CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metal contamination is one of the most pervasive forms of water pollution as metal elements do not disintegrate rapidly in aquatic environment; in fact, they further impair the marine ecosystem due to relatively high densities and toxicity even at low concentrations. Exposure to heavy metals, even at trace levels, poses a high risk to human health (Bosch, 2003). Industrial wastes are sources of major anthropogenic pathways of metal ions in contact with the environment.

Heavy metals discharged into water systems have to be managed efficiently, otherwise it is impossible to degrade naturally and to be safely released without treatment. The most common treatment technologies for water contaminated with heavy metals include chemical precipitation, adsorption by activated carbon, ion exchange/chelation, as well as membrane processes (Bhattacharya, 2006; Kojima, 2001). Another method applied for removal of metal ions is electrochemical technology for low heavy metal content or for complex effluent compositions (Weinberg, 1992). Although these methods of treatment are commonly utilized for wastewater treatment of heavy metals by industries, the technical and economical hindrance make these efforts limited in actual application (Puranik, 1999).

Enforcement of environmental protection has recently increased through legislation, especially for waste discharge limits to surface waters from industrial heavy metal ions effluents.

Requirements for heavy metals discharge to be treated first are restricted to factories and industries that handle contaminant metals before they are permitted to be discharged to surface water. Based on Malaysia Environment Quality Report 2011, the national water quality standard Class IIB for zinc, lead, and chromium (VI) are 5 mg/l, 0.05 mg/l and 0.05 mg/l respectively, but there is currently no data on chromium (III).

In order to address the heavy metals problems, current technology has come up with an alternative, which is Polymer Enhanced Ultrafiltration (PEUF), described previously in the works of Muslehiddinoglu, et al. (1998a, 1998b) and Uludag et al. (1997). In this process, an adsorptive mechanism of polymers efficiently bound to metal ions to form a molecular complex of metal ions-polymer that are then rejected by the ultrafiltration process (Baharuddin et al., 2014). A diluted permeate that can be discharged into the sewage or employed for a specific purpose is thus obtained (Sabate et al., 2002).

PEUF is known to have great potential for effectively removing metal ions from aqueous solutions (Uludag et al., 1997). Formation of the metal ion-polymer complex is a crucial aspect for metal ion removal by the PEUF process. The metal ions-polymer complex is able to be retained by the membrane whereas uncomplex metal ions are allowed to flow through the membrane. Attraction caused by electrostatic forces and coordination of the electron is the main contributor to the interaction of electron donors and acceptors that generate the metal ion-polymer bonds for metal ion-polymer complex formation (Labanda et al.,2009). Currently, application of PEUF for removal of metal ions has great potential to be explored further by researchers.

Most applications of PEUF focus on the commonly used binding polymers, such as polyethyleneimine (PEI), polyacrylic acid (PAA) and polyacrylic acid sodium salt (PAASS), which have been applied in heavy metal ion removal for decades via the ultrafiltration process (Islamoglu & Yilmaz, 2006; Kadioglu et al., 2009). The preferred polymers for metal ions removal in the PEUF system are mostly modified by crosslinking, grafting or any method that could change their molecular structure to enable reaction with metal ions to form macromolecules that are easily removed from aqueous solutions (Jianxian, 2009). The use of biopolymer without any modification of the structure is not discussed in open literature. Thus, unmodified starch as a water soluble polymer that mostly has no negative impact on our environment is proposed in this work as a binding polymer.

The unique criteria of unmodified starch are that it is an inexpensive agricultural material and is environmentally friendly; these are the reasons for introducing this polymer into the PEUF system. Although it is preferable to modify starch to improve its end-use properties, it can even be used without modification in the separation process. Hence, unmodified starch was proposed in this study for complexation of ultrafiltration system towards the metal ion-polymer interaction.

However, if the starch is disposed of with its load of heavy metals, it will have an environmental impact. In this research, low metal ions and polymer concentrations will be applied in the PEUF process do not have any issues on concentration of heavy metals that may contribute to sludge production at the final stage of the metal ions separation process. The final retentate metal ions concentrations are observed and measured by Inductive Coupled Plasma (ICP) and recycled back into the PEUF system until the metal ions concentrations are within the limits of Department of Environment (DOE) discharged standards. Overall, the PEUF process requires metal uptake/separation, a metal recovery and a polymer regeneration step, but the latter two are not the objectives of this research but are included in recommendations of future study in Chapter 5. This thesis deals with the uptake/separation aspect.

1.2 Problem statement

Water pollution due to heavy metal discharge into waterways is one of the issues faced in Malaysia. Out of the 464 rivers monitored, 275 (59.3%) were found to be clean, 150 (32.3%) slightly polluted and 39 (8.4%) polluted (DOE, 2011). The National Water Quality Standard of Malaysia (NWQS) has performing data for Pb(II) and Zn(II) in Class IIB where the discharge of metals waste is observed according to the allowable limits. The most important water management legislation in Malaysia is the Environmental Quality Act (EQA) which was applied for monitoring the quality of water resources.

In the 2011 Environmental Quality Report for Malaysia, heavy metal, namely lead, zinc and 99.95% chromium, data were listed under Class IIB limits of the National Water Quality Standard of Malaysia (NWQS)(DOE, 2011). The metal elements found to be pervasive in water bodies are Zn(II), Pb(II), Cr(III) and Cr(VI). They come from industries such as smelting, mining, plating, manufacture of storage batteries, ceramic and glass besides, chromium waste from dyes and paints.

Based on a study conducted by Idris et.al, lead (100%), zinc (80%), chromium (100%) and copper (52.7%) were found to be generated from diffused pollution sources rather than point sources in the Serdang area of Selangor, Malaysia (Idris, 2005). This caused critical water pollution, and the discharge of heavy metal wastes was uncontrolled from many industrial areas, negatively impacting the water system in Malaysia. In consequence, the case that occurred at Serdang can be used as guidelines for preparation against similar cases that can occur at others industrial areas, such as Shah Alam and Klang which are affected by the discharge of these types of heavy metals. Hence, finding a solution for removal of these four types of metals is of utmost importance.

The preferred polymers for metal ions removal in the PEUF system are mostly modified by crosslinking, grafting or any method that could change their molecular structure (Jianxian, 2009). However, present modification of polymers with toxic chemicals can cause environmental pollution, which means that researchers did not realize they were creating new problems as they tried to overcome the issue of heavy metals. Some researchers are focusing on modified starch, such as insoluble starch xanthate and water-insoluble carboxyl-containing polymer, for heavy metal ion removal (Rayford, 1978; Chang, 2007), and in combination with filtration process (Kim, 1999). The process involves xanthation of highly crosslinked starches prepared under various conditions (Doane, 1975), which can cause acute toxicity (Alto, 1977) to biotic species in water bodies such as rivers.

In this study, unmodified starch is proposed as a binding reagent for removal of target metals, namely Zn(II), Pb(II), Cr(III) and Cr(VI) ions, from aqueous solutions. Investigation of water-soluble starch as a biopolymer is a new application in complexation-ultrafiltration since it is a less toxic polymer and has a high potential for metal ion removal from aqueous solutions in the PEUF process. Hence, this unmodified starch is suitable as a potential binding reagent which has no adverse effect to the environment as the sources are plant-based (Baharuddin et al., 2014). The high concentration of unmodified starch will not be used in this work as it corresponds to no issues on the over loading of unmodified starch at the end of the PEUF process.

The common polymers, PEG and PEI, were also selected in this research in addition to unmodified starch for comparison purposes. In PEUF studies, one of the most important operating parameters is pH. As indicated from previous studies, pH shows significant effects on flux and retention (Aroua et al., 2007).

1.3 Objectives

The research is carried out to study removal of selected metal ions: Zn(II), Pb(II), Cr(III), and Cr(VI) from aqueous solutions via the PEUF system. In this study, unmodified starch is proposed as an alternative binding polymer for removal of selected metal ions species from aqueous solutions. Thus, the objectives of this research are:

1. To evaluate the performance of the unmodified starch as a new binding biopolymer for the removal of selected heavy metals from aqueous solutions through the Polymer Enhanced Ultrafiltration (PEUF) process

2. To compare the performance of the unmodified starch with that of commonly used PEUF polymers, such as polyethylene glycol (PEG) and polyethyleneimine (PEI) for heavy metal removal

3. To apply Canizares's Model to predict the flux and the concentration of the selected heavy metals in the permeate solutions

1.4 Scope of study

The experimental works implementing the laboratory batch scale were carried out continuously. The operating parameters and the parameter's range are chosen based on the Design of Experiments (DOE) by Box-Behken Model using Minitab 16 Software.

a) Operating parameters

- pH (2, 4, 6, 8, 12)

- transmembrane pressure (TMP): 1-2 bar

- flowrate: 80-150 ml/min

- polymer concentration: analytical starch (w/v %; (g/ml)): 0.05, 0.525, 1%, PEG and PEI (v/v% ;(ml/ml)): 0.01, 1, 2%

- metal ion concentration: 10-50 mg/l

b) Fitting experimental data with existing model related in the PEUF study: Canizares Model (Canizares et al., 2004, 2008). The retention coefficient of metal ions from experimental data is fitted into the established metal ion-polymer model. Canizares Model was used for analysing the potential for the unmodified starch to be used commercially for removal of heavy metal ions from aqueous solutions. ANOVA statistical analyses was employed at the end of the study to investigate how much experimental data fitted the theoretical Canizares Model (Canizares et al., 2004, 2008), as proof that the unmodified starch can be used as a new biopolymer in the PEUF system compared to commonly used polymers, PEG and PEI.

A laboratory scale unit will be used throughout this research. The ultrafiltration membrane used is polysulfone hollow fiber membrane having a molecular weight cut off (MWCO) of 10 kDa, and the effective surface of a module with 8 fibers is 0.026 m^2. In this work, the analyses of the binding mechanisms are only focusing on the ability of selected polymers to bind with metal ions to enhance the metal ions' retentions based on the objectives of study, not the used of membrane in terms of removal of metal ions.

1.5 Thesis Outline

The thesis is organized as follows:

Chapter 2: The literature related to the study is reviewed.

Chapter 3: The experimental set-up and procedures are described.

Chapter 4: The experimental results obtained for retention of coefficient and permeate fluxes studies for single and simultaneous solutions are analyzed and discussed. Discussions on the proposed model for single and simultaneous metal solutions which fit the research data are also included in this chapter.

Chapter 5: The investigations conducted in this study are summarized and suggestions for future work are discussed.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals and the Environment

2.1.1 Definitions

The term “heavy metals” has been used to identify a group of metals or semi-metals associated with contamination and potential toxicity. Metals are defined as elements that have characteristics, such as good electrical conductivity, metallic luster, malleable, ability to form cations and the presence of basic oxides. Elements containing metals can be referred to in the Periodic Table.

Definition of heavy metals is significant based on their atomic number as having atomic numbers above 20, namely with sodium (Lyman, 1995). When the atomic number is greater than sodium, it is considered “heavy”, meaning that it includes essential metals such as magnesium and potassium. Besides that, heavy metals have densities that range from 14.5 g/cm^{-3} for 76% weight, 20% Cu(II), 4% Ni(II) to 16.6 g/cm^{-3} for 90% weight, 7% Ni(II), 3% Cu(II) (Birchon, 1945). Heavy metals even include the semimetals, arsenic and tellurium, and the nonmetal, selenium (Burrell, 1974).

There is often some confusion in differentiating between the terms “heavy metals” and “toxic metals”. Heavy metal refers to its element and compounds, and categorization is based on their specific density and biological properties. Toxic metal refers to the fundamental rule of toxicology where all substances, including carbon, other elements and their derivatives, are toxic if exposed to at high doses (Lenntech, 2004).

The problem of heavy metal contamination has become a crucial issue in water pollution as these metal elements impair marine ecosystems due to their relatively high densities and toxicity even at low concentrations. They persist in the aquatic environment which further increase their environmental impact. This water pollution causes adverse impact on human beings and various biota species because aquatic organisms are at high risk of exposure to the heavy metal contaminated water. Exposure to heavy metals increases the risk to aquatic organisms even when those metals are detected at trace levels (Bosch, 2003) as they can cause bioaccumulation, sometimes known as bioconcentration.

2.1.2 Uses of Heavy Metals

According to the Environmental Protection Agency in the United States of America (USEPA), environmental hazards can be prevented by practicing waste management consisting of reuse, recycling, and reclamation of precious metals. In fact, when natural resources are protected, material and energy are saved as well. Many electronic products are made using costly natural resources, such as heavy metals, other metals and materials that require tons of energy to produce.

Use of recycled waste metal known as reclamation is a good practice to minimize the production of metal waste, as its' production requires a lot of energy and cost. In terms of reducing new metal production, electronic products are produced based on recycled metal waste, which are commonly lead, cadmium, zinc and copper. Recycling of heavy metals and materials is prominently practiced because of the production of heavy metals requires high energy and cost. Otherwise, it will be better to recycle than it will be only left heavy metal as the wastes (Lyman, 1995). Currently electronic products have utilized mercury, lead, cadmium and zinc in industrial applications, for example in production of dyes, rubbers and paints (Battarbee, 1988; Garbarino, 1995; Hutton, 1986; Nriagu, 1988, 1989; Hawkes, 1997).

In addition to being used in batteries, lead is used for vehicles, electrical backup systems and industrial batteries. For chromium, metallurgical, refractory and chemical industries apply this metal to processes, such as leather tanning, color pigments for textiles, and trace minerals for human and animal nutrition (Habashi, 1992; Labor, 2004; Peplow, 1999).

2.1.3 Heavy Metal Toxicity

The characteristics of heavy metals which are not degradable or destroyed naturally are the reason why heavy metals contaminants are found to be persistent among other sources of environmental contaminants, in comparison to paper, glass or tin waste. The increase in toxicity is due to heavy metals which accumulate in the soft tissues in the human body. Food, air, water or even skin absorption are possible routes of heavy metal absorption into the human body during site activities in industrial or residential areas (Holum, 1983; Yarlagadda, 1995).

Another source is via industrial exposure in which ingestion accounts for the most common route of exposure to humans (Roberts, 1999). For children, the exposure to high toxic metals is generally from hand-to-mouth activities as they come into contact with dirt or paint chips (Dupler, 2001).

On the other hand, toxicity of heavy metals depends on the total dosage absorbed, whether exposure was acute or chronic, and toxicity profiles based on the types of heavy metals formed. For example, human exposure to heavy metals during working days based on the World Health Organization, WHO, the following were the limits that are permitted in the human body (quantity per person/per week) that otherwise can cause the severe effects for body functions (taking an average human body weight of approximately 70kg) (OSHA, 2004): Hg: 0.35 mg/person/week, Cd: 0.49 mg/person/week, Pb: 1.75 mg/person/week, Cu: 245 mg/person/week, Zn: 490 mg/person/week, Ni: 2.45 mg/person/week, Fe: 392 mg/person/week and Mn: 68.6 mg/person/week. For example, the severe effects of several heavy metals are as follows: cadmium can cause lung inflammation, mercury causes diarrhea and vomiting, lead causes brain dysfunction and gastrointestinal hemorrhage, while chromium causes acute exposure of hemolysis (OSHA, 2004).

Emission of heavy metals, elements, and compounds, whether organic or inorganic, comes from industrial sources, such as mining sites, smelters and by-products of chemicals (UNEP/GPA, 2004). One of the other sources of environmental pollution originates from old mining sites, and pollution is reduced the sites farther away from the mining area (Peplow, 1999). Water bodies are polluted by these metals when metals leach out and enter the sea by the polluted run-off water or acid river downstream (Duruibe, 2007).

The issue of heavy metal pollution is related to chronic toxicity. In some circumstances, toxic substance accumulation in the human body is the result of continuous exposure caused by living near hazardous sites and exposure to contaminated water, air and dust. Once the exposure to the contaminated areas is repeated, some symptoms of chronic toxicity, such as asthma and colon damage, may not be easily recognized when entering the human body system, especially through ingestion and inhalation (Duruibe, 2007).

The treatment of wastewater is continuously improving in order to enhance the efficiency of hazardous material removal, such as heavy metal ions. One reason is that regulatory and legislative requirements have become more stringent, and industries, as well as society, are now much more aware of the need for clean processes. The guidelines of discharged standards are prominent in controlling the toxicity of wastewater to be within the permissible limits.

2.1.4 Discharge standards

According to the Department of Environment (DOE), standards have been established for the allowable quality of effluents to be discharged to receiving water. These take the form of the upper limit for various effluent contaminants. In order to ensure that the heavy metal effluents comply with the standards, effluents from treatment plants are regularly sampled and tested in laboratories. This is crucial in order to ensure treatment plants are well operated.

Discharge of selected heavy metals in Malaysia can be found in rivers. Sources of water pollution include bathing, laundry, fishing, crop irrigation and aquaculture from village development projects; heavy metals can contaminate the source of drinking water (Teck-Yee, 2012).

Excessive input of trace metals, especially cadmium, copper and zinc due to poor management practices from agricultural activities, accelerates the leaching of metals to the ground and surface waters, thus deteriorating water quality and affecting aquatic organisms (Vries, 2002). Due to their persistence and concentrations exceeding the standard limit through bioaccumulation and the food chain, human beings are potentially affected.

According to Ling et al. (2010) (Ling et al., 2010a, 2010b), concentration of heavy metals in feed and manure were decreasingly correlated in the order of Cu>Zn>Cr>Pb>Ni>Cd. After the oxidation pond treatment, the trend was Cr>Zn>Cd>Pb>Ni>Cu with a low concentration of less than 0.9 mg/L and 0.1 mg/L for Cr and all other trace metals respectively (Semiao & Schafer, 2009).

Based on the Department of Environment, permissible limits of Zn(II), Pb(II), Cr(III) and Cr(VI) effluents that can be discharged in water bodies in Malaysia are 2.0 mg/l, 0.5 mg/l, 1.0 mg/l and 0.05 mg/l, respectively (DOE, 1994). Methods commonly practiced for the removal of organic and inorganic contaminants include coagulation, air floatation, gravity settling or separation via electrostatic and electro-coagulation. Unfortunately, these commonly used separation techniques can lead to sludge management issues as well as system operations at the end of the process.

In Malaysia, the DOE has enacted its own effluent standards; discharge limits are shown in Table 2.1. Two of the metal elements found to be pervasive in water bodies are Zn (II) and Pb (II). Contamination of these two metals comes from industries such as smelting, mining, plating, manufacture of storage batteries, ceramic and glass.

Table 2.1 Acceptable Conditions for Discharge of Industrial Effluent for Mixed Effluent of Standards A and B Extracted from Environmental Quality (Industrial Effluents) Regulations 2009 [Paragraph 11(1) (a)](DOE, 1994).

Parameter		**Unit**	**Standard**	
1		2	3	4
			A (upstream)	**B (downstream)**
i)	Temperature	°C	40	40
ii)	pH value	mg/L	6.0-9.0	5.5-9.0
iii)	BOD5 at 20℃	mg/L	20	40
iv)	Suspended Solids	mg/L	50	100
v)	Mercury	mg/L	0.005	0.05
vi)	Cadmium	mg/L	0.01	0.02
vii)	Chromium, Hexavalent	mg/L	0.05	0.05
viii)	Chromium, Trivalent	mg/L	0.20	1.0
ix)	Arsenic	mg/L	0.05	0.1
x)	Cyanide	mg/L	0.05	0.1
xi)	Lead	mg/L	0.10	0.5
xii)	Copper	mg/L	0.2	1.0
xiii)	Manganese	mg/L	0.2	1.0
xiv)	Nickel	mg/L	0.2	1.0
xv)	Tin	mg/L	0.2	1.0
xvi)	Zinc	mg/L	2.0	2.0
xvii)	Boron	mg/L	1.0	4.0
xviii)	Iron (Fe)	mg/L	1.0	5.0
xix)	Silver	mg/L	0.1	1.0
xx)	Aluminium	mg/L	10.0	15.0
xxi)	Selenium	mg/L	0.02	0.5
xxii)	Barium	mg/L	1.0	2.0
xxiii)	Fluoride	mg/L	2.0	5.0
xxiv)	Formaldehyde	mg/L	1.0	2.0
xxv)	Phenol	mg/L	0.001	1.0
xxvi)	Free Chlorine	mg/L	1.0	2.0
xxvii)	Sulphide	mg/L	0.5	0.5
xxviii)	Oil and Grease	mg/L	1.0	10
xxix)	Ammonical Nitrogen	mg/L	10.0	20
xxx)	Colour	ADMI*	100	200

Notes: ADMI: American Dye Manufactures Institute

2.1.5 Typical Malaysian Wastewater Containing Heavy Metals

Wastewater treatment technology is continuously improving and enhancing the efficiency of hazardous material removal, such as heavy metal ions. This may be due to regulatory and legislative requirements which have become more stringent, and industries as well as society becoming much more aware of the need for cleaner processes. Methods commonly practiced for the removal of organic and inorganic contaminants include coagulation, air floatation, gravity settling or separation via electrostatic and electro-coagulation. Unfortunately, these techniques can lead to sludge management issues as well as system operations at the end of the process.

Water pollution due to heavy metal discharge into waterways is one of the water issues faced in Malaysia. Out of 464 rivers monitored, a total of 275 (59.3%) were found to be clean, 150 (32.3%) slightly polluted and 39 (8.4%) polluted (DOE, 2011). Heavy metals analyzed were Mercury (Hg), Arsenic (As), Cadmium (Cd), Chromium (Cr), Plumbum (Pb) and Zinc (Zn).

With reference to the National Water Quality Standard of Malaysia (NWQS); all Pb and Zn data were within the Class IIB limits, 99.98% of the Cd data were within the Class IIB limits, followed by Cr (99.95%), As (99.93%) and Hg (99.43%) (DOE, 2011).

Recovery of metal ions from valuable metal discharge by industrial or domestic effluents is well practiced through the separation technique for dilute or concentrated solutions over the past few years (Mavrov, 2003). Major species of heavy metals that cause chronic disorders to organisms are chromium, copper and zinc; these disorders can occur through ingestion if taken accidentally at limits beyond what is acceptable to human bodies (Prakasham, 1999).

The Environmental Quality Act (EQA) of 1974 became the main legislation for protecting the environment and water quality in Malaysia and is based on three main objectives: pollution prevention, abatement and control, as well as environmental enhancement. The role of the legislation is to sets limits for allowable pollutant levels, including land, sea-based sources, and prescribed activities specified under the Environmental Impact Assessment Regulations (1987).Various types of domestic and industrial wastes are controlled by regulations which constitute the standards and procedures for handling waste. Rivers with municipal, industrial and agricultural waste loads eventually discharge to estuaries and end up polluting the marine water system.

In 2011, river water quality was assessed based on a total of 4,249 samples taken from 464 rivers, using 812 manual stations (MWQM) and 10 continuous water quality monitoring stations (CWQM) for the purpose of early detection of pollution influx. For the period of January to December 2011, no distinctive incidence of pollution flux was observed by the DOE throughout the country.

Chemical characteristics were measured through the assessment of water quality and compared to national water quality standards. River quality in terms of status and trend for the period between 2005 and 2011 is shown in Figure 2.1

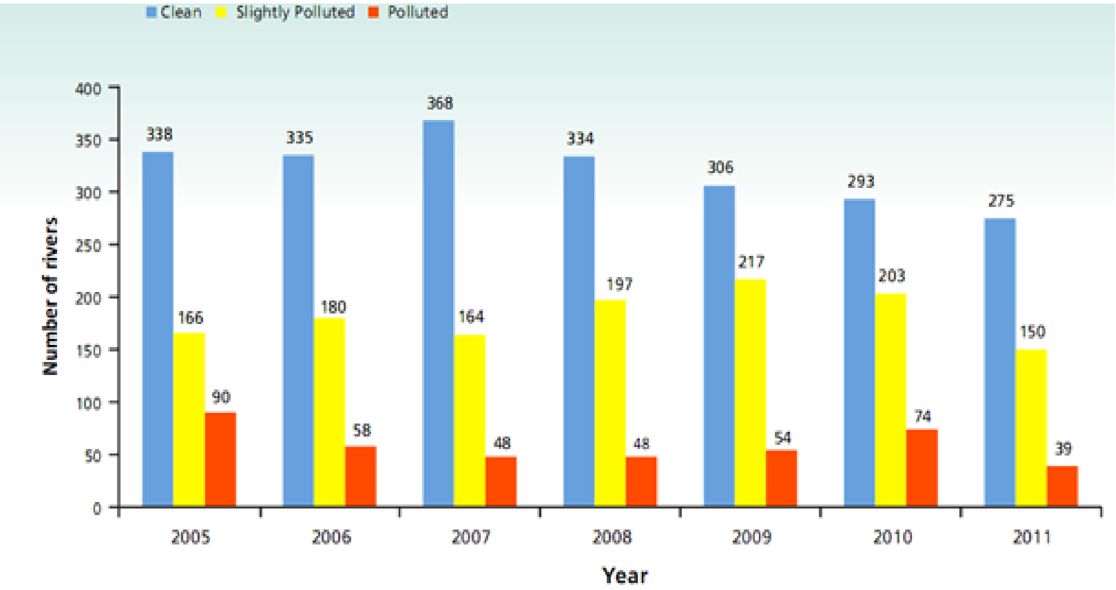


Figure 2.1 Malaysia River Water Quality Trend (2005-2011) (DOE, 2011).

Heavy metal sludge is the 4th most important waste based on the load discharged to the water as referred to in Table 2.2. The quantity of waste can be controlled if the selection of suitable treatment is practiced to reduce the concentration prior to discharge to water bodies.

Table 2.2 Quantity of Scheduled Waste Generated by Category, 2011(DOE, 2011).

No	Waste Category	Waste Code	Quantity of waste	
			MT/Year	Percentage (%)
1	Dross / Slag / Clinker / Ash	SW 104, 107, 406	370,789.09	22.86
2	Gypsum	SW 205	278,139.00	17.15
3	Mineral Sludge	SW 427	207,445.01	12.79
4	Heavy Metal Sludge	SW 204, 105, 108	173,837.06	10.72
5	E-Waste	SW 110	152,722.04	9.42
6	Oil & Hydrocarbon	SW 305, 306, 307, 308, 309, 310, 311, 312, 314, 315, 415	133,260.91	8.22
7	Clinical/Pharmaceutical	SW 404, 403, 405	44,674.52	2.75
8	Batteries	SW 102,103	41,246.65	2.54
9	Acid & Alkaline	SW 206, 401, 414	38,152.48	2.35
10	Used Container / Oil Filter	SW 409	36,706.83	2.26
11	Spent Solvent	SW 322, 323	30,976.89	1.91
12	Paper & Plastic	SW 410	23,332.03	1.44
13	Ink & Paint Sludge	SW 416, 417, 418	19,224.56	1.19
14	Residue	SW 501	18,118.39	1.12
15	Rubber Sludge	SW 321	16,130.66	0.99
16	Mixed Wastes	SW 422, 421	10,708.41	0.66
17	Phenol/Adhesive/Resin	SW 325, 319, 303	7,904.42	0.49
18	Catalyst	SW 202	6,229.05	0.38
19	Others	NA	5,505.33	0.34
20	Arsenic	SW 101	2,131.57	0.13
21	Chemical Waste	SW 430, 429	1,327.61	0.08
22	Contaminated Land/Soil	SW 408	1,072.87	0.07
23	Photographic Waste	SW 423	587.63	0.04
24	Contaminated Active Carbon	SW 411	510.03	0.03
25	Pesticide	SW 426	487.10	0.03
26	Mercury	SW 109	434.18	0.03
27	Asbestos	SW 201	194.11	0.01
28	Thermal Fluids	SW 327	178.00	0.01
29	Sludge Contain Cyanide	SW 412	5.09	0.00
	Total		1,622,031.54	100.00

Table 2.3 and Table 2.4 show the latest National Water Quality Standard for Malaysia consisting of the Class of River I until V. In Malaysia, the limits of heavy metals

concentrations are referred to Class III to be acceptable for daily water use (DOE, 2011).

Table 2.3 National Water Quality Standards for Malaysia (DOE, 2011)

PARAMETER	UNIT	CLASS				
		I	IIA/IIB	III	IV	V
Al	mg/l		-	(0.06)	0.5	
As	mg/l	↑	0.05	0.4 (0.05)	0.1	↑
Ba	mg/l		1	-	-	
Cd	mg/l		0.01	0.01*	0.01	
Cr (VI)	mg/l		0.05	(0.001	0.1	
Cr (III)	mg/l		-	1.4 (0.05)	-	
Cu	mg/l		0.02	2.5	0.2	
Hardness	mg/l		250	-	-	
Ca	mg/l		-	-	-	
Mg	mg/l		-	-	-	
Na	mg/l		-	1	3 SAR	
K	mg/l		-	0.02*	-	
Fe	mg/l		1	(0.01	1 (Leaf) 5	L
Pb	mg/l		0.05	0.1	(Other	E
Mn	mg/l		0.1	0.004	5	V
Hg	mg/l	N	0.001	(0.000	0.2	E
Ni	mg/l	A	0.05	0.9*	0.002	L
Se	mg/l	T	0.01	0.25 (0.04)	0.2	S
Ag	mg/l	U	0.05	0.0002	0.02	
Sn	mg/l	R	-	0.004	-	A
U	mg/l	A	-	-	-	B
Zn	mg/l	L	5	0.4*	-	O
B	mg/l		1	(3.4)	2	V
Cl	mg/l	L	200	0.1	0.8	E
Cl_2	mg/l	E	-	-	80	
CN	mg/l	V	0.02	-	-	
F	mg/l	E	1.5	(0.001)	-	
NO_2	mg/l	L	0.4	-	1	
NO_3	mg/l	S	7	-	-	
P	mg/l		0.2	-	5	IV
Silica	mg/l		50	-	-	
SO_4	mg/l		250	-	-	
S	mg/l	O	0.05	-	-	
CO_2	mg/l	R	-	5000	-	
Gross-α	Bq/l		0.1	(200)	-	↓
Gross-ß	Bq/l		1	N	-	
Ra-226	Bq/l		< 0.1	N	-	

Table 2.3, continued National Water Quality Standards for Malaysia (DOE, 2011)

	Bq/l		< 1	6 (0.05)	-	
Sr-90	µg/l		500	-	-	
CCE						
MBAS/BAS	µg/l		500			
O & G (Mineral)	µg/l		40; N	0.2 (0.01)	-	
O & G (Emulsified	µg/l	A	7000;	9 (0.1)	-	
Edible)	µg/l	B			-	-
PCB	µg/l	S	N	2 (0.02)		-
Phenol	µg/l	E		(1)	-	
Aldrin/Dieldrin	µg/l	N	0.1	-	-	-
BHC	µg/l	T	10	0.9 (0.06)	-	-
Chlordane	µg/l	↓	0.02	3 (0.4)	-	-
t-DDT	µg/l		2	450	-	-
Endosulfan	µg/l		0.08	160	-	-
Heptachlor/Epoxide	µg/l		0.1	850	-	-
Lindane	µg/l		10	1800	-	-
2,4-D	µg/l		0.05		-	-
2,4,5-T	µg/l		2		-	-
2,4,5,TP	µg/l		70		-	-
Paraquat			10		-	-
			4			
			10			

Table 2.4 Important Parameter of National Water Quality Standards for Malaysia (DOE, 2011)

Parameter	Unit	Class					
		I	IIA	IIB	III	IV	V
Ammoniacal Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	> 2.7
Biochemical Oxygen Demand	mg/l	1	3	3	6	12	> 12
Chemical Oxygen Demand	mg/l	10	25	25	50	100	> 100
Dissolved Oxygen	mg/l	7	5-7	5-7	3-5	< 3	< 1
pH	-	6.5-8.5	6-9	6-9	5-9	5 - 9	-
Colour	TCU	15	150	150	-	-	-

Table 2.4, continued Important Parameter of National Water Quality Standards for Malaysia (DOE, 2011)

Electrical Conductivity*	µS/cm	1000	1000	-	-	6000	-
Floatables	-	N	N	N	-	-	-
Odour	-	N	N	N	-	-	-
Salinity	%	0.5	1	-	-	2	-
Taste	-	N	N	N	-	-	-
Total Dissolved Solid	mg/l	500	1000	-	-	4000	-
Total Suspended Solid	mg/l	25	50	50	150	300	300
Temperature	°C	-	Normal + 2°C	-	Normal + 2°C	-	-
Turbidity	NTU	5	50	50	-	-	-
Faecal Coliform**	count/100 ml	10	100	400	5000 (20000)[a]	5000 (20000)[a]	-
Total Coliform	count/100 ml	100	5000	5000	50000	50000	> 50000

Notes :

N: No visible floatable materials or debris, no objectionable odour or no objectionable taste

*: Related parameters, only one recommended for use

**: Geometric mean

a: Maximum not to be exceeded

2.2 Membrane Processes as Emerging Technologies for Heavy Metal Removal

Membrane technology has emerged as a standard technology for pollutant separation, either independently or for mixtures, to assist conventional removal technologies that are able to remove contaminants at very low concentrations before allowing the wastewater to be discharged to water bodies (Canizares et al., 2007; Korus, 1999; Deshmukh, 1998). New ideas to combine ultrafiltration and other physical or chemical processes are reported as an alternative for heavy metal ion removal from aqueous solutions (Juang, 1993).

Applications of membrane for metal ions separations are practiced in several industries for wastewater treatment. The effect on selection of appropriate treatment, namely membrane technology, can make a difference in water quality by employing certain design parameters based on the types of substances that have to separate from the solutions. Membrane configuration, material of construction, removal efficiency and design of the system are complex characteristics which are profound in addressing the issues of the raw water quality and volume of finished water. The use of membrane technology is dependent on the purpose of membrane use in the industry (GEA, 2012).

The membrane is likely a barrier of two solutions that has two phases of feed solutions (that contain metal ions-polymer complex in the case of Polymer Enhanced-Ultrafiltration) known as permeate solutions (that contain water and uncomplex substances) as shown in Figure 2.2 (Pinto, 1999).

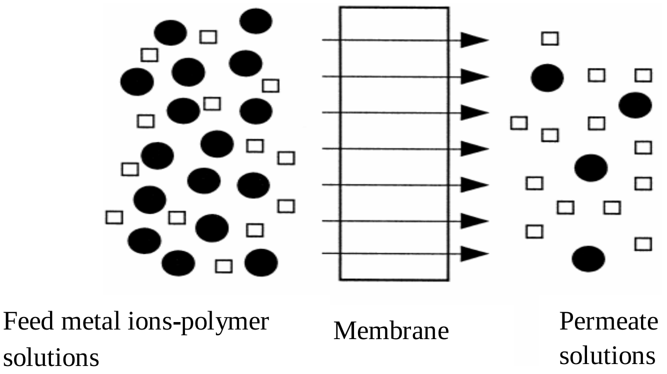


Figure 2.2 Tangential flow of the membrane separation process for cross flow type (Pinto, 1999).

Force must be applied to produce flow for mass transport to occur. The relationship between flow generated and force applied is governed by factors that depend on the nature of the chemical species and the membrane (Stratman, 1986).

$$\text{Flow} = f(\text{force, solubility, mobility}) \tag{2.1}$$

The selectivity terms in membrane applications are generally described as different from the rate ratio of two species mixed together in the solutions. They are able to flow through the membrane because of their permeability behavior, but they only allow uncomplex species and water to pass through its membrane surface, while the rest of the complex species are retained. In consequence, it has been chosen as an efficient technology for processing separation as it is faster than any other separation technique (Rawa-Adkonis, 2003).

Suspended solids and organic compounds can be removed by membrane filtration based on sizes of the substances able to be removed. UF, NF and RO are commonly used for wastewater treatment for heavy metals removal.

UF membranes with pore sizes ranging from 1×10^{-9} to 5×10^{-8} m are capable of retaining the species of 300-500000 Da of its molecular weight by an applied pressure-driven technique in the UF separation process (Hamza, 1997). Polymer molecules and small species are rejected by membranes, and diluted permeates can be discharged as waste. A retentive stream containing high concentration of metallic ions-polymer complexes (Pujola et al., 2006) is able to be adsorbed onto the surface or into the membrane pores, which are mostly polymeric material (Hamza, 1997).

This application intends to apply this process for wastewater treatment especially for metal ion removal. Selectivity of water-based polymer towards metal ions will form macromolecules that are able to be rejected from the membrane surface and could be enhanced by certain parameters: pH, flowrate, transmembrane pressure, etc. (Barakat, 2010).

2.2.1 Dead-end filtration

The process by which fluid tends to pass through the membrane while macromolecules are retained at the membrane surface is generally known as the dead-end filtration technique or batch filtration. The particles that accumulate on the membrane surface, called ‘filter cake’, are unable to pass through the membrane. This negatively influences filtration efficiency and permeate flux unless backwashing is applied to remove this filter cake. Pressure is employed whenever backflushing is practiced, and water is pushed through membrane; therefore, the pressure drop is monitored throughout this process as the cake build-up increases with time.

2.2.2 Cross-flow filtration

Cross-flow filtration membrane systems are widely used in the separation process depending on the pore size. The cross-flow mode (which could be any membrane) implies tangential flow which could be pumped cross-flow, stirred or bubble induced. In principle, (if no fouling occurs) the cross-flow mode remains at a steady state, whereas the dead-end is in an unsteady state with time dependent polarization. Dead-end and cross-flow modes of membrane filtration (could be MF, UF, NF, RO) imply there is no tangential flow to control concentration polarization. The processes differ from normal or dead-end filtration processes as shown in Figure 2.3.

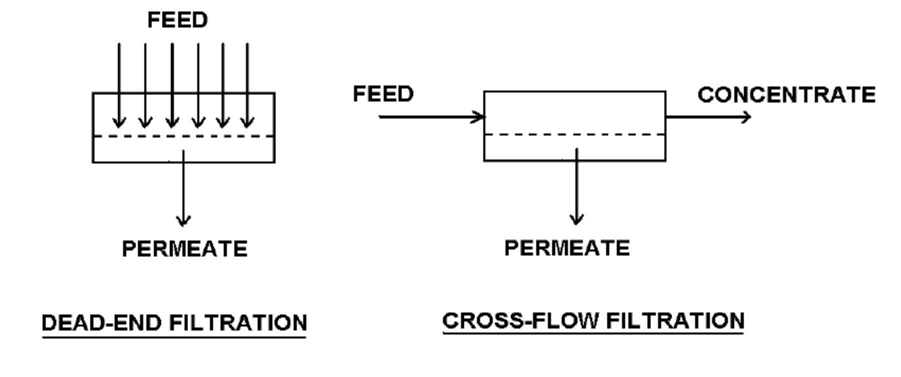


Figure 2.3 Dead-end and cross-flow filtration processes (Wagner, 2001).

In normal filtration as the feed water flows through the membrane filter, only deposited contaminants are removed; in contrast, membrane filtration employs pressurized water through the membrane. A small fraction of the incoming stream permeates through the membrane while the remaining streams are allowed to flow to the membrane surface with contaminants rejected by the membrane filtration. Filtered solutions are called ‘permeate’, while retained solutions are called ‘retentate’.

Rapid development and improvement of membrane application allows for operation at lower pressures, providing better product quality, reducing membrane fouling and recovering the energy in membrane operation system.

2.3 Polymer Enhanced Ultrafiltration (PEUF) Process for Heavy Metal Removal

2.3.1 Complex binding

Metal ion removal by employment of water-soluble polymers and ultrafiltration for complexation is known as polymer-enhanced ultrafiltration (PEUF). PEUF is known to have great potential for effectively removing metal ions from aqueous solutions (Uludag et al., 1997). Formation of a metal ion-polymer complex is a crucial aspect for metal ion removal by the PEUF process by ascertaining the binding of metal ions to selected polymers and its' adherence to membrane surface, while fluid streams and unbound metallic ions are permitted to flow through the membrane. Electrostatic attraction or electron coordination is the main contributor to the interaction of electron donors and acceptors that generate the metal ion-polymer bonds for metal ion-polymer complex formation (Labanda et al., 2009). Current application of PEUF for removal of metal ions has great potential to be explored further by researchers.

Most applications of PEUF are focused on commonly used binding polymers, such as polyethyleneimine (PEI), polyacrylic acid (PAA) and polyacrylic acid sodium salt (PAASS) which have been applied in heavy metal ion removal for decades via the ultrafiltration process (Islamoglu & Yilmaz, 2006; Kadioglu et al., 2009). The preferred polymers for metal ion removal in the PEUF system are mostly modified by crosslinking, grafting or any method that could change their molecular structure to enable reaction with metal ions to form macromolecules, hence easy removal from aqueous solutions (Jianxian, 2009).

PEUF is the process of metal retention, polymer regeneration and metal recovery. Metal ions react with a water-soluble polymer to form a macromolecular complex which are bigger than the membrane pore. The metal ions-polymer complexes are pressurized tangentially to pass through the UF membrane. The solution retains the metal ion-polymer complex while permitting a non-complex solute to pass through (Camarillo et al., 2010).

Macromolecules of metal ions in the form of homo- or copolymers may contain one or more coordinating and/or charged groups placed at the backbone, side chain, or directly through a spacer group. Polyelectrolytes may be distinguished from chelating polymers (polychelatogens) which have charge groups or easily ionizable groups in aqueous solutions and functional groups with the ability to form coordination bonds. Amines, carboxylic acids, amides, alcohols, amino acids, iminos, present in polychelatogens are mostly investigated by researchers (Rivas, 2009).

Property profiles of materials are improved by the application of advanced technology as most polymer modification is done by crosslinking and grafting other chemicals employed to restructure molecules and make the donor/share ions active as acceptors. The example of using chitosan as a polymer in PEUF is modified by cross-linking with glutaraldehyde (imine function) to decrease the ability of amine for chelation of metal cations, hence the bounded behavior is drastically decreased (Chen et al., 2007; Dzul Erosa, 2001).

Most PEUF works have been developed in lab-scale modules (Aroua et al., 2007; Camarillo et al., 2010) as all parameters are more easily monitored and controlled for high retention of metal ions from solutions. Important parameters like pH, loading metal/polymer ratio and feed concentration are mostly observed in continuous mode in the PEUF process to enable observation of retention (Islamoglu & Yilmaz, 2006). The ability of metal ion-polymer to become complex under certain working conditions is the main criteria with which to apply PEUF systems by this process mode (Camarillo et al., 2010).

Theoretical and experimental parameters are crucial in the PEUF system to determine the range of parameters that can be optimized for removal of metal ions from wastewater (Fatin-Rouge, 2006). Understanding the chemical mechanism and selectivity of water based polymers to metal cations are important prior to selection of polymer to ensure that complexation between metal-polymer occurs when the polymer used was either ionic or non-ionic but still able to form macromolecules for membrane retention.

Complexation of metal ions-polymer occurs by employing major operating parameters in the UF system (i.e. pH, loading (metal/polymer ratio)); other parameters include ionic strength (Islamoglu & Yilmaz, 2006) which may affect the complexation of metal ions-polymer in the performance separation process. The influence of polymer towards metal ion binding is enhanced by upgrading the polymer to activate the active group for electron donors to the metal ions as electron acceptors. For example, the established polymer used in PEUF study is polyethyleneimine (PEI) which has an active functional group of amino and the ability to interact well with metal ions that neutralize excess anions charges of metal species under acidic and neutral pH regions.

Thus, a suitable polymer is important in the interaction of metal ions-polymer for complexation in PEUF study. The least toxic polymer is the first selection criteria, besides the availability of polymers to bind with metal ions species in aqueous wastewater.

2.3.2 Adsorption of metal ions onto polymers

Metal ion species present in dilute solutions, which are able to compete with each other to bind with polymers, are treated as a surface phenomenon. Interactions of metal ion-polymers changed by the rate of desorption of metal ions released from polymer are known as polymer conformation (Rivas, 2002). Interaction between water-soluble polymers and metal ions are assisted by other parameters, such as pH and ionic strength (Fu et al., 2009).

Other than the presence of opposing charges of metal ions and polymer surfaces, continuous mixing of solutions enhances the binding mechanism within metal ion-polymer until it forms macromolecule complexes bigger than the molecular cut off membrane (MWCO), hence increasing retention of metal ions. By employing a high molecular weight of polymer, molecules can be enlarged and the permeate solutions are able to attain acceptable levels before discharge.

A useful water soluble polymer carrying a net charge is called a polyelectrolyte. To attract cationic metal ion species via adsorption, the net charge may be anionic by introducing carboxylic or cationic groups, as in the case of quaternised acrylic esters or Diallyldimethylammonium Chloride (DADMAC). This ionicity in copolymer influences the behavior of polymer in solutions and is a useful characteristic to quantify (Williams, 2007).

As the PEUF method increases the molecular size of metal ion species, it is not only limited by chemical interactions between metal ion-polymers but also by the physical interaction of metal ion-polymer complexation binding to polymer molecule surfaces to increase the size of metal ions (Kadioglu et al., 2009). Applying natural polymer to dissolve in water to interact with metal ions species can also enhance the size of metal ion-polymer until achieving the necessary sizes to be removed via UF system. Unmodified starch and synthetic PEG are examples.

Polymers are molecules of high molecular weight and limited chain flexibility. The skeleton of an adsorbed macromolecule is usually portrayed by chain segments (train) in direct contact with a solid surface, chain segments (loop) protruding into the bulk connected to the solid by their two ends, and chain segments (tail) connected to the solid at only one end (Pefferkorn, 2008). Processes leading to achievement of equilibrium characteristics after adsorption at the liquid/solid interface are summarized under the term "reconformation". Reconformation includes modifications in the macromolecule spatial configuration and electric charge distribution (for electrolytes) that accompany the progress of the adsorption processes or the changes in the stability of colloidal dispersions.

Surface modification on adsorption factors are mostly influenced by the structure of the polymer, length of chain, and nature of interaction of the polymer with the solvent surface, concentration of polymer in the solution and temperature (Williams, 2003).

Attraction of metal ions to a polymer known as adsorption can occur through chemical or physical mechanisms where most of them are attracted chemically by electrostatic force or physically adsorbed to the molecular surface. It is not a certainty that the chemical mechanism is a major attraction between metal ion-polymer and polymer-membrane, as indicated in the study of Manuel Palencia et al. (2009). From their investigations, a membrane–metal interaction coefficient (R_0) was found to be associated with a decrease of the hydrated ionic radius, indicating that electrostatic nature is not the main interaction of the metal ion adsorption mechanism on the clean and fouled membrane during PEUF when using polyvinyl sulfonic acid, PVSA (Palencia et al., 2009).

2.3.3 Polymer reagents for metal ions' adsorption

The present modification of polymers with toxic chemicals can cause environmental pollution, which means that researchers did not realize they were creating new problems as they tried to overcome the issue of heavy metals. Some researchers are focusing on modified starch, such as insoluble starch xanthate and water-insoluble carboxyl-containing polymer, for heavy metal ion removal (Rayford, 1978; Chang, 2007), and in combination with filtration process (Kim, 1999). The process to enhance reaction between metal ions and polymer will form high toxicity in the environment, especially after modification such as insoluble starch xanthate (Wing, 1975) which can cause acute toxicity (Alto, 1977) to biotic species in bodies of water.

The following requirements are necessary when employing polymer reagents for successful separation process in PEUF (Geckeler, 1980). They are displayed in Table 2.5.

Table 2.5 Criteria in selection of polymer reagent in the separation process

Major criteria of polymer chosen for separation process	• Affinity of polymer to selected metal ions and inactivity towards non target metal ions • Complexation of metal ion-polymer with high molecular mass • Regeneration of polymer and inexpensive • Stability of polymer chemically, mechanically and environmentally friendly

Three main groups of polymer reagents can be classified as basic polymers such as poly(ethylenimine), (PEI) and poly(vinylamine), (PVA); bio-polymers such as polyglycols, (PEGs) and polyalcohols, (PAs); and acidic polymers such as (poly(acrylic acid), (PAA) and poly(vinylsulfonic acid), (PVSA).

Three biopolymer or synthetic polymers, namely unmodified starch, polyethylene glycol (PEG) and polyethyleimine (PEI), were selected in this study. The natural polymers of unmodified starch has adsorptive affinity towards metal ions through either non-ionic behavior or through the active group of hydroxyl ions containing in their polysaccharides structure which can serve as donor bonds to interact to metal ions; unmodified starch has proven successful as an adsorbent for metal ions from aqueous solutions (Rammika, 2010). While PEG interacts with metal ions as non-ionic and ionic interaction, when more hydrogen ions and HO-(CH_2CH_2O-) were produced there was an increase in the uptake of metal ions to bind together at a certain pH level. PEI as the synthetic polymer has the ability to neutralize excess anionic species at a certain pH range as the active group of nitrogen atoms is able to interact with metal ions to form macromolecules complexes.

2.3.4 Binding conditions

2.3.4.1 Binding Degree

Interaction factors for affinity of metal ions to the polymer mostly depends on functionality of the chelating group density, metal electronic configuration, stereochemistry and electrostatic metal ions charges to polymer (Zalloum, 2008).

Functional charged chelations , neutral oxygen donor groups, or mono-, bi- with nitrogen acting as a Lewis base have the ability to act as electron donor to interact with the metal. The behavior of ligand chelates are considered the spaces of its functional groups to react to a selected polymer (Micioi, 2007). It corresponds to the donor groups of ligand chelates that interact to be a closer to polymer chain by means, although only the little hindrance of ligand chelates to attach to polymer's chain. This reaction is called a "poly-dentate ligand". In this condition, metal ions are able to fold locally, and polymer chains induce the crosslinking. The nature of the intervening groups, such as small spacing group flexibility of the polymer, causes folding on polymer chains, but types of rigid and bulky groups of ligand chelates will negatively influence the binding degree of polymers to grab metal ions (Micioi, 2007).

The pKa of the polymeric backbone and ligands also has a significant effect on the metal-ligand interaction (Li et al., 2008). By increasing the pH over pKa value for carboxylic acid functional groups, deprotonation occurs, and the ability of the electron donor is activated in relation to enhance the electrostatic repulsion by polymer charged groups which correspond to positively affecting the ligation efficiency. At a low pH, many polymers with the presence of a nitrogen group have lower binding behavior to metal cations caused by amine group protonation and loss of electron donation (Rivas & Maureira, 2007). Mostly the factor of binding degree towards metal ions-polymer has a relationship with the pH value of the solutions containing of metal ions which interact well in a certain pH range dependent on if the charges of metal ions are favorable to bind with the active group in the polymer structure.

2.3.4.2 pH Value

In PEUF studies, one of the most important operating parameters is pH. As indicated from previous studies, pH shows significant effects on flux and retention (Aroua et al., 2007). Generally, it is due to competition between hydrogen ions with metal ions, which can be trapped in the polymer structure at a low pH. Nevertheless, pH may influence retention by competing with metal ligands, resulting in a high retention value for metal ion removal. As described by Zeng et al. (2009), pH has great influence. For investigation on cadmium removal, it was shown that competing complexing agents can eliminate the complexation of metal ion-polymer when pH is increasing, leading to fluctuation of retention and flux (Zeng et al., 2009).

In PEUF studies, pH becomes prominent in the operating parameters for metal ions to attract by the selected polymer. As molecules of metal are able to form complexation of metal hydroxyl that could increase to sizes greater than membrane pores at a high pH region, the latter is effectively rejected, particularly for Zn(II) (Trivunac, 2006). The implications of this finding is at a certain pH range and metal ion concentration, there is a high possibility of achieving great retention of metal ion-polymer as well as the behavior of metal ion-polymer (non-ionic or ionic interaction) occurring during the experimental works.

The protonation of acidic and basic polymers are important in controlling chelation properties (the process of removing a heavy metal from the stream by means of a chelate from an aqueous wastewater system). Rivas et al. (2009) studied the effect of changing the pH on metal ion retention of poly(2-acrylamido glycolic acid) (Rivas & Maureira, 2009) and found retention of metal ions increases with pH by presence of selected metal ions in solutions. The effect of pH on polymer presents nitrogen as active groups, and it is found that fully protonated and positively charged nitrogen cannot donate electron density to the metal (Zander, 2009).

It is interesting to note that lower pH does not influence the Cu^{2+} and Pb^2+ retention as the groups of nitrogen of PEI actively play the roles as the donors and are mostly protonated (Zander, 2009) during complexation of metal ions-PEI. As PEI is a commonly used polymer in the PEUF process, it is particularly susceptible to pH changes. The metal ions and ammonium are unable to form complexation as ammonium groups cannot donate the electron; thus pH is much less than the pKa of PEI (Bell, 2006) to increase the binding behavior of metal ions and PEI.

2.3.4.3 Selectivity of polymer on binding behavior of metal ions in aqueous solutions by employed ultrafiltration process

The selectivity of polymer upon the metal ions uptake becomes the prominent factor to remove metal ions from aqueous solutions with the presence of a metal ions charger to be able to bind to the active groups of polymer. One importance of the polymer's selectivity on heavy metal ions is the remediation process.

Remediation is one of the important aims for wastewater containing complex metallic ions depending on the selectivity of the polymeric ligand to interact with metal ions. The process of metal ion removal from wastewater and metal recovery allows the separation between waste and valuable metals. Waste streams containing Ethylenediaminetetraacetic acid (EDTA) and acid (H^+) have the ability to compete with the chelating polymer to bind to target metals or protonate, inactivate the donating ability of the polymer, respectively (Fu, 2006; Li et al., 2008), and increase the efficiency on metal ions' removal from the metal ions solution.

The competitor ligands present in a solution are one of the factors in decreasing the ability to remove target metal ions from the solutions. Thus, by altering the pH of solution in advance, there will be negative effects on the affinity of metal ions to bind to the selected polymer. In consequence, the competitor ligands take place as a substance that is going to be removed from solutions, not the target metal ions. On the other hand, the target metal ions will remain in the solution.

Ligand substitution kinetics is considered in designing the chelate group in addition to the factors of operating other parameters, such as time and temperature. The size of target ion metal ions-polymer complex encapsulating the polymer's functional groups is the important characteristic to be considered because the polymer structure is contributed as the medium to trap metal ions (Bell, 2006; Micioi, 2007) in the solutions.

2.3.5 Ligand Composition

As mentioned above, ligand composition and pH are prominent factors in environmental remediation in chelating polymer selectivity. Metal ion-polymer complex induces precipitation that can be removed from the solution through filtration.

A demonstration of the effectiveness of this ligand-surfactant interaction for separating mobile contaminants from the real waste stream was carried out by Rouse et.al (2004) where Hg(II) ions are removed by obtaining different pH ranges during Hg(II) ions' separation process (Rouse, 2004). Solutions containing Hg(II) ions complex would pass secondary UF stage, allowing retention and reuse of the ligand-surfactant colloid. Removal of metal ions occurs because isolation of the target metal ion from the complex is desirable to allow for ligand and surfactant reuse. As a function of the ligand type, this can be achieved by precipitation, pH stripping, or ligand to ligand exchange (Rouse, 2004).

2.3.6 Synergism

The influence of the binding mechanism of one substrate to another substrate is known as synergism. In one study, synergism involved mercury recovery by employing a PEUF filtration system. In other research, chloride is used as synergism to chitosan polymer to enhance the performance of the PEUF process when applying PEI. It indicates the binding mechanism or contribution of electrostatic attraction and chelating mechanisms at a certain pH range. By using chloride as synergy, successful mercury recovery is achieved as the polymer and synergy dissolved together to enhance the sorption sites capacity in the PEUF system (Kuncoro et al., 2005).

2.4 Studies of Polymer Types Used in the PEUF Process

2.4.1 Overview

Glucose units combined with glycosidic bonds structures are formerly known as carbohydrates, and the structure developed is starch or amylum. Starch is a polysaccharide produced by green plants as energy storage contained in staple food, such as potatoes, wheat, maize (corn), rice and cassava.

Pure starch is a white, tasteless and odourless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear helicalamylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight (Brown, 2005).

The unique criteria of unmodified starch are that it is an inexpensive agricultural material and is environmental friendly; these are the reasons for introducing this polymer into the PEUF system. Although it is preferable to modify starch to improve its end-use properties, it can even be used without modification in the separation process. Hence, unmodified starch was proposed in this study to make the ultrafiltration system more complex towards the metal ion-polymer interaction.

There are a limited number of studies on cation binding by starch in the previous decade. Hollo et al. (1962) suggested that cation binding was related to phosphate content of starch (Hollo et al., 1962). Wettstein et al. (1961) showed that divalent cations were bound by cross linked starch phosphate, where selectivity increased in the order Zn < Ca < Ni < Cu (Wettstein et al., 1961). One of the most important findings has been that the adsorptive affinity of starch towards alkaline metals does not markedly affect the species of starch, content of linear fraction, granule size or micellar organization within the granule (Leach, 1961).

Natural starches are mixtures of amylose (10-20%) and amylopectin (80-90%). The long polymer chain of glucose units connected by alpha acetal linkage is the basic structure of amylose. Alpha -D-glucose and all the alpha acetal links connect C # 1 of one glucose to C # 4 of the next glucose in all the monomer units.

Polyethylene glycol (PEG) is a polyether compound also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight. Molecular mass below 20,000 g/mol is referred to as oligomers and polymers. PEG tends to refer to oligomers and polymers with a molecular mass below 20,000 g/mol.

The form of PEG is liquids which are prepared by polymerization of ethylene oxide depending on their molecular weights. PEG is available in molecular weights from 300 g/mol to 10,000,000 g/mol. The form of PEG is highly dependent on the initiator used for the polymerization process; it is commonly a monofunctional methyl ether PEG, methoxypolyethylene glycol, which is abbreviated mPEG. Monodisperse, uniform or discrete are pure oligomers of PEG with low molecular weight and crystalline in the form of high purity PEG, which can be seen by a x-ray to clearly view its crystal structure (French, 2009).

Different geometries of PEGs are also available, such as branched PEGs (three to ten PEG chains), star PEGs (10–100 PEG chains) and comb PEGs (multiple PEG chains normally grafted to a polymer backbone) emanating from a central core group. The weight of PEG polymer is important in determining their melting points.

Branched Polyethyleimine (PEI), which contains primary, secondary and tertiary amino groups, is a liquid at all molecular weights. PEI is known as a cationic polymer. A negative charge at the outer cells attracts to coat the PEI cell which provides a strong attachment of cell and plate. A three-membered ring with two corners consists of -CH_2- linkages and =NH of secondary amine group at the third corner and isconverted into a highly branched polymer (25% primary amine groups, 50% secondary amine groups, and 25% tertiary amine groups).

A highly branched polymer known as "pure polyethyleneimine" is different from copolymers of ethyleneimine and acrylamide. Polyethyleneimine (PEI) used as water soluble polymer in the PEUF system provides electron-donating amino groups whose protonation cause amino groups to become positively charged. This means it is negative to form chelates with cations (Aroua et al., 2007).

2.4.2 Details of Unmodified Starch

Several thousand monosaccharide units contained in polysaccharides of carbohydrate develop the structure called unmodified starch. Polysaccharides are stored to make structural support for plants, human and animals as well as for food and energy.

a) Sources for starch

Starch is found in granules contained in tubers and seed endosperm which typically has several million amylopectin and a small number of amylose. Maize, potato and tapioca are some examples of starch sources (Buleon, 1998). Starch has been recently improved by genetic modification to enhance their function for commercial purposes (Jobling, 2004).

b) Structural unit

The composed starch structure consists of 20-30% of amylose (linear polysaccharide) and 70-80% of amylopectin (highly branched polysaccharide). α-D-glucose units in the $^4C_1$ conformations contains in both starch units where carbon are located in -(1⟶4)- where amylose oxygen is linked at the same side. Carbon at position of -(1⟶6)- forming branch-points with one residue carbon in each twenty units. In hot water, a colloidal dispersion is formed by amylose to thicken the gravies and is insoluble for amylopectin. Figure 2.4 shows the structure of amylose containing in starch.

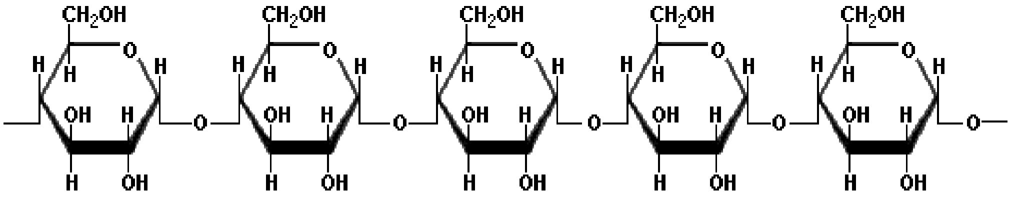


Figure 2.4 Amylose Structure (Zamora, 2012).

A typical helix consists of 200 to 20,000 glucose units for amylose structure as there are bond angles within their glucose units. Highly branched amylopectin are linked with 30 glucose unit at 1α→6 linkages for every twenty to thirty glucose units in their chain, and their structures are able to contain about two million glucose units as shown in the structure in Figure 2.5.

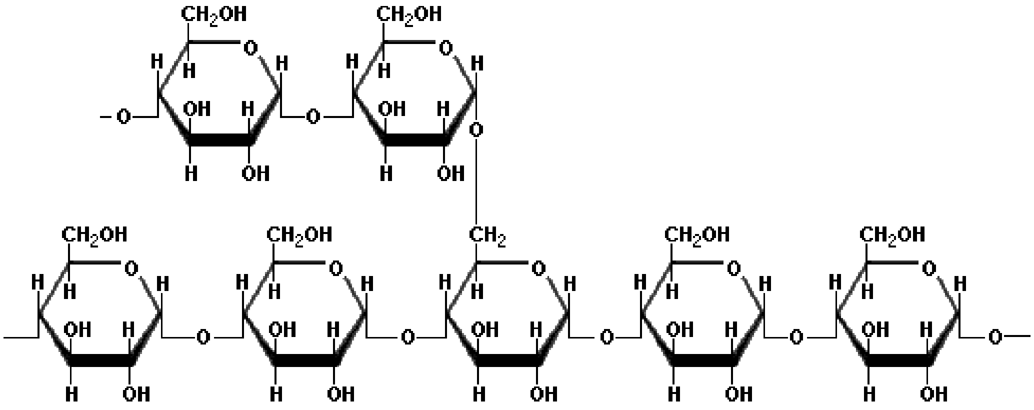


Figure 2.5 Amylopectin Branched Structure (Zamora, 2012).

One of the most important behaviors of natural adsorption by non-ionic starch to bind to target metallic ions is by its granule structure. Figure 2.6 illustrates the details of a starch granule.

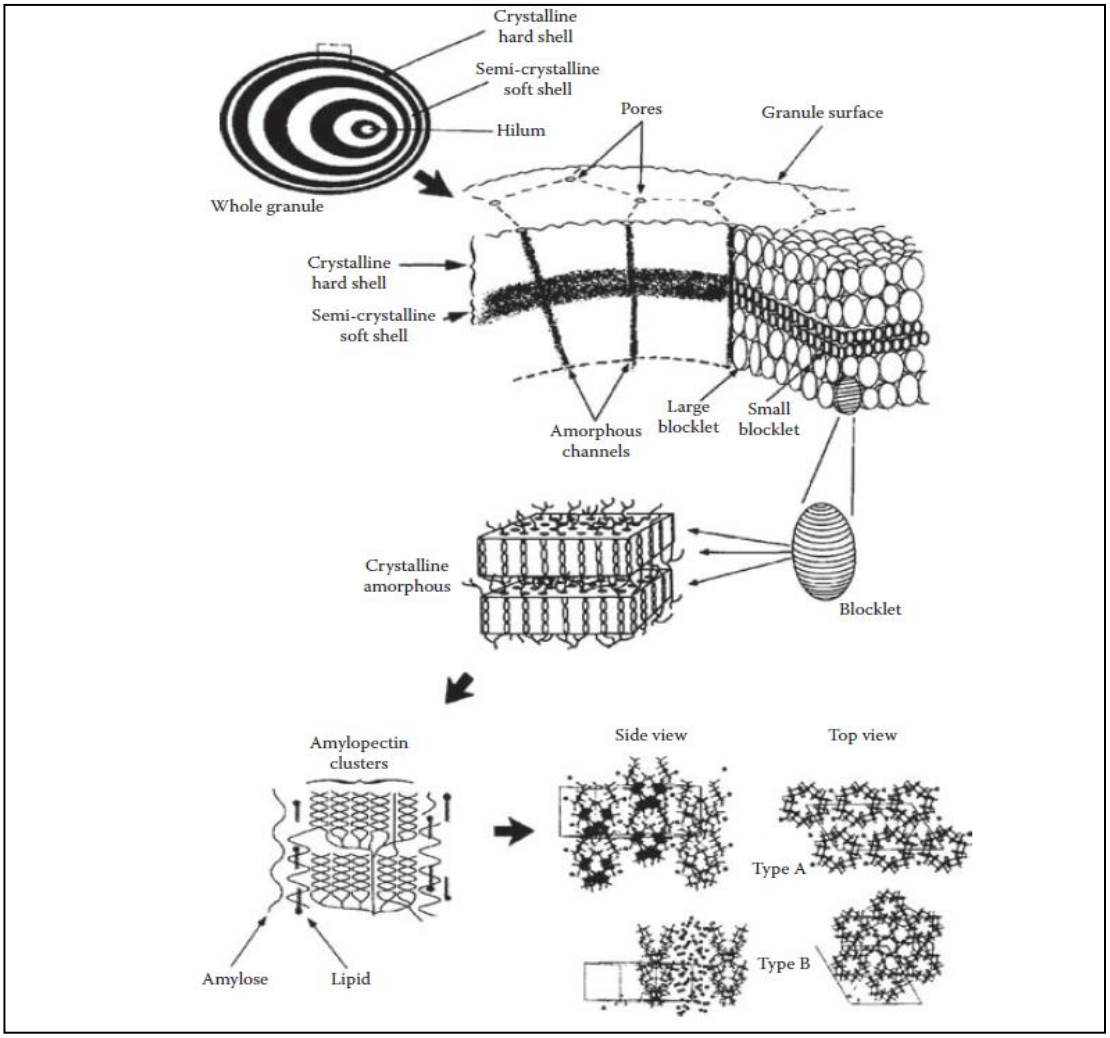


Figure 2.6 Detailed structure of starch granule (Bertolini, 2010).

c) Molecular structure

The shape of amylose and amylopectin are incompatible, as the lower molecular weight of amylose causes their structure to extend their shape in comparison to large and compact molecules of amylopectin. Distribution of starch molecular weight is difficult to determine and generally depends on their structure (Gidley, 2010).

Amylopectin crystallinity tends to be reduced in the presence of amylase. In fact, it causes water to penetrate its surface structure. Free rotation of α-(1⟶4) links around the (φ) phi and (ψ) psi torsions, where between O_3 and O_2 oxygen atoms hydrogen bonding led to stiff helical conformation with hydrophobic surfaces.

i) Amylose

Unbranched chains of amylose molecules have 500-20,000 α-(1⟶4)-D-glucose units mostly dependent on source with α-1⟶6 branches found to be linked with a few phosphate groups (Hoover, 2001) which did not have a significant effect on its molecule's behavior (Buleon, 1998). Extended shape of amylose with a hydrodynamic radius of 7-22nm (Ring, 2001) is estimated to form a stiff single helix on the left side or an even stiffer double helical in its junction sites (Imberty, 1988).

On the outside surface of amylose, O_2 and O_6 atoms bond with hydrogen single helix are consisting with only oxygen located inwards. Double stranded hydrogen bonding chains may cause resistance to amylase, resulting in reaction of hydrophobic behavior with low solubility which negatively influences starch formation.

The inner surface of amylose is hydrophobic which is easily bound to chains of iodine molecules. For example, the polyiodides (chains of I_3^- and I_5^-) are then able to form as I_9^{3-} and I_{15}^{3-}; whereas iodine in I_2 molecules cannot react with amylose unless it is in an anhydrous condition.

ii) Amylopectin

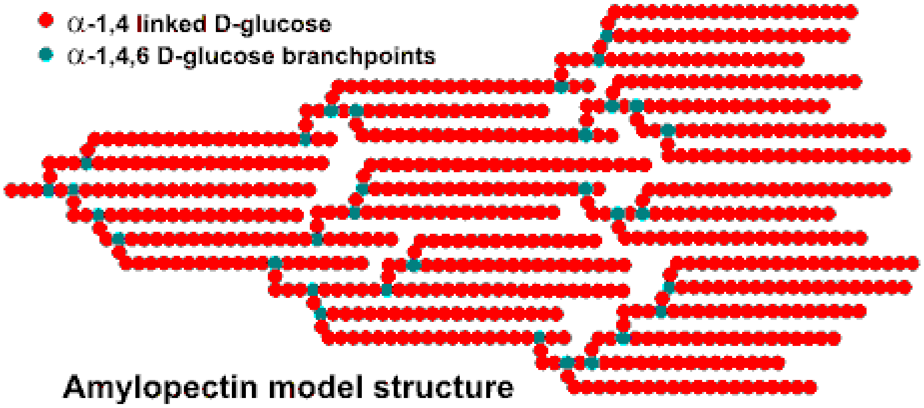


Figure 2.7 Amylopectin structure (Ring, 2001).

α-1⟶6 branching of the amylose-type α-(1⟶4)-D-glucose structure is the base structure of amylopectin (see Figure 2.7). Branching enzymes contain about 30 glucose residues, and only 5% are able to form branch points which can be divided into three; A-chains are outer unbranched chains, B-chains are inner branched chains, and the last group is a single reducing group called C-chains. Approximately 13-23 residues are contained in A-chains (Bertoft, 2008).

B-chains have long and short chain fractions of which more than 23-35 residues of longer chains are connected between clusters whereas the length of shorter chains is the same length as A-chains (Bertoft, 2008). Compact amylopectin (Bertoft, 2008) which contain about two million glucose residues (Ring, 2001) is structured radially with the increase of the radius. In fact, more branches are required to be filled by concentric regions of the crystalline structure (Juna, 2011).

Figure 2.8 shows the details of the amylopectin structure. A: features of amylopectin. B: Light microscopy view of amorphous and crystalline regions structure. C: Cross section of amylopectin granule orientation. D: Double helix structure effects on crystallinity of the granule.

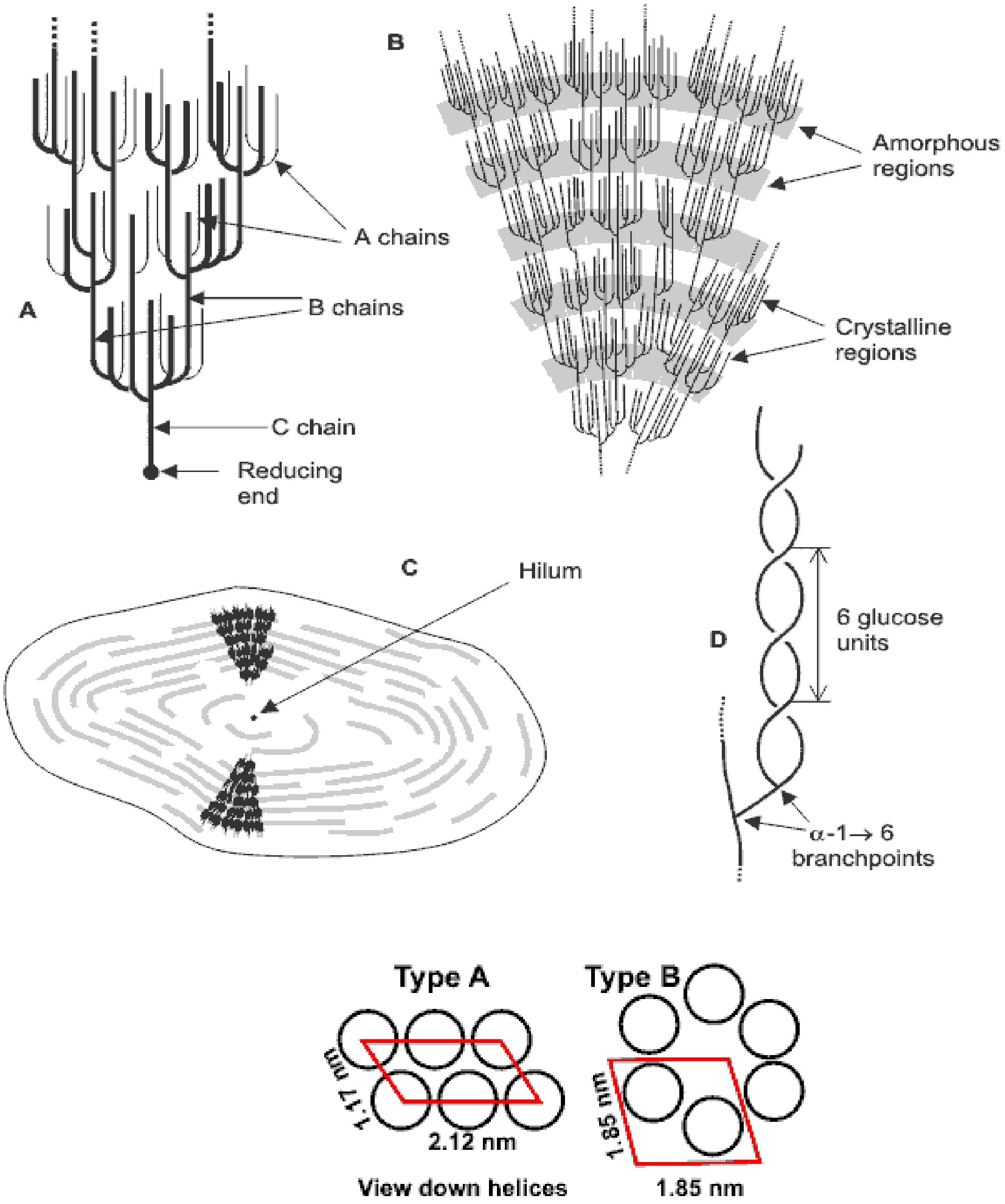


Figure 2.8 Schematic features of different amylopectin structures (Ring, 2001).

Amylopectin has two types of double-helical chains: Type A as denser crystallites with monoclinic packing (depending on plant source granules) and Type B as hexagonal crystallites (Ring, 2001).

23-29 unbroken chain length units of glucose are known as Type A which are mostly found in cereals, whereas 30-44 of slightly unbroken longer chain length units of Type B are found in bananas and cereal. A combination of Type A and B led to the development of Type C structures found in peas and beans (Tang, 2006).

d) Functionality

Water binder, emulsion stabilizer and thickener are examples of starch uses with criteria of versatility, inexpensiveness and availability. Recently, starch functionality has led to further technology applications (Copeland, 2009). Starch is naturally packed tightly into dehydrated granules with specific shapes and various sizes, such as maize 2-30 μm and potato 5-100 μm (Jobling, 2004).

The swelling functionality determined by its sizes are known as A-starch for larger sizes (like a lens) and B-starch for smaller sizes and slightly lower in swelling (spherical shape) (Jane, 2007). Swelling power and gel strength are lower when the starch contains high amylose even at the same concentration. Low swelling power and gel strength are obtained at high amylose containing the same starch concentration.

It can be summarized that amylose is more useful as a hydrocolloid. High viscosity and little effect due to variations in temperature cause extended conformation that has the specialty of a hydrophobic inner surface that does not hold tightly on water. In consequence, high ability to lose their helical chain makes it easier for other soluble substances to penetrate into its surface structure. Starch stickiness may decrease whereas gel firmness increases as with amylose concentration (Chung, 2009). For amylopectin, solutions may loss viscosity and possess slimy consistency as they contribute to interaction of the amylose chain. In regard to control viscosity, starch is partially hydrolyzed where two bonds are hydrolyzed to form dextrin (Qi, 2011).

Unmodified starch used in this research is derived from natural plant sources which can be found easily in tropical Asian countries. No additional chemical is added to enhance the binding mechanism of starch, but unmodified starch still can be bounded successfully with metal ions. The availability, relatively inexpensive costs and simple handling are the criteria behind the selection of starch as a water soluble polymer without modification. The lower feed concentration and final concentration of the sample of metal ions-polymer makes the treated solutions safe for discharge to the environment. The issues on concentration of permeate and retentate metal ions solutions are monitored to remain at a limit of discharged standards. Concentrated metal ions solutions will be recycled back to the PEUF system until the final metal ions' concentration is satisfied to be discharged into bodies of water.

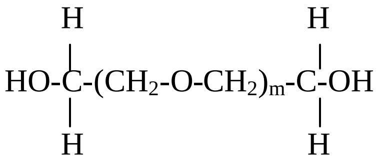
2.4.3 Details of Polyetylene Glycol (PEG)

PEG has a wide range of technical applications as a thickening agent, detergent's additive and for research purposes as it is water soluble (Harris, 1997). The modification of PEG, focusing on the molecular surfaces, may change the solubility that can affect protein adsorption (Blume, 1993; Hinterdorfer, 1996).

Polyethylene glycol with the general formula $H(OCH_2CH_2)_nOH$, is categorized as a condensation polymer, where n is the average number of repeating oxyethylene groups of 4 to about 180. Diethyleneglycol, triethylene glycol and tetraethylene glycol respectively are low in molecular weight of PEG and are known as pure compounds.

a) Molecular structure

The structure of PEG is illustrated in Figure 2.9 where it can be used as an adsorbent to remove metal ions from aqueous solutions.



$$HO\text{-}CH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_m\text{-}CH_2\text{-}OH$$

Figure 2.9 PEG polymer structure

Interaction of PEG is based on the reaction of ethylene oxide with water or on the oligomers of ethylene catalyzed by acidic or basic catalysts. PEG's oligomers, ethylene glycol and its oligomers are preferable compared to water as a starting material because of its low polydispersity as shown in Equation 2.2.

$$HOCH_2CH_2OH \quad + \quad n(CH_2CH_2O) \longrightarrow HO(CH_2CH_2O)_{n+1}H \qquad (2.2)$$

The polymerization mechanism is mostly dependent on whether the catalyst type is categorized as cationic or anionic. In fact, priority is given to an anionic mechanism as it may provide PEG with low polydispersity. Polymerization (polycondensation) of ethylene oxide is an exothermic process. Suspension of polymerization synthesized polyethylene oxide to enable polymer chain growth is called a polycondensation process in which magnesium and aluminium are used as catalyzers, and chelating additives of dimethylglyoxime resist coagulation of polymer in the solution.

2.4.4 Details of Polyethyleneimine (PEI)

Polyethylenimine (PEI) has been widely used in oil-water emulsion and in the paper industry as a flocculant and wastewater treatment (Dautzenberg, 1994). Cationic polymers of branched polyethyleneimine (BPEI) which contain primary, secondary and tertiary amines have buffer pH potential, and polymer protonation behavior has led to its selection as a commercial polymer used for industrial applications (Palmer et al., 1994). PEI copolymer is commonly modified to add value to its performance as a water soluble polymer, especially when tested in a wide range of pH to remove metallic ions from solutions (Labanda et al., 2009).

a) Molecular Structure

PEI has a branched structure resistant to molecule penetration flow through the fiber wall during filtration. Criteria of turbidity of filtrate, charge of the colloidal and characteristics of drainage are the basis to be monitored for optimization of PEI dosage. Heavy metal removal from aqueous solutions employing PEI as polymer, due to their affinity to the presence of an amine functional group, will make it possible for further dissociation of formed macromolecular complexes by their protonation. As the pH of aqueous medium decreases, polymer regeneration and recovery of metal are achieved by the UF process (Canizares, 2002). Application of PEI polymer employed in ink compositions increased water fastness. However, PEI may decrease the dye solubility, or worse, degrade the dye (reduction of the azo-linkage is the chemical group responsible for the ink color by the primary amino-group functional groups of PEI). The pure PEI structure is shown in Figure 2.10.

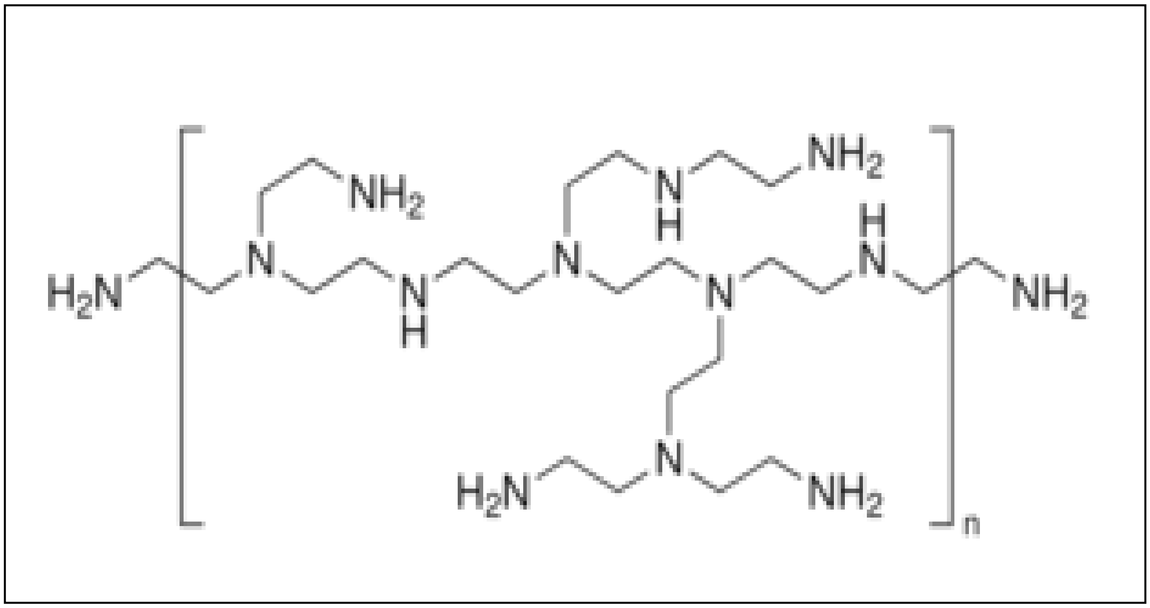


Figure 2.10 PEI polymer structure (Volchek & Dytnersky, 1994).

2.5 Previous work on the applications of heavy metal ion removal by PEUF: Limitation and Gaps

Table 2.6 Previous works on the applications of heavy metal ion removal in single metal ion solutions

Heavy Metals	Polymer	Brief research description	Findings
Single solutions			
1) Cu(II)	Sodium poly(styrene-sulfonate);(PSS)	Ultrafiltration and equilibrium dialysis method, are applied to measure mole ratios by polystyrenesulfonate to total copper (Sasaki et al., 1989).	• Measurement of mole ratios is carried out at range (10:1 to 3:1) at NaCl concentration of 0 to 80 mM. Large retention ratio of 10^3 is measured in the solution containing PSS-Cu(II). • As total concentration of copper decreased, retention ratio was increased. In conclusion, the UF and dialysis are well correlated with the ion-binding model proposed in micellar-enhanced ultrafiltration (MEUF).
2) Cr(III), Cu(II), Cd(II)	EDTA-polyester, DTPA-based copolymer	Investigation on efficiency and selectivity on separations of inorganic ions using polymeric agents with combination by membrane filtration and technique liquid-phase polymer-based retention (LPR).	• Low-molecular substances can be bound to macromolecules by all intermolecular forces (by ionic or complex bonds or the combination of both). • Complex bonds are significantly more selective than ionic interactions. A number of factors influence the interactions and binding conditions: binding degree, pH value, solution composition, and synergism.

		Polysulfone, polyamide, or cellulose membranes with a molecular mass cut-off (MMCO) of 10 kg mol^{-1}in connection with polymeric reagents of molar masses in the range between 20 and 100kg mol^{-1} are employed (Geckeler, 2001)	• Liquid-phase polymer-based retention (LPR) has been shown to be an effective and powerful technology for metal ion separation and enrichment in the homogeneous phase using the environmentally benign solvent water (this method can be an alternative for conventional chemoremediation methods).
3) Pb(II), Ca(II)	Poly(acrylic acid)(PAA)	Removal of Pb(II) ions from hard water by a semi-continuous PEUF system (Canizares et al., 2007)	• PEUF process with PAA is a viable technique for retention and further selective separation of calcium and lead ions. (great difference in affinity of these two metal ions towards PAA). • Optimum pH values making it possible to develop satisfactorily the three stages of proposed treatment are 7 for the concentration stage, 4 for the selective separation stage and 1 for the regeneration stage. The largest discrepancies between model and experimental data appear in the regeneration stage since the model does not take into account membrane fouling at very acidic pH values.
4) Cu(II), Ni(II), Cd(II),	Water insoluble	Water-insoluble starch xanthate was prepared by xanthation of highly	• Starch is crosslinked at 40% solid, followed without isolation by xanthation at 25% solid for 1-4 hr, and the separated product is isolated by spray or flash

Pb(II), Cr(III),Ag, Zn(II), Fe(II), Mn(II), Hg(II)	starch xanthate	crosslinked under various conditions. After isolation of drying or spray drying, their properties were determined. These products were very effective in removal of heavy metals from wastewater (Wing, 1975).	drying. Effluents from the crosslinking of the starch. • Conditions have been evaluated to give a method for making these products on a large scale. • Insoluble starch xanthate has been shown to be effective in removing heavy metals from water to concentrations below established discharge limits.
5) Cr(III)	Polyvinyl alcohol (PVA), polyacrylic acid-co-maleic acid (PACM), polyethylenimine (PEI), ethoxylatedpolyethylenimine (EPEI), polyacrylic acid-co-maleic acid (PACM).	The reversibility of the polymer metal binding was studied by operating in a dead-end operating system. Tubular ceramic membranes of 15 kDa MWCO were used in all experiments (Labanda et al., 2009)	• Complexation and decomplexation of chromium(III) ions with water-soluble polymers (PVA, PACM, PEI and EPEI) were studied under the ultrafiltration technique with two operation modes. • High chromium linked to the polymer surface was identified by high chromium retention values. • For the dead-end mode, comparison of the four polymers showed that carboxylic groups formed stable and irreversible bonds with chromium(III) ions, while alcohol groups did not interact with chromium(III) ions. • The amino groups complex and decomplex these metal ions by means of the formation of chromium hydroxo-complexes with pH. • EPEI was the polymer that best realized both reactions, since EPEI contains amino and alcohol groups in the molecular chains.

			- Chromium ions can be removed from wastewater by complexation with EPEI molecules at pH=5, while these ions can be recovered by decreasing the pH. - At high NaCl concentrations, the chromium retention and hydraulic permeability - decreased slightly by an increase in the membrane fouling.
6) Cu(II)	Poly(acrylic acid) sodium salt	Recovery of copper(II) ions from synthetic aqueous solutions is the main design determined by carrying out metal ion retention, regeneration of polymer and metal recovery by using bench-scale plant configured in a closed-loop equipped with 10 kDa of UF ceramic membrane (Camarillo et al., 2010).	- It is possible to tackle a linear scale-up of a PEUF process for the recovery of metal ions, since permeate fluxes and solute retention coefficients at bench-scale are similar to those obtained in a lab scale installation. For this, it is necessary to use membranes with identical hydraulic diameter and MWCO in both installations. - Increase in membrane length (from 20cm in lab-scale installation to 120cm in bench-scale plant) has provoked neither an increase in pressure drop nor a decrease in permeate flux. Furthermore, introduction of a closed-loop and parallel configuration of different membranes mean important energy savings during pumping. - Technical viability of the metal retention stage during the PEUF process has been proved at bench-scale, since at pH 5.5, 99.5% of copper (II) ions are retained. Moreover, as we have used Colloid 208® as a source of polyacrylic acid, raw materials’ costs

			come down. • Electrodeposition is not only a technically feasible regeneration alternative (reaching very high current efficiencies and with recovery of copper in its most valuable form), but it also avoids the main drawbacks of the chemical regeneration: the high water consumption and the generation of a final process stream to be reused. • Furthermore, it has been verified that polymer does not suffer oxidation or reduction reactions because of the electrochemical stage.
7) Cu(II)	Polyethylenimine (PEI)	The model is studied based on the equation of mass conservation and kinetics molecular complex formation reactions comprising of a metallic ion and a water-soluble polymer. Prediction of the model is according to temporal evaluations of metal concentration in permeate and rejected streams (Camarillo et al., 2012).	• A new kinetic model has been successfully applied to predict the temporal evolution of metal concentration in both permeates and rejected streams of a batch polymer enhanced ultrafiltration process. • Specifically, the removal of copper ions by poly ethyleneimine has been selected to verify its practical application. • This model allows us as well to determine not only the most suitable operating pH values for metal retention (pH=4–5) and polymer regeneration processes (pH=1) at 25 °C, but also calculating pH- and temperature-dependent conditional complex formation constants whose values are significantly similar to those obtained in previous works by means

			of potentiometric and spectrophotometric methods.
8) Cd(II)	Chitosan	The model is obtained to determine the influence of physicochemical and operation variables on metal reduction and productivity of treated water streams. Computations revealed the variables and found that influence are mostly acid and base reagents expended on the process, amount of polymer used and recycling stream flow (Sabate et al., 2006).	• The proposed continuous metal separation process by polymer enhanced ultrafiltration can produce good quality water at high production rates using a convenient polymer–metal system by fixing the appropriate operating variables. Two outcome variables are important: the maximum reachable metal reduction, MR_{max}, and the minimum expenditure of chemicals af_{min}. • The effects of the polymer–metal system on MR_{max} and af_{min} are determined by log β1 and pKa. The most important variable is log β1 whose value directly affects MR_{max}. The effects of the operating variables, pp, ro, and p on MR_{max} and af_{min} are varied and interrelated. Variables pp and ro have similar effects on MR_{max}. • An increase in either allows one to reach a higher value of MR_{max}. The value of af_{min} is inversely affected by pp. As expected, variable p reduces MR_{max} and increases af_{min}. However, it should be pointed out that the intensity of the effect of any of these operating variables on MR_{max} and af_{min} depends on the values of the rest of them. • As a result, the values of operation parameters that lead to the stable attainment of a treated water at a

			desired quality and production is determined.
9) Cu(II)	Poly(vinyl alcohol)(PVA)	The study on removal of cupric ions employed organic UF membrane in polyethersulfone which is complex before carrying out handling of polyvinyl alcohol from aqueous solutions. Metal ions' retention is highlighted by using viscometric and UV–vis spectroscopic analysis initial feed and permeates solutions (Mimoune & Amrani, 2007).	• This study shows the hydrodynamic behavior of an ultrafiltration organic membrane used in the concentration of aqueous solutions of macromolecular complexes of cupric ions and its adaptation in this specific application. • It is shown that membrane surface is modified as of its setting in contact of any macromolecular solution and that the flux through the modified membrane can be improved by cleaning with chlorine. • A relative concentration of the species in the solution, the pH and the ionic strength of the medium influence the solvent flux through the membrane when the cupric macrocomplex solutions are ultrafiltred. • The flow is thus enhanced when the pH of formation of the complex is reached. • It is finally shown that the cupric macrocomplex is most effectively concentrated when its pH formation is reached and that it is possible to meet the best operating conditions without affecting the retention rate by a judicious choice of the applied pressure and the relative concentration of the species in the

			solution.
10) Hg(II)	Polyethylenimine(PEI)	Separation of mercury from aqueous solutions by continuous PEUF was investigated. Polyethyleneimine (PEI) was added to the solutions as a complexing agent before circulating the solution in a laboratory-scale continuous UF system. Effects of mercury-to-polymer ratio, pressure drop and feed solution circulation rate on retention of mercury and permeate flux were studied (Uludag, 1997).	• A constant R value of 0.98 was observed until the mercury-to-PEI ratio of unity, after which R decreased sharply. • Mercury capacity of 1 kg of PEI can be taken as 1 kg of mercury at pH 5 for practical purposes. • Retention of mercury was dependent on the mercury-to-PEI ratio rather than their concentrations. • This enables possibility of treatment of heavily polluted streams via multistage operations. UF pressure drop, feed flowrate and concentration of the species did not cause any change in the R values. • Permeate flux increased linearly with the UF pressure drop. This gives an opportunity for optimizing the process parameters considering only the retention or the permeate flux. • Therefore, it can be concluded that, for determination of realistic metal binding capacities and investigation of effect of operating parameters, the continuous mode of operation is very useful.
11) Cr(III)	Ethoxylatedpolyethylenimine	Recycle polymer is started by desorption of metal ions. For	• The use of EPEI allows a substantial desorption of Cr(III) ion at pH 1, which makes the recycling of the

	(EPEI)	diavalent ions, quantitative desorption is achieved but less desorption for trivalent ions is obtained at an acidic pH value. The sorption isotherms of Langmuir, Freundlich, Redlich–Peterson and Temkin were tested to investigate the binding mechanism of chromium (III) to EPEI (Labanda et al., 2011).	polymer feasible. • The chromium (III)-EPEI bond is well described by the Freundlich sorption isotherm. The permeate flux is favored by low Cr(III) concentration and low pH due to a decline of osmotic pressure across the membrane and membrane fouling. • Intermediate pore blocking is the membrane fouling mechanism that gives a better description of the permeate flux decrease observed in long term experiments.
12) Cr(III), Cr(VI)	Chitosan, polyethyleneimine (PEI) and pectin	Investigation on polymer composition, retention and flux is carried out by employing chitosan, polyethyleneimine (PEI) and pectin at a constant pressure (Aroua et al., 2007).	• This study showed that PEUF is a promising method for the removal of chromium species from dilute aqueous solutions. • Pectin, a new polymer introduced in this research, showed better performance for the separation of Cr(III) than chitosan and PEI. Whereas PEI showed better performance for the removal of Cr(VI) compared to the two other polymers. • pH was found to be the major factor which controls the retention of both chromium species. • For Cr(III), high retentions approaching 100% were obtained at a pH more than 7 for the three tested polymers.

			• Cr(VI) showed different behavior for each type of polymer. • Little effect of pH is obtained for the retention of Cr(VI), which remained almost constant around a value of less than 50% with chitosan and pectin. • An interesting result was obtained with PEI where the retention of Cr(VI) approached 100% at a low pH and sharply decreased at pH 9 and above. This behavior is opposite to what one can expect in the polymer-enhanced ultrafiltration of heavy metals. • The effect of the pectin and PEI concentrations on the retention of both chromium ions are also investigated. A large impact is obtained on the removal of chromium, especially for Cr(VI) retention. The retention increased with the change of pectin and PEI concentrations but reduced when the concentration is very high. • For Cr(III), retention was high and not significantly affected by the change of both pectin and PEI concentrations.
13) Hg(II)	Polyethyleneimine(PEI)	Separation of mercury from aqueous solutions by complexation was investigated. Polyethylenimine	• In an acidic medium, the mercury retention strongly depends on pH and chloride ion concentration. • The zero retention pH varies in the range from 1

		(PEI) was used as a polymeric complexing agent. Effects of pH and chloride ions' concentration on mercury retention were studied (Barron-Zambrano et al., 2002)	without chloride ions and up to 5 for a 1 mol/l chloride ion concentration. • For neutral pH, mercury retention is not affected by chloride ion concentration and the retention reaches values higher than 95%. • Mercury retention close to 100% can be obtained for pH 2-7 if the PEI solution is previously filtered. A process allowing mercury separation and concentration was studied. • It couples two ultrafiltration steps: the first step concentrates mercury/PEI complex and the second one enables mercury separation and polymer recycling. • This process was experimentally tested. In the chosen conditions, adsorption does not affect the mercury concentration step while polymer recycling is accompanied by a non-negligible quantity of metal. • A concentrated solution of mercury (about 10 fold the feed concentration) is obtained in the second stage, and a depleted stream is obtained from the first step.
14) Ca(II)	Poly(acrylic acid–maleic anhydride)	Calcium is found to replace two sodium, whereas two protons replace calcium is	• An industrial grade PAM-Na seems a good polymer to work as a soluble ion-exchanger in the water softening processes.

	sodium salt (PAM-Na)	obtained quantitatively. A two-phase model inspired by ion-exchanger calculations is developed. Prediction of calcium and sodium separation carried out through ultrafiltration in the presence of polyelectrolytes is investigated based on the theory in this study (Sabate et al., 2002).	• The two key features involved are as follow: first of all, the presence of weak acid groups, which tend to easily protonate at low pH values and secondly, its preference to adsorb calcium counter ions more than sodium ones. The model proposed is able to explain the behavior of a PEUF system.
15) Cu(II)	Partially ethoxylatedpolyethylenimine (PEPEI)	Chemical regeneration is employed as an alternative to electrochemical regeneration and results in a decrease of pH effect on reducing the ability to form macromolecular complexes. The following step is used in electrochemical cells for study on metal ion electrodeposition (Llanos et al., 2008).	• The viability of a PEUF process to recover copper using PEPEI as a water-soluble polymer has been demonstrated in the present work. In the metal retention stage, retention coefficients over 97% have been obtained working with a loading ratio of 208mg Cu/g PEPEI, at50 ◦C,$\Delta P = 4$ bar and pH 6. • From this result it can be concluded that the substitution of –NH2 groups by –OH in polyethylenimine does not have a marked negative effect on its capacity to retain copper ions. • The polymer electrochemical regeneration has been tested to verify that PEPEI does suffer neither oxidation nor reduction processes when the target solution is regenerated under our working conditions. • Moreover, the optimal working pH has been

T h e s			determined with studies at a constant voltage. It has been verified that the optimal working pH is higher than that necessary if the regeneration were carried out chemically. • This represents a clear advantage as lower reagents consumption and less extreme working conditions are required. • Furthermore, a used ultrafiltration membrane has been used as cathodic material. Although this option offers the possibility of re-use of this material, low deposition velocities have been obtained which diminish with time on stream. • For this reason, in future works a new electrochemical cell that maximizes mass transfer will be designed in order to achieve higher values of both current efficiency and deposition rate.

The single solution of listed experiments in Table 2.6 were carried out mostly using different heavy metals with combination of modified and conventional polymer such as PEPEI, PAA, PVA and many types of membrane module. Overall operating parameters tested for single solutions of metal ion removal via PEUF were pH, metal ion concentration, pressure, flowrate, time and temperature to investigate retention and flux.

The factors of different polymers are used to provide the binding mechanisms between favorable active groups to metal ions especially in the presence of different charges (metal ions and polymers). Metal selectivity can be improved by selecting the polymer's side chain functionality which can enhance metal ions removal from aqueous metal ions solutions. A number of interactions are possible, but one of the most useful is that of chelation. The two main components that enhance the adsorptive mechanisms are the polymer backbone, which provides the solubility and stability of the reagent, and the functional groups, which are necessary for the selective reactivity of the polymer.

In conclusion, from Table 2.6, the active groups contained in polymers play important roles for metal ions-polymer binding mechanisms. For example, the carboxylic groups of the polyacrylic acid can link metal ions by electrostatic forces and/or formation of complexes by means of acid–base Lewis reactions. Both mechanisms take place in different magnitudes depending on the pH. At a high pH, the contribution of the electrostatic effect is stronger than at a low pH when the formation of complexes is of major importance. The carboxylic groups can act as mono-dentate and bi-dentate ligands according to the amount of oxygen that interacts with the metal ion. Amino groups also form stable complexes with the metal ion according to the acid and base Lewis theory. These complex bonds are significantly more selective than electrostatic interactions.

In consequence, at optimum operating parameter conditions, an increase in the ionic strength of the medium not only acts in reducing the viscosity of the medium, but it also favors increasing the concentration of the polarization layer formation phenomenon. It is finally shown that whenever a macro complex is formed, the most effective retention is achieved when the major parameter, pH, is reached (Mimoune, 2007). Experiments conducted on a laboratory scale have been used before, and common polymer was used as a binding reagent without proposing a new polymer to be used in their works. Performance on retention by modifying polymers in removal of selected metal ion types was almost successful. Most achieved the standard EQA limit of permitted effluent discharge for industries and are allowable for release to water bodies.

Table 2.7 Previous works on the applications of heavy metal ion removal in mixed metal ion solutions

Heavy Metals	**Polymer**	**Brief research description**	**Findings**
Heavy metals mixtures			
1) Ni(II), Cu(II), Cr(III)	Carboxymethyl Cellulose (CMC)	The UF membrane process with polyethersulfone membrane and a 10,000Da cut-off is obtained throughout this study. Experiments are carried out with metal ions in the mixture solution (Barakat & Schmidt, 2010)	• The complexation–ultrafiltration process has been successfully applied for removal of Cu(II), Ni(II), and Cr(III) ions from synthetic wastewater solutions. • Polyethersulfone (FUS 0181) was used as ultrafiltration membrane, while carboxymethyl cellulose was used as a metal complexing agent. • It was shown that the complexation and filtration processes are pH dependent, and the metal retention was more efficient in neutral and alkaline conditions than in acidic. • The metal retention efficiency values with an initial metal ion concentration of 10 mg/L were 97.6, 99.5 and 99.1% for Cu (II), Cr (III), and Ni (II) ions, respectively at pH 7. • The membrane worked efficiently on a wide range of concentrations up to 100 mg/L for both Cu(II)

			and Cr(III) ions, while the Ni (II) ions' retention efficiency decreased to 57%. • The sequence with regards to complexing abilities of CMC were Cu(II)>Cr(III)≫ Ni(II). • The process is characterized by low-energy requirements involved in the ultrafiltration, the very fast reaction kinetics, and the high selectivity for the metal ion separation. • The membrane selectivity was confirmed by the simultaneous separation of the three metal ions in one boot.
2) Cd(II), Ni(II)	Polyethyleneimine (PEI)	Ionic strength, counter ions and pH are the parameters in this study that mostly affect complexation of metal ions-polymer. In this work, the effect of ionic strength on retention of binary solutions of metal ions is investigated (Islamoglu & Yilmaz, 2006).	• Waste waters containing heavy metals may have high ionic strength, therefore investigation of the effect of ionic strength on the performance of selective separation of Cd(II) and Ni(II) by PEUF is important. • Experiments performed with single component solutions of Cd(II) and Ni(II) by using PEI as a complexing agent showed that high salt concentrations (up to 1 N) did not render the complexation between PEI and metals Cd(II) and Ni(II) appreciably. • Selective separation of Cd(II) and Ni(II) may be achieved by changing the pH and salt concentration.

3) Cd(II), Pb(II)	Poly(acrylicacid) (PAA)	Performance of the semi-continuous PEUF process has been investigated for the metal recovery of cadmium and lead from binary mixtures. The proposed process includes three different stages: total retention of metal ions, selective separation and polymer regeneration. For all experiments, polymer concentration (0.1%, w/w PAA), ionic strength (0.15M $NaNO_3$) and temperature (50°C) have been kept at the same values as in single studies. The quotient between both metals was fixed at 1:1 in weight, the feed flowrate was increased to 300 L h^{-1}, and transmembrane pressure (TMP) was fixed at 5 bar (Canizares et al., 2008).	• The optimum value of loading ratio (12.5 mg of each metal ion per gram of PAA corresponding with molar loading ratios of 8.006 mmol of cadmium and 4.344 mmol of lead per mole of PAA) has been established at pH5 for retention stage of both metals. • Also, a pH range of 3.5–4 has been fixed for the separation stage, and pH 2 for the total regeneration stage. • With these conditions, a semi-continuous process comprising of three different stages has been studied. Thus, in the first stage one stream with 12.5 mg/l of each metal is treated and has obtained a retentate stream with 26.7 mg/l of lead and 23.5 mg/l of cadmium approximately. • After that, the separation stage is applied, but it is observed that no pH value allows selective separation. • Finally, total polymer regeneration is carried out. Concentration of both metals after this regeneration in the polymer solution is lower than 7 mg/l, and regenerated polymer can be recycled in a new metal retention stage.

			• In general, a very good agreement between theoretic and experimental data for retention and total regeneration stages has been observed, but the model does not reproduce as well in the selective separation process. • Presence of other metals may influence formation constants, which are introduced as parameters in the mathematical model. • Polyacrylic acid was chosen as a water soluble polymer because it possesses a simple functional group. In order to simulate its behavior, there is a need for the study of new functionalized polymers in the PEUF process.
4) Hg(II), Cd(II)	Polyethyleneimine (PEI)	Polyethyleneimine (PEI) as a water soluble polymer is employed in the removal of mercury and cadmium from the UF system. Two separate streams, namely retentate and permeate, were obtained after running the experiment. The former contains mainly metal–polymer complexes and free polymer molecules, while	• Analysis methods are very important to determine the metal concentrations in permeate and feed streams correctly. AAS can be used successfully to determine the concentrations of mercury, calcium and cadmium at the end of the PEUF experiments. • It was found that existence of one metal did not affect the analysis of others in binary metal solutions. Also, permeate streams contain almost no PEI therefore they cause no deviation from the correct atomic absorption signal.

		the latter contains free metal ions. For the former, the membrane used was Osmonics flat sheet type having a 5 kDa molecular weight cut off. For the latter, it was a Amicon spiral wound (S10Y10) type having an effective area of 0.93 m^2 and MWCO 10 kDa (Muslehiddinoglu, et al., 1998).	• Therefore, there is no difficulty in determining the concentration in the permeate streams. • However, for the samples taken from the retentate streams, the existence of PEI affects the analysis results. • This effect can be eliminated by means of adding a certain amount of HCl to the sample solutions for the mercury analysis in CVAAS. • For cadmium and calcium analyses in FAAS, two approaches using standard solutions containing PEI and no PEI were applied to acheive corrected concentration results.
5) Cu(II), Zn(II)	Poly(acrylicacid) (PAA)	Polyacrylicacid (PAA) is employed in the removal of copper and zinc ions carried out in the batch mode of the UF process (Ruey-Shin & Ji-Feng, 1993).	• Factors affecting retention and permeate flux, such as membrane pore size and applied pressure, were investigated. • The basis of the known chemical equilibrium constants were obtained from a monoionic system. • Prediction of retention coefficient is studied by taking into account separation factor in a bi-ionic solution
6) Zn(II), Ni(II)	Sodium polyacrylate	Hybrid complexation in the UF process is obtained in removing metal ions. The	• The results presented definitely confirm that there is a possibility for applying low-pressure driven membrane operations to separation of Zn(II) and

		research was conducted on synthetic solutions containing Zn(II) and Ni(II) ions by employing sodium polyacrylate as a complexing agent (Korus et al., 1999).	Ni(II) ions from aqueous solutions after their prior linking with macromolecular ligands. • By changing the pH values appropriately, it is possible to carry out the separation of metal ions obtaining high retention coefficients or to decompose polymer–metal complexes which may result in recovery of the concentrated metal present in the feed and regeneration of the complexing polymer applied.
7) Hg(II), Cd(II)	Polyethyleneimine (PEI)	Performance of the continuous PEUF method was investigated for removal of mercury and cadmium from binary mixtures. This method included the addition of polyethyleneimine (PEI) as a water soluble polymer and carried out UF in the laboratory and pilot scale systems. Operating parameters, such as temperature, metal/polymer ratio, presence of calcium ions and pH on retention of metals and permeate flux, were investigated	• Continuous PEUF appears to be an attractive method for the selective removal of mercury and cadmium ions. Effects of various parameters on the performance of this process are investigated in detail. • In the pilot scale system, it was observed that increasing the temperature caused reduction of retention of mercury and an increase in permeate flux. • Presence of calcium does not affect the retention of mercury and permeate flux. • The pH and loading are the most critical parameters in the PEUF process. Effects of pH and loading are analogous on retention of two metals. This means that in all curves, showing retention as a function pH or loading, a flat plateau was observed: A

		(Muslehiddinoglu et al., 1998).	constant R value, about 0.98, was observed until the critical loading or pH values were exceeded. Then, decreasing the pH or increasing the loading ratio resulted in decreasing retention for both metals. • In conclusion, before developing a practical PEUF process, industrial effluents should be studied to see the effects of other contaminants on the separation of target metal ions. • Then, other important factors, such as membrane life time, regeneration of polymeric agents, effect of pretreatment, etc., must be investigated.
8) Cu(II), Ni(II), Zn(II)	Poly(acrylicacid) (PAA)	Cu(II), Ni(II) and Zn(II) ions removed from the model and real galvanic wastewater are investigated by applying the hybrid complexation- UF process. Instar AS containing PAA is obtained as a complexing agent. Porous membranes made from polycaprolactam were used as a membrane filtration medium in the separation process. Water permeability of the membrane was 6.5×10^-^{10} m^3/m^2.s.Pa. UF of the model	• The application of the porous polycaprolactam membranes to metal ion separation was feasible to the use of the agent binding metal to be complex in terms of molecular size which enabled to be retained on the membrane. • A satisfactory value of permeate flux of the model and real galvanic wastewater was obtained. • In the case of the ions examined (Ni^{2+}, Cu^{2+} and Zn^{2+}), separation was effective and the application of the optimum amount of complexing polymer in relation to the amount of metal and suitable pH enabled us to obtain high values of retention coefficients (85-97%). • In summarizing the characteristics of the

		solutions were carried out in the dead-end mode capacity: 400 cm^3, surface of real wastewater was conducted in cross-flow mode (total area of 336 cm^2). Research was conducted on the model and real galvanic wastewater which contained Ni(II), Cu(II) and Zn(II) ions (Bodzek et al.,1999).	membranes made from polycaprolactam, it is necessary to point out their good stability and high chemical resistance marked by a lack of changes in transport and separation properties during all tests carried out.
9) Cd(II), Pb(II)	Poly(acrylic acid) sodium salt (PAASS)	The complexation–UF process was investigated for mercury and cadmium removal from binary solutions by using polyacrylic acid sodium salt (PAASS) as a complexing agent (Jianxian et al., 2009).	• The complexation–ultrafiltration process is viable and suitable to remove mercury and cadmium ions from aqueous solutions with the help of the water-soluble polymeric ligand, PAASS. • At pH 5.5, the kinetics of complexation reactions of PAASS with the metal ions were investigated in the presence of a large excess PAASS. • Effects of various operating parameters on metal retention coefficients were investigated in detail. The binding capacities for PAASS to both metal ions are 1.0 g mercury/g PAASS and 0.033 g cadmium/g PAASS. Compared to the mercury case, the cadmium complexation is more sensitive with changing pH.

			• The influence of the added salt is great at a low pH, whereas the influence is weak at a high pH. Low molecular competitive complexing agents do not affect the complexation behavior of PAASS with mercury but reduce the retention of cadmium. • In the process of the concentration, permeate fluxes decline insignificantly, and retention coefficients of both metals are very high. • In the diafiltration process, cadmium in the retentate can be extracted effectively, and a purified PAASS is obtained. For mercury's case, however, it is the contrary. • At a special pH value, the selective separation of mercury and cadmium ions can be achieved by controlling the concentrations of metal ions and PAASS. Almost all cadmium is in the permeate, while mercury is retained in the retentate.
10) Ca(II), Mg(II), Fe (II)	Polyvinyl alcohol (PVA), Polyethyleneimine (PEI)	In the present study, polyethyleneimine (PEI) and polyvinyl alcohol (PVA) were used as water-soluble polymeric macro ligands. The UF experiments were carried out in stirred dead-end cells.	• Satisfactory results were obtained for metal and COD removal from pulp and paper industry wastewater by coupling complexation with water-soluble polymeric ligands and the ultrafiltration process. • The complexation–ultrafiltration process has increased the final quality of wastewater when

		The membrane used was formed from polyvinilidene fluoride (PVDF). The performance of water-soluble polymeric ligands was evaluated by determining metal removal and chemical oxygen demand (COD) from pulp and paper industries (Vieira et al., 2001).	compared to simple ultrafiltration. The contact time significantly influenced metal removal in both systems (PVA and PEI added wastewater). • In order to assure good water quality with complexation–ultrafiltration, further tests with low cut-off membranes are necessary, and the influence of other operational parameters must be studied, especially for the reduction of the contact time between water soluble polymeric ligands and the wastewater.
11) Pb(II), Zn(II), Cu(II), Ni(II), Ca(II), Mg(II)	Alginate	Removal of divalent metal ions from hard waters or galvanic wastewater by polymer assisted membrane filtration using alginate was investigated. The ability of this natural polymer to form aggregate sand gels in the presence of metal ions were studied in order to carry out metal removal by UF or MF (Fatin-Rouge et al., 2006)	• The use of alginate to soften hard waters and remove Pb^{2+},Cu^{2+}, Zn^{2+} and Ni^{2+} from galvanic wastewater using polymer assisted UF was successfully tested, except for Ni^{2+}. • Treatment in real conditions of natural hard waters by directly adding Na-alginate powder to water and having an alginate concentration $\approx 4x10^{-2}$M was very efficient in terms of permeate fluxes and retention. • In that case, poorly crosslinked agregates were formed, and alkaline earth concentrations were about $8x10^{-4}$M after treatment. The softening can be efficiently carried out in MF as well. • Metal ions have shown the following affinity for alginate: $Pb^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}$

			- Very good retentions were obtained for Pb^{2+}, Cu^{2+} and Zn^{2+}. Alginate regeneration can easily and rapidly be achieved in a strong acid medium.
12) Zn(II), Cd(II)	Diethylamino ethylcellulose (DEAE),poly ethyleneglycol (PEG), dextrin	Complexation of bonding the metals to a bonding agent is a promising process in metal ions' removal by employing membrane filtration. Factors in choosing water-soluble macro ligands play an important role in developing this technology. The effects on type of complexing agent, pH value and applied pressure on retention coefficients of Zn(II) and Cd(II) complexes were investigated (Trivunac & Stevanovic, 2006).	- The results presented confirm that there is a possibility to apply this method for the separation of Zn and Cd ions after their prior linking with macroligands. Flux of purified water and retention coefficients of Zn(II) and Cd(II) complexes, depending on the type of complexing agent, pH value and applied pressure, were investigated. It was concluded that with some care the process could be described by the osmotic pressure model. - In the complexation–filtration process, the strong influence of pH on retention of metal ions was observed. By changing the pH values, it is possible to carry out the separation of metal ions by obtaining high retention coefficients or to decompose macroligand complexes which may result in recovery of the concentrated metal present in the feed, and regeneration of the complexing agent applied. - It was shown that the bonding process was more efficient in alkaline conditions than in neutral or acidic ones. - The lowest retention coefficients were obtained with dextrin, as expected due to its lowest

			molecular weight. Polyethylene glycol performed as a more efficient complexing agent, but the highest retention coefficient was achieved using diethylaminoethyl cellulose (95% for cadmium and 99% for zinc). • The removal of Zn(II) is more efficient than Cd(II) due to its higher coordination ability with macroligands.
13) Radioactive cobalt, caesium, europium and lanthanum	Instar AS (ICSO Chemical Production, Poland) containing sodium acrylatecopolymer,Polyethylenimine (PEI) and cyanoferrates.	Radioactive wastes processing generally employ inorganic membrane in this case; ceramic membranes in NF and UF range are obtained. Non-active and radioactive model solutions and original radioactive waste samples are prepared. The UF process is developed as “seeded UF” to achieve high decontamination which is enhanced by chemical complexation (Zakrzewska-Trznadel, 2003).	• Ceramic membranes in nanofiltration and ultrafiltration pore size range can be used for a removal of radioisotopes in an ionic form only in combination with complexation in which effectiveness is pH-dependent. • Efficiency of removal depends on the complexing agent used, its molecular weight and concentration. • The molecular weight of chelating polymer has to be selected experimentally for each membrane cut-off (Mw dependence on cut-off is not monotonic). • The use of macromolecular ligands improving the efficiency of the UF process results in the need of regular membrane cleaning to avoid decrease of the permeate stream and membrane blockage. • A proper selection of the process conditions (membrane complexing agent, pH, concentration of the ligand) may result in a good purification of the

			effluent, comparable to one-stage reverse osmosis. • The regeneration and reuse require an additional stage of filtration after proper pH adjustment. Another possibility is to use an inexpensive industrial grade complexing agent or industrial by-products, which do not need regeneration.
14) Cu(II), Ni(II), Cd(II), Zn(II)	Partially ethoxylatedpoly ethyleneimine (PEPEI)	Acid-base potentiometry is the initial study before experimental works are carried out on a laboratory-scale study to understand characterization of the polymer and macromolecular complexes. This work obtained the evaluation of effects of pH and loading ratio, (LR) on Cu^{2+} and Zn^{2+} selective separation (Llanos et al., 2010).	• The affinity order of PEPEI towards four industrially valuable metal ions, can be established as follows: $Cu^{2+}>Ni^{2+}>Cd^{2+}>Zn^{2+}$. The global complex formation constant (β_{102}) between this polymer and Cu^{2+} is close to two orders of magnitude higher than the rest of the formation constants. • Cu^{2+} and Zn^{2+} selective separation by PSU is technically feasible. • Process selectivity increases with pH and loading ratio, reaching a selectivity coefficient of 12.31 at the optimum working conditions (pH 6, T=50◦C, $\Delta P = 3$ bar; LR = 286.74 mmol $Me^{2+/}$mol PEPEI). • The proposed model accurately adjusts retention coefficients evolution for monometallic solutions, when the pH is close to neutrality. • Prediction error increases at lower pH values. This model also allows calculating complex formation

			constants from metal retention data. • These constants are similar to those obtained by acid–base potentiometry, although constants predicted from UF data are slightly lower. Model prediction is improved when these constants are used, instead of those calculated by potentiometry, as prediction error is lower for all single experimental points.
15) Cu(II)	Polyethyleneimine(PEI)	The metal ion (Cu^{2+}) is a target metal to be removed by employing a water-soluble polymer (PEI) in this study. The simple kinetic model is proposed as a prediction of copper ions in permeates and retentions on streams for conditional formation constants of PEI–Cu macromolecular calculations. The theory of metal ions complex formation influenced by the pH value in the reaction of complex formation between Cu(II) ions and amine groups by considering the latter as a polyfunctional	• Permeate fluxes and solute retention coefficients at bench-scale are similar to those obtained in a lab scale installation. • For this, it is necessary to use membranes with identical hydraulic diameter and MWCO in both installations. • Increase in membrane length (from 20cm in lab-scale installation to 120cm in bench-scale plant) has provoked the effects neither an increase in pressure drop nor a decrease in permeate flux. • Furthermore, introduction of a closed-loop and parallel configuration of different membranes mean important energy savings during pumping. • Technical viability of the metal retention stage during the PEUF process has been proved at bench-scale, since at pH 5.5, 99.5% of copper(II) ions are retained. Moreover, as we have used Colloid 208®

		ligand. The ceramic membranes with MWCO 15 kDais obtained an effective membrane area of 0.004 m^2 in this research. In order to study the effect of transmembrane pressure, polymer concentration and feed flow rate on permeate flux, and a series of previous experiments in the total recirculation mode were accomplished (Camarillo et al., 2010).	as a source of polyacrylic acid, raw materials costs come down. - Electrodeposition is not only a technically feasible regeneration alternative (reaching very high current efficiencies and with recovery of copper in its most valuable form), but it also avoids the main drawbacks of the chemical regeneration, this is to say, the high water consumption and the generation of a final process stream to be reused. - Furthermore, it has been checked that polymer does not suffer oxidation or reduction reactions because of the electrochemical stage.

For mixture solutions, the overall procedures, such as operating parameters, selected heavy metal ions, or membrane types, are similar to single mixtures but are more complicated for mixture solutions. The ability of each metal ion to attract and bind to the polymers has increased or decreased depending on the interaction between polymers and metal ion operating parameters, thus the selection of polymer for mixtures solutions was important in terms of achieving high retention of metal ions from aqueous solutions or real wastewater. Nevertheless for mixture solutions, selectivity coefficients are found in an acidic or alkaline pH range higher than that foreseen for monometallic solutions depending on metal ion and polymer interactions. In contrast, separation was more pronounced at slightly acidic pH values for mixture solutions. The difference because the amount of free macromolecular ligand available to form the weakest complex is smaller if a metal ion with higher preference for polymer is present (Llanos et al., 2010). The factors that influenced the binding interactions (metal ions-polymer) were discussed previously (after Table 2.6). The pH and loading ratio were found to influence the performance of mixtures solutions, as shown in Table 2.7.

2.6 Canizares Models applied as a theoretical model to predict concentration of permeate, retentate and permeate volume of metal ions in comparison with experimental data (Canizares et al., 2004, 2008).

The Canizares Model is simple and easy to apply as the PEUF Model. This method provides the mathematical calculation based on the solution's concentration of metal ions by carrying out the significant parameters of the experimental study either in single or mixture solutions. The important aspects of the Canizares Model chosen in this research study are:

a) Similar experimental procedures based on metal ion removal were carried out by using polymer in the PEUF system, but this model proposed the calculation based on handling similar procedures in larger effluent volumes which have commercial value.

b) The Canizares Model provides two independent formulas for metal retention and polymer regeneration, but polymer regeneration was not an objective of this study. Since retention is most affected by operating parameters in this experiment, the model also provides the same findings as the focus is on retention of metal ions.

c) In the Canizares Model, predictions of metal ion concentration in permeate and retentate solutions can be determined by assuming that polymer dissociation and polymer–metal ion complexes are constant. In this case, it is easier to calculate the theoretical value of metal ion-polymer concentration such as initial feed concentration with application to the Canizares Model, hence comparisons of permeate, retentate and feed solutions can be made between experimental results and theory.

d) Throughout the Canizares Model, the metal retention calculation used a fixed pH. In this study the pH value was 7, resulting in retention at this stage. It was concluded that these models provided the calculation for polymer capacity by applying retention results at fixed a pH of experimental data. In this model, a maximum metal concentration to polymer concentration ratio in the reactor was assumed by dismissing the permeate concentration limit for disposal purposes.

e) They also carried out single and mixed metal ion solution methods in their model in which metal ions are selected as target ions to be removed. The theory of their model is carried out for commercial use as they developed this model by assuming that metal ions can exist in single or in mixed solutions in actual industrial waste streams and perform as larger waste volumes.

f) The assumptions based on the Canizares model fulfill the requirements of this methodology study which are:

(i) Equilibrium is reached whenever operation is started.

(ii) 1:1 to 1:n is the stoichiometries ratio for complexation form.

(iii) In the considered pH interval, the formation of metal-hydroxy complexes is neglected. Metal-hydroxide formation is neglected.

(iv) The reactor behaves like a continuous stirred tank. The operation tank is assumed to be continuously stirred throughout the PEUF process.

(v) The pH value is the same on both sides of the membrane and remains unchanged.

(vi) The complex metal ion retention coefficient is the same as the polymer retention coefficient (meaning that retention is represented by macromolecular complexes of metal ions-polymer) which is carried out at room temperature of 25°C.

g) For mass balance calculation, polymer and metal ion balance can be calculated by setting the working time of operation and can be practiced if handling different contact times as tested parameters.

h) This model omitted the metal ion and polymer charges because the concentration of metal ions and polymer is the only objective in this study and is significant enough to be calculated.

i) If the metal ion concentration is known (in this experiment 10 mg/l is used as feed concentration [M]), the metal retention coefficient can be calculated in any moment as it is an equation of complex analytical resolution.

j) By carrying out the related assumption of the Canizares Model which suits this work, initial metal ion retention, R_0, R_M and R_L, metal and polymer concentrations in permeate stream and permeate volume can be calculated.

k) Since the Canizares model carried out the study of the polymer's acid-based behavior, it is significant to this research that potentiometric analysis of polymer is carried out with or without the presence of metal ions studied potentiometrically and is in same line with the Canizares study. In this case, it is applicable to be utilized in this research (for a calculation of complex formation constants and polymer binding capacity based on experimental results carried out previously).

2.7 Summary highlighting gaps addressed in research

The PEUF system in this study operated at a continuous mode investigating the retention and flux efficiency at different operating parameters: pH, metal ions and polymer concentration. The pH parameter is investigated as the first major parameter before metal ions and polymer concentration are analyzed. The performance of starch as a biopolymer in the recovery of multivalent metal ions, namely Zn(II), Pb(II), Cr(III) and Cr(VI), from aqueous solutions using a PEUF process is investigated and compared to PEG and PEI.

Starch is known as a water soluble biopolymer with excellent binding properties towards metal captions, but starch has not yet been academically tested and explored in conjunction with PEUF without modification by means of using native starch where no changes are made to its granular structure.

A low concentration of unmodified starch is applied to reduce gelatinization behavior. No additional chemicals are added to enhance the binding mechanism of starch but unmodified starch can still be bounded successfully with metal ions. The availability, relatively inexpensive price and simple handling are the criteria behind the selection of starch as a water soluble polymer without modification. The lower feed concentration and final concentration of the unmodified starch used as a water soluble polymer makes the treated solutions safe for discharge into the environment at the end of the PEUF process. The new findings of unmodified starch as a biopolymer for heavy metal removal are incorporated with the existing PEUF model, the Canizares Model, to prove that this biopolymer can be commercialized and used to treat larger volumes of metal waste in the water system.

CHAPTER 3

METHODOLOGY

3.1 Flowchart

This chapter provides the details pertaining to the methodology and procedures adopted to achieve the objectives of this research. The overall steps in the methodology are given in Figure 3.1.

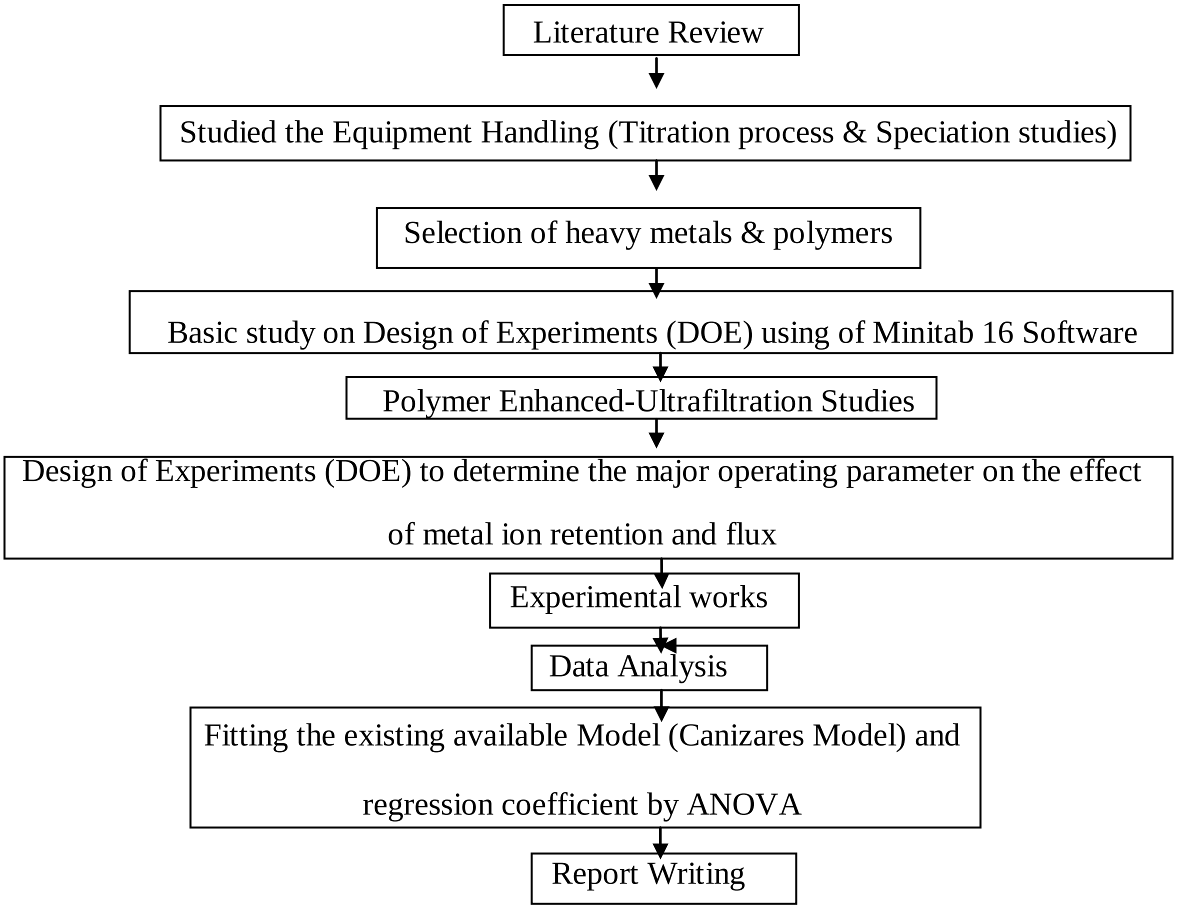


Figure 3.1 Flow diagram of research methodology

The details of all the steps shown in Figure 3.1 are given in the following sections.

3.2 Literature Review

Before starting the research work, a study was conducted on previous research on the PEUF system and polymers used as binding reagents. The guidelines on the gaps and limitation of their studies were benchmarked in this work.

3.3 Study of the equipment handling (Titration process and Speciation Studies)

Analytical techniques on handling the equipment, namely Inductive Coupled Plasma (ICP) and potentiometric titration, were studied at an earlier stage to identify their application in the following research works.

3.3.1 Titration process

a) Potentiometry

The purpose of the potentiometry study is to measure the analytical quantity of various polymer concentration reactions with or without the presence of metal ions carried out in acid-base solutions under the same operational conditions conducted in the experimental study. This study stands independently in the examination of the potential of acid-base characteristics of polymers used in the complexation study. Potentiometry is categorized as a fundamental technique where a variable pH range was tested for investigation of acid-base reactions and at the same time to understand metal-ligand interactions.

b) Chemicals and Reagents used in titration

Titrations works were conducted using the same polymers used in actual experimental works (PEUF system), namely starch, PEG and PEI. Three of these polymers solutions were prepared based on optimum polymer concentrations; they were kept in separate containers and stored in room temperature of 25ºC. Used polymer concentration was 0.05 (w/v) % for starch, 1.0 (v/v) % for PEG, and 0.01(v/v) % PEI. All polymers were used without further treatment.

Simulated wastewater containing heavy metals were prepared for 1000ml of each stock solution containing 1000 mg/l of Zn(II), Pb(II), Cr(III) and Cr(VI) and were diluted using Milipore ultrapure water. Zn(II), Pb(II), Cr(III) and Cr(VI) were prepared using $Zn(NO_3)_2.6H_2O$ (MW: 297.46 g/mol), $Pb(NO_3)_2$ (MW:331.2 g/mol), $CrCl_3.6H_2O$ (MW=266.45g/mol) and $K_2Cr_2O_7$(MW=294.19 g/mol) respectively. These preparations on metal ions solution procedures are similar to those procedures conducted in the experimental works. In contrast, only 10 mg/l are required for each polymer in the potentiometric titration test.

Sodium hydroxide (NaOH) and hydrocloric acid (HCl) concentration of 0.5 M were prepared in potentiometric titrations. During experiments, a carbon dioxide trap is used to keep NaOH free from carbonate during experiments while NaOH beads are held and fitted on flask cap.

c) Apparatus for potentiometric titration studies

An automatic titrator (Auto-tritino 785 DMP Titrino, Methrom) was employed for potentiometric analysis. It was equipped with an electronic burette fitted with a glass-combined electrode. Calibration of the electrode was monitored continuously after using two buffers during titration. Automatic data recording for every change of pH versus acid/base volume made the data more accurate. For data processing, the software provided by Methrom is obtained for titration derivative (dpH/dV) calculation which allows the inflexion points to be visualized. Data was printed automatically via an HP Laser Jet P1006 printer upon the completion of each experiment.

d) Analytical procedures for titration

Measurements were carried out at 25ºC under nitrogen atmosphere using cell analysis which contained 250 ml of the sample. To remove oxygen, nitrogen gas was added into the cell containing solutions. There are three tested polymers, starch, PEG and PEI, which were used for acid-base analysis. Starch titration was done using acid and base because starch generally has a neutral pH. For starch titration, 0.5 M of acid and alkali was applied, and for the PEG test, ionic strength of 0.5 M of NaOH is required since the pH is slightly acidic at pH 6. PEI titration used was 0.5 M of HCl since the basicity of PEI polymer was alkaline. All samples were prepared at pH 7 since high retentions were detected at this pH.

Analysis was done using samples with or without the presence of metal ions at constant volume containing single or more selected polymers. Sample titrations were carried out with carbonate-free NaOH, and stirring was maintained at a pace conducive for solution homogenization.

Curves of derivative titrations were directly recorded. After each additional NaOH solution and concentration of hydroxide ions was calculated, the proton concentration was measured. For the analysis at room temperature, 25ºC, the pKw is found to be ≈13.823 as calculated from the experimental data collection.

3.3.2 Speciation studies

The importance of the speciation studies is to identify the species of metal ions present in solutions and their concentrations at certain pH range. Studies carried out were related to the results and discussions section (in Chapter 4) to justify that the binding interaction between metal ions and selected polymers in the presence of ionic charges in metal ions solutions at a certain pH range will interact with the polymers.

The brief protocol on how to develop metal ions speciation using Visual Minteq Software Version 3.0 is as follows:

pH: Calculated from mass balance

Ionic strength: Fixed at... 0.001

Activity: Davies

Concentration unit: mg/l

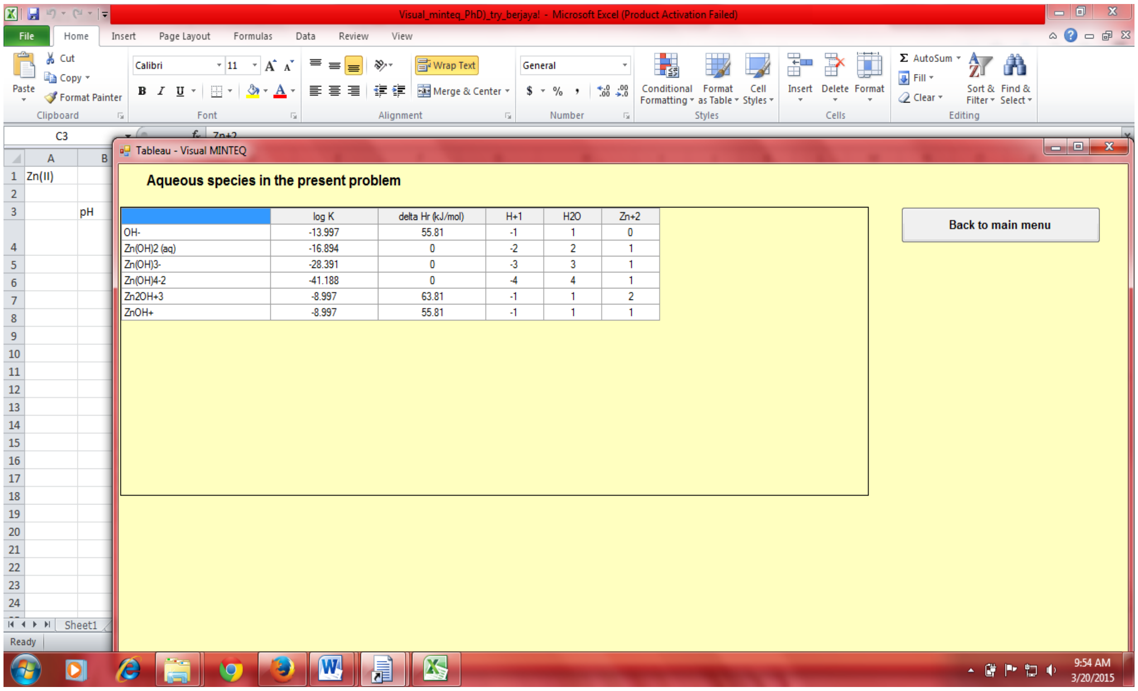
Temperature: 25 deg C

Component name: Zn+2

● Total concentration: 10 mg/l

○ Fixed activity

Figure 3.2 : The example of selection on selected metal ions conditions to develop speciation studies using Visual Minteq Version 3.0



Aqueous species in the present problem

	log K	delta Hr (kJ/mol)	H+1	H2O	Zn+2
OH-	-13.997	55.81	-1	1	0
Zn(OH)2 (aq)	-16.894	0	-2	2	1
Zn(OH)3-	-28.391	0	-3	3	1
Zn(OH)4-2	-41.188	0	-4	4	1
Zn2OH+3	-8.997	63.81	-1	1	2
ZnOH+	-8.997	55.81	-1	1	1

Figure 3.3 : The example of metal ions species presents in unit log K in Visual Minteq Version 3.0

1) Select the menu of pH to be calculated from mass balance and ionic strength= 0.001, choose metal ions species, and set the concentration unit to 10 mg/l with a constant temperature of 25°C.

2) After that, select the ‘view/edit list’ and finally, select ‘species tableau’ and the different species of metal ions presents in different pH ranges are ready to be studied.

3) The data exported to Microsoft Excel were plotted into the graph of metal ions speciation of species concentration versus pH) and data of log K form Visual Minteq Version 3.0 were converted to pH using the common used formula, pH= - $\log_{10}$ [H^+].

3.4 Selection of heavy metals and polymers

The selection of heavy metals and polymers in the investigation of heavy metal waste in water simulated the local wastewater scenario in Malaysian wastewater problems. For polymers, the selection was based on the criteria of least toxicity, local availability and least cost to be applied by comparing with a common polymer used for membrane application in wastewater treatment.

3.5 Basic study on the Design of Experiments (DOE) using Minitab 16 Software

The study on the Design of Experiments (DOE) was carried out using Minitab 16 software by applying Response Surface Methodology (RSM) employed using a Box-Behken method to identify the major factors that may influence retention and permeate flux by identifying important parameters that affect the PEUF performance in this study. The DOE study is important as a guide to determine the required number of experimental runs and the parameters (i.e. metal ions concentration, polymers concentration, pressure and flowrate) carried out for each run. As a result, we can know which parameter has a greater effect on retention and flux in this work.

3.6 Polymer Enhanced-Ultrafiltration Studies

3.6.1 Materials

Simulated wastewater containing heavy metals were prepared for 1L of each stock solution containing 1000mg/l concentration of Zn(II), Pb(II), Cr(III) and Cr(VI) diluted using deionized water obtained using a Millipore water purification system.

For polymer solution preparations, each polymer was prepared by adding 1000 mL of Millipore water and mixed until it is equal to 1L volumetric. These three polymers, namely unmodified starch, PEG and PEI, were kept in separate containers and stored at ±4°C temperature. Sodium hydroxide and hydrochloric acid are used for pH adjustment. Chemicals were used without further treatment. Dilutions and preparation of feed solutions were carried out using deionized water obtained using a Millipore water purification system.

The prepared metal ions concentration is mixed with selected polymers before starting the experimental works based on the parameters tested during that time. The mix of metal ions-polymer solutions will be continuously stirred during the experiment (with the purpose of forming molecular complexes of metal ions polymer), and the experiment is run for two hours.

The membrane used was polysulfone hollow fiber from GE Healthcare (Model: UFP-10-C-MM06A) with an effective filtration area, A, of 26 cm^2 with a molecular cut-off (MWCO) of 10 kDa and pure water permeate flux, J_w, of 0.9421 $cm^3/cm^2.min$ obtained after 20 minutes (stable condition) of operation at 1.5 bar. Polysulfone polymer is selected as the membrane material as it is generally designed for particulate removal from solutions during filtration. It should be noted that this work is carried out using water soluble polymer employing polysulfone as the membrane material, and the focus is not on fouling studies. The work is carried out by frequent backwashing using Millipore water and NaOCl before each run to ensure the pore membranes are not blocked by sample particles. In consequence, water flux also is determined before each run to be no less than 20% of the initial water flux.

A detailed review of the scope of works used in this experiment is shown in Table 3.1.

Table 3.1 The scope of work (chemicals and polymers) used in this research

	Chemicals	**Grade**	**Molecular Weight(MW)**
Heavy Metals	• Zinc nitrate hexahydrate 98% extra pure, $Zn(NO_3)_2.6H_2O$ • Lead nitrate, $Pb(NO_3)_2$ • Chromium(III) nitrate hexahydrate, $CrCl_3.6H_2O$ • Potassium dichromate, $K_2Cr_2O_7$	Analytical from ACROS organics	• 297.46 g/mol • 331.2 g/mol • 266.45g/mol • 294.19 g/mol
Polymers	• Unmodified starch $(C_6H_{10}O_5)_n$ • Polyethylene glycol (PEG 200), $C_{2n}H_{4n+2}O_{n+1}$ • Polyethyleneimine (PEI) 50% (w/v)	• Form of powder • Form of liquid • Branched PEI form of liquid All polymers used were analytical from ACROS organics grade except PEI (Brand Fluka from Sigma Aldrich)	• ≈162 g/mol • 180-220 g/mol • 750,000 g/mol

3.6.2 Experimental Setup

In this study, a laboratory bench system (batch scale) of cross flow filters was employed as shown in Figure 3.2 which consist of the functional ultrafiltration process reservoir feed, retentate and permeates, connections with tubing and backpressure valves, a peristaltic pump, manual pressure control clips, a flow meter with a digital panel meter/display, a stirrer for mixing and a power supply. For all pH measurements, a Methrom pH meter was used.

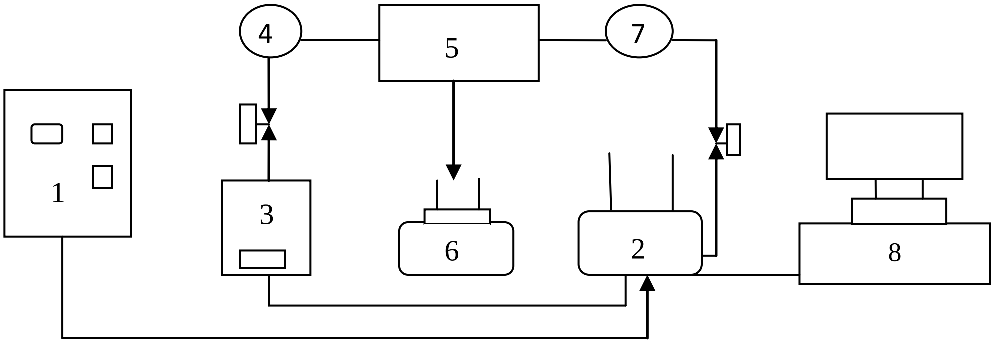


Figure 3.4: Schematic diagram of laboratory-scale ultrafiltration system. (1) – power supply and digital meter of flowrate and pressure (in and out), (2) - magnetic stirrer and 250 ml of feed solutions, (3) – peristaltic pump, (4) – pressure in, (5) – hollow fibre filtration cell, (6) - electronic balance and permeate solutions, (7) – pressure out, (8) - personal computer.

3.6.3 UF Experimental Procedures

a) Retention studies

The Design of Experiments (DOE) done by Minitab 16 software is the first UF experimental step to identify the major factors of parameters (i.e. metal ions concentrations, polymer concentrations, pH, flowrate, and transmembrane pressure (TMP)) which mostly influence the retention and permeate flux in this work. It is also used as a guide for the selection of a wide range of parameters tested to obtain more specific and consistent results. By applying Response Surface Methodology (RSM) from DOE, the exact number of experimental runs and the analysis of the results could be done systematically, and results presented will be more precise.

The highest retention value and flux are obtained after running the experiment based on the Design of Experiment (DOE) from Minitab 16 software. The factors of evaporation and sampling techniques (from feed and permeate stream) influence the deviation of feed solution and metal concentration preparation. Deviations of preparing the sample concentration were due to evaporation and handling techniques while sampling feed and permeate solutions.

Hence feed stream should also be analyzed. Retention values were calculated from the formula:

$$\text{Retention, (R)} = 1- \frac{C_p}{C_f} \tag{3.1}$$

where C_p is the concentration of the metal ion in permeate and C_f is the concentration of the metal ion in the feed.

Permeate flux can be defined as:

$$\text{Permeate Flux} = \frac{\text{Volume of permeate sample through membrane}}{\text{Effective area of membrane filtration x time}} \tag{3.2}$$

Millipore water is used to clean the membrane immediately after the end of experiment by rinsing with Millipore water and a sequence of 0.1 M of NaOH and 0.1 M NaOCl. Water flux is always measured to ensure the cleanliness of the membrane.

b) Polymer concentration studies

For the best identification of polymer concentration for complexation (in percentage) of selected metal ions Zn(II), Pb(II), Cr(III) and Cr(VI), 10 mg/l of synthetic wastewater was prepared in addition to various polymer concentrations of unmodified starch (w/v %), PEG (v/v %) and PEI (v/v %) of 0.01%, 0.05%, 0.5%, 1.0% and 2.0% (measured by weight %). Concentration of each polymer tested was designed using Minitab 16 at the initial experimental stage.

Four species of selected metal ions were added at desired concentrations (optimum 10 mg/l of metal ions solutions) to unmodified starch solution and were stirred for about 30 minutes to enhance complexation within metal-polymer until the equilibrium stage was reached. The pH was kept at a constant pH 7 by using HCl and NaOH for pH control and was continuously monitored during each run throughout the experiment. This procedure was repeated whenever a different polymer was used for the next run.

During the experiment, the UF system was run with constant operating parameters where different polymer concentrations were used with 10 mg/l of metal ion solutions (Zn(II), Pb(II), Cr(III) and Cr(VI)). The system pressure was controlled using the back pressure valve; meanwhile flowrates and feed solution were adjusted by changing the capacity of the pump.

After a two-hour run, the membrane was flushed with an alkaline solution with open circuit (without recycling) prior to subsequent UF. Performance of the membrane was monitored using runs of ultrapure water by Millipore before and after experiments to evaluate permeability after UF runs. Membranes with water flux (J_w) deviation of less than 20% were reused. Metal ion retention which measures the efficiency of the UF system is mainly known as Retentions, (R) (refer to Equation 3.1 for metal ions retentions calculation). Range of value for each parameter tested can be referred to in Table 3.2.

Table 3.2 The scope of experimental work for major parameters tested

Concentration of heavy metals	Concentration of polymer	pH
10, 20, 30, 40, 50 mg/l	Unmodified starch (0.05, 0.525, 1.0) (w/v)% : g/ml PEG (0.01, 1.0, 2.0) (v/v)% : ml/ml PEI (0.01, 1.0, 2.0%) (v/v)% : ml/ml	2, 4, 6, 8, 10, 12

3.7 Design of Experiments (DOE) to determine the effect of the major operating parameter on metal ion retention and flux

Designing the operating parameters is a crucial factor at the initial stage of the experiment before certain parameters have been decided to avoid trial and error experiments and to save the time on experimental works as well.

Industrial physicists can no longer afford to experiment in a trial-and-error manner, changing one factor at a time. DOE provides information about the interaction of factors and the way the total system works, something not obtainable through testing one factor at a time (OFAT) while holding other factors constant.

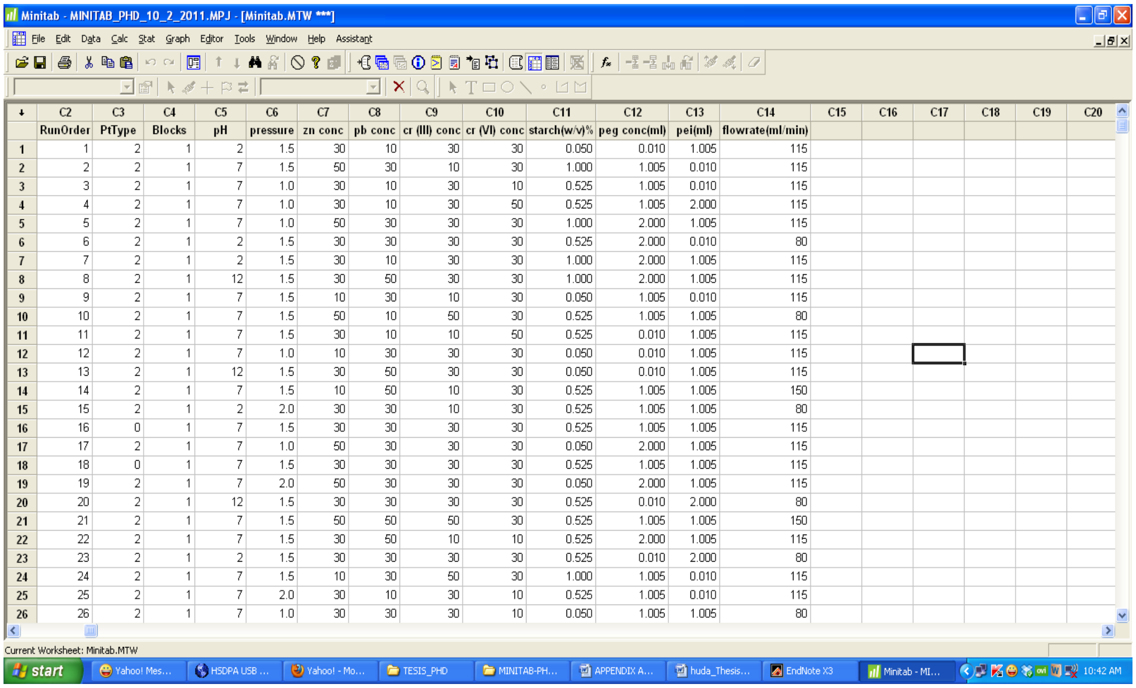
Simple steps for DOE were practiced during this research:

a) Ten wide ranging parameters were designed during the initial stage: pH, transmembrane pressure (TMP), flowrate, Zn(II), Pb(II), Cr(III), and Cr(VI) feed concentrations, unmodified starch, PEG and PEI concentrations (%). The range is based on related literature of PEUF study for metal ion removal using a laboratory scale and also the encountered ability of the equipment itself during UF.

b) As ten parameters with several variables are to be tested, DOE using Response Surface and Box Behnken type of design is chosen to minimize the number of runs needed to identify the major parameters in this work and to minimize the cost of operations. The number of runs is about 500 with a wide range of parameters for single and mixture solutions.

c) Since there are three types of polymer (unmodified starch, PEG and PEI) and four metal ion samples for single solutions, 27 runs x 3 x 4 = 324 runs are required to accomplish an experimental work as only one polymer and one metal ion species is used in each single metal ion solution experiment. For every complete cationic species experiment, we can identify the significant TMP, flowrate and pH which contribute towards high retention and flux. Finally, after significant pressure and flowrate of the PEUF system is obtained, experiment is run based on optimum conditions in this PEUF system.

d) For mixed metal ion solutions, procedures are the same since we carried out the optimum conditions employed in single solutions compared to the performance of four metal ions complexes with selected polymers in one solution. For each selected polymer, 62 runs were required for experimental works; to conduct experiments on three polymers, 62 runs x 3 = 186 runs for experiments were carried out in mixed metal ion solutions and are referred in Figure 3.5.



Minitab - MINITAB_PHD_10_2_2011.MPJ - [Minitab.MTW ***]

↓	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
	RunOrder	PtType	Blocks	pH	pressure	zn conc	pb conc	cr (III) conc	cr (VI) conc	starch(w/v)%	peg conc(ml)	pei(ml)	flowrate(ml/min)						
1	1	2	1	2	1.5	30	10	30	30	0.050	0.010	1.005	115						
2	2	2	1	7	1.5	50	30	10	30	1.000	1.005	0.010	115						
3	3	2	1	7	1.0	30	10	30	10	0.525	1.005	0.010	115						
4	4	2	1	7	1.0	30	10	30	50	0.525	1.005	2.000	115						
5	5	2	1	7	1.0	50	30	30	30	1.000	2.000	1.005	115						
6	6	2	1	2	1.5	30	30	30	30	0.525	2.000	0.010	80						
7	7	2	1	2	1.5	30	10	30	30	1.000	2.000	1.005	115						
8	8	2	1	12	1.5	30	50	30	30	1.000	2.000	1.005	115						
9	9	2	1	7	1.5	10	30	10	30	0.050	1.005	0.010	115						
10	10	2	1	7	1.5	50	10	50	30	0.525	1.005	1.005	80						
11	11	2	1	7	1.5	30	10	10	50	0.525	0.010	1.005	115						
12	12	2	1	7	1.0	10	30	30	30	0.050	0.010	1.005	115						
13	13	2	1	12	1.5	30	50	30	30	0.050	0.010	1.005	115						
14	14	2	1	7	1.5	10	50	10	30	0.525	1.005	1.005	150						
15	15	2	1	2	2.0	30	30	10	30	0.525	1.005	1.005	80						
16	16	0	1	7	1.5	30	30	30	30	0.525	1.005	1.005	115						
17	17	2	1	7	1.0	50	30	30	30	0.050	2.000	1.005	115						
18	18	0	1	7	1.5	30	30	30	30	0.525	1.005	1.005	115						
19	19	2	1	7	2.0	50	30	30	30	0.050	2.000	1.005	115						
20	20	2	1	12	1.5	30	30	30	30	0.525	0.010	2.000	80						
21	21	2	1	7	1.5	50	50	50	30	0.525	1.005	1.005	150						
22	22	2	1	7	1.5	30	50	10	10	0.525	2.000	1.005	115						
23	23	2	1	2	1.5	30	30	30	30	0.525	0.010	2.000	80						
24	24	2	1	7	1.5	10	30	50	30	1.000	1.005	0.010	115						
25	25	2	1	7	2.0	30	10	30	10	0.525	1.005	0.010	115						
26	26	2	1	7	1.0	30	30	30	10	0.050	1.005	1.005	80						

Current Worksheet: Minitab.MTW

Figure 3.5 Example of experimental parameters after design with Minitab 16 before starting the research.

e) All parameters are run, and results for retention and flux are added to columns C15 and C16 for the optimization process. Concentrations of metal ions are analyzed by ICP (Inductive Coupled Plasma) before the calculation of retention and flux.

f) The last part is optimization of operating parameters, and all 10 parameters were set up before the experiments (the following page shows an example of major interactions and optimization results of unmodified starch and Zn(II) ions in the PEUF study carried out in single solutions).

g) After determining all parameters that have a major effect on retention and flux in this PEUF study, the same range of parameters are used to be tested in mixture solutions. The optimization plot of significant operating parameters is shown in Figure 3.6, 3.7 and 3.8. Comparison of the experimental performances of three selected polymers during single and mixture solutions was discussed in Chapter 4.

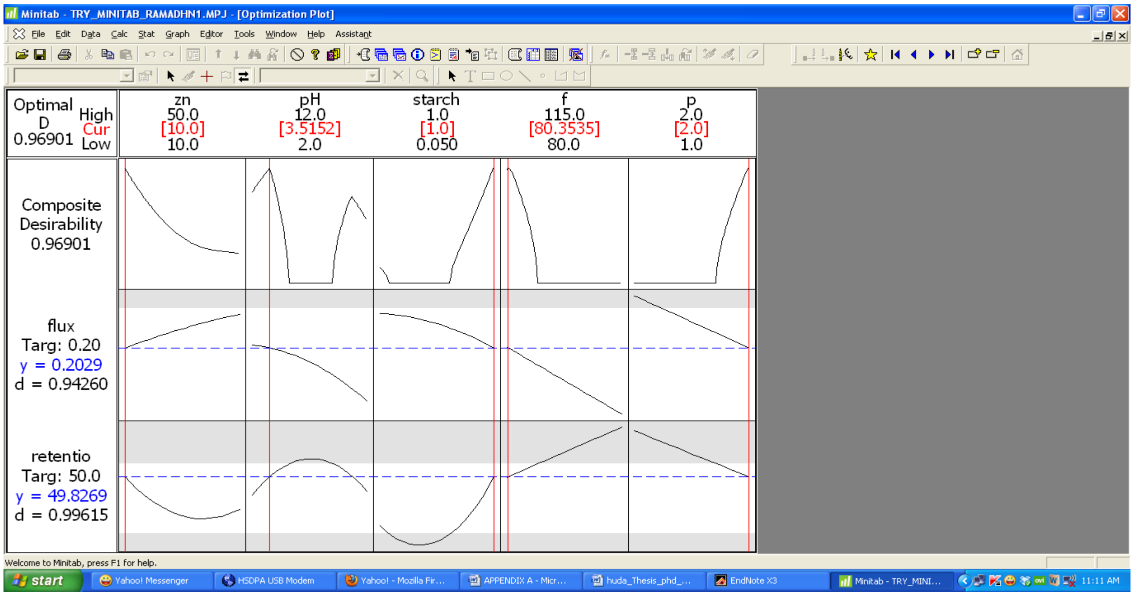


Figure 3.6 Optimization plots of unmodified starch and Zn (II) showing the major effects at each tested parameter range.

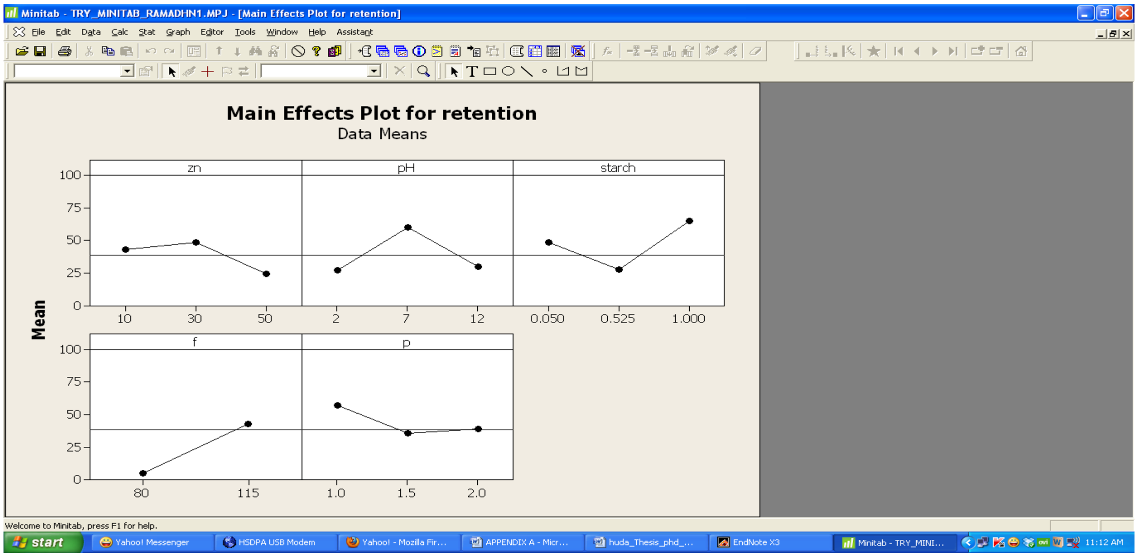
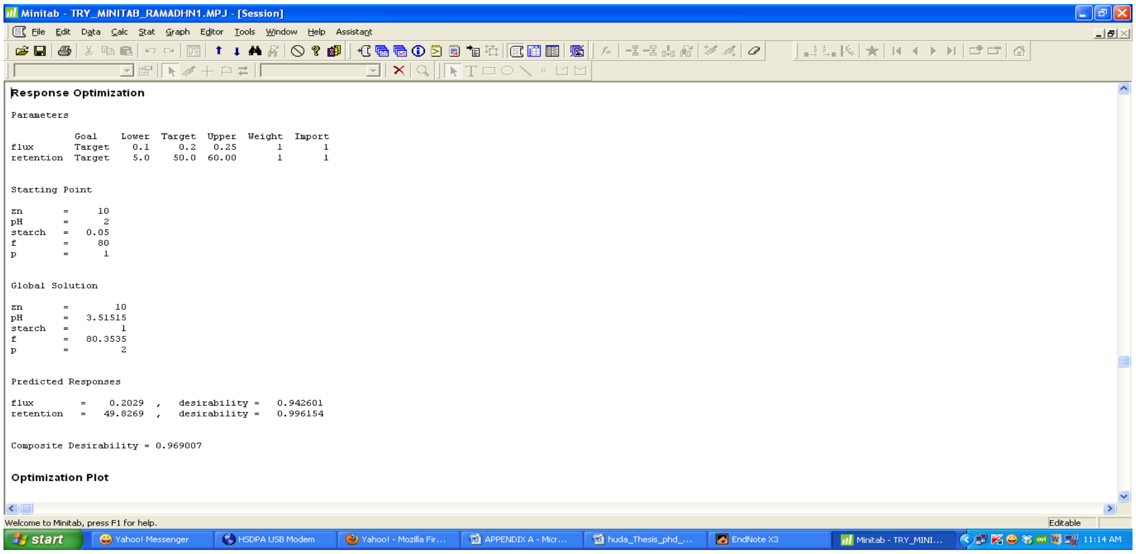


Figure 3.7 The selected range of operating parameters for Zn (II) bound with unmodified starch effects on retention.



```
Response Optimization

Parameters

           Goal    Lower  Target  Upper  Weight  Import
flux       Target    0.1     0.2   0.25       1       1
retention  Target    5.0    50.0  60.00       1       1


Starting Point

zn        =     10
pH        =      2
starch    =   0.05
f         =     80
p         =      1


Global Solution

zn        =        10
pH        =   3.51515
starch    =         1
f         =   80.3535
p         =         2


Predicted Responses

flux         =    0.2029  ,   desirability =   0.942601
retention    =   49.8269  ,   desirability =   0.996154


Composite Desirability = 0.969007


Optimization Plot
```

Figure 3.8 Response optimization using unmodified starch polymer and Zn(II) achieved about 97% in this experimental work, indicating highly accurate results.

3.8 Experimental works

3.8.1 First phase of experimental works (single metal ion solutions)

Zn(II), Pb(II), Cr(III) and Cr(VI) were prepared as single metal ion solution containing the desired amount of water soluble polymer. The pH of the metal feed solutions was adjusted to the desired value by using NaOH or HCl. In this work, low metal ions and polymer concentrations were used to avoid metal hydroxide precipitation that would negatively influence the PEUF system. This can be clearly demonstrated in speciation studies that are explained further in the discussion. For mass of polymers studies, the concentration of polymer used was 0.05 to 2.0 (w/v%, g/mL) of starch, 0.01 to 2.0 (v/v%, ml/ml) of PEG and PEI used are mixed with metal ions concentration of 10 mg/l at a pH of 7. For each selected polymer concentration used for each tested parameter, the polymer was diluted to 100 cm^3 of Ultrapure water at first and stirred together with selected metal ions solutions to be 250 cm^3 of feed metal ions single solutions.

A feed volume of 250 cm^3 containing selected metal ions with polymer was prepared. Monitoring of pH, temperature, feed flowrate and pressure differences were constant and continuously observed during the UF process. In this study, the PEUF process was employed to find effects of important operating parameters for single metal solutions. All experimental work was conducted at 1.5 bar and 115 ml/min of flowrate at room temperature of 26°C with a variation of ±1°C.

The feed metal ion solution was kept stirred and circulated continuously through the peristaltic pump and passed through the hollow membrane fiber for 2 hours over range of experiments. The feed metal ions concentrations are regularly measured using Inductively Coupled Plasma (ICP) before starting the experimental works. For solutions carried out as single solutions, 10 mg/l to 50 mg/l of each metal ions concentration are prepared. For each experimental run (for each tested parameters), the selected polymer concentration is added (based on required concentrations designed using the Design of Experiments (DOE)) and is stirred continuously to ensure the polymers concentration used is favorable to complex with metal ions during the PEUF process.

At the end of the UF experiments, the membrane was immediately rinsed with Ultrapure water obtained using a Millipore water purification system and a sequence of 0.1 M of NaOH and 0.1 M NaOCl.

3.8.2 Second phase of experimental works (mixed metal ion solutions)

Different types of chemicals were used in these experiments. These include analytical grade starch in the form of powder, polyethylene glycol (PEG) 50% (w/v) from ACROS Organics, Polyethyleneimine (PEI) 50% (w/v) as a binding reagent solution, Zinc nitrate hexahydrate 98% extra pure for preparation of Zn(II) solutions, lead nitrate for preparation of Pb(II) solutions, chromium nitrate for preparation of the Cr(III) solution, potassium dichromate for preparation of the Cr(VI) solution, and sodium hydroxide with hydrochloric acid for pH adjustment. Molecular weight of PEG in this work is 200 g/mol, and starch ($C_6 H_{10} O_5$) is 162 g/mol used in powder form. All chemicals obtained from ACROS Organics were used without treatment.

Ultrapure water obtained using a Millipore water purification system was used for dilution and preparation of a feed solution.

A polymer concentration of 0.01 to 1 (w/v%; unit g/mL) of unmodified starch in aqueous water is recommended based on the Design of Experiments (DOE) using Minitab 16 software carried out at the initial stage of research study. The DOE has significant effects on metal ions retention in single metal ions solutions, hence the similar optimum polymer concentration was applied for mixed metal ions solutions. Higher concentrations of unmodified starch can form gelatin that can reduce the flux during the ultrafiltration process. As a result, lower polymer concentration is applied to reduce adsorptive affinity due to gelatinization.

The mixture solutions experiment commenced after accomplishing the investigation of single solutions. Optimum conditions for single solutions (i.e. pH, transmembrane pressure, flowrate, feed concentration and optimum polymer concentration) could be represented for mixture experimental works. In this study, the PEUF process was employed to determine the effect of important operating parameters for single metal containing solutions. All experimental works were conducted at 1.5 bar at room temperature.

In all experiments, the feed volume was 250 cm^3, and the first 10 cm^3 was discarded. During UF runs, solution pH, temperature, feed flowrate and pressure difference were kept constant and monitored continuously. For 2 hours, feed solution was stirred, circulated through the peristaltic pump, and passed through the hollow membrane fiber. Although feed concentration was adjusted for certain concentrations, evaporation may cause deviation of the sample's volume and concentrations due to a sample of the permeate or retentate metal ions solution taken from a container without a proper closing apparatus. To avoid these deviations, proper keeping and handling the samples are required, and storage of the metal ions samples can last no longer than a week in a refrigerator at the temperature ± 4°C.

3.8.3 Complexation–ultrafiltration procedure

The mixed metal ion feed consists of 10 mg/l each of Zn(II), Pb(II), Cr(III) and Cr(VI). The solution containing the desired amount of water soluble polymer is adjusted to certain pH values using NaOH or HCl. Low concentrations of heavy metal cations were used to avoid metal hydroxide precipitation that can interfere with the PEUF process. These can be demonstrated in speciation studies that are explained further in the discussion. For solutions of single metals, 10 mg/l to 50 mg/l concentration of each metal ion was used. Runs with single metal ion solutions were performed prior to those with mixed metal ion solutions.

A feed volume of 250 cm^3 of mixed metal ion solutions was prepared, and an initial volume of feed solution was dispensed. Feed solution was maintained, stirred and circulated through the peristaltic pump and passed through the hollow membrane fiber for a period of two hours.

At first, the appropriate pH solution and polymer concentrations were determined using single heavy metal solutions at a constant transmembrane pressure of 1.5 bar and a constant linear velocity of 4.423 cm/min (based on water flux). All experiments were conducted at room temperature 26°C with a variance of ±1°C. Before the start of each experiment, water flux were monitored at not more than 20% of the reduction from the previous initial water flux reading to maintain membrane performance in the ultrafiltration process. The best pH and polymer concentrations were used in the subsequent heavy metal mixture runs. All experiments were carried out twice, and no significant differences were observed between the two runs.

Statistical work was carried out using Design of Experiment (DOE) by Minitab software version 3.0 for analysis of major operating parameters (pH, metal ion concentration, polymer concentration, flowrate and transmembrane pressure). The major operating parameter was selected from this software for use in the experiments but was not included as much data needed to be analyzed before the experiments began.

To simplify the PEUF process employed in this work, the PEUF process used is a batch scale of polymer solution which is circulated through the UF module. Feed containing the metal ions is introduced into the system, and the ions complex and/or combine with the polymer, so they are reduced in concentration in the permeate metal ions solutions. Over time the polymer will become ‘loaded’ with metal ions, and the batch will have to be regenerated (though this is not part of this study but is included in the recommendations). However to maximize the batch process, the aim would imply that the use of low polymer concentrations is ‘reliable enough’ to remove the selected metal ions since the polymer is continuously added to metal ions solutions to maintain the metal ions-polymer complexation at feed solutions for each run of experimental works.

3.9 Data analysis

Inductively Coupled Plasma (ICP-OES) Optical Emission Spectrometer (Model Optima 7000 DV) from Perkin Elmer is employed for precise analysis of metal concentration in the feed, permeate and retentate solutions. There is a standard use to check the concentration of selected metal ions by ICP. The initial preparation is done before analyzing by using ICP. Volume of each sample is 25 ml, and ICP is set up to then operate automatically after certain data is included in the software. The measure is considered for metal ion concentration in feed, retentate and permeates solutions for each run. For selected metal ions calibration curve, refer to Appendix A.

3.10 The similarities and differences in using single and metal ions solution

The use of single metal ions solutions with (Zn(II), Pb(II), Cr(III) and Cr(VI) ions) by employing three selected polymers, unmodified starch, PEG and PEI, has obtained high retention values of each metal ions solutions tested at three operating parameters (pH, polymer concentration and metal ions concentrations). By using single metal ions solutions, the behavior of each metal ion can be observed individually when compared to polymers (retentions and fluxes values). For mixed metal ions solutions, the presents of (Zn(II), Pb(II), Cr(III) and Cr(VI) ions) in a solution is observed by employing the optimum operating conditions found in single metal ions solutions (to compare the performance of metal ions-polymers complexes).

Mixed metal ions solutions are practical to be practiced in actual experiment (cause heavy metals are found to be mixed in water) which comes from industrial discharged waste. Overall, the research procedures of single and mixed metal ions solutions are similar. However, by analyzing mixed metal ions solutions, we will determine the performance of proposed biopolymer; unmodified starch either to be practically used in the PEUF system or in removal of Zn(II), Pb(II), Cr(III) and Cr(VI) ions in single metal ions solutions (further details are included in Chapter 4 and Chapter 5.

3.11 Fitting the existing available model (Canizares Model) and regression coefficient by ANOVA (Canizares et al., 2004, 2008)

3.11.1 Fitting Canizares Model

The criteria of selection to fit this data to the established Canizares Model caused by parameters tested on Canizares research works were similar to this work with the difference being the use of PAA polymer as the binding reagent in the Canizares Model (Canizares et al., 2004, 2008). In their research, Canizares determined that pH had the greatest effect on retention. Their findings were similar to this experimental work and can be applied to obtain theoretical data as a comparison to the experimental findings (Canizares et al., 2004, 2008). The theoretical data and calculation can be referred to in Appendix B.

3.11.2 ANOVA application for regression coefficient analyses

By using the Canizares Model, the theoretical data could be calculated, and comparisons to experimental data could be made (Canizares et al., 2004, 2008). The ANOVA was used for regression coefficient analysis to identify the degree of difference between the experimental and theoretical data which indirectly shows whether the experiment was successful or not. In ANOVA analysis, a small p-value indicates that there is a small chance of obtaining this data if no real difference exists, and therefore it indicates that expression data is significant. The term ‘small’ indicates a typical P-value of 0.05; on the other hand, if probability of obtaining a P-value more than 0.05 was actually observed that the null hypothesis is true.

ANOVA was the medium used as a guide to check that the experimental work was on the right track by referring to the theoretical data of the established Canizares Model (Canizares et al., 2004, 2008).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results and discussions of the experimental investigation of PEUF of Zn(II), Pb(II), Cr(III) and Cr(VI). This chapter is divided into two sections: the first section deals with the results obtained for single metal ion systems, and the second section concerns solutions containing mixtures of metal ions.

4.2 Single Metal Ion Solutions

4.2.1 Speciation studies

Understanding speciation profiles is important when investigating ionic species reactivity in solutions. Speciation allows for the identification of the forms present at certain pH values. Different chargers of species present at a certain pH that have an interaction with chargers of selected polymers may have developed the binding mechanisms of metal ions-polymer to become macromolecular metal ion-polymer complexes. These macromolecular metal ion-polymer complexes are bigger in size than membrane pore sizes and metal ion-polymer complexes are able to retain on the membrane surface and yet metal ion-polymer complexes will efficiently remove from aqueous wastewater by PEUF system. In this investigation, Visual Minteq Software Version 3.0 was used to produce species profiles for Zn(II), Pb(II), Cr(III) and Cr(VI) at concentrations of 10 mg/l.

4.2.1.1 Speciation profile of Zinc (II)

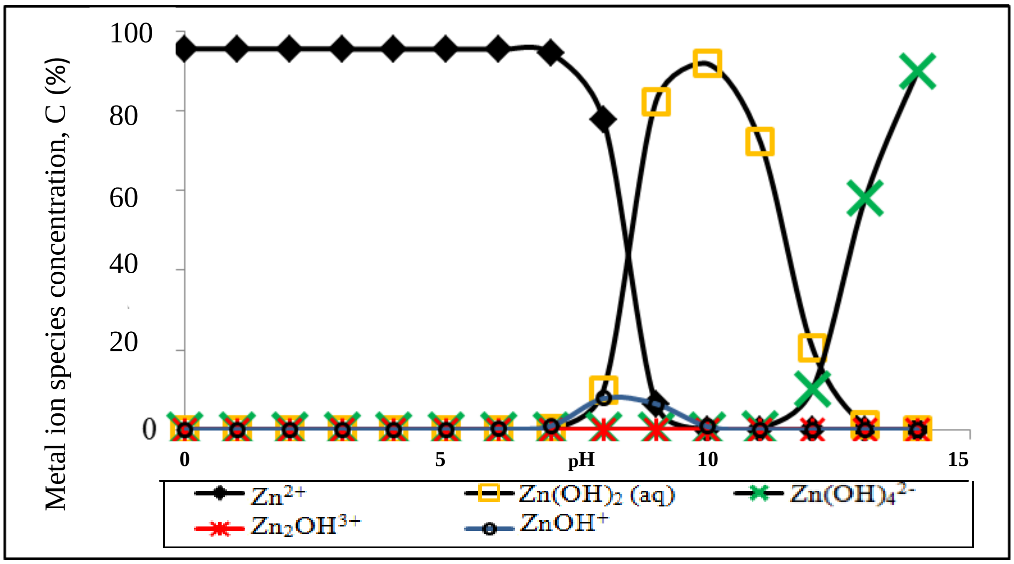


Figure 4.1 Speciation profile of Zn(II) in aqueous solutions

Figure 4.1 shows the speciation profile of 10 mg/l concentration for Zn(II). As shown in this figure, five soluble metal species of Zn(II) were identified, and their presence depended on the pH of the solution. Zn^{2+} appeared as a major species until pH 7 and represented 96% of total zinc concentration. Only $Zn_2(OH)_3^+$ cationic species appeared throughout the entire pH 7 range. In addition to monovalent species, $Zn(OH)^+$ only appeared at pH 8 and pH 9. Insoluble $Zn(OH)_2$ was the major component when the Zn^{2+} species disappeared at pH 10. These species disappeared at pH 13, and Zn(II) took the form of $Zn(OH)_4^{2-}$, which was the only species at pH 13 and above.

4.2.1.2 Speciation profile of Lead (II)

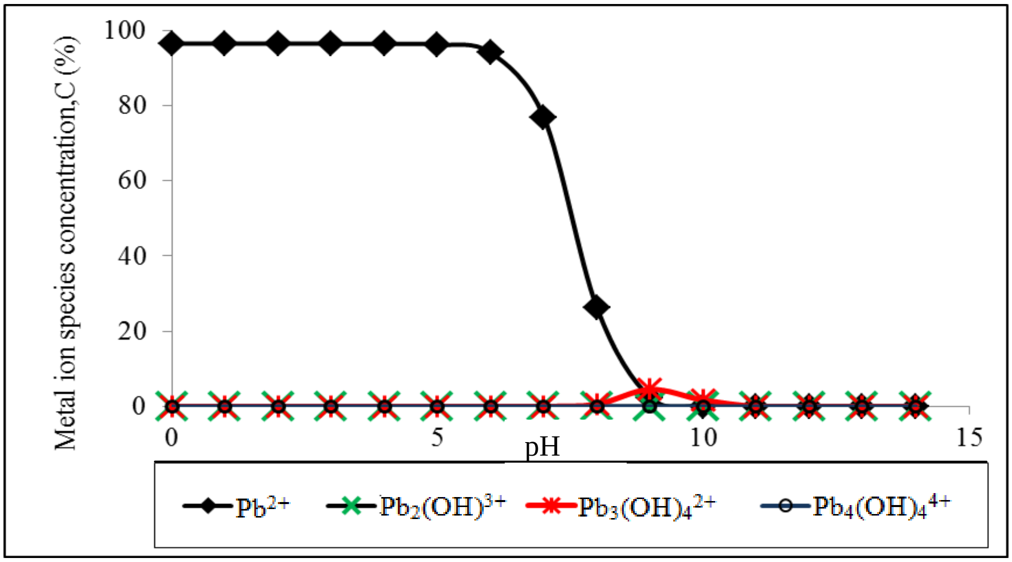


Figure 4.2 Speciation profile of Pb(II) in aqueous solutions

Speciation profiles for Pb(II) are given in Figure 4.2. As shown in this figure, four soluble species of Pb(II) exist at different pH levels.

For pH levels less than 6, about 98% of Pb(II) existed as Pb^{2+}. This species disappeared at pH 9. $Pb_3(OH)_4^{2+}$ concentrations were very low throughout most of pH range with a slightly high concentration at pH 9. The concentrations of the two other species, namely $Pb_2(OH)_3^+$ and $Pb_4(OH)_4^{4+}$, were very low and considered negligible over the entire range of pH values.

4.2.1.3 Speciation profile of Chromium (III)

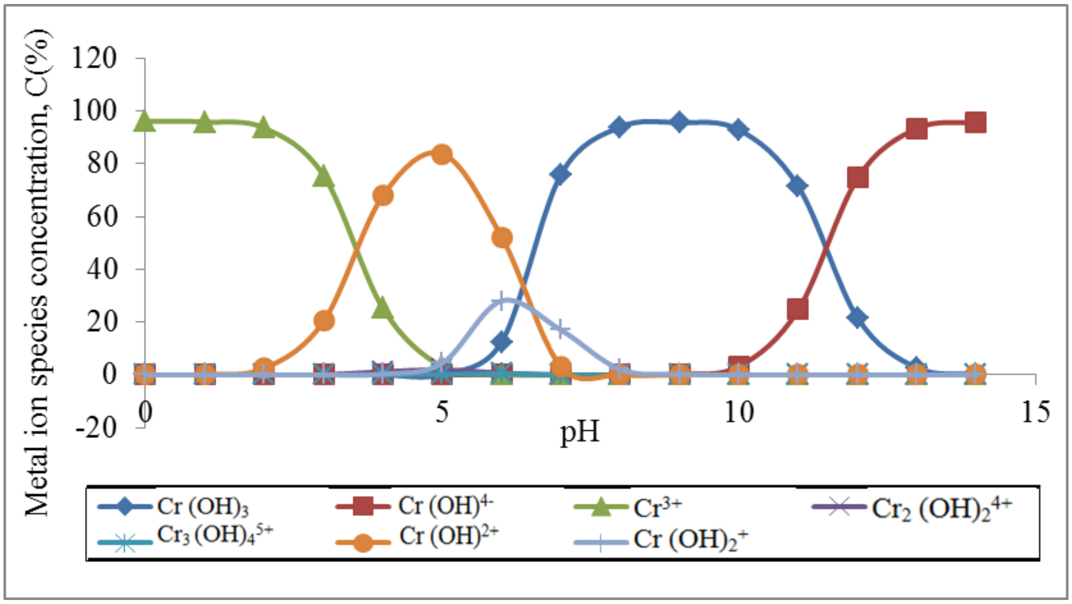


Figure 4.3 Speciation profile of Cr(III) in aqueous solutions

Figure 4.3 shows that Cr(III) existed in solutions as seven different soluble species. The proportions of these species varied with the pH. Up to pH 2, the major species was Cr^{3+}, which represented 99% of the total chromium until pH 5 when it disappears. $CrOH^{2+}$ became the major component at pH 5 then began to disappear at pH 7. Cr(III) took the form of $Cr(OH)_3$(aq), a neutral species, and $Cr(OH)_2^{+}$ a monovalent cation. In the range of pH 8 to 10, total Cr(III) was in the form of the neutral species $Cr(OH)_3$(aq). When pH level exceeded 10, $Cr(OH)^{4-}$ was the only species at pH 13 and above.

4.2.1.4 Speciation profile of Chromium (VI)

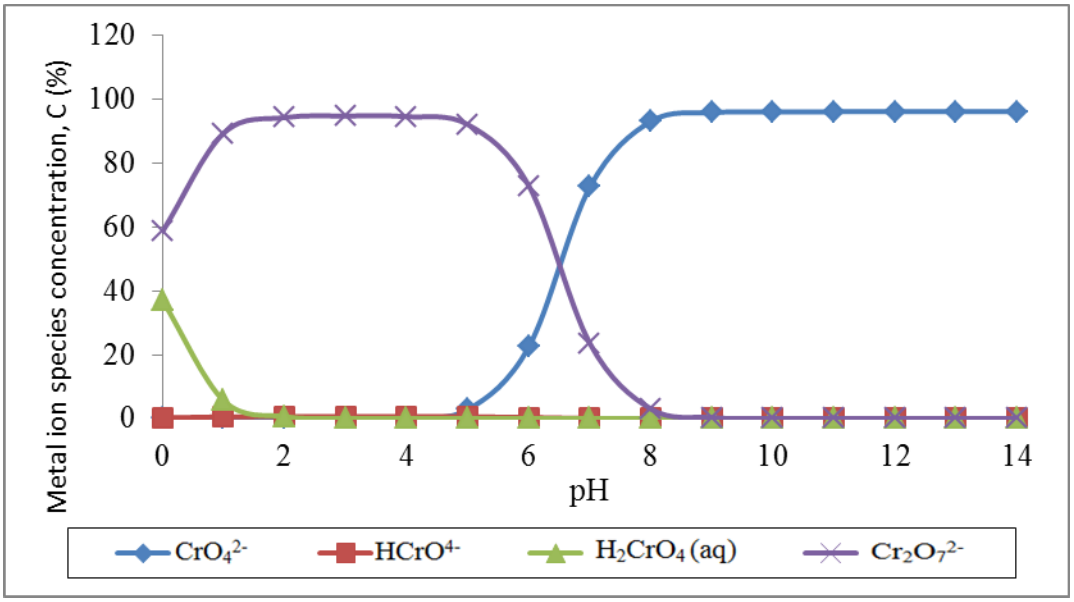


Figure 4.4 Speciation profile of Cr(VI) in aqueous solutions

Figure 4.4 shows the speciation profile for 10 mg/l of Cr(VI) in a 0.001 M solution that was obtained using Visual Minteq Software Version 3.0 as the concentration of Cr(VI) species versus pH. No precipitation of Cr(VI) species was observed in the solution at any pH value. As shown in Figure 4.4, Cr(VI) existed in four different soluble solutions. The proportions of these species varied with the pH. Up to pH 6, the major species was $Cr_2O_7^{2-}$ which represented 96% of the total chromium until it disappeared at pH 9. At very low concentrations of neutral species, H_2CrO_4 (aq) only appeared at pH 1 and 2. H_2CrO_4 existed in low concentrations throughout the pH range (pH 1-14). CrO_4^{2-} species began to form at pH levels higher than 6 and became the only species at pH 10 and above.

4.2.2 Potentiometric Titrations Study

The relative selectivity of metal ions depended on the overall pH of the compounds, thus the acid-base behavior was potentiometrically studied in this research. The effect of pH on the electrode potential at various selected metal ions' concentration of (Zn(II), Pb(II), Cr(III) and Cr(VI)) was studied by titration of the metal ion solution with diluted solutions of 1M HCl or 1M NaOH based on their original pH (to be neutralized by HCl or NaOH).

The strength of an acid or base determines the sharpness of the change (gaps appeared while potentiometrically studying the presence of metal ions compared to non-presence of metal ions to complex with the selected polymer). Wider gaps of graphs patterns (metal ions and polymers) compared to only polymers present in the acid-based solutions means the binding mechanism of metal ions-polymer was effective at a certain pH range. The end point was found by plotting a titration graph and determining the location of the sudden change in pH; the complexation between polymers and polymer-metals was slowest whenever both of the curved lines were close to the end of the titration. The influence of pH and ionic strength on polymeric molecule performance and reaction of selected polymers (unmodified starch, PEG and PEI) with and without presence of Zn(II), Pb(II), Cr(III) and Cr(VI) was clearly demonstrated in the acid-base titration curve in the potentiometry study.

4.2.2.1 Potentiometric titration study on Zinc (II)

Figures 4.5, 4.6, 4.7 and 4.8 represent the titration curves obtained for Zn(II) solutions by employing 1.0 M of HCl and 1.0 M NaOH for titration with unmodified starch. The unmodified starch had an original pH of 7.5 (could be tested by 1.0 M of NaOH and 1.0 M of HCl), while 1.0 M of NaOH was used for titration with PEG (origin pH= 5.5) and 1.0 M of HCl for PEI (origin pH= 10.2).

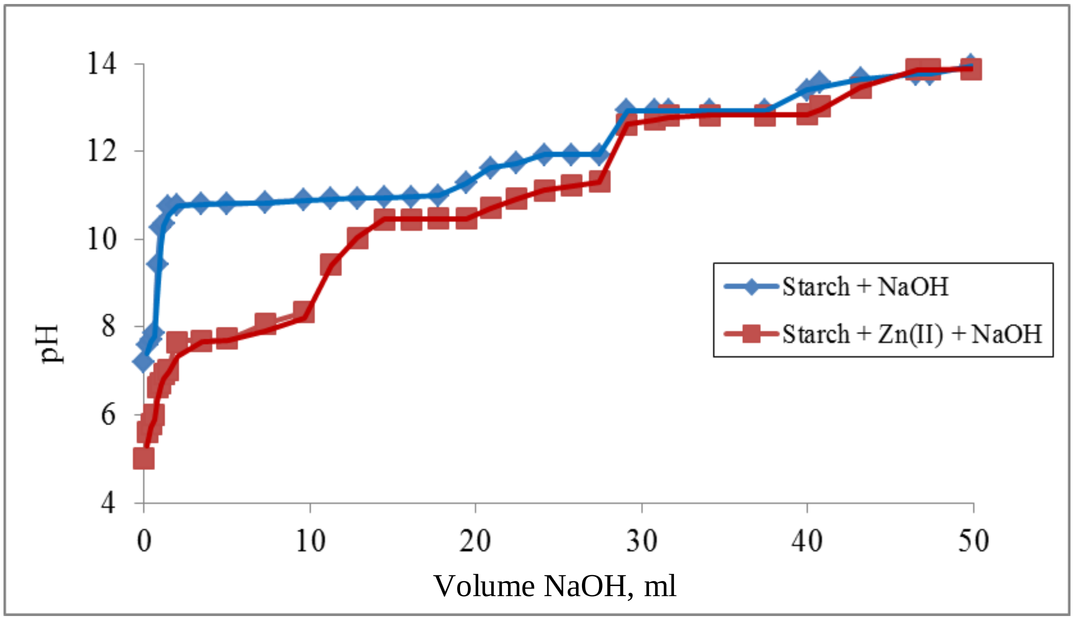


Figure 4.5 Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Zn(II)

As shown in Figure 4.5, the unmodified starch neutralization curve demonstrated dramatic shifts whenever Zn (II) was present in the solution. The shift in neutralization curve indicates that fast complexation occurred at the beginning of the titration (pH> 6). At higher pH values, more gaps appeared which indicated the presence of more complex species of unmodified starches and Zn(II) ions, through the adsorption of Zn(II) ions due to the branched structure of the unmodified starch. The branched structure of the unmodified starch allowed it to crumple, thus providing space for metal ions to penetrate the surface of the granules (Chabot, 1976). Smaller gaps appeared when unmodified starch-Zn(II) reached pH 10, representing the slow interaction of adsorption within unmodified starch-Zn(II). The adsorption behavior became constant at pH greater than 11.

The neutralization behavior of unmodified starch and Zn(II) when employing acid in titration is presented in Figure 4.6. At earlier stages of neutralization (pH 3), there are large gaps between the unmodified starches and the unmodified starches in the presence of Zn(II). Most complexation was extreme at this pH level as Zn(II) is effectively attracted to the surface of unmodified starch to form complexation. This phenomenon occurs at an earlier stage of the curve where it visibly follows the neutralization of unmodified starch alone and is not affected by the presence of Zn(II) ions when the pH level fell below 3.

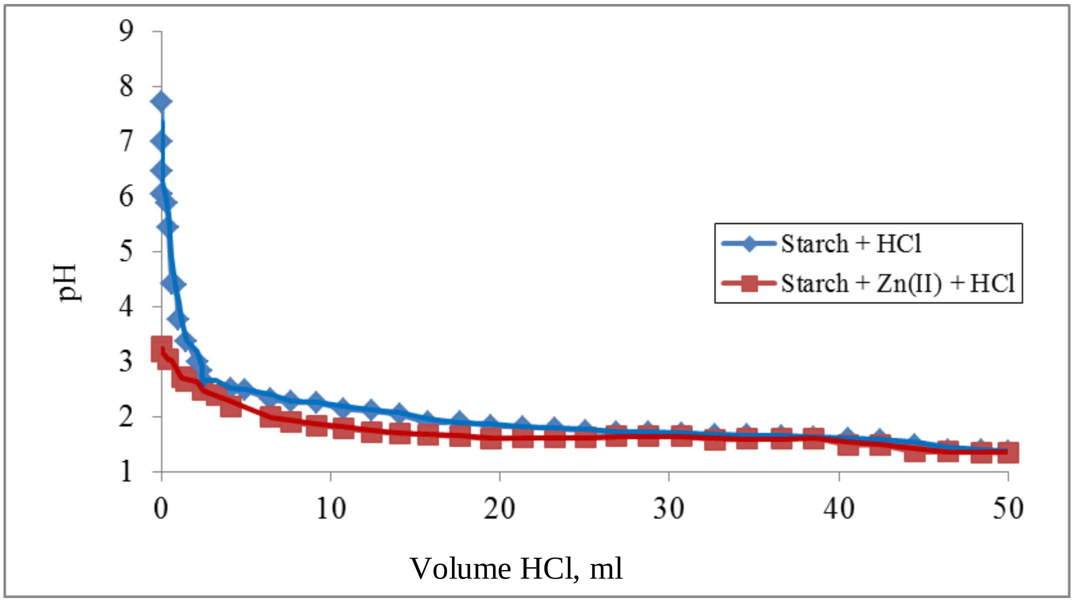


Figure 4.6 Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Zn(II)

The titration curve (V_{NaOH}, pH) at the moment of neutralization between PEG by sodium hydroxide in the presence of Zn(II) ions is presented in Figure 4.7. This titration curve shows wider gaps when initial neutralization occurred at pH>6 compared to PEG alone and in the presence of Zn(II) ions. Due to the attractive mechanism of Zn(II) ions, PEG developed through the adsorption process. The pH remained lower during 'Zn(II)-PEG' titration due to increased interactions compared to neutralization of PEG alone. As pH reached 10, a slower interaction of Zn(II)-PEG can be observed in Figure 4.7 when smaller gaps begin to appear at pH levels greater than 12.

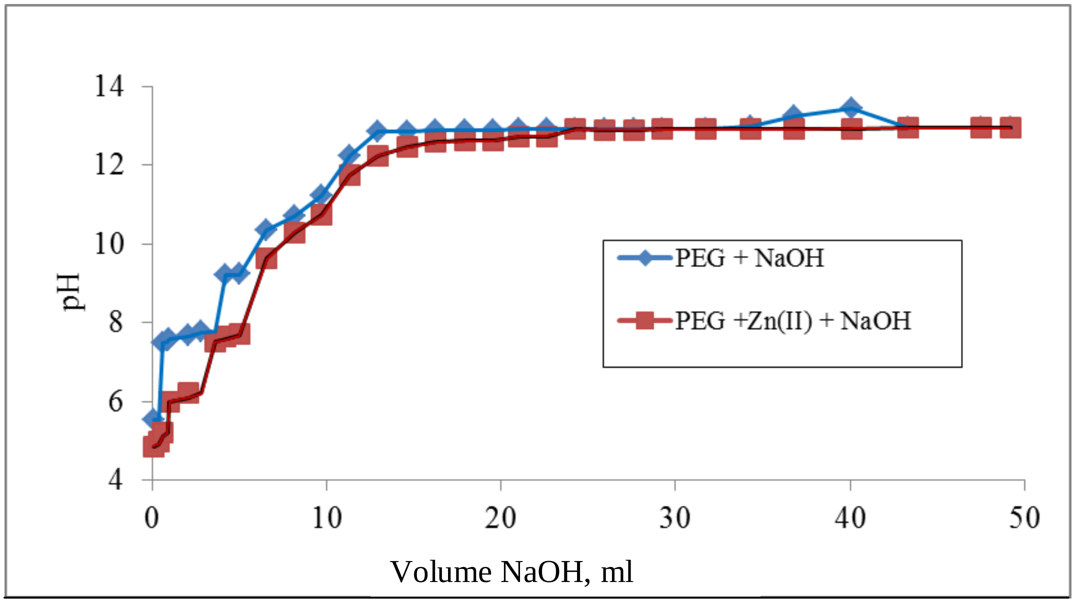


Figure 4.7 Acid-based titration with NaOH of PEG 1.0% (v/v) in the presence of Zn(II)

Different behavior was seen in the case of PEI neutralization using hydrochloric acid in the presence of Zn(II) ions as demonstrated in the curves (V_{HCl}, pH) presented in Figure 4.8. In the titration study of PEI with Zn(II) ions neutralization, the gaps began to appear in the initial titration process and continued until pH 4. As seen in this figure, the wide gaps for PEI alone in the presence of Zn(II) ions appear at pH 6 where the interaction of nitrogen atoms from the two amine functions of the secondary and tertiary amine groups of PEI with the coordination of Zn(II) ions occurs. This indicates that Zn(II)-PEI complexation took place in this range of pH levels.

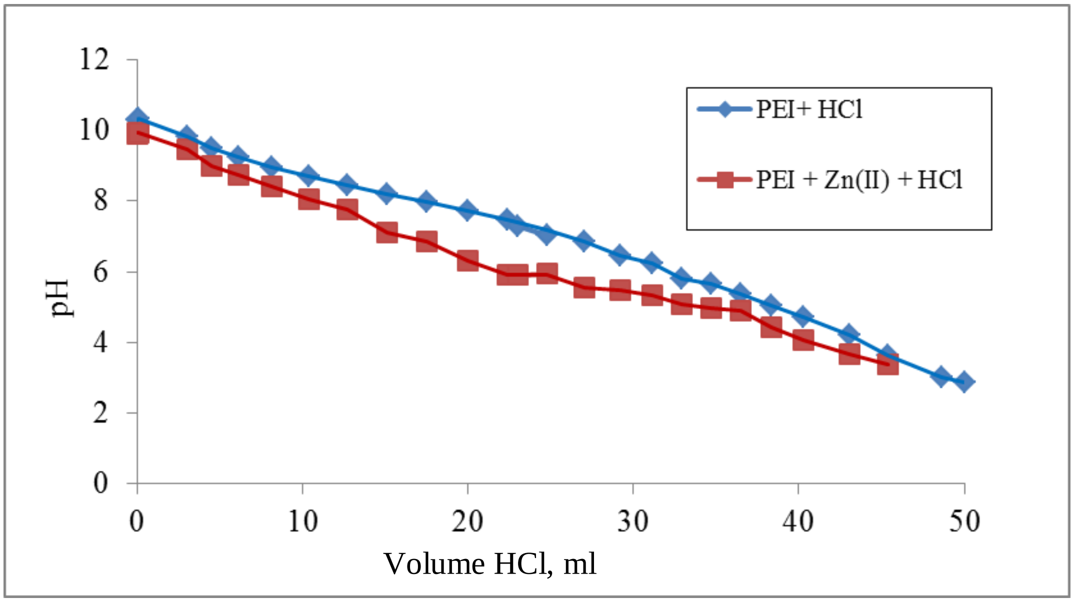


Figure 4.8 Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Zn(II)

4.2.2.2 Potentiometric titration study on Lead (II)

The titration curve (V_{NaOH}, pH) for neutralization using an unmodified starch was carried out using sodium hydroxide in the presence of Pb(II) ions and is presented in Figure 4.9. Complexation occurred at pH>5 of titration due to the dissimilarity between the neutralization curve for unmodified starch and by the presence of Pb(II) ions. At pH levels greater than 8, the gaps indicated greater adsorption of unmodified starches with Pb(II) ions. Adsorption occurred at most pH levels (pH > 9).

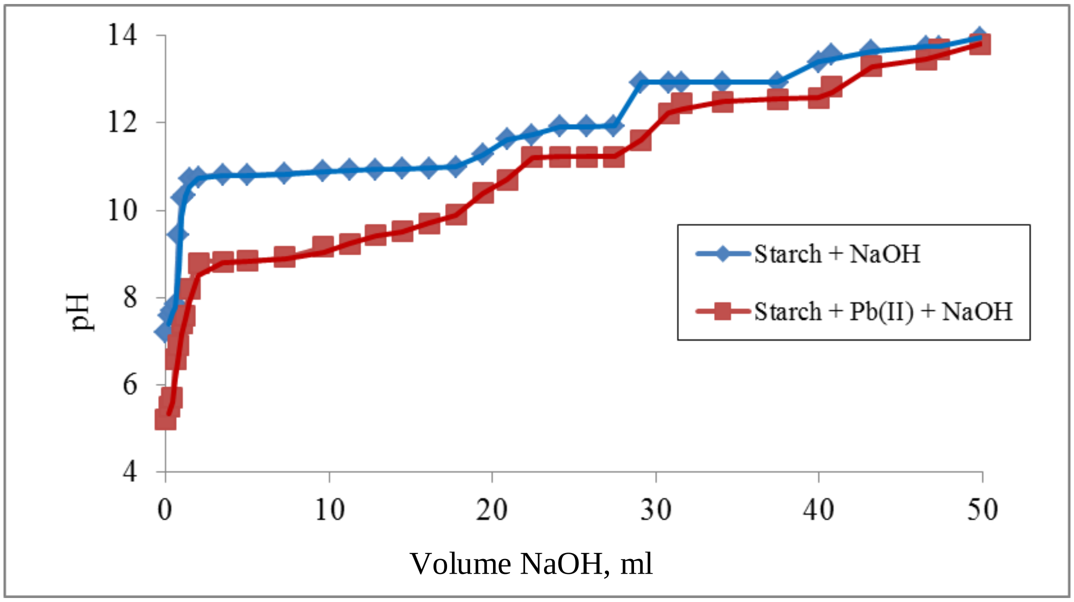


Figure 4.9 Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Pb(II)

Figure 4.9 demonstrates that pH remained low during this high level of interaction within the ‘Pb(II)-unmodified starch’ compared to the neutralization curve of the unmodified starch alone. The smaller gaps that appeared at pH 12 and above were due to most of the available sites on the unmodified starch being filled with Zn(II) ions that contributed to the slow interaction between Pb(II)-unmodified starch at pH levels higher than 12.

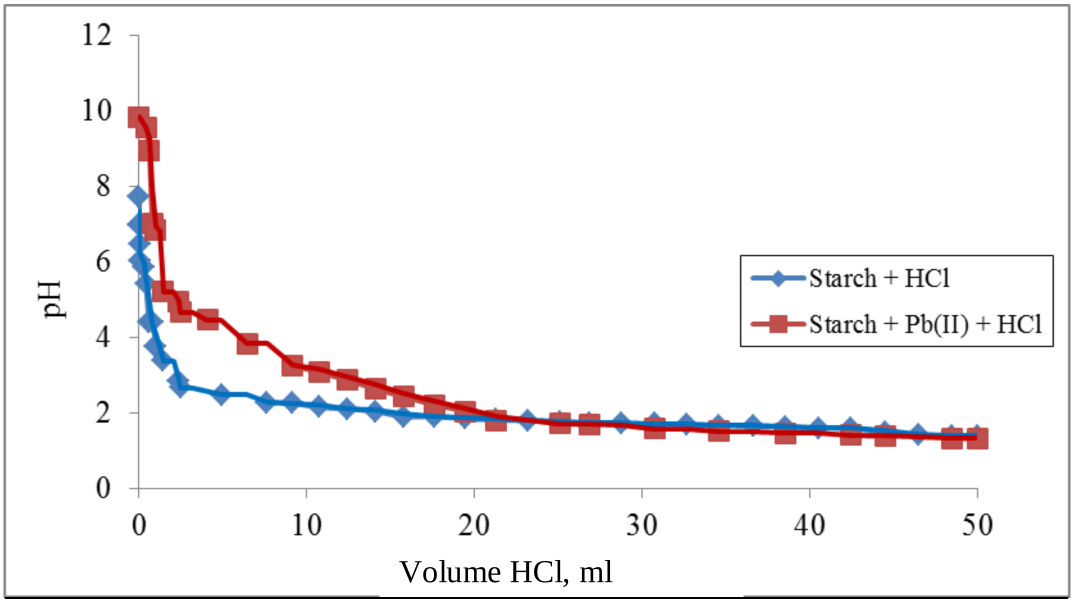


Figure 4.10 Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Pb(II)

In Figure 4.10, the curves (V_{HCl}, pH) for the neutralization of unmodified starches using hydrochloric acid in the presence of Pb(II) ion are presented. At the initial stage of neutralization, gaps that were caused by extensive adsorption appeared. This phenomenon continued until pH 2. The neutral adsorption process of unmodified starch and Pb(II) was slow whenever the curve for unmodified starch alone and the presence of Pb(II) ions was overlapped. Since there were no gaps at all, it can be concluded that there was no complexation at pH levels below 2.

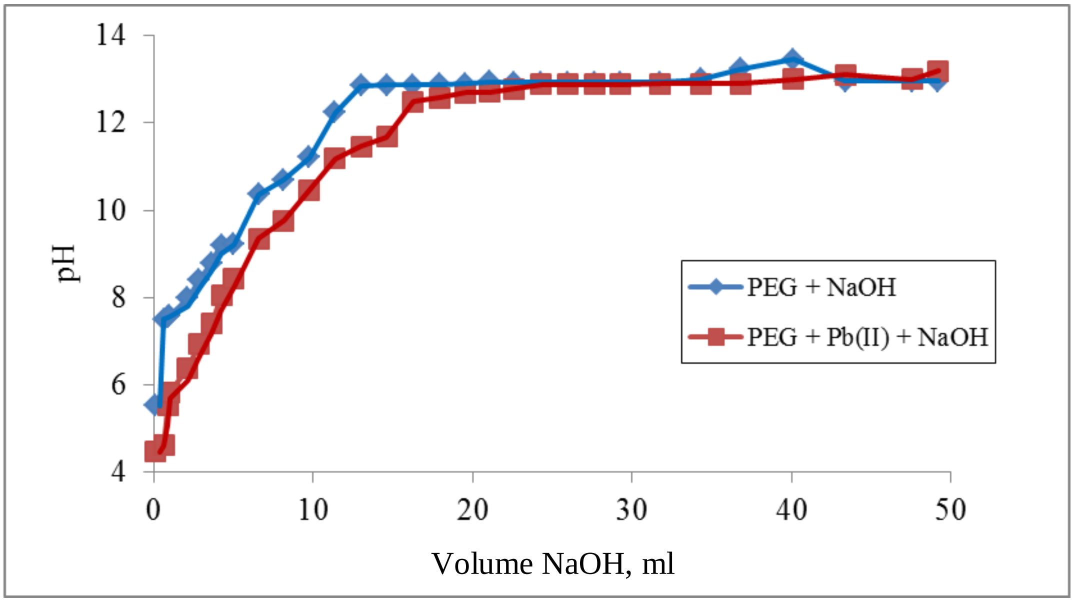


Figure 4.11 Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Pb(II)

The experimental titration curve for PEG using sodium hydroxide in the presence of Pb(II) is presented in Figure 4.11. The same behavior was found during the neutralization of PEG in the presence of Pb(II). The behavior of PEG with Pb(II) is more complex compared to Zn(II) ions. The wide gaps can be seen at the initial stage of neutralization and they continue until pH 13. Most of the gaps appeared at pH >12. Most probably, the hydroxyl groups in PEG effectively form complexation with Pb(II) in an alkaline environment, but as the pH reached levels greater than 13 there appears to be no complexation between PEG-Pb(II) ions.

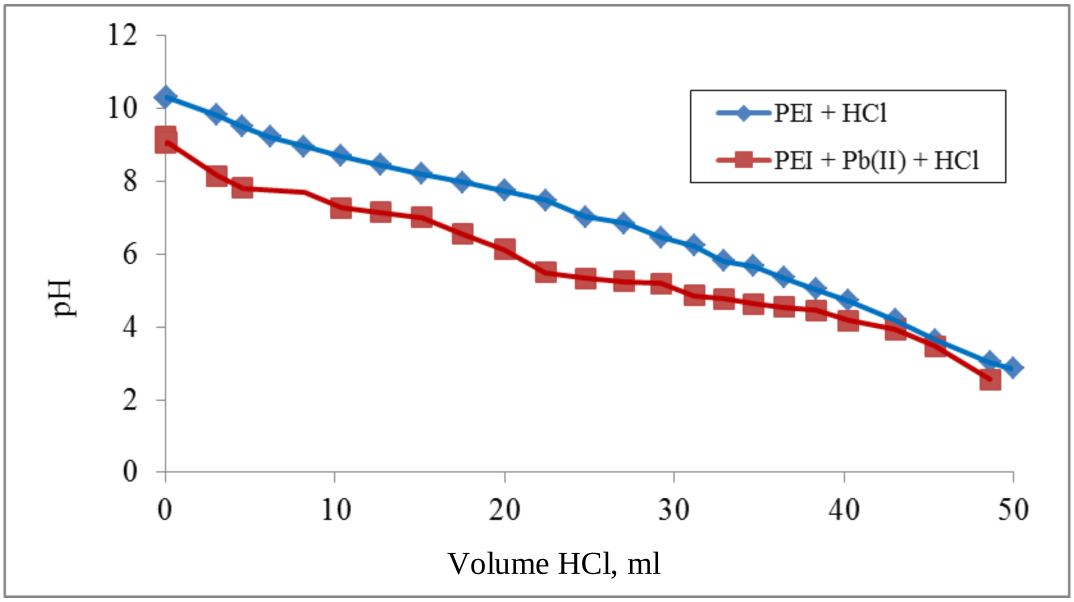


Figure 4.12 Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Pb(II)

In Figure 4.12, a different behavior was observed when PEI was neutralized using hydrochloric acid in the presence of Pb(II) ions as demonstrated by the curves (V_{HCl}, pH). For the neutralization of PEI and Pb(II), gaps appeared at the beginning of titration until pH 4. Extreme complexation was expected at pH> 6 as the curve for the presence of Pb(II) ions was lower than PEI alone. This was mostly due to the high interaction of 'Pb(II)-PEI' which indicates that two amine groups of PEI effectively developed complexation with coordination sphere of Pb(II) ions structure in this pH range (pH > 4).

4.2.2.3 Potentiometric titration study on Chromium (III)

Relative selectivity for metal ions depends on the overall basicity of the compounds, and the acid-base behavior was potentiometrically studied. The effects of pH on the electrode potential for various selected metal ions concentrations of Cr(III) and Cr(VI) were studied by adding diluted solutions of 1 M HCl or 1 M NaOH. The strength of an acid or base determines the sharpness of the change. Based on the acid-base titration curve from the potentiometry study, the influence of pH and ionic strength on polymeric molecule performance is clearly demonstrated by the reaction of selected polymers (unmodified starch and PEG with and without presence of Cr(III) and Cr(VI)).

The titration curve (V_{NaOH}, pH) during the neutralization of unmodified starch by sodium hydroxide in the presence of Cr(III) ions is shown in Figure 4.13. There were no complexations between unmodified starch and Cr(III) in the early stages of titration as shown by the curve of unmodified starch alone with the presence of Cr(III) that had no gaps at all. Complexation occurred at pH>10 as shown by the curve between the two species of unmodified starch alone and in the presence of Cr(III) that depicted more and wider gaps at pH 11-12. This was mostly due to unmodified starches that were able to adsorb Cr(III) ions at this pH level. This phenomenon is demonstrated in Figure 4.13 in which the pH remained low whenever there was an interaction between ‘unmodified starch-Cr(III)’ and where Cr(III) ions are capable of filling in the available space in the unmodified starch molecular granule. This attractive process between Cr(III) and unmodified starch began to slow down when most of the empty spaces in the unmodified starch were with Cr(III) ions at pH levels above 13.

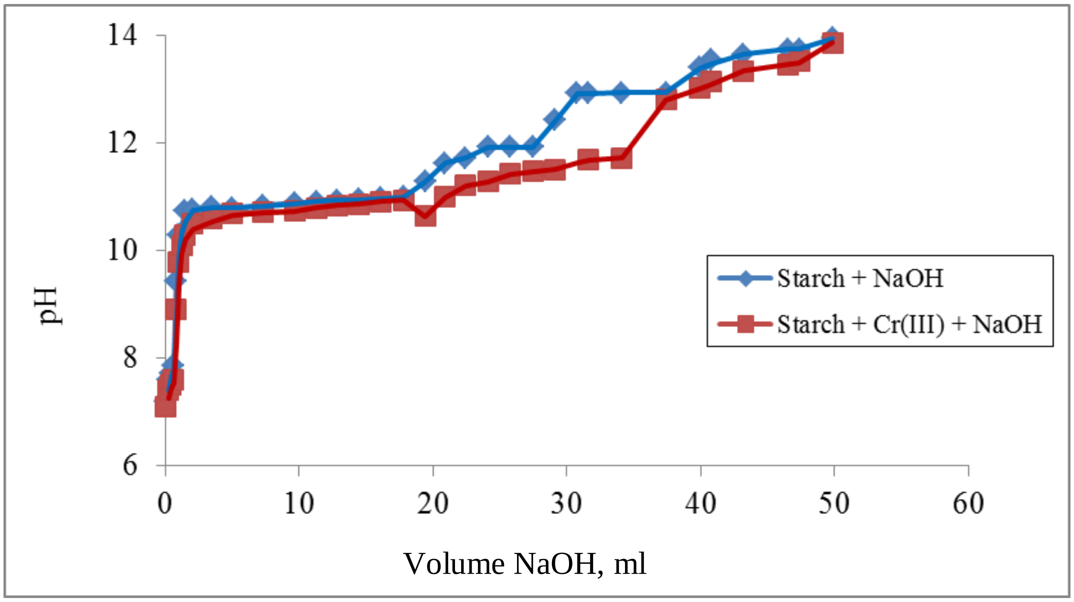


Figure 4.13 Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Cr(III)

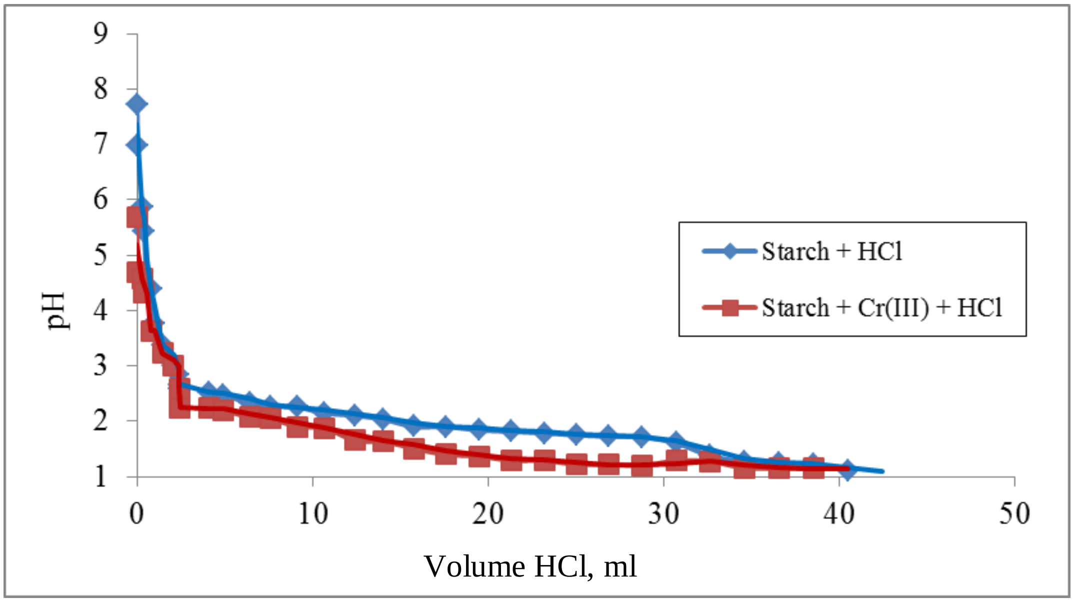


Figure 4.14 Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Cr(III)

Similar behavior was seen during the neutralization of unmodified starch by hydrochloric acid in the presence of Cr(III) ions, as demonstrated in the curves (V_{HCl}, pH) in Figure 4.14. Where the neutralization of unmodified starch using hydrochloric acid in the presence of Cr(III) is concerned, complexation occurred when the pH level reached pH 2 which also caused smaller gaps to appear. The attractive adsorption of Cr(III) ions by unmodified starch can be observed in the curve of unmodified starch in the presence of Cr(III) ions. This was due to the capability of unmodified starch approaching Cr(III) ions to fill its empty sites and form macromolecules because unmodified starch has the unique characteristic of having a neutral pH 7. The adsorption process was retarded when the region was too acidic, demonstrated by the overlapping curve for unmodified starch in the presence of Cr(III) at pH levels near 1.

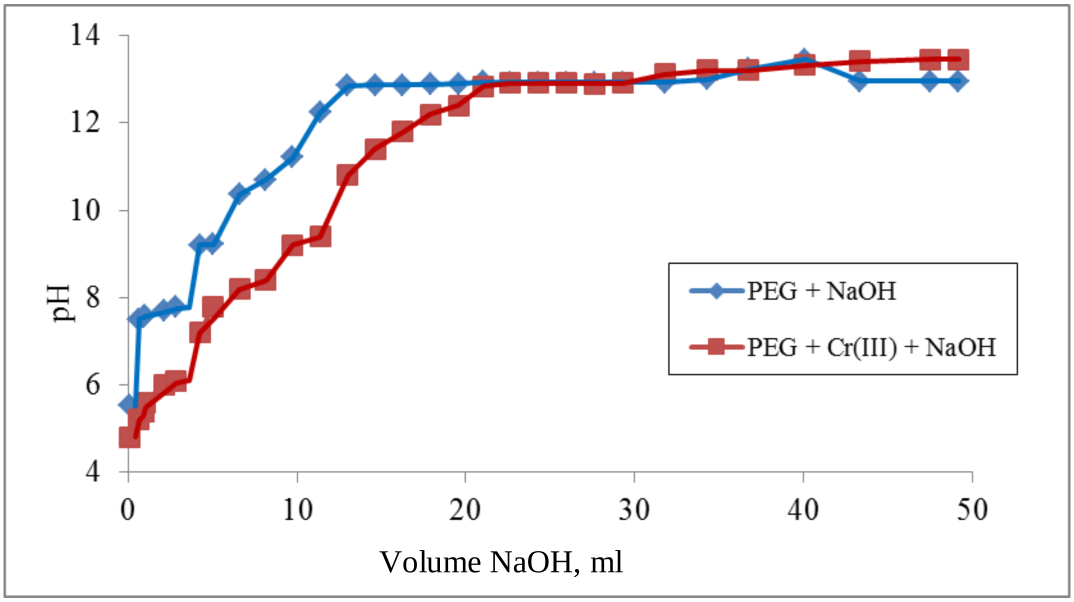


Figure 4.15 Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Cr(III)

Figure 4.15 shows the dramatic shift of the PEG neutralization curve when Cr(III) was present in the solution. The shift in the neutralization curve indicated the fast interaction of the adsorption process that started when titration began (pH < 6). More gaps appear at higher pH values, indicating the presence of greater adsorption for synthetic PEG that would provide available sites for Cr(III) ions to be attracted to and eventually form macromolecule complexes. Although the adsorption process occurred effectively over most of the pH range, the adsorptive mechanism between 'Cr(III)-PEG' became 'reluctant' once pH exceeded 13.

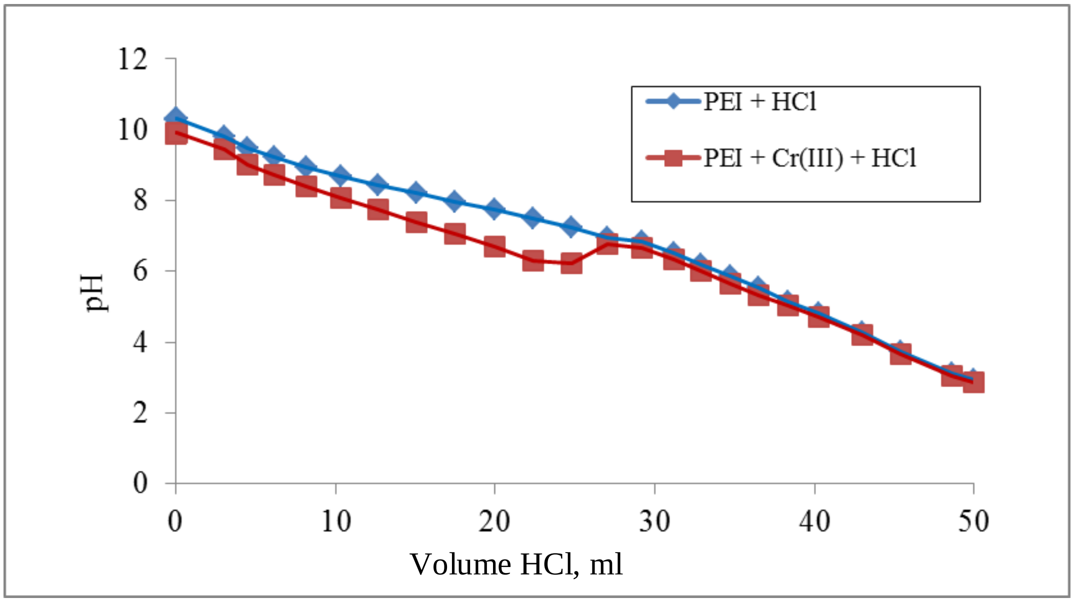


Figure 4.16 Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Cr(III)

The same behavior occurred when PEI was neutralized using hydrochloric acid in the presence of Cr(III) ions as depicted in Figure 4.16. In the initial stage of neutralizing PEI, the complexation between 'Cr(III)-PEI' appeared as a modification of the curve and demonstrated gaps indicating the presence of complexed species bringing into play the coordination of nitrogen atoms of two amine functions from secondary and tertiary groups of PEI with Cr(III) ions. The rest of the time, the pH level during titration was low due to the interactions between ‘Cr(III)-PEI’ compared to that of PEI alone. In acidic environments (pH<6), the curve followed the same curve as the neutralization of PEI alone, indicating that complexation occurred previously and was not affected by the presence of Cr(III) ions.

4.2.2.4 Potentiometric titration study on Chromium (VI)

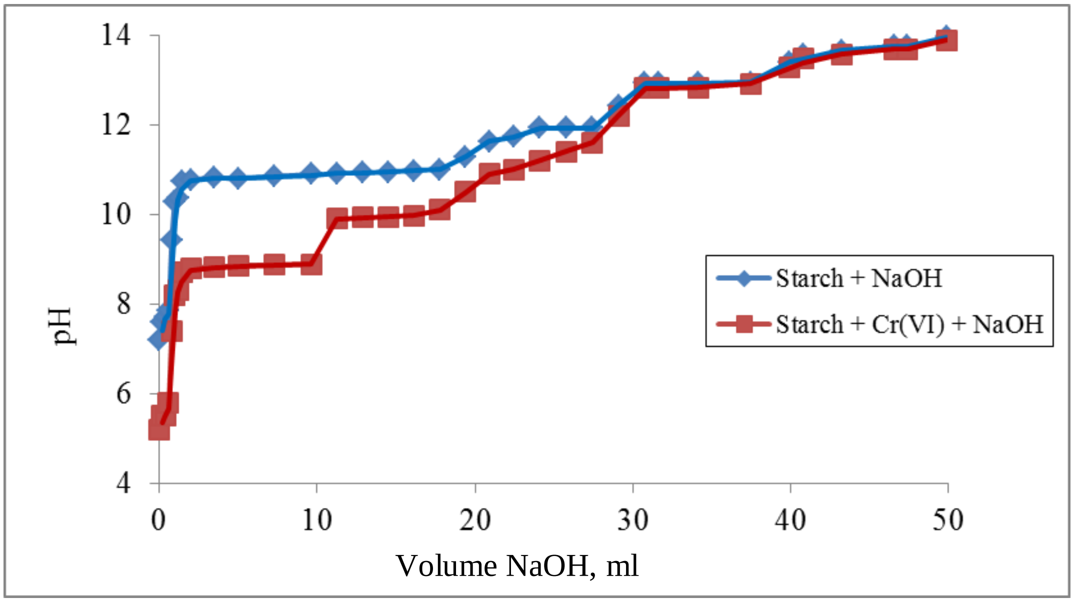


Figure 4.17 Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Cr(VI)

The titration curve (V_{NaOH}, pH) showing the neutralization of unmodified starch by sodium hydroxide in the presence of Cr(VI) ions is presented in Figure 4.17. Complexation occurred when titration began (pH > 5) due to the dissimilar neutralization curves between the unmodified starch by itself and in the presence of Cr(VI) ions. Wider gaps appear at pH levels above 9 indicating a greater adsorption mechanism where Cr(VI) was able to extensively penetrate the surface of unmodified starch. The pH remained low during ‘Cr(VI)-unmodified starch’ titration due to an increased level of interaction in comparison to the neutralization of unmodified starch alone. Gaps observed were smaller at pH levels above 10 in the case of unmodified starch, indicating that the adsorption process had ended.

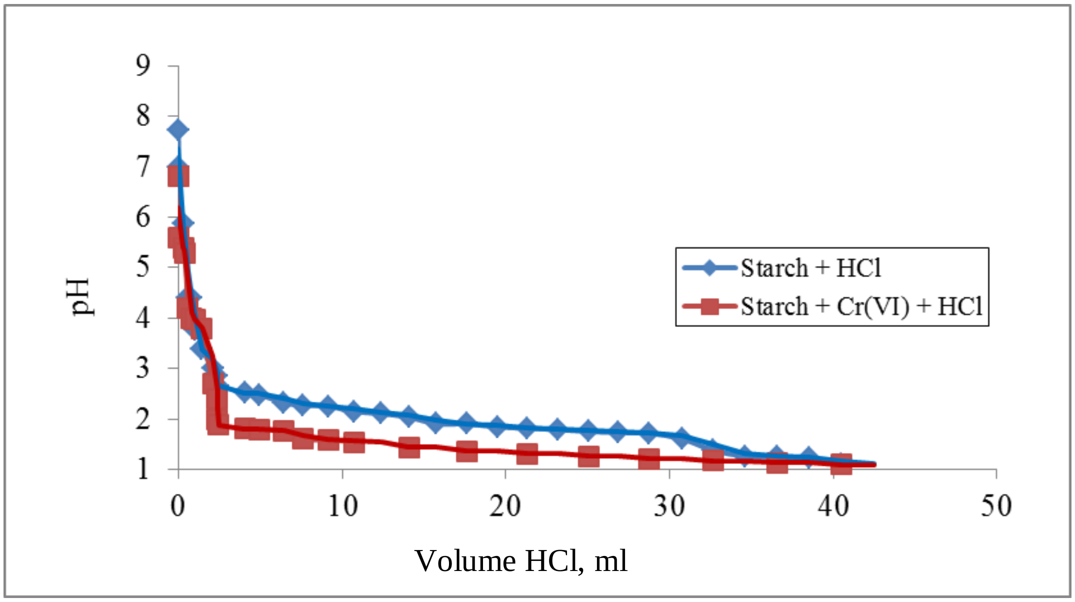


Figure 4.18 Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Cr(VI)

In the case of neutralizing unmodified starch in the presence of Cr(VI) ions, a different behavior was observed when hydrochloric acid was used, as indicated by the curves (V_{HCl}, pH) presented in Figure 4.18. During the initial titration process when neutralizing unmodified starch using Cr(VI) ions and HCl, the curve followed a trend similar to neutralizing unmodified starch by itself. The initial titration process was not affected by the presence of Cr(VI) ions. This indicated that when the pH range was higher than 3 (pH>3), no interaction between ‘Cr(VI)-unmodified starch’ occurred. At lower pH values, modifications appeared which indicated that the Cr(VI) ions were able to fill the available sites on the unmodified starch through an adsorption process. At this point, the pH during titration was observed to remain lower due to the effectiveness of the interactions compared to that of unmodified starch alone.

In the case of neutralizing unmodified starch in the presence of Cr(VI) ions, a different behavior was observed when hydrochloric acid was applied, as demonstrated by the curves (V_{HCl}, pH) presented in Figure 4.18. At the beginning of the titration process for neutralizing unmodified starch with Cr(VI) ions by HCl, the curve followed a trend similar to that for neutralizing unmodified starch by itself. This process was not affected by the presence of Cr(VI) ions. This demonstrated that in this pH range (pH>3), there was no interaction between ‘Cr(VI)-unmodified starch’. At lower pH values, modifications indicated that Cr(VI) ions were capable of filling the sites available on unmodified starch using an adsorption process. In this stage, the pH during titration remained low due to effective interactions compared to the interactions for unmodified starch alone. The adsorptive ability of unmodified starch attracting Cr(VI) ions was lacking due to slower interactions between ‘Cr(VI)-unmodified starch’ at pH levels near to 1.

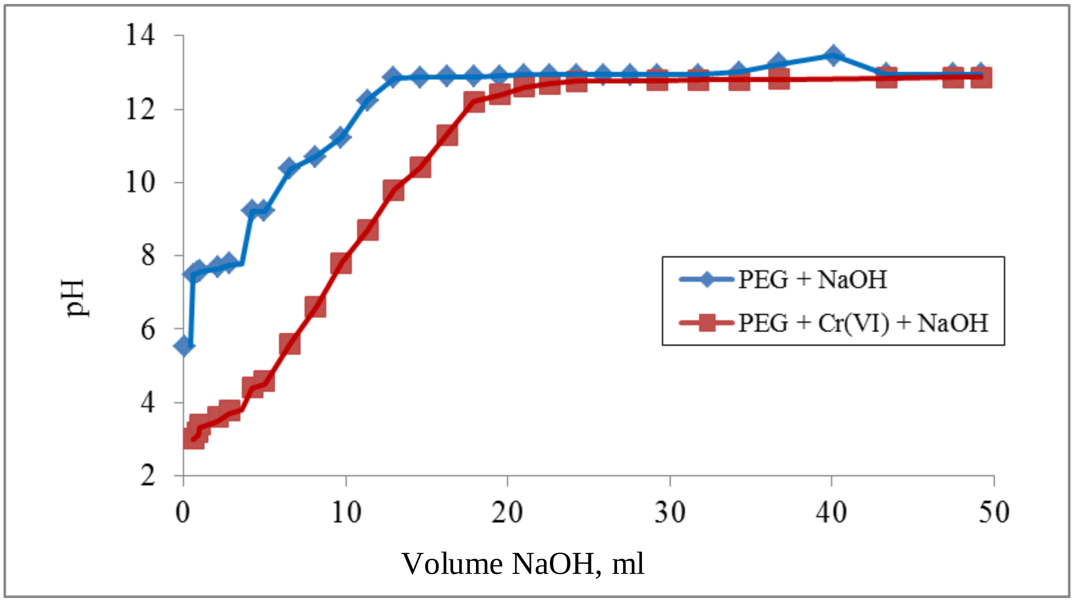


Figure 4.19 Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Cr(VI)

The titration curve (V_{NaOH}, pH) for neutralizing PEG using sodium hydroxide in the presence of Cr(VI) ions is presented in Figure 4.19. Complexation occurred at the beginning of titration (pH>3) due to larger gaps that appeared between the neutralization curve of PEG by itself and in the presence of Cr(VI) ions. These wider gaps during neutralization likely remain due to the high volume of interactions between Cr(VI) ions that provided space on the surface of unmodified starch molecules which occurred at most pH levels forming larger molecules. This extensive adsorption mechanism was observed until the pH rose above 12. Slower interactions took place after that point until the presence of Cr(VI) ions had no effect at pH over 13.

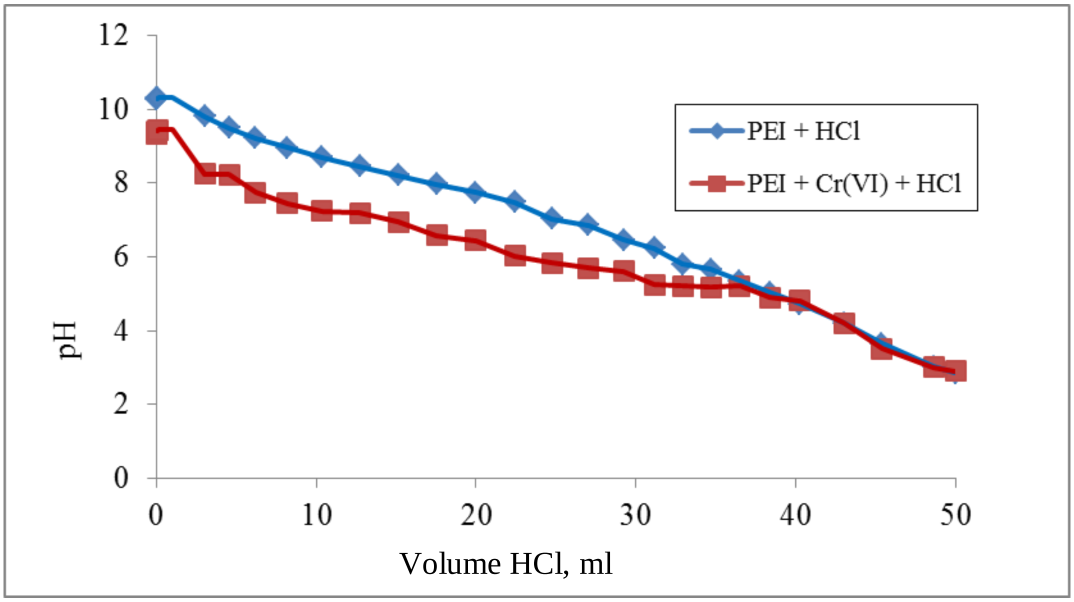


Figure 4.20 Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Cr(VI)

The experimental titration curve for PEI was the result of employing hydrochloric acid in the presence of Cr(VI) ions as revealed in Figure 4.20. Similar behavior was observed during the neutralization of PEI where complexation took place at the initial stage of titration at pH 10. The behavior observed during the neutralization of PEI with Cr(III) was similar to Cr(VI). The complexation of PEI to interact with Cr(VI) ions occurred until the pH level reached 5 compared to Cr(III) ions that were formed only at pH 7. The pH remained low compared to PEI alone as nitrogen atoms from the amine group were able to form complexation in the coordination sphere of Cr(VI), and it continued until pH 5. Wider gaps were sustained as extensive interactions dominated most pH regions. Fewer interactions of 'Cr(VI)-PEI' appeared at pH turns below 5.

By comparing the neutralization curve for the polymer alone between selected metal ions and polymer, it can be concluded that the polymer-titration curve study revealed that possible interaction of polymer-metal corresponded to the supplementary release of protons and could be observed due to the formation of metal complexes. The selected metal ions' (Zn(II), Pb(II), Cr(III) and Cr(VI)) interaction with polymers during titration contributed to the challenges facing metal ions that were attracted to the reactive sites of functional groups of polymers either by chemical or physical mechanisms. For each titration study using a different polymer, complexation became increasingly more significant at each pH level with the presence of Zn(II), Pb(II), Cr(III) and Cr(VI). The significant pH range for 4 ions is shown in in Table 4.1.

Table 4.1 pH complexation range of four selected ions with unmodified starch, PEG and PEI as polymer

Titration metal ions with polymer	pH complexation ranges
Zn(II) + NaOH + starch	6 - 10
Zn(II) + HCl + starch	2 - 3
Zn(II) + NaOH + PEG	6 - 12
Zn(II) + HCl + PEI	5 - 9

Table 4.1, continued pH complexation range of four selected ions with unmodified starch, PEG and PEI as polymer

Pb(II) + NaOH + starch	9 - 12
Pb(II) + HCl + starch	2 - 10
Pb(II) + NaOH + PEG	5 - 12
Pb(II) + HCl + PEI	4 - 9
Cr(III) + NaOH + starch	11 - 13
Cr(III) + HCl + starch	1.5 - 2.5
Cr(III) + NaOH + PEG	5 - 13
Cr(III) + HCl + PEI	6 - 9
Cr(VI) + NaOH + starch	5 - 12
Cr(VI) + HCl + starch	1.5 - 3
Cr(VI) + NaOH + PEG	2 - 12
Cr(VI) + HCl + PEI	5 - 9

4.3 Polymer Enhanced Ultrafiltration of Single Metal Ion Solutions

4.3.1 Effect of pH on metal ions retention by unmodified starch

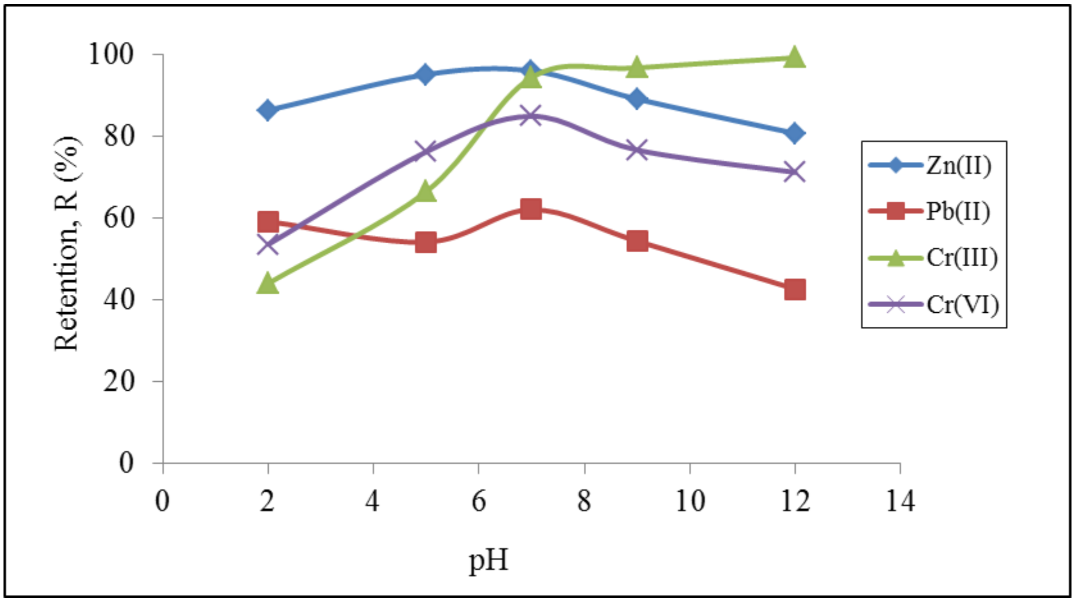


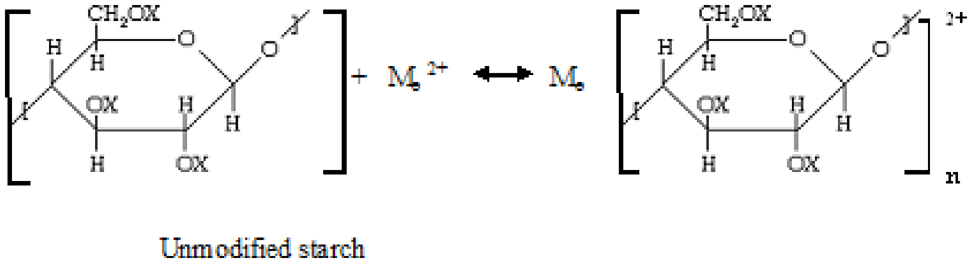
Figure 4.21 The effect of pH on retention using 0.05% (w/v; g/ml) unmodified starch (TMP= 1.5 bar, flowrate= 115 ml/min, metal ion concentration= 10 mg/L))

Figure 4.21 shows the effects of pH on the retention of Zn(II), Pb(II), Cr(III) and Cr(VI) ions using unmodified starch. The studied pH range was from 2 to 12, and applied pressure was 1.5 bar at room temperature. These retention values were carried out an error of ±0.1 of all experimental data. More Zn(II) was retained than Pb(II) for the entire range of pH tested, but it decreased when pH level rose to 7, concurring with the potentiometry titration study of Zn(II) and starch. The potentiometry titration study of Zn(II) and starch indicated that active complexation initially occurred at pH 4-6 and decreased at pH 10 and above. As pH increased, the formation of the complexes was enhanced and eventually increasing the retention of

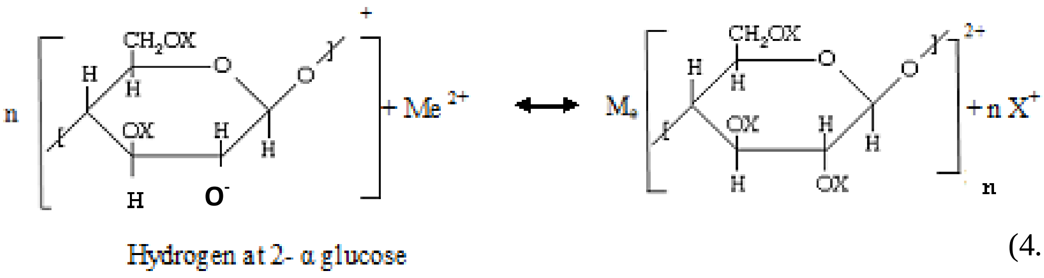
Zn(II) (Barakat & Schmidt, 2010). This was due to an adsorptive mechanism for metal ions using an unmodified starch caused by a physical mechanism of adsorption in which metal ions are able to bond to the starch surface.

At pH 7, unmodified starch acts as a binding biopolymer and Zn(II) removal meets permissible limits for the discharged effluent standards of the EQA, which is 96% removal per 0.4 mg/l using a PEUF process to remove metal ions.

The unmodified starch uptake of selected metal ions by adsorption is high in certain situations because of chemical adsorption. In these situations, the metal component bonds to the unmodified starch because the hydrogen ions form pendant hydroxyl (OH) groups capable of forming hydrogen bonds. H^+ at position 2-, 3- and 6- in glucose is capable of forming donor bonds to grab metal ions. Hence, there is a high possibility that adsorption can occur via chemical interactions as expressed in Equations 4.1 and 4.2:



(4.1)



(4.2)

X= represents hydrogen ions

Me = metal ion

As expected, metal retention was highly dependent on the pH of the solution. Metal retention was lower at low pH levels due to protons competing for available active sites on the macromolecular ligand, which caused the loss of the Zn(II) complex stability (Camarillo, 2012).

Increased pH resulted in an increase in retention of up to 96% at pH 7. This concurs with a study conducted by Bertolini who found that solubility of Zn(II) ions in most types of waters was greater at pH levels between 7.0 and 9.2. Consequently, the ability of Zn(II) to bind to starch is better at this pH range (Bertolini, 2010).

When the pH of the solution was greater than 7, Zn (II) ions retention decreased. This may be due to the negative effect of insoluble metal hydroxides. Furthermore at such high pH levels, starch granular reactions take place and produce heterogeneous granular patterns that reduce the metal ions' ability to diffuse and disperse throughout the granule matrix prior to the slow reaction between metal ions-polymer (Gray, 2004; Huber, 2001). Theoretically, as the pH increase, the reaction efficiency should also increase (Gray, 2005; Han, 2006; Lim, 1993; Van Warners, 1994; Wu, 1990). However, at a certain pH range, the granular reaction pattern of starch, metal ions and the species of metal ions in a solution negatively affected the ability of metal ions to adsorb to starch, (Bertolini, 2010; Patterson, 1983) and metal ions retention consequently decreased.

Unmodified starch has long chains and can have a forked and branched structure that allows macromolecules to be strongly attracted to each other. The long chain's structure can shorten the molecule through physical adsorption. As the structures of unmodified starch molecules do not contain straight chains like those in cellulose, it has the ability to lose its structure to provide a chance for solvents to penetrate its surface. As a result, starches are able to bond, increase their molecular weight, and form macromolecule structures that can be removed via PEUF, especially at low pHs.

The behavior demonstrated for Pb(II) was similar to that of Zn(II). Between pH 1 and pH 7, retention increased then started to gradually decrease until the pH level rose to 12. According to previous studies, adsorption of metal ions by polymers increases as pH increases. These studies state that at a neutral pH, Pb^{2+} is present, in accordance with the Pb(II) speciation diagram. At alkaline pH values, interaction of metal ions and polymer can cause precipitation of metal hydroxide, but metal ions are still able to be removed via polymer-assisted ultrafiltration (Alpatova et al., 2004; Barakat & Schmidt, 2010). These studies also concluded that at pH levels higher than 7, most Pb(II) species present in metal solutions were in a low concentration. However, the possibility of membrane fouling remained high due to metal ion-polymer complexes that were retained on the membrane, which enhanced membrane pore blocking (Alpatova et al., 2004).

At pH 10, Pb(II) ions retention decreased due to presence of three cationic species, namely $Pb_2(OH)_3^+$, $Pb_3(OH)_4^{2+}$ and $Pb_4(OH)_4^{4+}$, (refer to speciation diagram) which caused desorption. This was due to very low concentration of these three species and their ability to bind to the available macromolecular starch-PEI sites.

Low retention of chromium ions complexation was found at low pH levels. For Cr(III) ions, it increased as pH increased but decreased for Cr(VI) ions as illustrated by the potentiometric curve that shows the adsorptive behavior of starch was effective at certain pH levels and formed macromolecular complexes with chromium ions. The retention coefficient for Cr(III) and Cr(VI) ions approached 94.5% and 84.9% respectively at pH 7, which meant that chromium ions were efficiently removed from the membrane outlet at this optimum pH range.

Removal of chromium ions was most probably due to the physical adsorptive mechanism of unmodified starch containing amylopectin, which has a highly branched molecular structure that allows chromium ions to penetrate the surface of the molecules (Chabot, 1976). Removal of Cr(III) by unmodified starch under optimum working conditions meets the permissible limits recommended by the Department of Environment (DOE) for effluent discharge of 1 mg/l (DOE, 1994). Using starch without modification was found to efficiently remove Cr(VI) ions without reducing them to Cr(III), indicating that it can also avoid precipitation.

There is a high possibility that bonding occurred between unmodified starch and chromium ions via chemical interactions since starch can also have pendant hydroxyl (OH) groups capable of forming hydrogen bonds H^+ at position 2-, 3- and 6- in glucose to adsorb metal cations.

On the other hand, low chromium retention was only observed at pH=2 due to metal ions being entrapped by the bulky polymers at the surface of the membrane (Rivas, 2003). At lower pH levels, nearly all chromium ions were recovered in the permeate stream. Retention of both chromium ions reached a plateau when the pH level rose to 9. This might be caused by saturation of the active polymer sites by chromium ions, thus limiting retention. Both chromium ions showed less significant adsorptive mechanisms at low pH levels (between 2 to 6). This can be seen in the potentiometric study where the behavior with or without the presence of chromium ions for complexation was similar which indicates that there was no complexation between chromium ions and unmodified starch.

4.3.2 Effect of pH on retention of metal ions by PEG

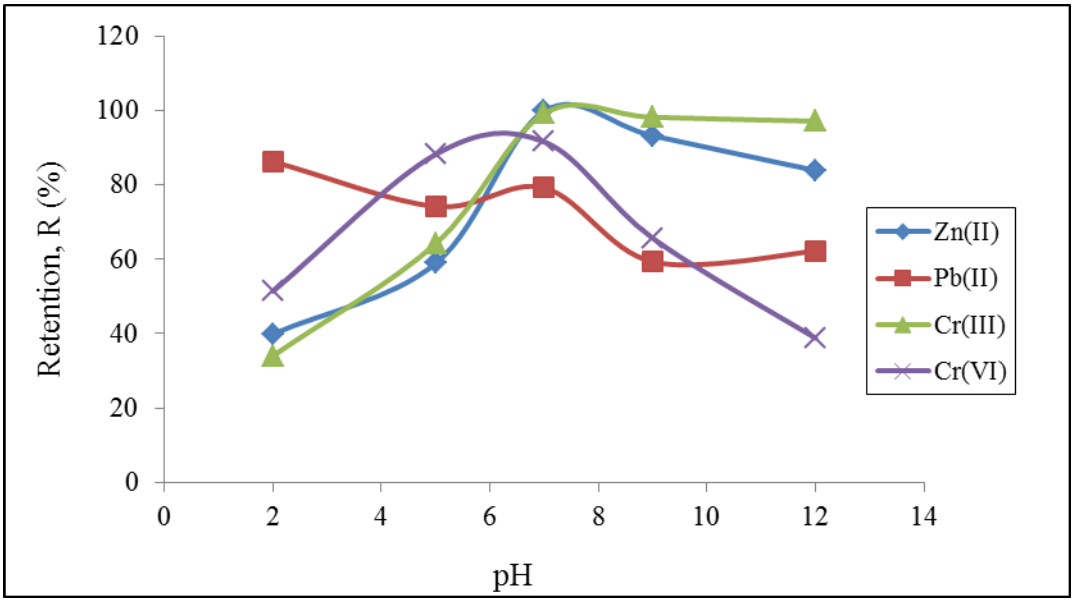


Figure 4.22 Effect of pH on retention when using 1.0% (v/v; ml/ml) PEG (TMP= 1.5 bar, flowrate=115 ml/min, metal ion concentration= 10 mg/L)

The results of experiments using different pH values reveals the fluctuating relationship between retention coefficients and pH, but the highest level of retention occurred at pH 7 for the selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) as shown in Figure 4.22.

In an acidic environment, Zn(II) ions retentions were low due to the decreased ability of Zn(II) ions to be adsorbed by available PEG sites. This is due to the ability of the positive charge of Zn(II) ions at the initial pH levels to efficiently bind to the surface of the PEGs which is negatively charged. This explanation corresponds to the results of the Zn(II) speciation study where retention increased. The adsorptive mechanism occurred continuously until the anion of Zn(II) species took place which may have caused the adsorption process to slow down as the environment became more alkaline, as demonstrated in Figure 4.22 where the retention of Zn(II) ions slightly decreased.

The different behavior exhibited by Pb(II) is presented along the pH levels tested. The adsorption and desorption behavior of Pb(II) ions were unstable causing the retention curve of Pb(II) to fluctuate in the acidic to alkaline pH region. The highest level of Pb(II) ions retention was obtained at a low pH level caused by cation species of Pb(II) that were adsorbed by the PEG surface which was then replaced by the desorption processes.

At low pH levels, the concentration of monovalent H^+ ions competed with Cr(III) as cations to be adsorbed by PEG. As a result, few adsorptive interactions were found between Cr(III) and PEG. The plateau extended from pH 7 to 12, representing 99.8% retention of Cr(III) ions at neutral pH levels. This is in accordance with the results from the potentiometric titration studies for Cr(III) ions where more gaps appeared at pH 7 which indicates that the complexation of Cr(III) and PEG occurred rapidly as the pH increased and became alkaline. As there was no complexation between Cr(III)-PEG, retention dropped. For Cr(III) ions, the high level of retention was probably due to Cr(III) attaching to the surface of non-ionic PEG by physical adsorption.

PEG provided the available space for Cr(III) ions to attach when the pH level was neutral and where cationic species of Cr(III) ions dominate. Most probably the surface of PEG was filled with negative charges that were capable of absorbing the cation charges of Cr(III). Additionally, metal hydroxide precipitation is possible at neutral or alkaline pH values as suggested by the results of a study conducted by Arthanareeswaran et al. (Arthanareeswaran et al., 2007). Based on DOE discharge standards B for industrial effluent limits, both chromium ions species met the requirements of 1.0 mg/l and 0.05 mg/l for Cr(III) and Cr(VI) (DOE, 1994), when PEG is used as a binding reagent in certain circumstances and at pH 7 in the UF process.

These results contradict the results for Cr(VI) where the retention coefficient dropped as pH increased to become more alkaline. The retention behavior of Cr(VI) was similar to those from the potentiometric studies of Cr(VI)-PEG where the effective adsorptive mechanism occurred at pH 7-12 with the appearance of more gaps. As with the presence of Cr(VI) ions, the reactions indicated the complexation of Cr(VI)-PEG compared to neutralization by PEG alone. The retention coefficient values for different pH levels illustrated in Figure 4.22 show the fluctuating behavior of both chromium ions species but the highest level of retention was obtained at pH 7.

4.3.3 Effect of pH on retention of metal ions by PEI

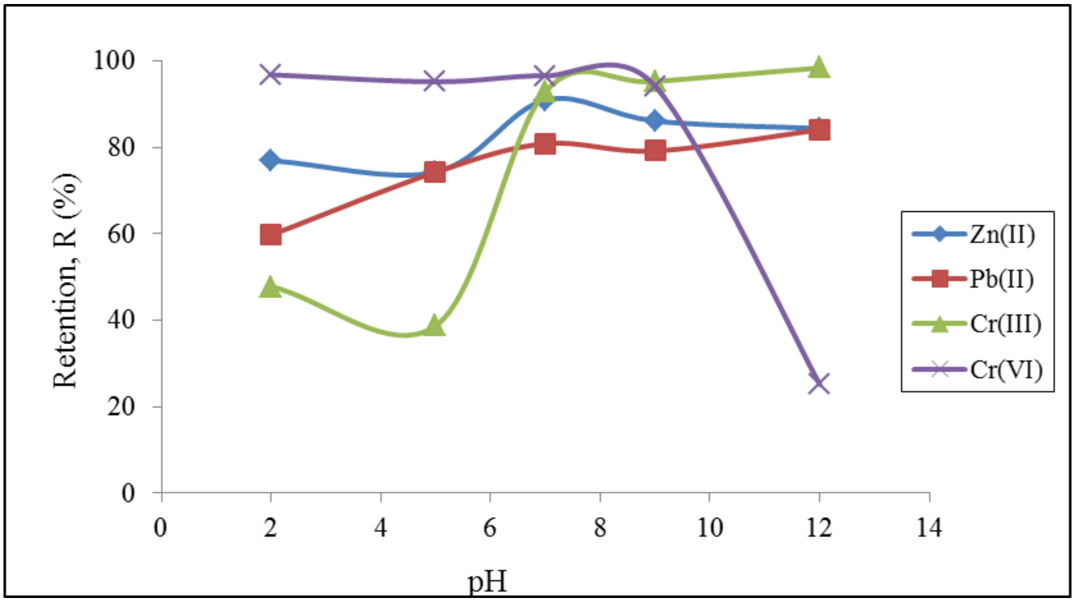


Figure 4.23 The effect of pH on retention using 0.01% (v/v; ml/ml) PEI (TMP= 1.5 bar, flowrate= 115 ml/min)

The retention values for metal ions are shown in Figure 4.23. The effect of pH on selected metal ion removal from aqueous solutions was determined using PEI. Graphs for both Zn(II) and Pb(II) are slightly similar at an acidic to neutral pH levels, but differ slightly at alkaline levels. As PEI is a cationic polymer that is able to neutralize excess anionic species, retention increases as it reaches an alkaline pH. This is in accordance to the speciation profile of Zn(II) species, where at a pH over 10, Zn(II) with negatively charged species starts to appear. This contributes towards forming macromolecules by complexation, through interaction of the active amino group of PEI with Zn(II) ions.

The behavior demonstrated for Pb(II) is somewhat similar to that of Zn(II), where at pH 1 to 7 retention is low due to high concentrations of Pb(II) ions. Repulsive interactions between PEI and Pb(II) occurred and decreased as pH rose to 10. Low concentrations of Pb(II) species at this pH levels caused minimum repulsion between PEI-Pb(II). Consequently, it influenced adsorption resulting in an increase of Pb(II) ions uptake by PEI at pH 9 and above. This PEI-Pb(II) interaction is in accordance with Pb(II) speciation profiles which demonstrate the low concentration of cationic species in the solution at pH levels between 9 and 14.

These cations cannot be completely complexed by the protonated PEI. Retention decreased at lower pH (pH< 7) levels, which is connected to the competition between H^+ and cationic Pb(II) forms. In acidic environments the retention of Pb(II) decreased, but in alkaline environments Pb(II) retention increased. This was due to lower concentration of cationic Pb (II) present in the solutions, hence little competition between H^+ and cationic Pb(II) resulted in increased retention. According to an earlier study conducted by Aroua et al., using PEI as a binding polymer increased retention by as much as 99% for Cr(III) ions as pH increased. This is in contrast to the results for Cr(VI) where retention dropped as pH increased to pH 12 (Aroua et al., 2007).

At lower pH values, Cr(III) retention first decreased retention, sharply increased when the pH level reached 5, and plateaued at pH 7 and above. This follows the actual phenomenon where higher complexation occurs between metal and PEI at pH> 5 as shown in the previous potentiometric titration study. Different behavior was demonstrated by Cr(VI) where retention values were nearly perfect: constant to 1 at most pH levels until pH 9 was reached which is in accordance with the potentiometric titration study. In spite of this, retention drops when pH was greater than 9. This is due to pure PEI effectively neutralizing excess anionic colloidal charges under acidic and neutral pH conditions. This situation and different behavior of Cr(VI) retention required further investigation, especially the effect of pH on Cr(VI) ions corresponding to potentiometric titration study.

Performance of starch, PEG, PEI on retention values, and the effect of pH should be compared to the theoretical values for effluent discharged standards set by the Malaysian DOE; pH is an important parameter in the PEUF study. The Malaysia DOE discharge standards for Zn(II), Pb(II), Cr(III), and Cr(VI) ions are 2 mg/l, 0.5 mg/l, 1.0 mg/l and 0.05 mg/l, respectively. By using starch, Zn (II) and Cr (III) ions meet DOE standards as the retention value reached 95% and 94.5%, respectively. The final metal ions concentrations after the PEUF process were 0.55 mg/l for Zn(II) and 0.5 mg/l for Cr(III) ions. Similar results were found for PEG which safely removed Zn(II) and Cr(III) ions. It is likely that PEI could efficiently remove Zn(II), Cr(III) and Cr(VI) to meet discharge standards, which are 1.0 mg/l, 0.8 mg/l and 0.02 mg/l, respectively. The highest retention level for metal ions was at optimum pH 7.

4.4 Effect of polymer concentration on retention

4.4.1. Effect of unmodified starch concentration

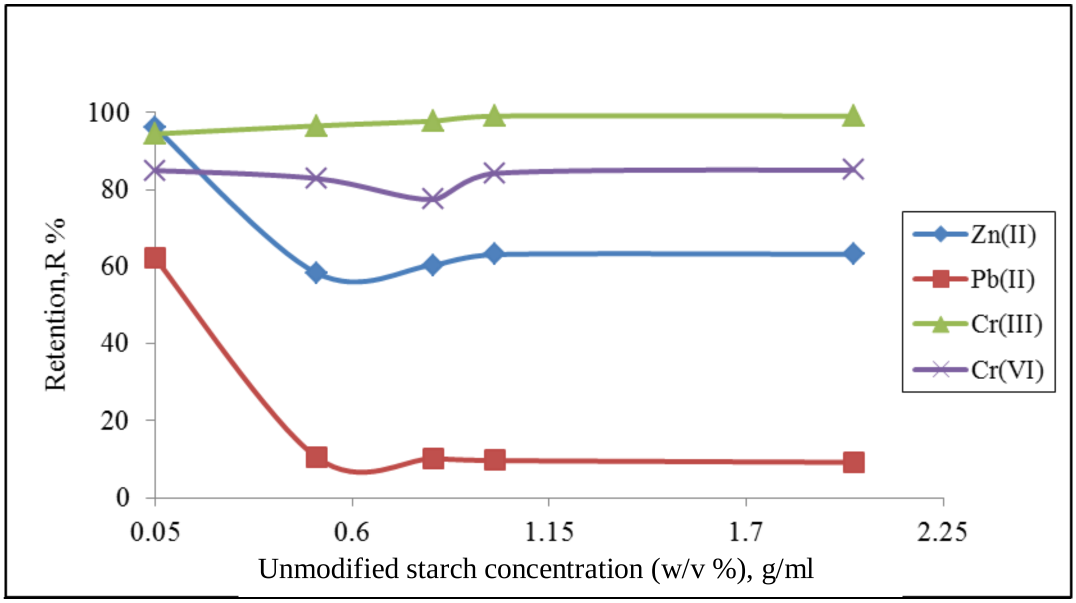


Figure 4.24 Effect of unmodified starch concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

Figure 4.24 shows the effect of the concentration of starch on the retention of Zn(II), Pb(II), Cr(III) and Cr(VI).

Figure 4.24 shows that Zn(II) and Pb(II) ions were affected by the concentration of starch and their retention is similar. As the concentration of polymers increased, the ability of starch to bind with metal ions decreased due to excessive availability of polymer sites bound with selected metal ions compared to metal ions present in solutions. The complexation metal ions and unmodified starch were observed to have more adsorption when the polymer concentrations were low and gelatinization behavior was avoided.

Retention remained consistent even though the concentration of starch increased to 1.0%. The experimental results supported the theory that when high concentrations of polymers are used, negatively influenced polyelectrolyte behavior causes the polyelectrolyte concentration decrease in the metal ions solutions. This phenomenon contributed to less production of ions and low ionic atmosphere in the metal ions solutions compared to the diameter of the polymeric coil of PEG because the repulsive ions increased towards the polymer corresponding to the decrease in polymer’s chain rigidity. This corresponds to the reluctance of polymeric coils to expand which caused a decrease in metal ions solution viscosity (Aroua et al., 2007) as well as a decrease of retentions. The reasons for employing low polymer concentrations are to minimize polymer loss in the solutions without complex to selected polymer and to increase the retention of metal ions (Yurum, 2013).

The retention coefficients for Cr(III) and Cr(VI) rose to 95% and 85%, respectively when unmodified starch concentrations were increased to 2.0% (w/v; g/ml), as shown in Figure 4.24. This was due to an increase of polymeric domains with local high and nearly constant ligand concentrations corresponding to an increase in the number of unmodified starch chains (Rivas, 2003). The difference caused by applying low or high polymer concentration had little effect on retention. Since unmodified starch can exhibit gelatinization behavior that may interfere with the UF process, using a low concentration of unmodified starch is preferable.

Increasing the concentration of unmodified starch resulted in a slight increase of retention. This was due to the interaction of chromium ions and unmodified starch that seemed to be stagnant. No effective complexation occurred when a very high concentration of starch was used. The bonding behavior of the metal-polymers was not complex enough to be retained by the membrane, thus allowing the retention coefficient to reach a plateau phase. This behavior had little effect on Cr(VI) retention when the concentration of unmodified starch was more than 0.5% as the metal-polymers became more complex at this stage.

4.4.2 Effect of PEG concentration

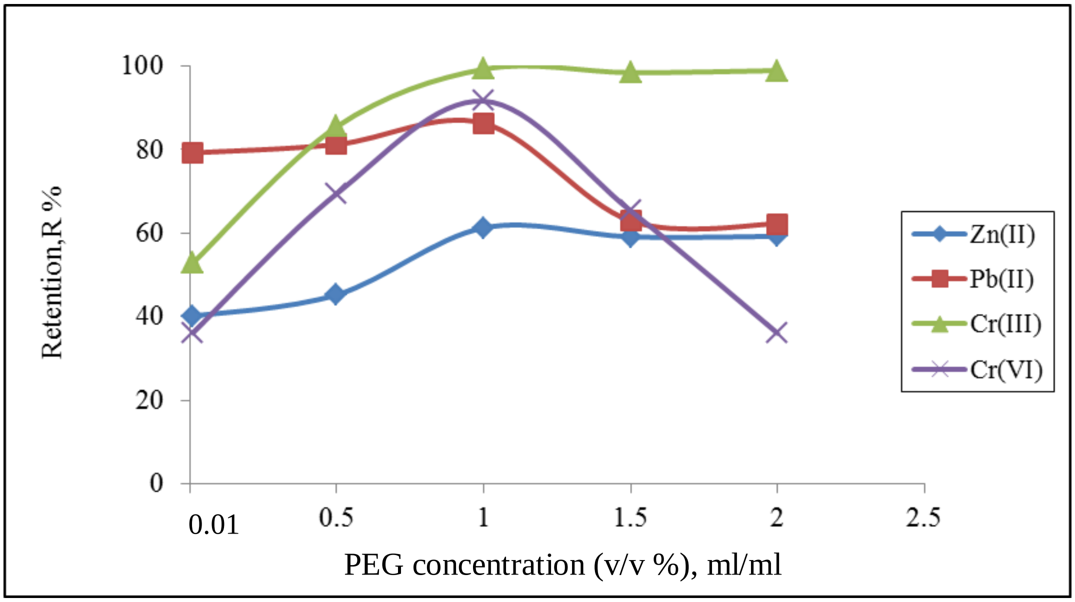


Figure 4.25 Effect of PEG concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

Figure 4.25 shows the effect of PEG concentration on the retention of the four metal ions discussed in this study. PEG is known to be an effective agent for removing heavy metal ions from aqueous solutions (Vella et al., 2008). Low PEG concentration of less than 0.5 (v/v %) shows the lowest retention of each selected metal ions, and constant retention values were obtained at 80% when PEG concentrations when tested at ranges of 0.01 to 0.5 (v/v %). Figure 4.25 shows that about 60% retention of Zn(II) ions remained constant at 1% (v/v; ml/ml) and are above PEG concentrations. On the other hand, Pb(II) displayed a contrast behavior compared to Zn(II) ions when Pb(II) ions retentions became constant (R≈ 0.80) at a low PEG concentration of 0.01 to 0.5% (ml/ml) and slightly increased when the concentration of PEG reached 1.0 (v/v%,) before it then decreased as the concentration of PEG increased. The group of HO-(CH_2CH_2O-) in the PEG structure and hydrogen ions were produced and provided the medium on the PEG surface to be completely bound to selected metal ions when 1.0 (v/v%) of the PEG concentration was achieved. Hence, it became the optimum polymer concentration for metal ions to be efficiently filled on PEG available sites (sufficient for metal ions uptake by PEG in metal ions-polymer solutions).

Cr(III) ions retention increased at the initial PEG concentration and then stabilized as the PEG concentration reached 1.0%. The retention of Cr(III) ions was due to the most favorable polymer being fully occupied by Cr(III) ions to form macromolecules, which are easier to retain by the membrane.

At the optimum polymer concentration 1.0% (v/v; ml/ml), Cr (VI) are able to bind completely with PEG until the concentration of PEG was increased up to 1.5%. The behavior of Cr(VI) ions trapped in PEG chains' structure when the local concentration of ligands is higher compared to the polymer domain. It corresponds to the higher interaction between the backbone segments in PEG chains caused the coiled-globule like conformation in the PEG structure that resulted in reduced PEG viscosity in order to complete complexation with Cr(VI) solutions (Aroua et al., 2007) when the PEG concentration was increased. As the concentration of feed solution increased to 2%, higher resistance of PEG to be bound to Cr(VI) ions occured since the higher PEG concentration makes the flow of metal ions-polymer solutions become stagnant at the membrane surface due to the excess PEG concentration present in the metal ions solutions compared to Cr(VI) ions (Camarillo et al., 2010) which negatively affected the retention coefficients.

4.4.3 Effect of PEI concentration

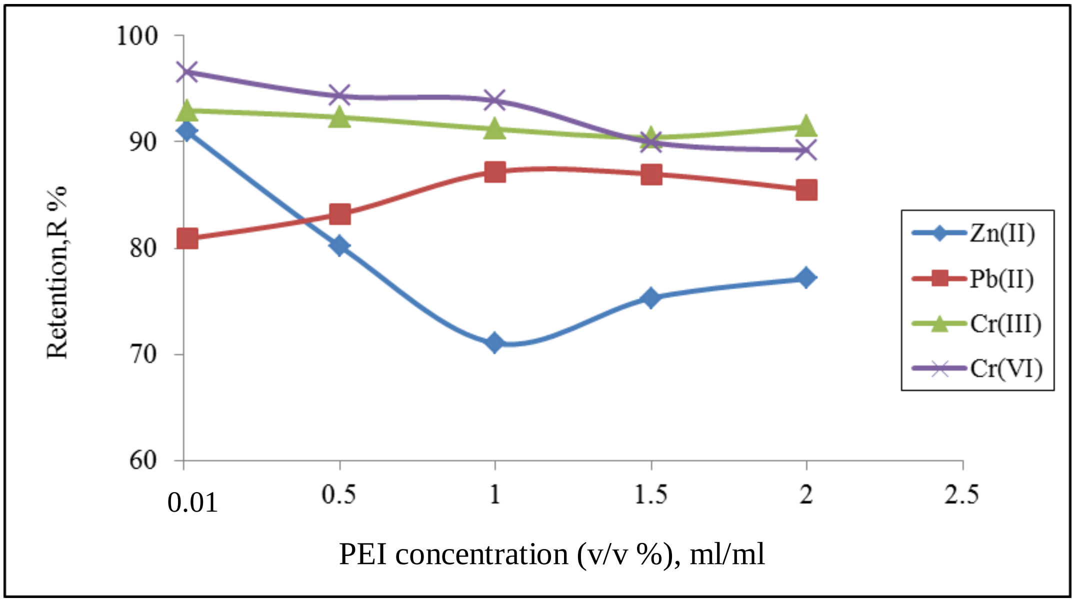


Figure 4.26 Effect of PEI concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

The effect of PEI concentration on Zn(II), Pb(II), Cr(III) and Cr(VI) ions retention is shown in Figure 4.26. The binding mechanism of Zn(II), Cr(III) and Cr(VI) ions on PEI were greatly successful; when practiced at low concentration of 0.01 (v/v%) which results the highest metal ions retention. In contrast, the presence of cationic species of Pb(II) ions at pH 7 in concordance to Pb(II) ions speciation species was found to cause ineffective binding with cationic PEI, but it still had effects on retention value even if this has not greatly influenced Pb(II) ions retentions at PEI concentrations more than 1 (v/v%). This figure also demonstrated that Zn(II) ions were influenced by low concentrations of PEI and that there was only a slight effect on Pb(II) ions retention created by increasing the concentration of PEI to 2.0%. This behavior can be interpreted using the previous findings regarding an adsorptive mechanism by complexation between several divalent metal cations and PEI (Takagishi, 1985). PEI has the ability to become a polymer with high complexation behavior towards metal adsorption because it has an active group of PEI of primary, secondary and tertiary imine groups in the ratio of 1:2:1 (Bolto, 1995).

In our study, at a very low concentration of PEI, the equilibrium state for free Zn(II) ions with PEI was achieved. When as the concentration of PEI increased, retention decreased until a critical ratio was reached where the most favorable sites for metal ions were filled. Decreasing the concentration of polymer increased the viscosity of the metal ion-polymer solution in which the PEI structures constructed their chain structure closer indicates Zn(II) ions effectively interacted with free amino groups and protonated PEI, which increased the Zn(II) ions retentions during optimum pH conditions. In contrast, the interaction of uncharged PEI with metal ions reduced viscosity because the ability of the backbone structure to form a coiled globule-like configuration increased; results the desorption of Zn(II) ions from PEI structure (Rivas, 2003), and Zn(II) ions retentions consequently decreased when PEI concentrations achieved 1.0 (v/v %).

The retention of Pb(II) ions was almost constant despite an increased concentration of PEI. This was due to a number of polymer and metal ions interactions that had a negative influence on metal ions retention because the macromolecules that formed on the membrane surface were blocked as the polymer concentrations were too high (Uludag et al., 1997). The previous study illustrated that retention is slightly reduced at higher concentrations of PEI, and most chromium ions were removed when the concentration reached 0.05% (Aroua et al., 2007). These results indicate that low PEI concentrations can be exploited to achieve the highest level of Zn(II) and Pb(II) ions retention resulting in an economical application for wastewater treatment.

The most Cr(III) ions were retained at constant value about 90% in all tested PEI concentration ranges, suggesting that PEI was appropriate for Cr(III)-PEI interactions to form macromolecular complexes in the PEUF study. Similar behavior was shown by Cr(VI) species even though they were not very affected by PEI concentrations. The most retention occurred at lower PEI concentrations. These retention results confirmed that by using high concentrations of PEI, the typical polyelectrolyte behavior of metal ions decreases corresponding to a reduction in the viscosity of the solution and decreasing retention.

As pH becomes the fundamental factor in PEUF studies, the equilibrium of protonated and free amino groups are greatly dependent on pH as equilibrium shifts to the free amino group as pH increases. Uncharged PEI allows for increased interactions of backbone segments adopting a coiled globule-like configuration that results in less viscosity (Aroua, et al., 2007).

The retention values of starch, PEG, and PEI compared to the discharge standards of DOE in Malaysia indicate that Zn(II) and Cr(III) ions could be efficiently removed using 0.05% of unmodified starch which retained > 90% of metal ions. Only Cr(III) ions were discharged by 1.0% of PEG, whereas a 0.01% concentration of PEI efficiently removed Zn(II) and both chromium ions.

4.5 The effect of metal ion concentration on retention

4.5.1 The effect of metal ion feed concentration by unmodified starch

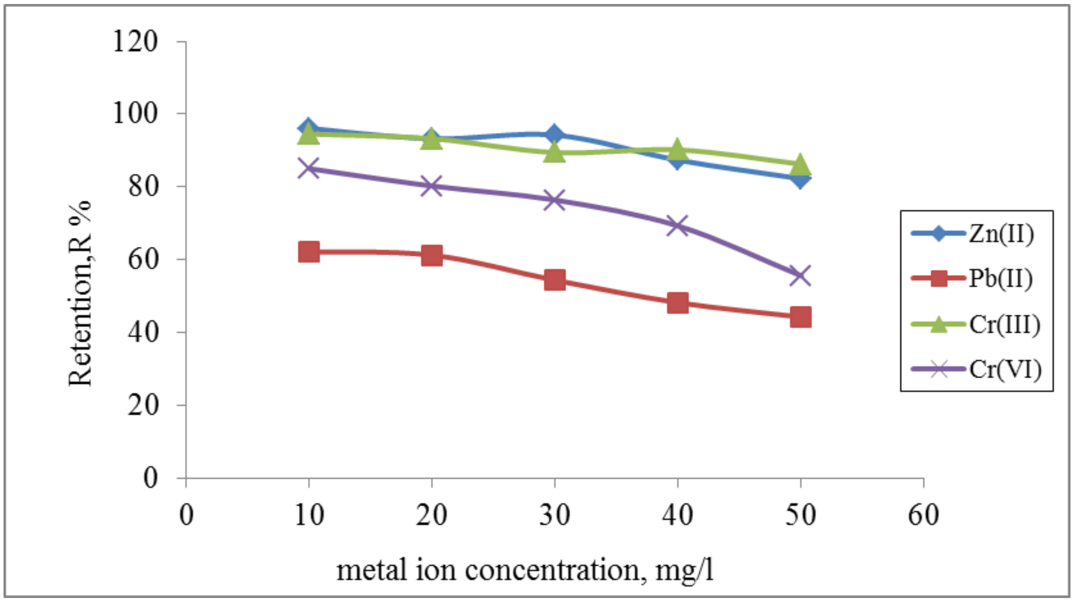


Figure 4.27 The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch concentration= 0.05 (w/v %), g/ml)

Figure 4.27 shows the effects of four metal ions species feed concentrations on retentions' coefficient. Here, a 0.05% unmodified starch concentration was used for different metal ion feed concentrations. The initial 10 mg/l of Zn(II) ions had the highest retention value of about 94.5%. The lower the feed concentration of metal ions, the more effective it was for binding unmodified starches to form macromolecules without causing membrane fouling. It corresponds to a high possibility of membrane fouling that can occur when using high feed metal ions concentrations as they can cause an excess of metal ions present in the solutions without complexation with unmodified starch that are then retained on the membrane surface, which will negatively affect the retention coefficient values.

The same behavior was exhibited by Pb(II) ions species, where retention was insignificantly affected by metal ions feed concentration whenever higher concentrations were used.

For Cr(III) ions, retention was almost constant for each tested metal ion concentration. This was most likely due to Cr(III) ions being partially bonded to the surface of the unmodified starch. Consequently, the retention coefficient was constant for the entire metal ions concentration of 10 to 50 mg/l but slightly decreased at 30mg/l of metal ions concentrations. Cr(III) ions obtained high retention levels at the initial metal ion concentrations before they then decreased.

By contrast, Cr(VI) ions retentions declined gradually at metal concentrations of 10 to 50 mg/l; this is most probably because as the metal ions concentrations increased, their ionic strength reflected too. Thus, the dissociation of Cr(VI) ions towards unmodified starch constants was found to be increased, corresponding to a decreased ability of metal ions-polymer complex on metal ions retentions (Rivas, 2003).

4.5.2 Effect of metal ion feed concentration by PEG

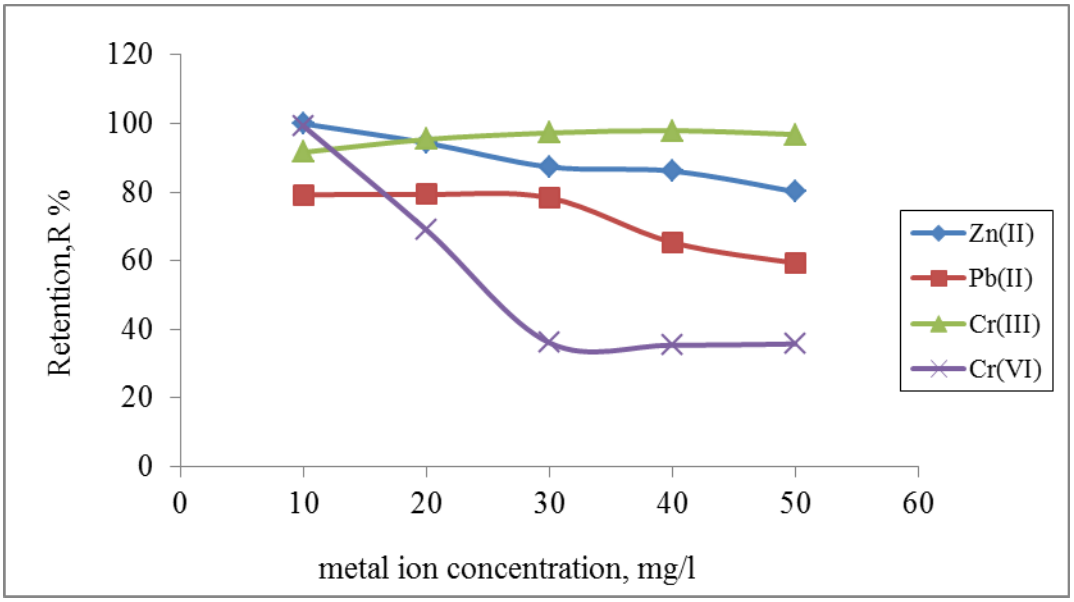


Figure 4.28 The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration= 1.0% (v/v %), ml/ml).

Figure 4.28 shows the retention behavior of Zn(II), Pb(II), Cr(III) and Cr(VI) independently using 1.0% of PEG at different metal ions feed concentrations. It was found that the retention of the selected metal ions species decreased as metal concentrations increased, but different behavior on retentions was obtained for Cr(III) ions. The change of metal ions concentration affected Zn(II) retention, which dropped as the feed concentration rose to 50mg/l. On the other hand, the same pattern was found with PEG on Pb(II) ions retentions, but it achieved only about 60% at 50 mg/l of feed metal ions concentration. The decreased metal ions retention was probably due to the low availability and affinity of metal ions to bond with PEG at high concentration of metal ions species present in metal ions solutions. The polarization phenomenon negatively influenced metal ions retentions whenever high metal ions applied in the PEUF system. In this case, it was a natural process as the gel layer of metal ions-polymer complex can be easily removed (Wang et al., 2011) by backwashing or feed flow scouring that are efficiently practiced to obtain high metal ions retention after a certain time of the PEUF operation.

With regards to the retention of Cr(III) ions using 1.0% PEG, the performance pattern of retention coefficients was similar when 0.05% of unmodified starch was used (Figure 4.27). By employing 1.0% of PEG, Cr(III) ions demonstrated a less significant effect on retention for feed metal ions concentrations which indicates that there was little change in the metal ions retention coefficient.

The pattern was different for Cr(VI) ions retention as Cr(VI) ions decreased drastically as the feed metal ions concentration increased from 10 mg/l to 30 mg/l until it then reached a plateau at 40 mg/l. It seems that low metal ions concentrations applied in selected metal ions removal was favorable instead of high metal ions concentrations, since a high retention level of chromium ions could be achieved. This corresponds to metal ions that would partially bond to the polymer when high metal ions are applied in the PEUF process, resulting in decreasing of metal ions retention (Barakat, 2010). This partially bond of Cr(VI) ions to PEG is most probably due to the presence of anions charges of Cr(VI) (refer to Cr(VI) speciation study) that were found to be excessive in the solutions at 30 mg/l and above of metal ions concentrations when 1 (v/v%) of PEG was found to be concentrated to grab these excess Cr(VI) anions in these metal ions concentrations ranges.

4.5.3 Effect of metal ion feed concentration by PEI

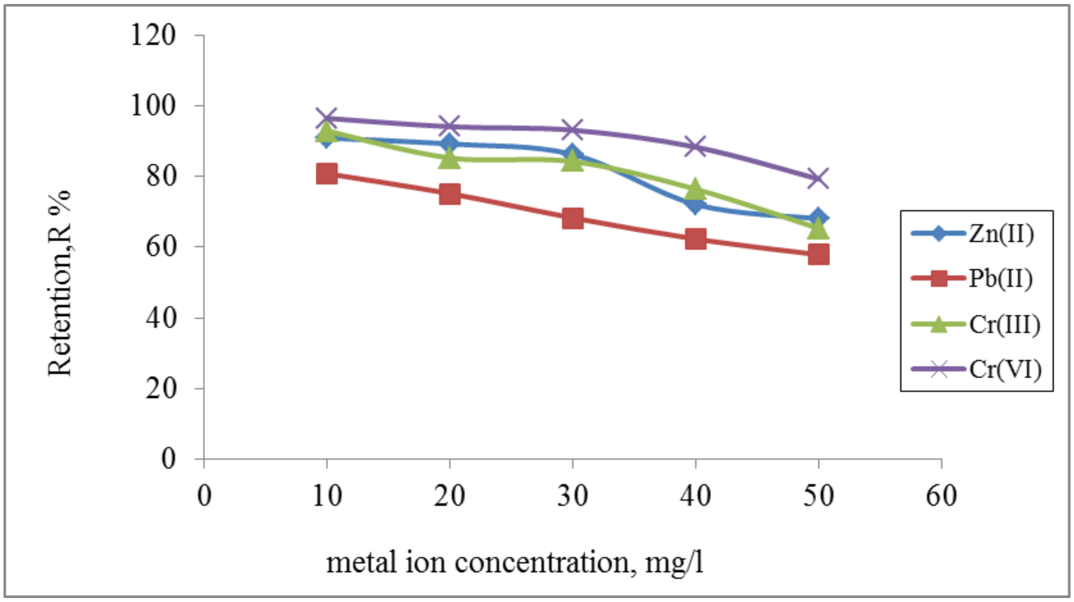


Figure 4.29 The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration= 0.01% (v/v %), ml/ml)

Figure 4.29 revealed the effect of the behavior of four metal ions species; Zn(II), Pb(II), Cr(III) and Cr(VI) on metal ions feed concentrations using 0.01% of PEI applied to different feed concentrations. Figure 4.29 shows that there was a gradual decrease in the value of the retention coefficient when higher feed concentrations were used. For Zn(II) ions, the behavior shown with PEI was similar to unmodified starch (Figure 4.27). Changes to the retention percentage is clearly shown by the interaction of Pb(II)-PEI where 10mg/l results in the highest level of retention compared to high feed concentration practiced in the PEUF study. For the retention of Cr(III) and Cr(VI) ions, it was expected that the lower the feed concentration, the better the retention values would be. This was clearly demonstrated previously with selected metal ions and polymers, as well as unmodified starches and PEG.

The UF study conducted at a laboratory scale is suitable when employing low metal ions feed concentrations in order to avoid the formation of a filter cake on the membrane surface in the initial stages of the experiment.

The retention study using starch, PEG and PEI as polymers was investigated, and results were compared to the discharge standards recommended by the DOE of Malaysia. 10 mg/l had the highest retention of metal ions. Starch was found to efficiently remove Zn(II) and Cr(III) ions and obtained 95% and 93%, respectively of metal ions retention value, whereas PEG and PEI achieved allowable effluent concentrations for Zn(II), Cr(III) and Cr(VI) ions (retention of about 98% for Zn(II) and Cr(VI) ions, and 90% for Cr(III) ions by PEG. 96% of retention of Zn(II) and Cr(III) ions were obtained, and about 96% of retention of Cr(VI) ions was achieved using PEI as a polymer).

4.6 Effect of pH on PEUF flux

The effect of flux is a crucial parameter in the optimization process for the PEUF study. The higher the flux, the less membrane surface is necessary for solutions to be processed in a UF system.

4.6.1 Effect of pH on PEUF flux using unmodified starch

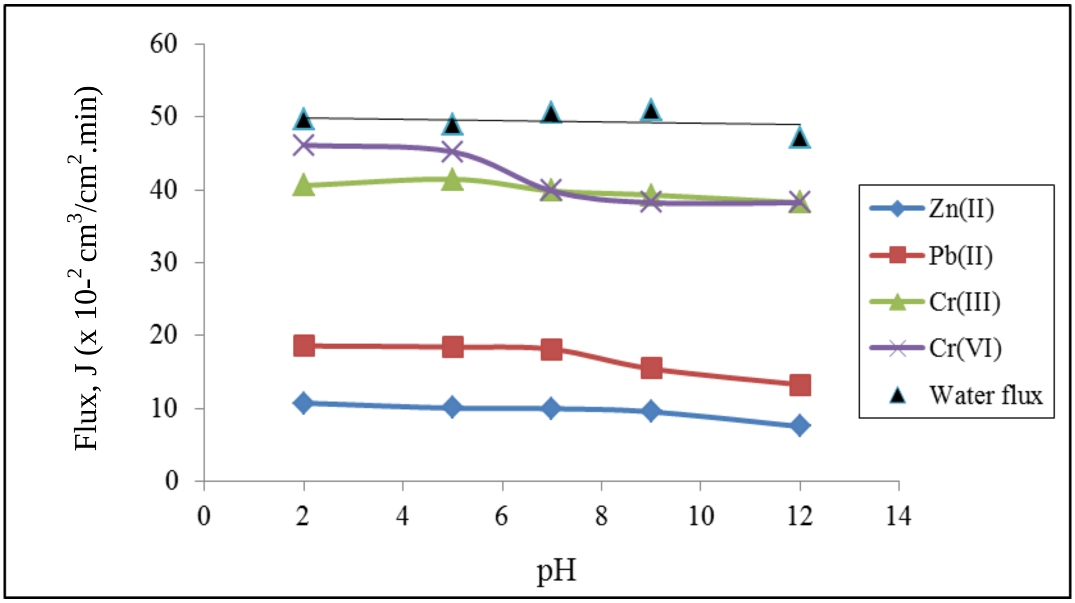


Figure 4.30 Permeate water flux on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) using 0.05 (w/v %), g/ml unmodified starch and 10 mg/l of metal ions concentrations at different pH values.

Permeate flux is one of the important parameters in the PEUF process. Figure 4.30 shows membrane permeability for water, Zn(II), Pb(II), Cr(III) and Cr(VI) using unmodified starch at various pH levels by carrying out an error of metal ions flux on experimental data about ± 0.1 in all discussions. As shown in this figure, pH has little effect on flux as the values fluctuated in range of 47-51 (x 10^{-2}) cm^3/cm^2.min of pure water flux. However, the unmodified starch systems showed slightly less flux when selected metal ions were used. As pH changed from 2 to 12, flux efficiency was about 10 and 20 (x10^{-2}) cm^3/cm^2.min for Zn(II) and Pb(II). For Cr(III) and Cr(VI), permeate flux was 41 and 44 (x 10^{-2}) cm^3/cm^2.min, respectively. Expectations for unmodified starch flux was low due to the behavior of the unmodified starch during the UF processes which was able to interrupt the membrane surface and negatively influence flux. It was observed that the effect of pH on permeate flux for the four selected metal ions was less significant as only small changes in the flux values were observed as the pH increases to 12.

In Figure 4.30, the permeate flux is not significantly influenced by pH. This was due to a gel layer forming on the membrane surface during the PEUF process for the entire range of pH levels tested (Bertolini, 2010).

The lower permeate flux of Zn(II) ions indicated that its ability to form complexes with unmodified starch was low because the starch was able to conduct gelatinization behavior resulting in a starchy formation on the membrane surface that resisted to the flow of metal ions complex solutions corresponding to a negative influence on flux efficiency (Bello-Perez & Paredes-Lopez, 2009).

It was observed that permeate flux was similar for Zn(II) and Pb(II) ions at various pH ranges of 10-20 (x 10^{-2}) cm^3/cm^2.min of flux by using starch. This indicated that the behavior of gelatinization on unmodified starch did not significantly influence the permeate flux in the PEUF system since low concentrations of 0.05 (w/v%) unmodified starch was practiced in the flux study. The same flux results demonstrated by Aroua et.al, showed that pH has little effect on the ability of flux to remove chromium ions from aqueous solutions (Aroua et al., 2007).

Cr(III) ions demonstrated similar behavior almost constantly throughout the range of tested pH levels of about 40% of permeate flux. Different behavior was illustrated by Cr(VI) as a slight decrease in permeate flux occurred when pH increased. The initial value of flux was high due to low ability of unmodified starch-Cr(VI) to form macromolecular sizes at the membrane surface. Eventually molecule sizes became large enough to be retained, hence decreasing the permeate flux value and allowing it to become constant at pH levels greater than 7. For each metal ions species tested in this PEUF study, the value of the permeated flux was almost constant at pH levels around 5 at about 49 (x 10^{-2}) cm^3/cm^2.min of pure water permeate flux.

These results show that pH had a less significant effect on flux when unmodified starch was used. The effect of pH on the PEUF flux was clearly shown; as the interaction of the metal ions tested, (Zn(II), Pb(II) and Cr(III)), towards unmodified starch was low, causing the unmodified starch to undergo gelatinization at higher pH ranges. The paste formation of starch was influenced by polysaccharides groups of starch containing active hydrogen ions at position 2, 3 and 6 of the starch granular structure to be less effective and to not easily to lose its structure for metal ions uptake compared to starch in a soluble form. On the other hand, paste formation of starch may resisted the flow of the metal ions solution through the membrane which negatively affected the flux value (Bello-Perez & Paredes-Lopez, 2009). Nevertheless, higher permeate flux was obtained by Cr(VI) ions, showing that the behavior of gelatinization on unmodified starch did not significantly influence the permeate flux in this research.

4.6.2 Effect of pH on PEUF flux by PEG

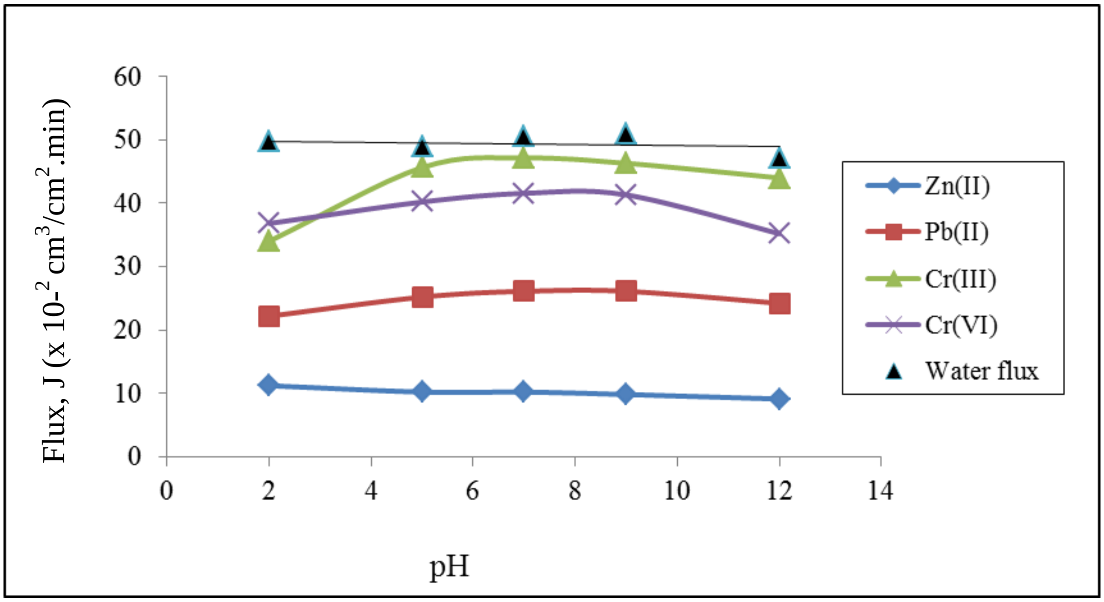


Figure 4.31 Permeate water flux on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) using 1.0 (v/v %), ml/ml PEG and 10 mg/l of metal ions concentrations at different pH values

Figure 4.31 shows the behavior of permeate flux for Zn(II), Pb(II), Cr(III) and Cr(VI) at 10 mg/l using 1.0% of PEG polymer at pH 2 to 12. It can be observed that the flux was present at a constant value over the entire pH range tested for Zn(II) and Pb(II), especially at around pH 5. The flux value fluctuated in a range of 47-51 (x 10^{-2}) cm^3/cm^2.min of pure water flux. Similar behavior was demonstrated by Zn(II) and Pb(II) ions on permeate flux using PEG and tested using unmodified starch.

For Cr(III) ions in very acidic pH environments, the permeate flux of Cr(III) ions was only 34% at a constant PEG concentration of 1.0% (v/v). This decrease in permeate flux could be explained by the changes in the structural formation of polymer molecules caused by pH, which promoted membrane fouling at acidic pH values (Canizares et al., 2005).

For Cr(VI) ions, permeate flux was low at very acidic pH levels but increased slightly until pH 7 was reached. After this point, it decreased until pH 12 due to metal hydroxide precipitation (Barakat, 2010). Lower flux at pH 2 (≅ 36 cm^3/ cm^2.min) was probably due to the membrane suffering from a serious fouling phenomenon at high pH values (Camarillo, 2012). In this study, it was likely that the size of the formed Cr (VI)–PEG complex was not larger than the pores of the studied membrane; consequently the complex could not be completely retained by the membrane.

4.6.3 Effect of pH on PEUF flux by PEI

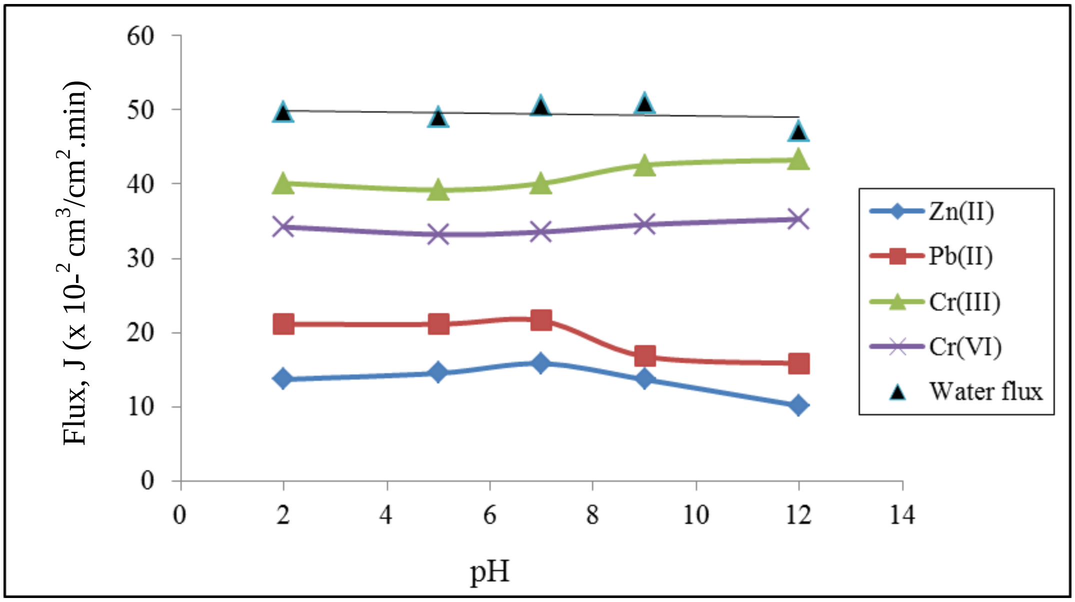


Figure 4.32 Permeate water flux on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) using 0.01 (v/v %), ml/ml PEI and 10 mg/l of metal ions concentrations at

different pH values.

Results of permeate flux of the four metal ions species with PEI in a PEUF system can be observed in Figure 4.32. In this figure, the flux fluctuated at pH levels between 5 and 9 and was constant at other pH ranges for Zn(II) and Pb(II) ions. The value of the flux decreased as pH increased and became more alkaline. This behavior was in contrast to the interaction of Zn(II) and Pb(II) with unmodified starch and PEG. For Cr(III) ions, there was only a slight increase in the permeate flux when pH was greater than 9 and no effect was observed on the Cr(VI) flux for the rest of the pH levels. Constant fluxes for each tested metal species are seen at pH 5 and have indicated about 47-51 (x 10^{-2}) cm^3/cm^2.min of permeate pure water flux in the UF study. The unstable flux values are probably due to the ultrafiltration process which was affected by concentration polarization corresponding to membrane fouling whenever cross-flow ultrafiltration studies were conducted.

4.7 Effect of polymer concentration on PEUF flux

4.7.1 Effect of unmodified starch on PEUF flux

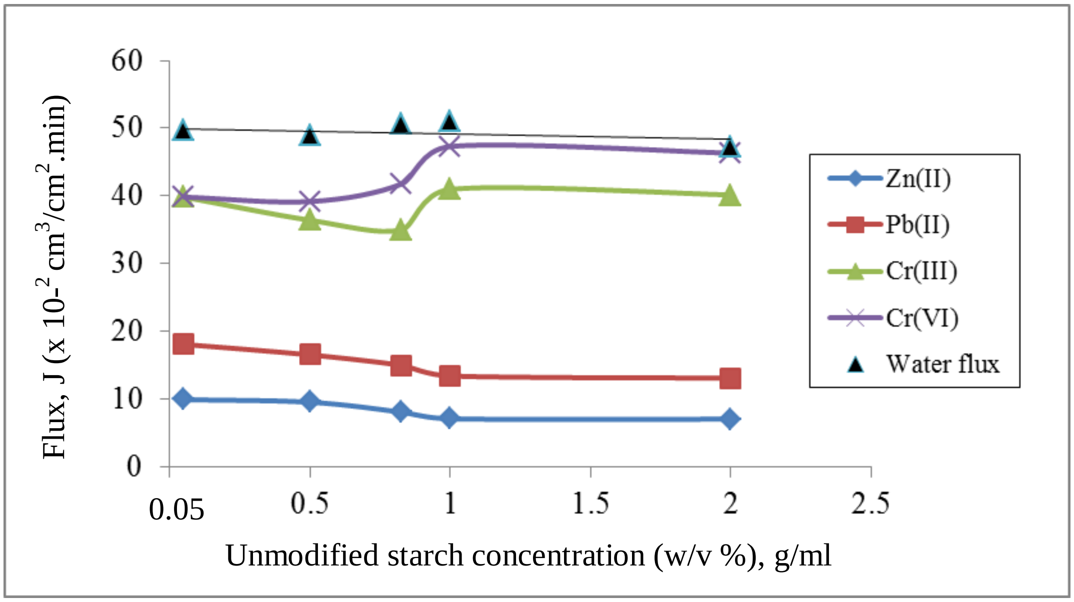


Figure 4.33 The effect of unmodified starch concentrations on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ions concentrations= 10mg/l)

In Figure 4.33, the permeate flux of the four metal ions species Zn(II), Pb(II), Cr(III) and Cr(VI), were different when unmodified starch concentration in single solutions were presented. The flux behavior demonstrated the same pattern for flux values for Zn(II) and Pb(II) ions. At first, permeate fluxes of Zn(II) and Pb(II) ions had slightly higher values of 10 and 20 (x 10^{-2}) cm^3/cm^2.min, respectively compared to only 8 and 18 (x 10^{-2}) cm^3/cm^2.min, respectively on fluxes' value when unmodified starch concentration increased to 2% (w/v). The constant value was reached when the concentration of unmodified starch increased to 1.5%, representing about 50 (x 10^{-2}) cm^3/cm^2.min of water permeate flux.

The different behavior of Cr(III) ions can be seen in Figure 4.33. For Cr(III) ions, the value of the permeate flux decreased with the increase of polymer concentrations. This probably occurred due to the sizes of the Cr(III)-unmodified starch molecules which had smaller sizes compared to membrane pore sizes, meaning that the substance deposited on the surface of the membrane was harder to retain, and low permeate flux remained constant as unmodified starch concentrations increased to 2% (w/v; g/ml). This behavior was similar to Cr(VI) ions on the permeate flux, where the value of permeate flux for Cr(III) and Cr(VI) ions were 42 and 48 (x 10^{-2}) cm^3/cm^2.min, respectively; these values were obtained not too high on flux values. The flux values were slightly lower for Zn(II) and Pb(II) ions compared to both chromium ions but were at a satisfactory level to be tested for the rest of the PEUF study.

4.7.2 Effect of PEG on PEUF flux

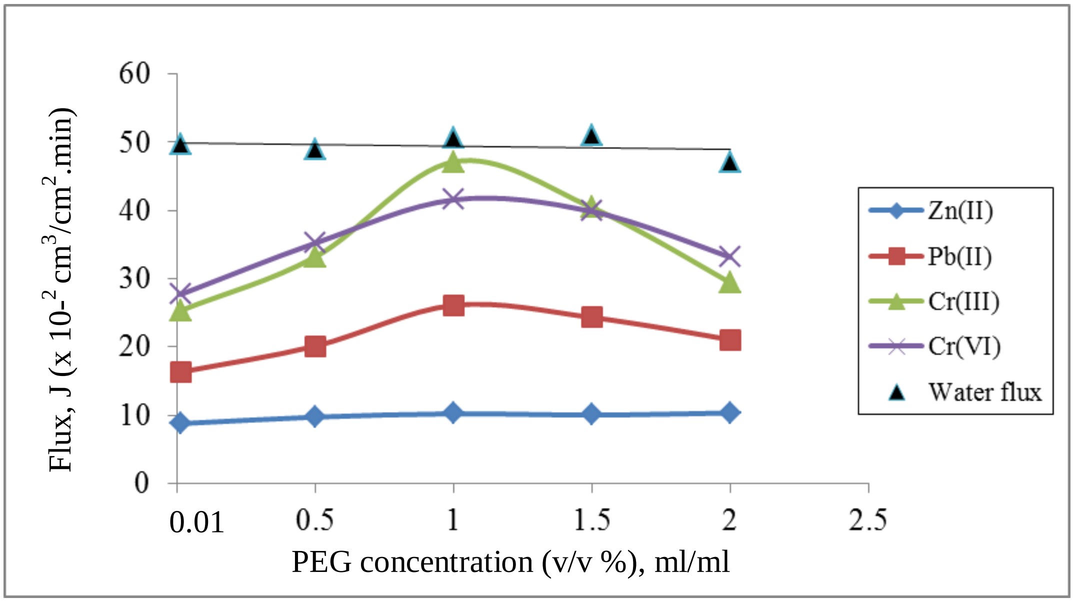


Figure 4.34 The effect of PEG concentrations on the selected metal ions of (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ion concentrations = 10 mg/l)

Figure 4.34 presents the results of permeate flux obtained when selected metal ion species at different PEG concentrations were removed by a single metal ions solution. Constant permeate flux was observed for the Zn(II) ions over the entire range of PEG concentrations values that were tested, representing around 10 (x10^{-2}) cm^3/cm^2.min of the flux value. For Pb(II) ions flux, the flux increased at 1 (v/v%) of PEG concentration and decreased when the polymer concentration increased up to 2 (v/v%). The behavior demonstrated by permeate fluxes was similar to that demonstrated by Cr(III) and Cr(VI) ions. For both chromium ions (Cr(III) and Cr(VI) ions), the highest level of flux (47 and 41 cm^3/cm^2.min, respectively) was obtained at 1(v/v%) of PEG concentrations. The mechanism of selected metal ions-

PEG has been shown in Equation 4.51 (Section 4.11.2) and occurred to form a macromolecular metal ions-polymer complex. The fluctuating value of the permeate flux is probably due to the attractive interaction of PEG and metal ions that form macromolecules as well as the negative effects of hydrodynamic conditions that generally occur whenever the cross-flow of the UF process is practiced in a system.

The lower tendency of PEG to bind to metal ions influenced the partial formation of metal ion–PEG complexes, causing the results for the permeate flux to be lower as shown in Figure 4.34. The size of the metal ion–PEG complex was too small to be completely rejected by the PEUF system. Thus, it can be concluded that the order for PEG on flux is Cr(III)> Cr(VI)> Pb(II) > Zn(II). Figure 8 and Figure 4.34 clearly show that Zn(II) and Pb(II) ions can cause gel formations on membrane surfaces through complexation with unmodified starch and PEG, thereby reducing flux.

It was observed that permeate flux had a constant value over the entire pH test range for Zn(II) and Pb(II), especially at pH values between 5 and 9. This indicated that the flux value was about 47-51 cm^3/cm^2.min for water at all pH levels when using UF. Similar behavior of Zn(II) and Pb(II) ions was demonstrated on permeate flux using PEG as tested with unmodified starch.

At very acidic pH levels, the permeate flux of Cr(III) ions was only 34 cm^3/cm^2.min at a constant PEG concentration of 1.0% (v/v). At acidic pH levels, slight changes in the formation structure of the polymer molecules were obtained, which caused membrane fouling in this pH range (Canizares et al., 2005). For Cr(VI) ions, permeate flux was low at very acidic pH levels but increased slightly until pH 7 before it decreased at the extreme pH level of 12 due to metal hydroxide precipitation (Barakat & Schmidt, 2010). Moreover, the lower permeate flux at pH 2 (≈ 36 (x10^{-2}) cm^3/cm^2.min) was probably due to the membrane which had suffered from serious fouling at high pH levels (Camarillo 2012). In this study, it was more likely that there was less complexation between the Cr(VI)–PEG, and consequently, it was able to pass through the membrane during the filtration process.

4.7.3 Effect of PEI on PEUF flux

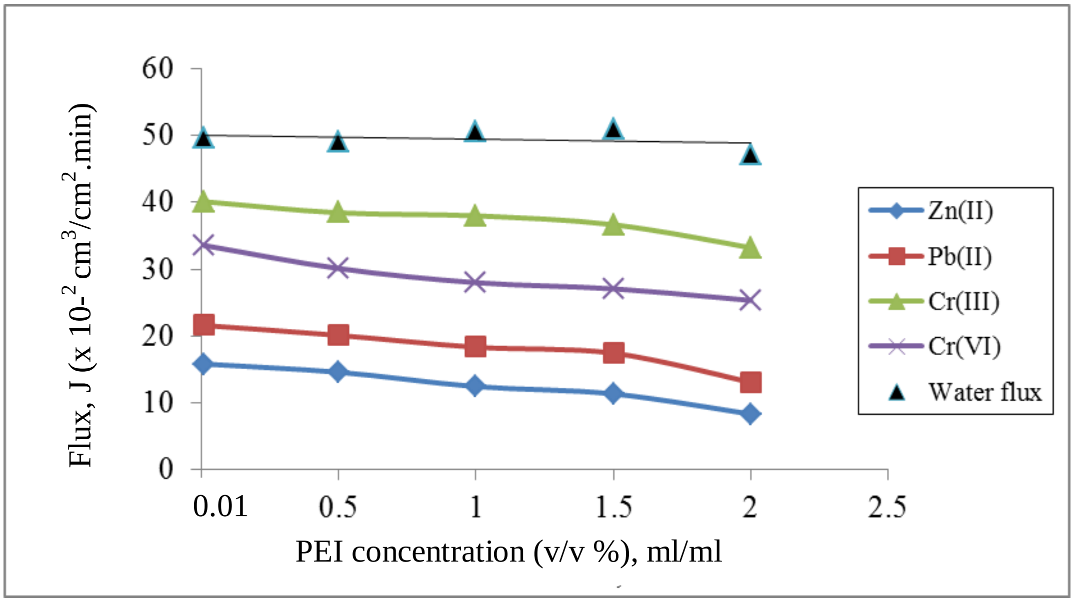


Figure 4.35 Effect of PEI concentration on the selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ions concentrations= 10 mg/l)

The effects of PEI on the flux of the four selected metal ions species at different PEI concentrations using single metal ions solutions is illustrated in Figure 4.35. The behavior of the four selected ions species, Zn(II), Pb(II), Cr(III) and Cr(VI), clearly presented similar behavior over the entire range of pH values that were tested. A low concentration of PEI polymer was used in this UF study, and the highest flux of the four species of ions dropped whenever the PEI concentrations increased from 0.5-2.0%. This behavior shows that low concentrations are favorable for PEUF studies if the goal is to achieve better metal ions-PEI interactions and to enhance the size of the molecules sizes for retention studies.

Low concentrations lower the cost of an operation by using low polymer concentrations in PEUF studies that correspond to the production of less toxic waste.

4.8 The effect of metal ion concentration on PEUF flux

4.8.1 The effect of unmodified starch on PEUF flux

During the optimization process, flux becomes a fundamental parameter in the PEUF study. Less filtration area is required to process the desired amount of solution as higher permeate flux for the membrane is achieved.

Metal ions concentration exerted an influence on the permeate flux of Zn(II), Pb(II) and the two chromium species in this PEUF study. This behavior was in contrast with pH that had less of an effect on flux. On the other hand, the effect of metal ions concentration on permeate flux was also limited to PEUF studies. Given these circumstances, it will be interesting to explain this phenomenon in the following section.

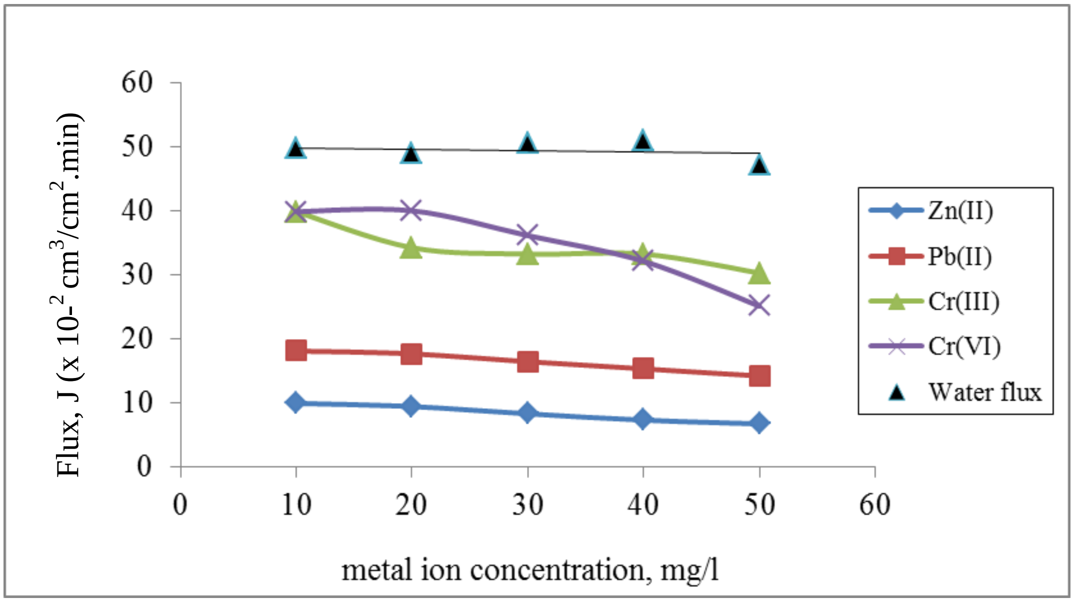


Figure 4.36 The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml), metal ions concentrations = 10 mg/l)

Figure 4.36 shows the effect of different metal ions concentrations on the flux of Zn(II), Pb(II), Cr(III) and Cr(VI) from aqueous solutions using 0.05% of unmodified starch. Lower concentrations of metal ions, 10 mg/l used in the UF process, provided favorable sites for both chromium ions to bond to unmodified starch which had the potential to form macromolecular complexes. In contrast, using high concentrations of metal ions did not assure higher flux efficiency for metal ions in the PEUF system.

The study on the effect of metal ions feed concentration on selected metal species during retention would not be complete if the effects of the feed metal ions concentrations on flux that used 0.05% of unmodified starch at different metal ions concentrations were not performed. It was found that flux efficiency was almost constant for Zn(II) ions at each tested feed concentration. Similar behavior was observed for Pb(II) ions. This shows that feed concentrations had a less significant effect on Zn(II) and Pb(II) ions in PEUF systems.

In contrast, whenever Cr(III) ions were present, low concentrations of 10 mg/l provided the highest flux value of about 40%. The inability of Cr(III) and unmodified starch to bond completely as feed concentrations increased may have led to surface membrane fouling which negatively affected flux. It was observed that the higher the feed concentration, the lower the flux efficiency presented by Cr(VI). This was due to unmodified starch behavior creating a starchy environment that caused gelatinization on the membrane surface that would negatively affect retention efficiency.

Higher feed concentrations were not used because they could affect UF performance in addition to causing reduction on fluxes and most probably the formation of polarization concentration of metal ions and starch. It is demonstrated in Figure 4.36 that the flux value of Cr(VI) ions gradually decreased when more than 20 mg/l of metal ions concentration was used.

4.8.2 Effect of PEG on PEUF flux

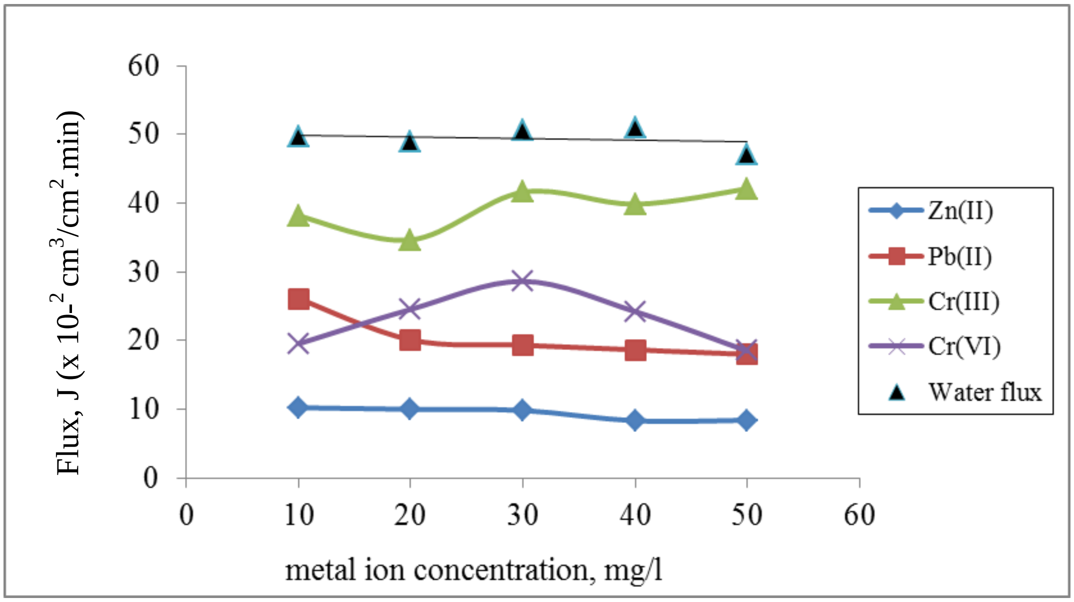


Figure 4.37 The effect of metal ion feed concentration on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG= 1.0% (v/v; ml/ml), metal ions concentrations = 10 mg/l)

Figure 4.37 demonstrated the effects of metal ions concentrations of the four selected metal ions species on flux by using 1.0% of PEG in a single solution.

The behavior of Zn(II) ions on unmodified starch was found to be similar to PEG where the feed concentration was observed to have no effect on Zn(II) ion flux as it remained constant for all tested feed concentration. Pb(II) ion flux was the highest at about 26 cm^3/cm^2.min and became constant whenever higher feed concentrations were used. Regarding membrane permeability, obvious transient flux decay was identified for both chromium cations. Lower concentrations of chromium ions (10 mg/l) provided favorable sites for both chromium ions to bond to unmodified starch, which had potential to form macromolecular complexes. On the other hand, applying high metal ion concentrations did not promise to increase the flux efficiency of metal ions in the PEUF system.

For results obtained on chromium ions flux by employing PEG, both chromium ions flux obtained almost fluctuated by feed metal ions concentrations tested from 10 mg/l to 50 mg/l. In contrast to Cr(VI), the tendency of PEG to form metal ions complexes was greatest at 30 mg/l meaning that the highest permeate flux obtained was 28.643 x 10^{-2} cm^3/cm^2.min. The difference in flux efficiency of Cr(VI) ions at 10 mg/l and 30 mg/l was less than 10 x 10^{-2} cm^3/cm^2.min., indicating that 10 mg/l could still be used as a metal ion feed concentration in the UF system. On the other hand, as Cr(VI) ions increase to 50 mg/l, their ability to form macromolecules declined, negatively influencing flux efficiency. Consequently, complex molecules between metal-polymer could not be completely retained on the membrane surface (Barakat & Schmidt, 2010).

4.8.3 Effect of PEI on PEUF flux

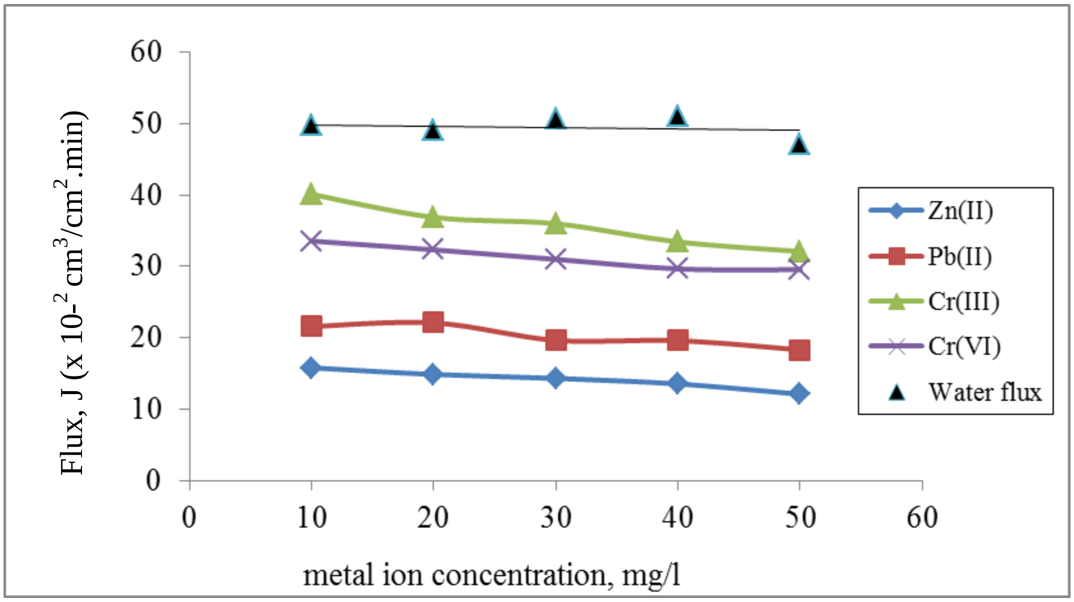


Figure 4.38 The effect of single solution metal ion feed concentrations on Zn(II), Pb(II), Cr(III), and Cr(VI) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI=0.01% (v/v; ml/ml))

Figure 4.38 shows the flux values for the metal ions species Zn(II), Pb(II), Cr(III) and Cr(VI) demonstrated using 0.01% of PEI at different metal ion feed concentrations. This study was carried out in single solutions on a laboratory scale and performed at pH 7.

It was found that most metal ion species had similar constant flux values at every feed concentration tested using PEI. Since feed metal ions concentration had no significant effects on flux when PEI was used, it can be concluded that 10 mg/l of feed concentration can be used in the PEUF study for Zn(II), Pb(II), Cr(III) and Cr(VI). This may be due to the interaction of metal ions species with PEI that forms incomplete macromolecule complexes due to high ionic strength at high feed concentrations that contributes to the dissociation of metal molecules to bond with PEI and prevents complex molecules’ formation. There were no changes to permeate flux values when high feed concentrations of metal ions were used.

The results from all the tested metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI) ions) in the PEUF study using selected polymers, unmodified starch, PEG, and PEI, and 10 mg/l of feed concentration were used to provide good retention coefficients and permeate flux performance. Even though there were other feed concentration values that lead to high retention or flux values, 10 mg/l remains appropriate because the difference in the percentage was not significant or acceptable (< 8%). The permeate water flux that was observed was 50% of the metal ions flux constant value.

4.9 Canizares’s Model employed as theoretical model on selected heavy metal ions removal through the PEUF system

4.9.1 Introduction

As a part of modelling, this study was carried out to fit the established model of single and mixed metal ions solutions obtained via Polymer Enhanced Ultrafiltration (Canizares et al., 2004). This equation for this model consisted of polymer dissociation, complexation of polymer-metal formation derived from conservation, and the equilibrium analyses of reactions occurring in aqueous solutions. The most important part of this model depended on metal ion concentration predictions either in permeate or retentate streams in terms of the behavior of polymer dissociation and the formation of polymer-metal complexation at a known and constant value (Morlay et al., 1998).

4.9.2 Model for metal ions removal via PEUF system

a) Model for single metal ion solutions (Canizares et al., 2004)

Since there were some differences between the theoretical modeling and our research project, we will focus only on the calculation of metal ions removal without including the polymer regeneration process. All modeling will be based on the objectives of study discussed previously in Chapter 1. Figure 4.39 shows the schematic diagram of Canizares's Model employed in this research.

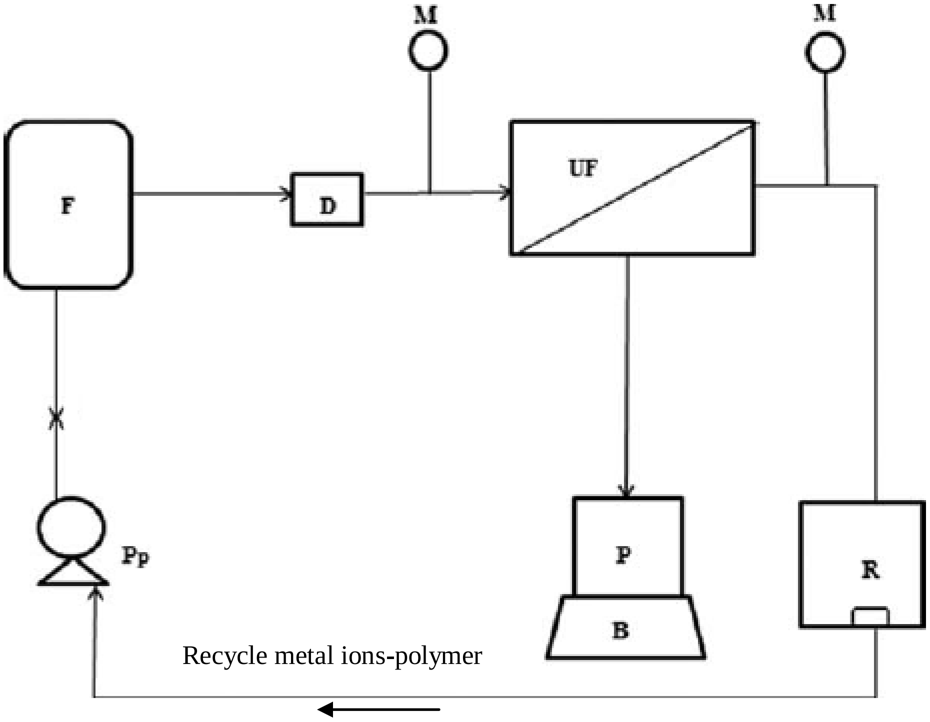


Figure 4.39 Schematic diagram of Canizares's Model employed in this research as theoretical model of the PEUF system. This would show the F: feed tank included

[M] and [L] in the reactor, UF: UF system, P: permeate stream included $[M_p]$ and $[L_p]$, R: retentate solutions included $[M_R]$ and $[L_R]$, B: Electronic balance, Pp: Peristaltic pump, M: pressure meter, D: Damper.

The metal ions charges were omitted throughout the modeling process to create the reactive ultrafiltration process and the equation below:

$$HL \leftrightarrow H + L;\ K_A = \frac{[H][L]}{[HL]} \tag{4.3}$$

$$M + L \leftrightarrow ML;\ K_1 = \frac{[ML]}{[M][L]} \tag{4.4}$$

$$M + nL \leftrightarrow ML_n;\ K_n = \frac{[ML_n]}{[M][L]^n} \tag{4.5}$$

([H] = free metal ions ligands concentration, [L] = polymer concentration, [M] = metal ions concentration)

To simplify these calculations, the following assumptions were made (Canizares et al., 2004):

(1) Equilibrium is reached instantaneously

(2) Complexes are formed from stoichiometries 1:1 to 1:*n*

(3) In the considered pH interval, formation of metal-hydroxy complexes are neglected

(4) Reactors behave like a continuously stirred tank

(5) pH value is the same on both sides of the membrane

(6) The complex retention coefficient is the same as the polymer retention coefficient which indicates that the metal ions bind together with polymers to form macromolecular complexes that are able to retain at the membrane surface, and the metal ions-polymer rejects from the PEUF system)

The model created in our study has been simplified and expressed in the following equations for ease of understanding and to interpret the theoretical calculations in this study:

Overall mass balance, polymer balance and metal ion balance are expressed as:

$Q_F = Q_P + Q_R$, $Q=VA$

$Q_F = Q_R + Q_P$

$$Q_F = V_R \underline{d[L]_R} + Q_P[L]_P \quad (4.6)$$

thus, $$V_R\left\{\frac{d[L]_R}{dt}\right\} = -\; Q_P[L]_P \quad (4.7)$$

$$Q_P(t) = Q_F(t) = V_R.\frac{d[L]_R}{dt} \quad (4.8)$$

Substitute Equation 4.7 in Equation 4.6, where $\mathbf{Q_R = Q_F - Q_P}$

$$V_R \frac{d[M]_R}{dt} = Q_F[M]_F - Q_P[M]_P \quad (4.9)$$

As a result, the equation for metal ions and polymer retention coefficients can be defined as:

a) For metal ion coefficient equation:

$$R_M = 1 - \frac{[M]_P}{[M]_R} \quad (4.10)$$

$$R_M = \frac{[M]_R - [M]_P}{[M]_R} \quad (4.11)$$

$$[M]_P = [M]_R - R_M[M]_R \quad (4.12)$$

Thus, $[M]_P = [M]_R (1- R_M)$ (4.13)

Substitute Eqn.4.13 in Eqn. 4.9,

$$V_R \frac{d[M]_R}{dt} = Q_F[M]_F - Q_P [M]_R (1- R_M) \quad (4.14)$$

b) For polymer retention coefficient equation:

$$R_L = 1 - \frac{[L]_P}{[L]_R} \quad (4.15)$$

$$R_L = \frac{[L]_R - [L]_P}{[L]_R} \quad (4.16)$$

$$[L]_P = [L]_R - R_L[L]_R \quad (4.17)$$

Thus, $[L]_P = [L]_R (1- R_L)$ (4.18)

Substitute Equation 4.18 in Equation 4.7,

$$V_R \frac{d[L]_R}{dt} = -Q_P[L]_R(1 - R_L) \quad (4.19)$$

c) For permeate metal ion concentration equation:

$$[M]_T = [M]_P + [L]_P \quad (4.20)$$

$$[M]_T = [M] + \sum_n [ML_n] \quad (4.21)$$

$$[M]_T = [M]_R(1 - R_M) + [L]_R (1 - R_L) \quad (4.22)$$

$$[L]_R = \sum_n [ML_n] \qquad (4.23)$$

Thus, when $[M]_P = [M]_T$ (4.24)

$$[M]_P = [M](1 - R_M) + \sum_n [ML_n](1 - R_L) \qquad (4.25)$$

d) For the metal ion retention coefficient equation:

$R_M = 1 - \frac{[M]_P}{[M]_T}$, where $[M]_P$ eqn. taken from Equation 4.25 and $[M]_T$ from Equation

4.21

$$R_M = 1 - \frac{(1 - R_{Ml})[M] + (1 - R_L)\sum_n [ML_n]}{[M] + \sum_n [ML_n]} \qquad (4.26)$$

$$= \frac{[M] - \sum_n [ML_n] - [(1 - R_{Ml})[M] + (1 - R_L)\sum_n [ML_n]]}{[M] + \sum_n [ML_n]} \qquad (4.26(a))$$

$$R_M = \frac{[M]\, R_{Ml} + R_L \sum_n [ML_n]}{[M] + \sum_n [ML_n]} \qquad (4.26(b))$$

Since, from Equation 4.5, $K_n = \frac{[ML_n]}{[M][L]^n}$,

thus, $[ML_n] = K_n[M][L]^n$ (4.27)

Substitute Equation 4.27 with Equation 4.26 (b),

$$R_M = \frac{[M]\, R_{Ml} + R_L\, [\sum n\, K_n[M]\, [L]^n]}{[M] + [\sum n\, K_n[M]\, [L]^n} \qquad (4.28)$$

$$R_M = \frac{R_{Ml} + R_L \sum n\, K_n[L]^n}{1 + \sum_n K_n[L]^n} \qquad (4.29)$$

**To calculate metal ion retention, Equation 4.29 is recommended.

e) For total ligand concentration equation:

$$[L]_T = [L] + [LH] + \sum_n n[ML_n] \quad (4.3)$$

which consist of the combination of Equations 4.30, 4.31 and 4.32:

$$[L]_T = [L] + \frac{[L][H]}{K_A} + \sum_n n[ML_n] \quad (4.31)$$

$$[L]_T = [L] + \frac{[L][H]}{K_A} + \sum_n n\, K_n[M][L]^n \quad (4.32)$$

f) For the free metal concentration equation:

From Equation 4.21, $[M]_T = [M] + \sum n\ [ML_n]$, thus,

$$[M] = [M]_T - \sum_n n\ K_n[M][L]^n \quad (4.33)$$

$$[M]_T = [M] + \sum_n n\ K_n[M][L]n \quad (4.34)$$

$$[M]_T = [M]\ (1 + \sum_n n\ K_n[L]^n \quad (4.35)$$

$$[M] = \frac{[M]_T}{1 + \sum_n K_n[L]^n} \quad (4.36)$$

Introducing Equation 4.36 in Equation 4.32:

$$[L]_T = [L] + \frac{[L][H]}{K_A} + \frac{[M]_T \sum_n nK_n[L]^n}{1 + \sum_n nK_n\ [L]^n} \quad (4.37)$$

g) Permeate volume calculation

Permeate volume as a function of time can be calculated with the following integral equation:

$$V_{P(t)} = \int_0^t Q_P(t)\,dt \qquad (4.38)$$

This equation can be solved numerically as shown below:

$$V_{P(t)} = \sum Q_P(t)\,\Delta t \qquad (4.39)$$

Where Q_P is the permeate flowrate at time t and Δt the size of each i interval of the total operation time.

(b) Metal and polymer concentrations calculation at time, t

An analytical solution is too complex, so this system has been solved by applying a finite growth method. In this study, this equation did not involve a theoretical calculation for metal ion concentrations. However, if this study was to be repeated using time as a parameter, the following equation could be used for theoretical metal and polymer concentrations based on Canizares modelling (Canizares et al., 2004).

For metal and polymer concentrations based on time, t respectively:

$$\frac{V_R\,[M]_{R,t}+1 - [M]_{R,t}}{\Delta t} = Q_{F,t}[M]_F - Q_{P,t}[M]_{R,t}(1 - R_{M,t}) \qquad (4.40)$$

$$\frac{V_R\,[L]_{R,t}+1 - [L]_{R,t}}{\Delta t} = -Q_{P,t}[L]_{R,t}(1 - R_L) \qquad (4.41)$$

Metal and polymer concentration at time $t + 1$ can be written as:

$$[M]_{R,t+1} = [M]_{R,t} + \frac{\Delta t}{V_R}\{Q_{F,t}[M]_F - Q_{P,t}[M]_{R,t}(1 - R_{M,t})\} \tag{4.42}$$

$$[L]_{R,t+1} = [L]_{R,t} - \frac{\Delta t}{V_R} Q_{P,t}[L]_{R,t}(1 - R_L) \tag{4.43}$$

This model is to estimate theoretically and commonly used to estimate the feed, retentate and permeate metal ions solutions in PEUF process, but it can be used for higher feed metal ions concentration and polymer concentrations in the feed stream whenever the real wastewater discharged issues are overcome.

In our study, we did not involve polymer regeneration processes in the experiments. Thus, we discarded this section according to theoretical analyses:

$$[M]_F \neq 0 \text{ for metal retention process} \tag{4.44}$$

$$[M]_F = 0 \text{ for polymer regeneration process} \tag{4.45}$$

The calculation sequence is:

(1) Initial polymer and metal concentrations in the reactor are:

$$[L]_{R,0} = [L]_0 \tag{4.46}$$

$$[M]_{R,0} = 0 \text{ for metal retention process} \tag{4.47}$$

$$[M]_{R,0} = [M]_0 \text{ for polymer regeneration process} \tag{4.48}$$

(2) Free polymer concentration [L] is calculated by means of Equation 4.37, and the initial metal retention coefficient $R_{M,0}$ is found using Equation 4.29.

(3) From R_M and R_L respectively, metal and polymer concentrations in permeate stream can be calculated.

(4) R_M, $[M]_{R,\, t+1}$ and $[L]_{R,\, t+1}$ can be calculated using Equations 4.42 and 4.43 once an integration step size Δt has been assigned. The calculation is carried out at constant Δt.

(5) In order to calculate permeate volume Equation 4.41 is solved.

(6) Steps 2–5 are repeated until final conditions are reached.

Following this calculation algorithm, it is possible to determine the temporal evolution of metal and polymer concentrations in the reactor and permeate stream in addition to the metal retention coefficients for both processes.

A typical concept of polymer regeneration processes is the metal retention coefficient(Golovanov, 1993):

$$R_M(\%) = \frac{[M]_{R,t}}{[M]_{R,0}} \times 100 \qquad (4.49)$$

The temporal development of this variable can be found using the previous calculation algorithm.

4.10 The ANOVA analyses of regression of experimental data and the Canizares theoretical model

a) Single metal ion solutions:

1) Effects of pH on metal ions retention (R) by using selected polymers

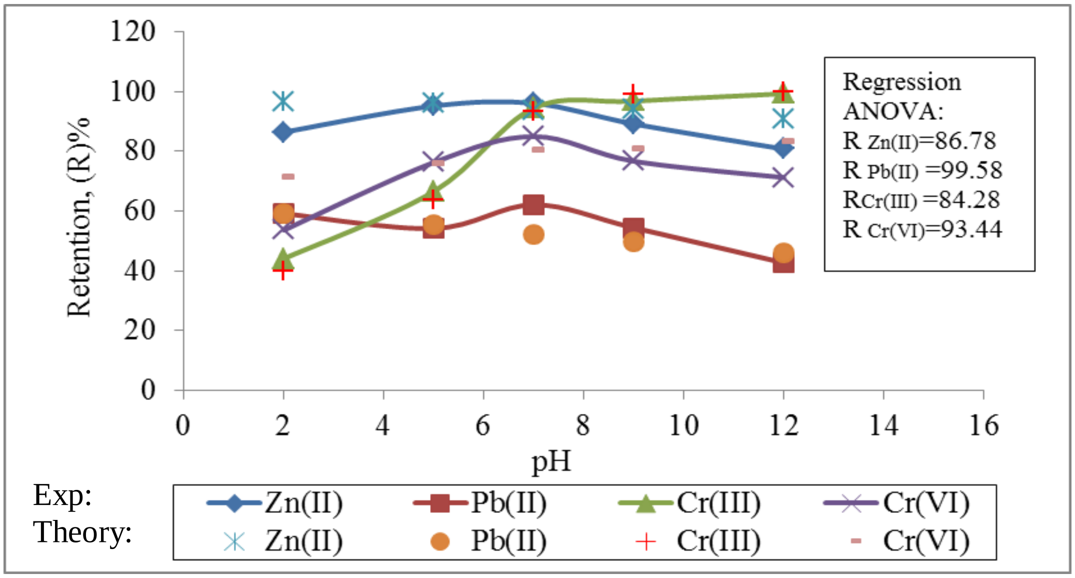


Figure 4.40 Regression coefficient (R^2) of the effect of pH on 10 mg/l concentration of the selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions using 0.05% (w/v; g/ml) of unmodified starch (TMP=1.5 bar, flowrate=115 ml/min)

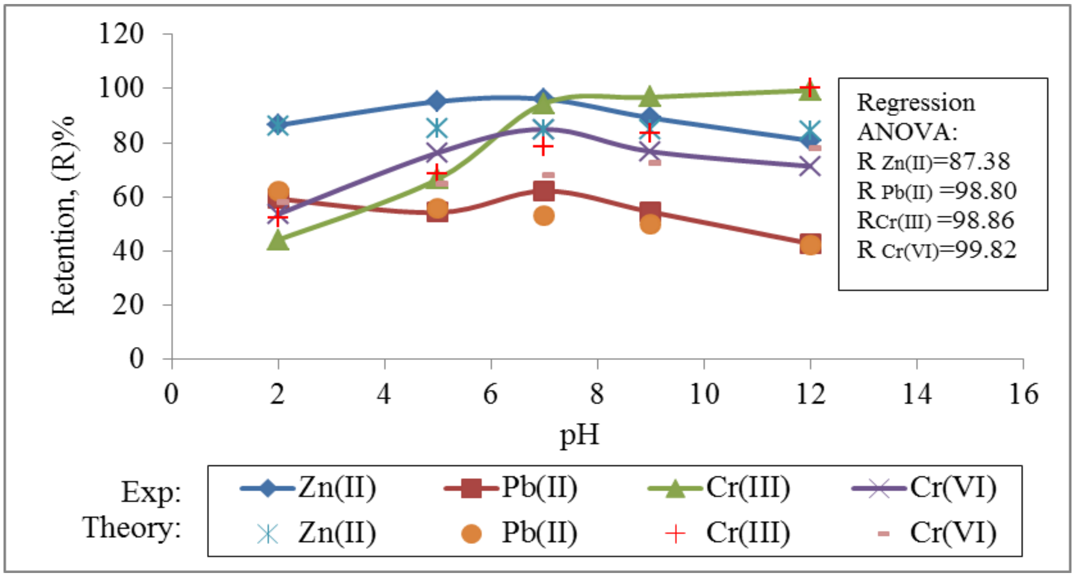


Figure 4.41 Regression coefficient (R^2) of the effect of pH on 10 mg/l concentration of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions using 1.0% (v/v; ml/ml) of PEG (TMP=1.5 bar, flowrate=115 ml/min)

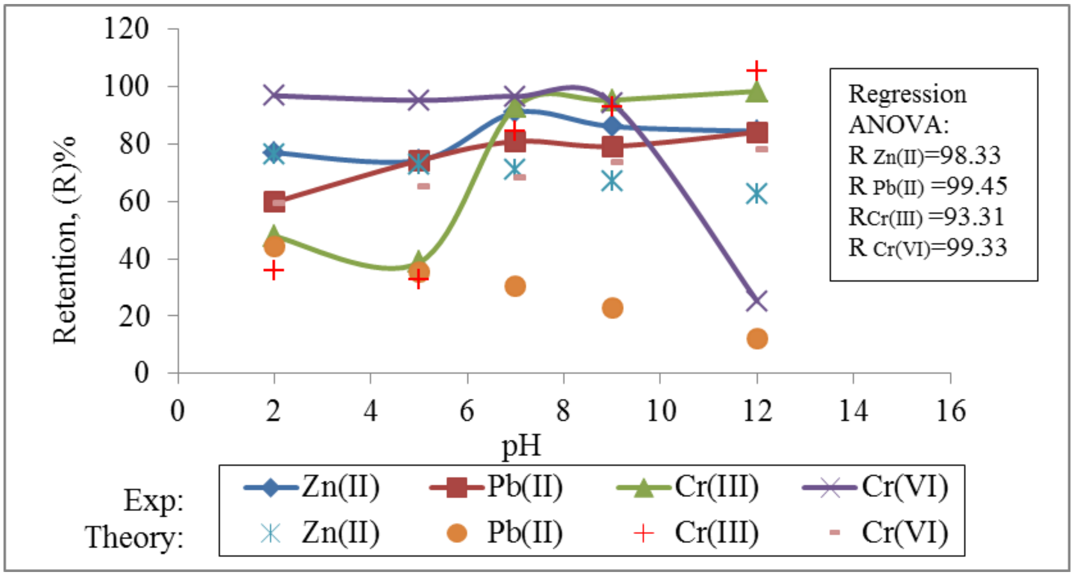


Figure 4.42 Regression coefficient (R^2) of the effect of pH on 10 mg/l concentration of selected metal ions using ANOVA to analyze Zn(II), Pb(II),

Cr(III) and Cr(VI) retentions using 0.01% (v/v; ml/ml) of PEI (TMP=1.5 bar, flowrate=115 ml/min)

2) Effects of polymer concentration on metal ions retention (R) by using selected polymers

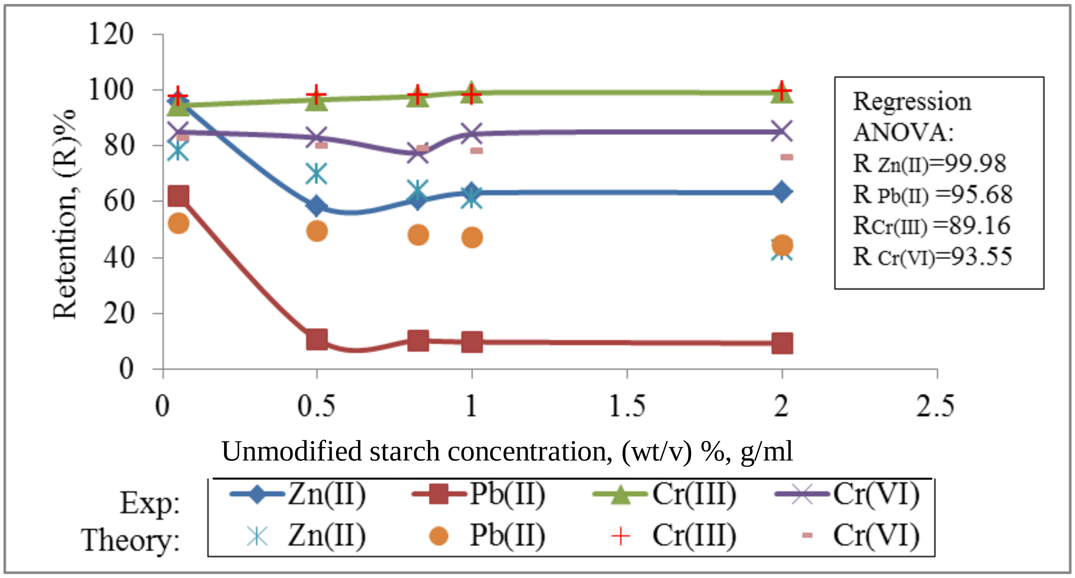


Figure 4.43 Regression coefficient (R^2) of the effect of unmodified starch concentration on 10 mg/l concentrations of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

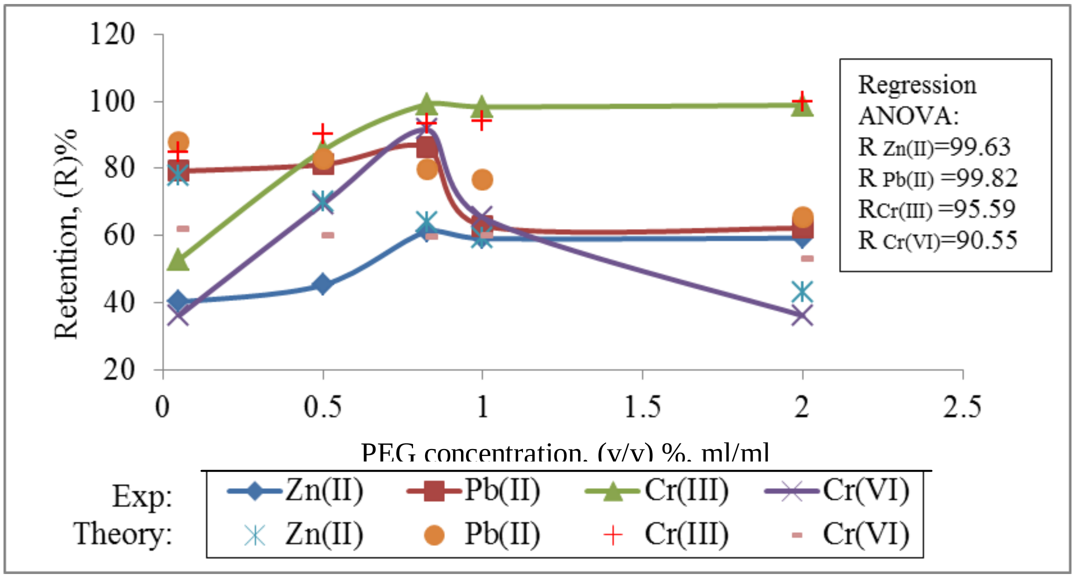


Figure 4.44 Regression coefficient (R^2) of the effect of PEG concentration on 10 mg/l concentrations selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

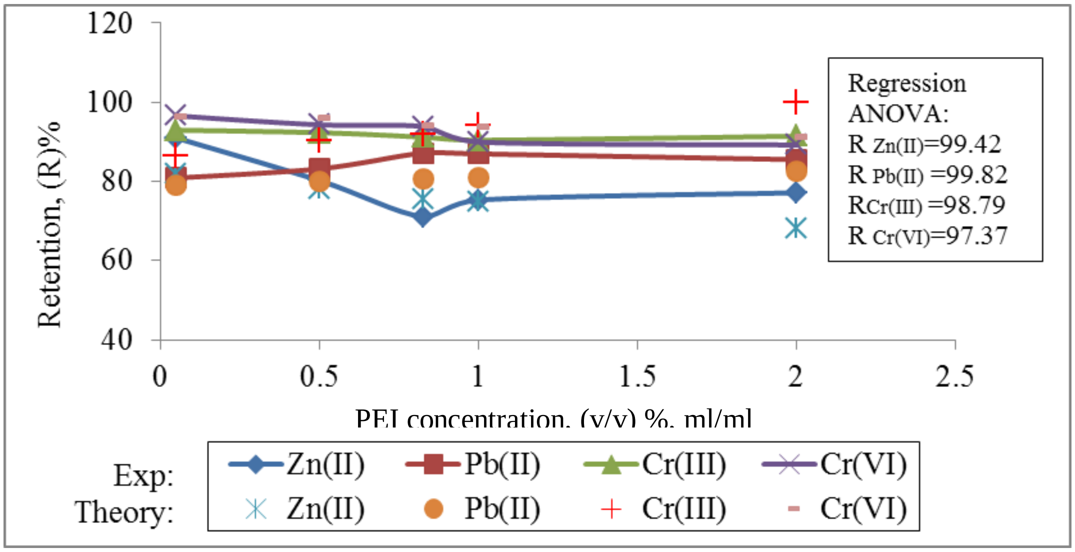


Figure 4.45 Regression coefficient (R^2) of the effect of PEI concentration on 10 mg/l concentrations selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

3) Effects of metal ions concentration on retention (R) by using selected polymers

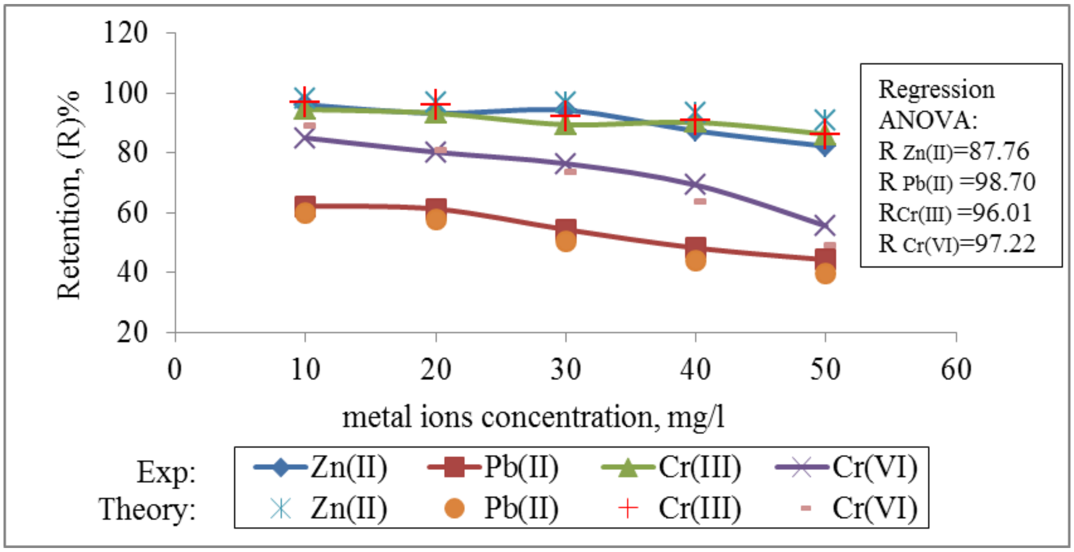


Figure 4.46 Regression coefficient (R^2) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch concentration= 0.05 % (w/v; g/ml))

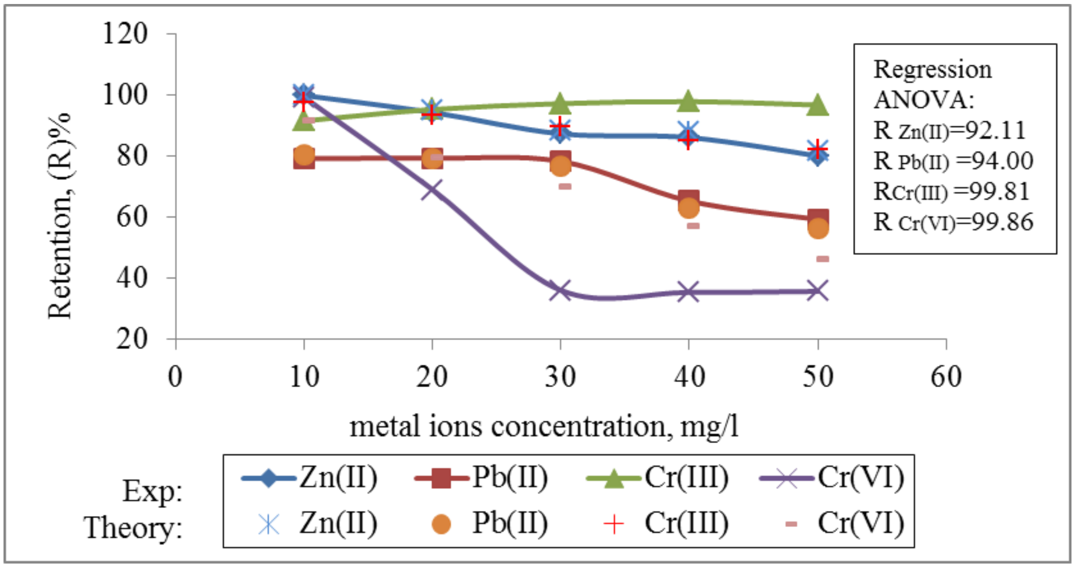


Figure 4.47 Regression coefficient (R^2) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI)

retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration= 1.0% (v/v; ml/ml))

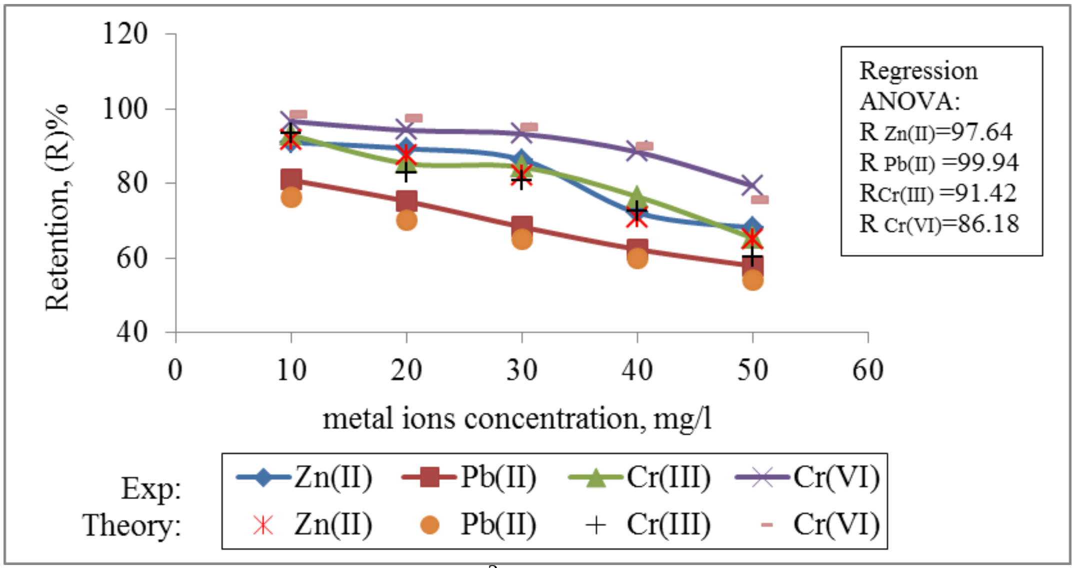


Figure 4.48 Regression coefficient (R^2) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration= 0.01% (v/v; ml/ml))

For overall conclusions of single metal ions solutions regression coefficient (R^2) using ANOVA, the numbers of regression coefficients were mostly higher than 90% and respectively obtained 67%, 78% and 89% for Zn(II), Cr(III) and Cr(VI) ions. Pb(II) ions were found to be well fit with the Canizares model for each parameter tested using a PEUF system.

The optimum working conditions for the single metal ions solutions (pH 7, flowrate= 115 ml/min, feed metal ions solutions concentration = 10 mg/l, polymer concentration = 0.05% of unmodified starch, 1.0% of PEG and 0.01% for PEI) were also used for the mixed solutions because of the high retention values achieved by the single metal ions solutions from synthetic metal ions solutions. Similar optimum working conditions were used for mixed metal ion solutions to investigate if more effective removal could be achieved using mixed solutions. The assumption was that little or no metal ions competition exists in single metal ions solutions leading to a high retention of metal ions. Therefore, in a mixed metal ion solution, the four metal ions in the solution would compete with each other to adsorb the polymers and influence retention. The studies were conducted on both conditions as neither single nor mixed metal ions solutions seem to be effectively removing metal ions by the PEUF system. The removal of metal ions in mixed metal ions solutions was practical since mostly metal ions are found in mixtures in real wastewater.

4.11 Polymer Enhanced Ultrafiltration of Mixed Metal Ion Solutions

4.11.1 Effect of pH on retention using unmodified starch

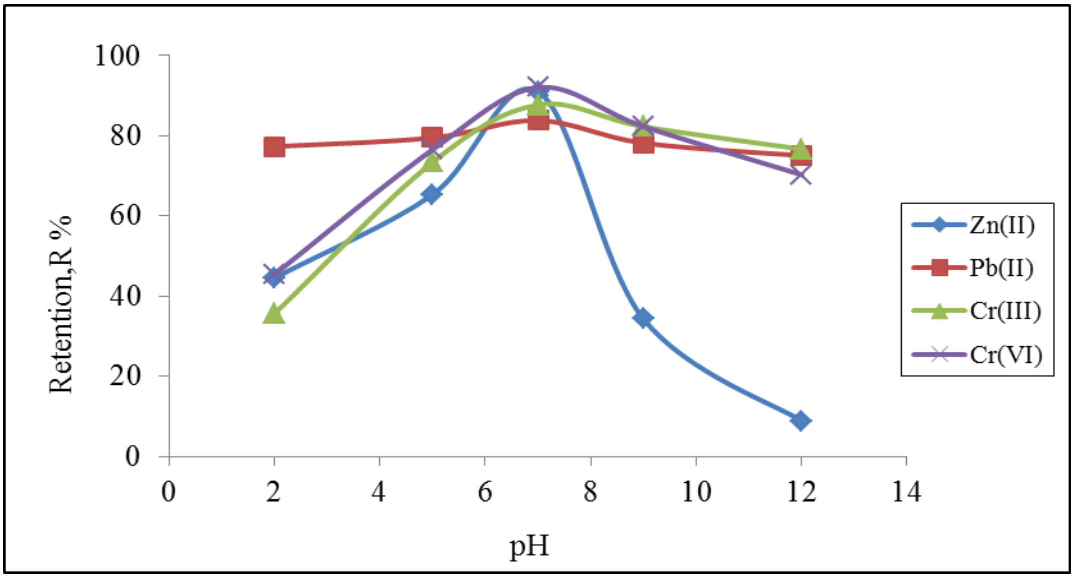


Figure 4.49 Effect of pH on 10 mg/l concentration of each metal ions (Zn(II),

Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 0.05% (w/v; g/ml) unmodified starch , TMP=1.5 bar, flowrate =115 ml/min)

Figure 4.49 depicts the influence of feed solution pH on retention in the presence of 0.05% (w/v) starch as polymer at 1.5 bar pressure. The adsorption of selected metal ions by the unmodified starch creates a non-ionic bond with selected metal ions in the solutions, and there is a high possibility that ionic interaction between unmodified starches towards metal ions will occur during metal ions-starch complexes.

For the binding mechanism of unmodified starch to occur chemically at pH 2, low metal ion retention was obtained due to the presence of metal ions and protons in the solution competing to be adsorbed onto the available sites on the polymer. The formation of protonated carboxylate groups decreased metal ion retention in situations where the complexation of metal ions is aggressively disassociated with a decreasing ability to agglomerate onto membrane surfaces.

The ability of metal ions to be adsorbed by unmodified starch is influenced by pH. At certain pH levels, the formation of macromolecular complexes decreased since the protonation of carboxyl groups decreased along with the starch. The interaction of the binding mechanism between starch and metal ions was lower which negatively affected retention. Consequently, the retention coefficient decreased. The dissociation of metal ions-polymer complexes caused by desorption that occurred at a too acidic pH level can cause the metal ions to pass through the membrane surface which corresponds to less metal ion retention. Consequently, an increase in metal ion retention is found when the pH increased to a neutral pH level (Canizares et al., 2007).

As pH increased to pH 5, the macromolecular metal ion-polymer was able to be complexed because of increased concentration of deprotonated carboxylic groups increased metal ion retention (Canizares et al., 2004; Choo, 2008). As expected, the retention of the four selected metal ions had the highest retention levels at pH 7 as more hydrogen ions and $CH_2\text{-}CH(COO^-)$ was produced, which increased the binding sites for heavy metal ions in ionic interactions as shown in the following equation:

$$n\,\{[\text{-}CH_2\text{-}CH(COOH)^-]_x + xM_e^{n+} \leftrightarrow \{[\text{-}CH_2\text{-}CH(COO^-)]_x\}nM_{ex}^{n+} + n\cdot xH^+ \quad (4.50)$$

According to Equation 4.50, the formation of complexes was due to an increase in pH value that caused an increase in metal ion retention.

The Zn(II) cations existed at the initial pH range (pH 0-9) in accordance to Zn(II) speciation species and bonded completely with unmodified starch, but they were replaced by Zn(II) anions species at high pH levels. Therefore, it was a high possibility that the adsorptive mechanism would occur chemically at pH range of 2 until the neutral pH of 7, where the polymeric binding of starch is generally influenced by two polysaccharide groups, namely amylose and amylopectin. Amylopectin has a highly branched (70-80%) molecular structure (Hoover, 2001) and as a result, has a high possibility of crumpling, losing its structure (Eilers, 1936) and allowing metal ions to penetrate surface of the molecules (Chabot, 1976). As pH range increased to a too alkaline pH range, repulsion of metal ions to polymer occurred due to anions charges of Zn(II) that were reluctant to bind together to unmodified starch (refused to form metal ions-polymer complex), which resulted in low metal ions retention.

Pb(II) exists as cations over the entire range of pH values that were tested, and the competition between H^+ and Pb^{2+} to bind to starch caused the number of retentions to remain constant over all pH levels. This trend was caused by a different metal ions species that existed at certain pH levels and that are adsorbed by unmodified starches. From pH 9 to 12, the retention of Pb(II) and Cr(III) reached a plateau at a value of about 80%. It was found that the retention of Pb(II) remained almost constant at a value of 80% over the tested pH range. The results showed the reduced ability of Pb(II) ions to bind to the unmodified starch. About 80% of Pb(II) ion retention was obtained throughout the tested pH range. Observed retention for Pb(II) was not due to a complexation mechanism but was due to the formation of a starch gel layer on the surface of the membrane. In this case, the Pb(II) trapped in this gel layer indicated the ineffectiveness of using unmodified starch as a binding biopolymer to remove Pb(II).

By contrast, the retention of Cr(VI) decreased at high pH levels due to the protonation of chelating groups, namely carboxylic functions. Cr(VI) anions existed over the entire range of pH values that were tested and did not completely undergo complexation with unmodified starch. Since retention of metal ions increased at higher pH levels when unmodified starch was used as a polymer, chemical interaction of metal ions polymer is not possible. Unmodified starch binding with metal ions could occur physically as well as chemically with high starch glucose groups containing starch that can bind chemically with metal cations.

The adsorptive mechanism is probably due to the formation of a number of pendant hydroxyl (OH) groups capable of forming hydrogen bonds. H^+ at position 2-, 3- and 6- in glucose are able to form donor bonds that can be grabbed by metal ions. Retention was constant for Pb(II) but decreased for Zn(II), Cr(III) and Cr(VI) at alkaline pH levels. This was because anion species were present in alkaline conditions for Zn(II), Cr(III) and Cr(VI) (Aroua et al., 2007), which perform the repulsive mechanism that enables binding to an unmodified starch at higher pH levels. These Cr(VI) anionic species are not expected to be complexed by carboxylic groups (Aroua et al., 2007). The complexation between Cr(VI) ions and unmodified starch occurred due to formation of an unmodified starch gel layer on the membrane surface that trapped Cr(VI) ions.

Using starch without modification efficiently removed Cr(VI) ions without reducing them to Cr(III) ions. As a result, it avoided precipitation. The interaction of unmodified starch is expected to occur by natural adsorption. Generally, starch categorized as non-ionic is bonded to the target metal ions influenced by granular structure. In addition, amylose is the larger component of starch and functions as a hydrocolloid that able to form complexation with metal ions. The high viscosity behavior of starch caused by extended starch conformation behavior is not significantly affected by temperature. Thus, temperature was not used as a parameter in this study.

Extended loose helical chains possess a relatively hydrophobic inner surface that does not hold water well, (Yeh, 2001) and in consequence metallic cations, namely Zn(II), Pb(II), Cr(III) and Cr(VI), can easily replace these chains. The second component of starch is amylopectin whose behavior makes it easy to lose viscosity in the solution due to the interaction between amylose chains and the retrogradation process leading to a slimier consistency (Chung & Park, 2009), which influences the possibility of metal ions-starch complexation. This factor caused the adsorptive mechanism between unmodified starch and metal ions to be activated during the ultrafiltration process. Since the granular structure easily loses its structure, the granules were easily replaced with metal ions and bound together which increased metal ion retention. In addition to the gelatinization behavior of starch as pH increasing, it should be noted that a polarization phenomenon took place that may have interfered with this study. This polarization was caused by alteration of the granular surface of the starch to became starchy in form, reducing the ability of the starch polymer to bond with metal cations, hence the decreasing retention (Chabot, 1976).

4.11.2 Effect of pH on retention by PEG

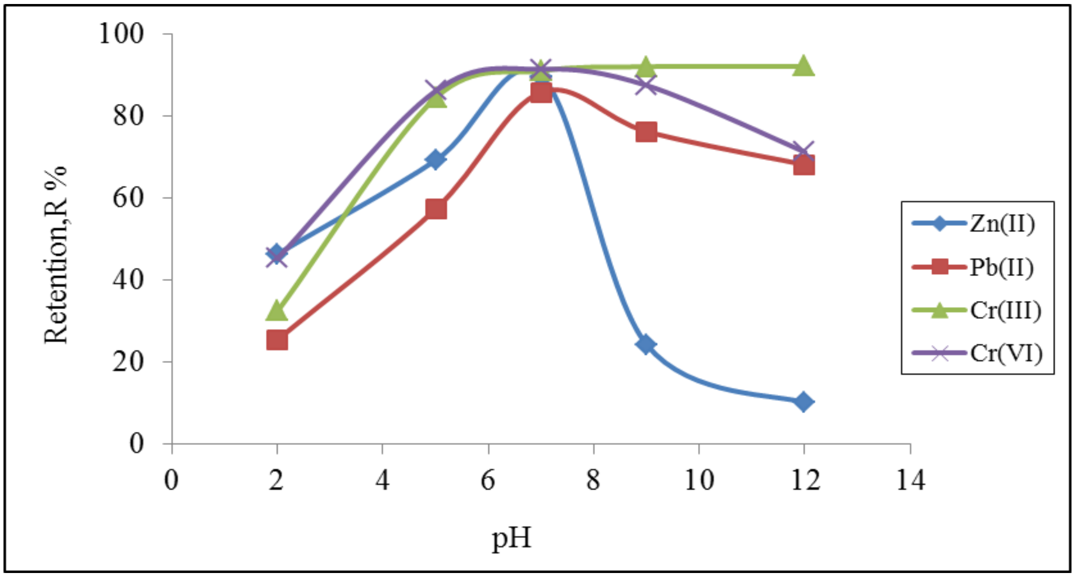


Figure 4.50 Effect of pH on 10 mg/l concentration of each metal ion (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 1.0% (v/v; ml/ml) of PEG, TMP=1.5 bar, flowrate=115 ml/min)

PEG is well known and is frequently used as a water soluble polymer in PEUF systems. Figure 4.50 shows the retention values caused by the influence of pH on a PEUF system in continuous circulated mode. It is found that the retention of Zn(II), Pb(II), Cr(III) and Cr(VI) increased with increasing pH levels, especially from pH 2 up to neutral pH. As pH reached 12, Zn(II) retention decreased drastically; while for Pb(II) and Cr(VI), retention increased until pH 7 and then decreased until pH 12.

In the speciation study, Zn^{2+} reached its highest concentration at pH 1 to 7, after which it was replaced by $Zn(OH)_2$ at pH 7-12. Zn_2OH^{3+} and $ZnOH^{+}$ were the least significant ion species to exist at certain pH levels. $Zn(OH)_4^{2-}$ existed at pH 12 and above. Consequently, Zn(II) ions were present in natural species form, which in this study was $Zn(OH)_2$ at pH levels from 7-to 12. Thus, no charges were observed for this species. Complexation did not occur completely between $Zn(OH)_2$ and the polymer resulting in low retention at pH 7-12, which is in accordance with Zn(II) speciation species study.

Regarding Cr(III) ions retention, it was found that a plateau was reached at pH 9. In the case of PEG bonding to Cr(III), the complexation was more dependent on anions than it was on cations (Bednar et al., 1991). These results were in agreement with the speciation studies of Cr(III), where most anion species were present at pH levels higher than 9 (Aroua et al., 2007) which increased metal ion retention by increasing the macromolecular complexation formation of Cr(III)-PEG. There was evidence that the adsorptive mechanism took place as an electrostatic attraction between metal ions and polymers and enhanced the formation of complexes at high pH levels (Labanda et al., 2009). At higher pH levels and in the presence of PEG, more hydrogen ions and $HO-(CH_2CH_2O-)$ were produced, increasing the binding sites for heavy metal ions in ionic interactions as shown in Equation 4.51:

$$n[HO–(CH_2CH_2O)n–H]x + x\,M_e^{n+} \Leftrightarrow \{[HO-(CH_2CH_2O)nO^-]x\}nM_e x^{n+} + n\cdot xH^+ \quad (4.51)$$

According to Equation 4.51, an increase in pH enhances the formation of the complexes, increasing metal retention.

At low pH levels, PEG has an active carboxylic group of polymer molecules that are unable to completely separate due to the highly flexible C–C bonds in the main chain and the development of cluster configurations by polymer

(Bednar et al., 1991). Alteration of the polymer structure at certain pH levels had a negative effect on metal ion retention (Choe et al.,1986; De Stefano et al., 2003; Volchek, 1993; Canizares et al., 2008) as groups of hydrogen bonds developed weak interactions with polymeric molecules and the surface of the membrane, which consequently decreased retention.

To reject Cr (VI) ions, PEG without modification can remove Cr(VI) ions without first reducing them to Cr(III) ions and thus avoiding precipitation, which occurs during the PEUF process.

4.11.3 Effect of pH on retention by PEI

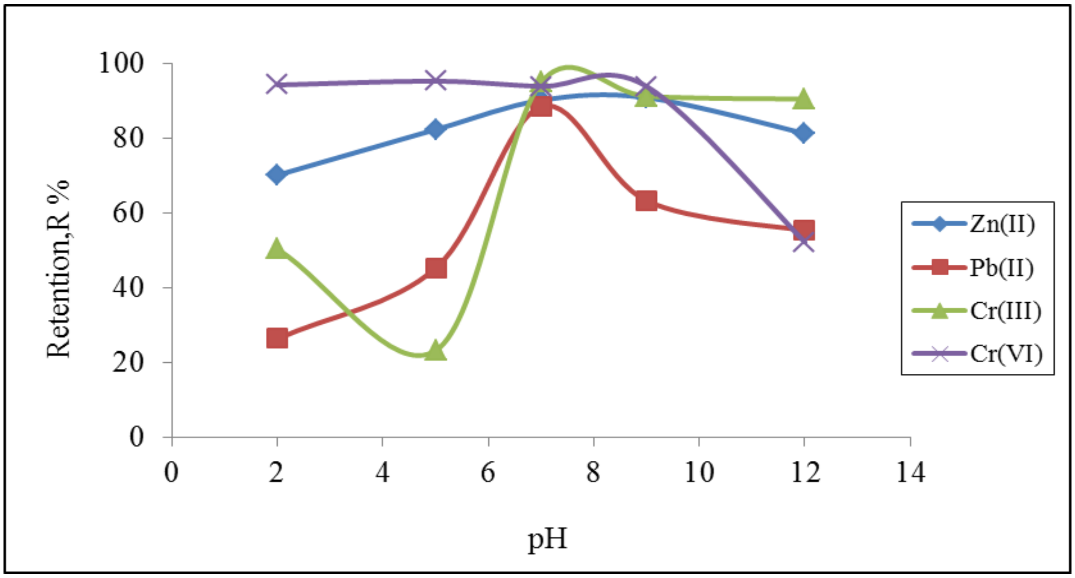


Figure 4.51 Effect of pH on 10 mg/l concentration of each metal ion (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 0.01% (v/v; ml/ml) of PEI, TMP=1.5 bar, flowrate=115 ml/min)

Figure 4.51 reveals the effects of pH on 10 mg/l of four species of metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) using mixed solutions to examine retentions in 0.01% PEI at a pressure of 1.5 bar in a PEUF system. It was found that behavior of metal ions in mixed and single solutions had little effect on retention, but the number of retentions in mixed solutions was slightly lower.

For Zn(II) ions retentions using PEI in mixed solutions, the number of retentions did not change much for every pH level tested, but the highest number of retentions occurred at pH 7. These results concurred with the potentiometric study of Zn(II) ions where the most active complexation occurred at pH 7, and the nitrogen atom of the PEI polymer amine function was in the coordination sphere of the Zn(II) ions species and subsequently performed the complexation within Zn(II)-PEI. Retentions achieved were 88%, lower than the 93% for single solutions due to the fact that there was more competition between metal ions in the mixed solution.

The behavior of Pb(II) ions in mixed solutions contrasts with the number of retentions. More retentions occurred in the mixed solutions due to the ability of Pb(II) ions to form macromolecules complexes when there is increased interaction with PEI at pH 7, as illustrated in potentiometric study of Pb(II) ions-PEI. The small differences between the effect of pH on Pb(II) ion retentions for single and mixed solutions were about 8%. The ability of PEI polymer to neutralize Pb(II) ions in neutral pH conditions shows that PEI can effectively remove Pb(II) ions from aqueous solutions even if more than one metal ion exists in the solution.

Cr(III) ions demonstrated similar retention behavior for both mixed and single solutions. It was found that Cr(III) ion retentions were not affected by other metal ions in the solutions. At pH levels greater than 10, most Cr(III) ions existed as anions species in agreement with the Cr(III) speciation study where the dominating anions had an advantage over PEI polymer. This effectively neutralizes excess anionic colloidal charges in acidic or neutral pH conditions (Aroua et al., 2007).

Similar behavior was demonstrated by Cr(VI) ions. The retention values were high over the entire range of pH levels tested in this study, even though there was a slight decrease in alkaline conditions. This behavior is in accordance with the Cr(VI) speciation species test where only anion species appeared at every pH level. These results indicate that PEI is capable of interacting well with Cr(VI) ions with pure PEI, which is very effective for neutralizing anionic species. This is clearly showed in Figure 4.50 where more than 90% of the retentions were present at acidic and neutral pH levels but suddenly dropped due to concentration polarization on membrane surface taking place.

Some metal ions species were influenced by the presence of Zn(II), Pb(II), Cr(III) and Cr(VI) existing in one boot, but some were not. This was due to the ability of the polymer (unmodified starch, PEG or PEI) to interact with selected metal ions using chemical complexation through ionic metal-polymer interaction or the physical formation of macromolecules through adsorption. Performance of metal ions-polymer in PEUF systems during the retention study was greatly influenced by important fundamental parameters, such as temperature, transmembrane pressure (TMP) and flowrate.

The metal ions retention of Zn(II), Pb(II), Cr(III) and Cr(VI) in mixed metal ion solutions with either starch, PEG or PEI were compared to the discharge standards set by the of DOE in Malaysia. Using starch and PEG, Zn(II) and Cr(III) ions can be safely removed according to DOE standards. Zn(II) and both chromium ions can be safely removed using PEI. The optimum pH value for achieving the highest retentions rates was pH 7.

4.12 The effect of polymer concentration on retention

4.12.1 The effect of unmodified starch concentration

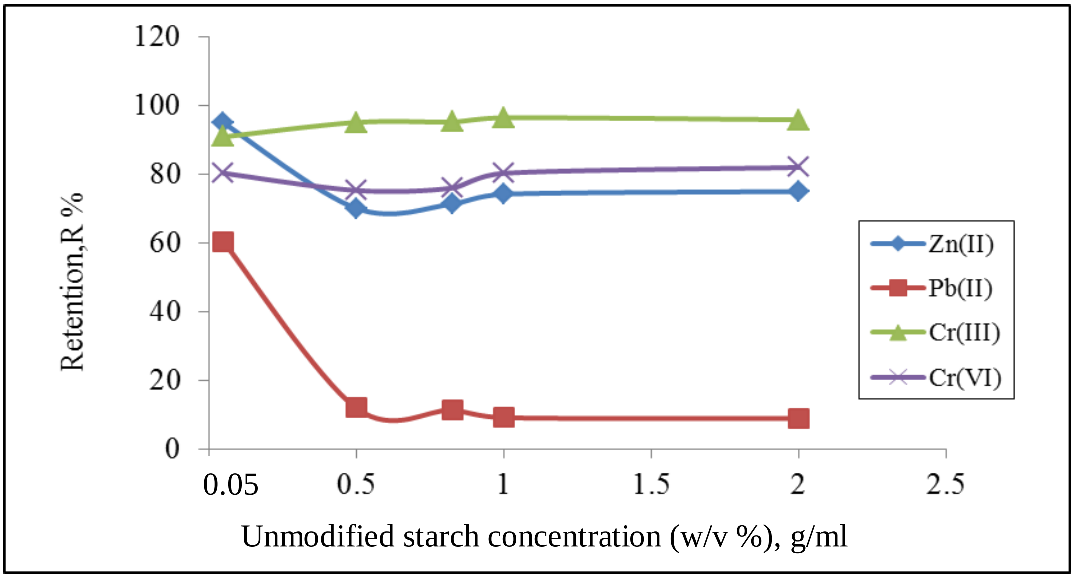


Figure 4.52 The effect of unmodified starch concentration on 10 mg/l concentration of each metal ion (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

The effect on retention by different unmodified starch concentrations in mixed solutions containing 10 mg/l of the four metal ions species at pH 7 is shown in

Figure 4.52. Most metal ions species had their highest retention levels at the initial polymer concentration of 0.05% of unmodified starch. This was especially true for Zn(II) and Pb(II) ions that reached 95% and 60% retentions, respectively. This interaction between metal ions and unmodified starch attracted polymers, and the low polymer concentration provided enough molecular sites for Zn(II) and Pb(II) ions to be adsorbed by the surface. The behavior of these metal ions in the mixed metal ion solutions was similar to their behavior in the single metal ion solution.

For Cr(III) and Cr(VI) ions, the curve demonstrated in Figure 4.52 is similar to those presented for single solutions. This is because mixtures of metal ion species were not affected by the presence of quantitative ionic species found in the solutions but were affected by the polyelectrolyte behavior of water-soluble polymers.

As mentioned previously, due to increased levels of polymers in single metal ion solutions, the polyelectrolyte also increased due to a reduction of polymer viscosity. This confirms that whenever polymer concentrations increase, the ionization degree will decrease. This behavior contributes to produce ions that create an ionic atmosphere higher than the diameter of the polymeric coil. Hence, repulsion between ions increases the rigidity of the polymer chain, consequently expanding the polymeric coil by increasing polymer viscosity.

Polymer concentrations with unmodified starch did not significantly affect the retention of metal ions species carried out either using single or mixed metal ions solutions. Lower concentrations of 0.05% unmodified starch were necessary to form macromolecules of the selected metal ions-polymer and to provide a satisfactory amount of retentions in the PEUF system.

4.12.2 The effect of PEG concentration

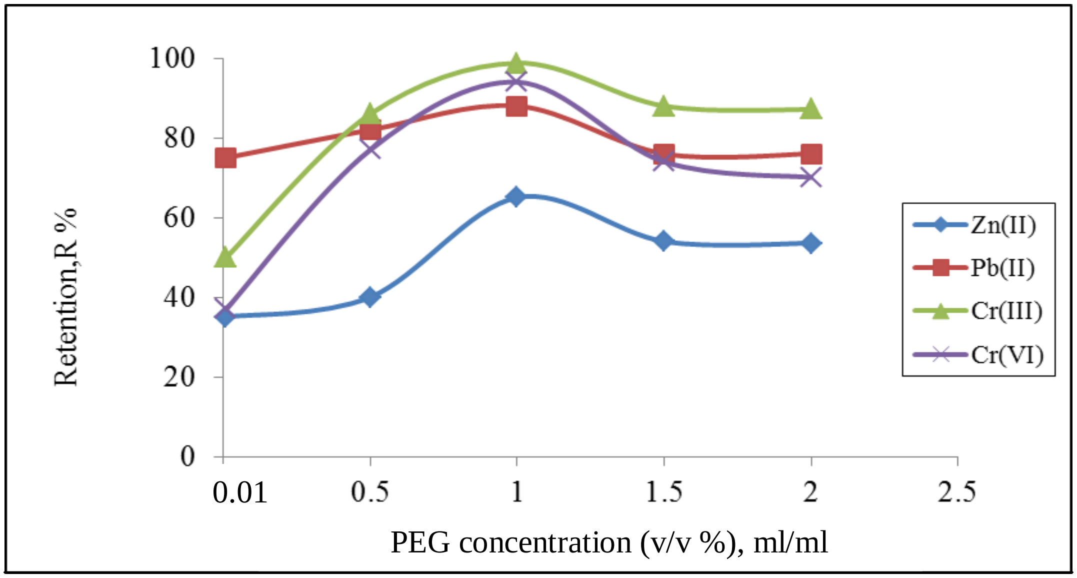


Figure 4.53 The effect of PEG concentrations on 10 mg/l concentration of each metal ion (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

Figure 4.53 reveals the performance of different PEG concentrations (0.01%, 0.5%, 1.0%, 1.5% and 2.0%) in mixed metal ions solutions by combining 10 mg/l of four metal ions species at pH 7 by the cross-flow filtration mode in the PEUF study. As shown in Figure 4.52, the behavior illustrated was similar to behavior exhibited in the single solutions. The tested polymer initially showed less retention due to the viscosity of polymer at 0.01% that prevented the rigid PEG chain to bind with the metal ions. Retentions suddenly increased when using a 1.0% concentration of PEG, where Zn(II), Pb(II), Cr(III) and Cr(VI) had the most retentions at 65%, 88%, 99% and 94% respectively and were tested in one boot of metal ion solution. It was found that the retentions in single and mixed solutions were similar, which indicates that 1.0% of PEG polymer was able to undergo complexation with metal ions and was not affected by polymer concentration.

The metal ions-polymer was able to interact physically through adsorption and reached the necessary molecular size even when it had to compete with other metal ions in mixed solutions. As a result, polymer concentration was not considered as one of the more important parameters for the PEUF study.

4.12.3 The effect of PEI concentration

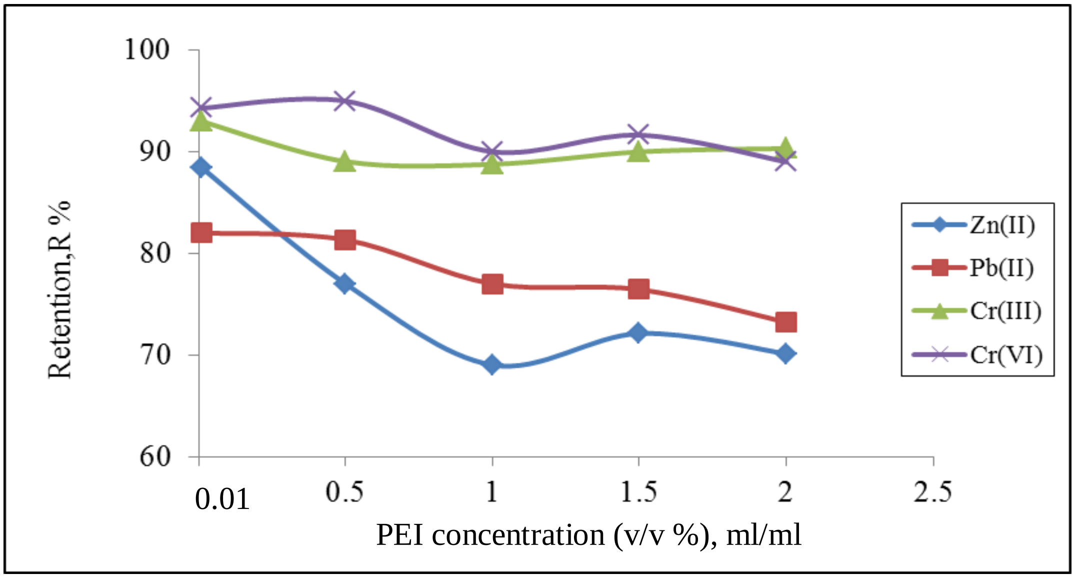


Figure 4.54 The effect of PEI concentration on 10 mg/l concentration of each metal ion (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 cm/min, pH=7)

The retention of metal ions in mixed metal ion solutions containing 10 mg/l of Zn(II), Pb(II), and Cr(III) and Cr(VI) ions at different PEI concentration is shown in Figure 4.54. The behavior of each metal ion had similar retention rates in single solutions at low PEI concentrations of 0.01%. The typical behavior of polyelectrolytes to retain metal ions species increased when the polymer concentration also increased. However, the viscosity of the solution decreased in these situations.

Whenever the viscosity of a solution decreased, the retention coefficient for the metal ions which strongly depended on pH had a shifted free amino group, but the equilibrium of the protonated and free amino group increased. Uncharged PEI permitted more interactions within the backbone segment, which contributed to coiled globule-like compounds that decreased viscosity in mixed solutions.

Looking at the effect of polymer concentration on the amount of retentions for three selected polymers, unmodified starch, PEG, and PEI, it was discovered that the concentration of the polymer affected metal ions retentions. Therefore, the smaller polymer concentrations are reliable enough to be used in the PEUF study in the removal of selected metal ions while encountering the other important parameters of pH, transmembrane pressure (TMP), temperature and flowrate; high metal ions retention values are obtained whenever single or mixed metal ions solutions are employed in the PEUF study.

The retention values obtained using the optimum polymer concentrations were compared to the discharged standards for three selected polymers recommended by the DOE in Malaysia. At concentrations of 0.05% starch and 0.01% PEI, the removal of Zn(II) and Cr(III) ions met DOE standards, but PEG only effectively removed Cr(III) ions when 99% of the metal ions was retained.

4.13 Effect of metal ion feed concentration on retention

4.13.1 Effect of metal ion feed concentration by unmodified starch

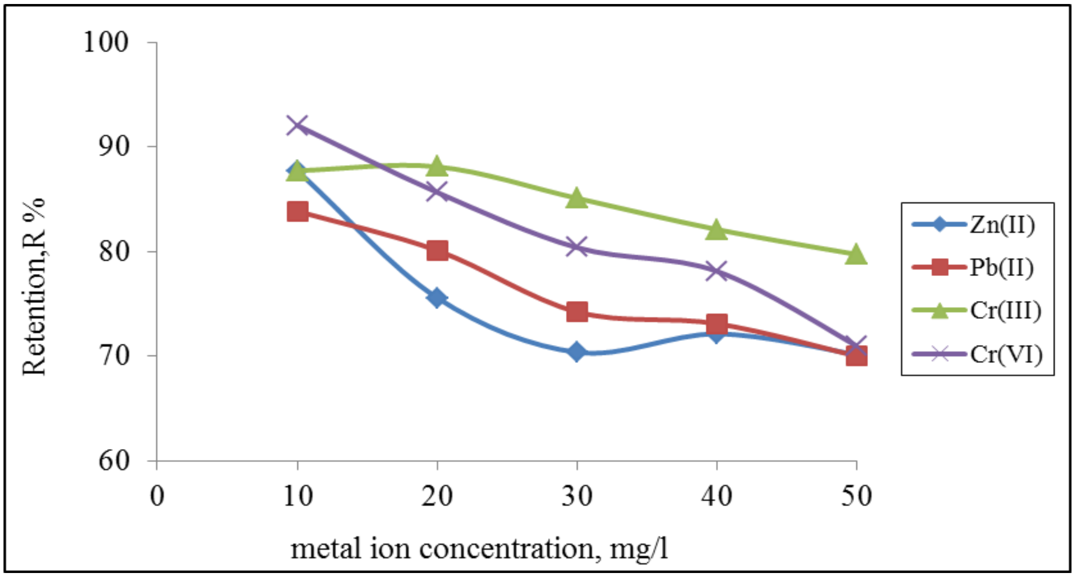


Figure 4.55 The effect of metal ion feed concentrations for mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml))

At first, a PEUF analysis was carried out to investigate the influence of pH on the retention of the four metal ion species with a constant polymer value and a metal ion concentration in single solutions. Next, the optimum pH that yielded the most retention in a single solution was chosen for mixed ion solutions to study the influence of metal ion concentrations on retention coefficients.

The effects of metal ion concentration on selected metal ion solutions using unmodified starch carried out in mixtures solution is shown in Figure 4.55. The graph shows that 10 mg/l of metal ions was used for all experiments. For Zn(II), Pb(II), Cr(III) and Cr(VI), the retention amounts were 87.82%, 83.86%, 87.74%, and 92.06% respectively. Unmodified starch was used in low concentrations because its adsorptive affinity is reduced by gelatinization behavior that occurs in high concentrations (Hood, 1976), and it decreased the retention coefficients for each tested metal ion species.

4.13.2 Effect of metal ion feed concentration by PEG

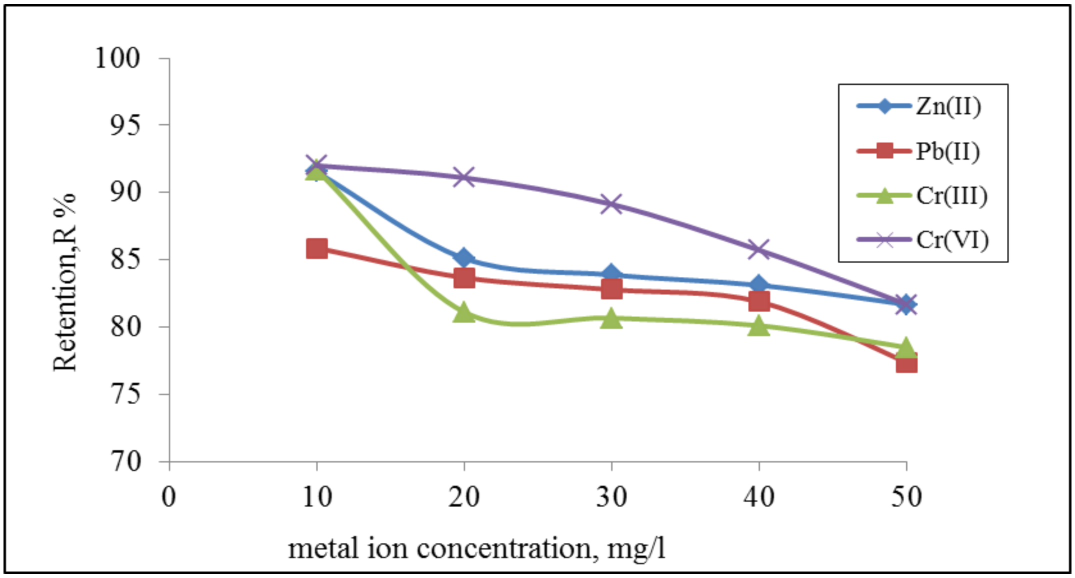


Figure 4.56 The effect of metal ion feed concentrations of mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG = 1.0% (v/v; ml/ml))

As the metal ion concentration increased, excess metal cations failed to bond with the polymer, resulting in diminished metal ion retention. As shown in Figure 4.56, the pattern is similar to unmodified starch being replaced with PEG. As metal ion concentrations increased from 10 mg/l to 50 mg/l, metal hydroxide precipitation took place and negatively affected metal ion retention by increasing the concentration of metal ions. Owlad et al. suggested that the efficiency of Cr(VI) ions removal decreased as feed ions concentrations increased due to the limited active adsorbent sites. In this study, the available polymer sites were replaced by metal ions (Owlad et al., 2010).

The metal hydroxide precipitation had little effect on retention since most of the experiments were run using low concentration of 10 mg/l. It was not possible for metal ions-polymer to pass through the membrane pores, but the metal ions that were not completely bound with the water soluble polymer were able to pass through the membrane at certain volumes and concentrations. It was found that Zn(II), Pb(II) and Cr(III) retention at concentrations of 20 mg/l to 40 mg/l of metal ions reached a plateau and then slightly decreased when the concentration rose to 50 mg/l. These findings suggest a slightly smaller affinity between metal ions and water based polymers such as unmodified starch and PEG at higher metal ion concentrations as they lack the ability to bind excess free metal ions present in mixed metal ion solutions.

When four metal ions are present in a solution, their ability to bond freely to starch was limited due to competition between the metal ions. The presence of too many saturated metal ions in the solution resulted in the starch not being able to provide sufficient space for the metal ions. In this case, the polymer deficiency that occurred at this stage resulted in the presence of free metal ions in the permeate stream (Canizares et al., 2007).

The change in metal ion concentration had a significant effect on Pb(II) and Cr(VI) metal ions but a less significant effect when PEG was used in a mixed solution. It can be observed that most of the selected metal ions obtained maximum retention at 10 mg/l.

A similar pattern emerged when PEG was used with Zn(II) and Pb(II), where retention rates reached only 80.12% and 59.32% respectively at 50 mg/l (Figure 4.56). This is likely because the affinity of metal ions to bind with PEG is lower at high concentration of metal ion species in addition to a polarization phenomenon which had a negative effect on retention coefficients. The behavior of Cr(III) ions was constant in terms of retention as metal ions concentrations increase. At lower concentrations, 10 mg/l, the highest retention rates were found for each metal ion. Otherwise only small changes in retention were obtained and a plateau phase for both chromium ions was reached when the metal ions concentration increased from 30 to 50 mg/l. There was a possibility of free metal ions in the solutions containing the four species being successfully bonded at 1 g/l of PEG using this UF process.

In Figure 4.56, selected multivalent metallic species were more likely to be removed at pH 7 at a concentration of 10 mg/l in mixed solutions. Generally, this was due to complexation formation between the metal ions-polymer, which was higher when the desired amount of free active forms of these complexes could bind effectively to the polymer present in solutions (Llanos et al., 2010).

4.13.3 Effect of metal ion feed concentration by PEI

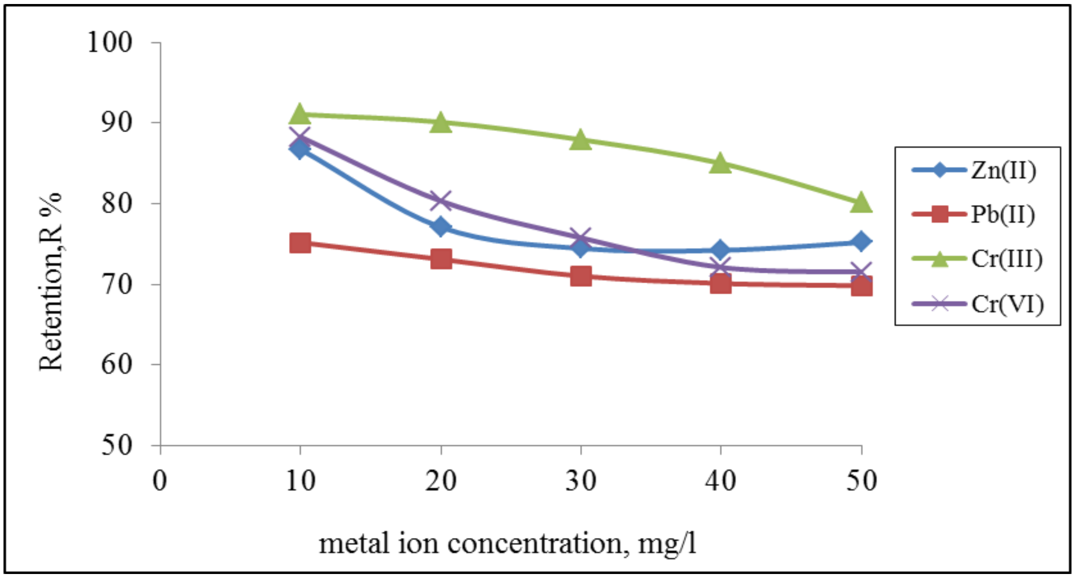


Figure 4.57 The effect of metal ion feed concentration of mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI= 0.01% (v/v; ml/ml))

Figure 4.57 presents the results of the investigation of retentions in mixed solutions containing Zn(II), Pb(II), Cr(III) and Cr(VI) tested using 0.01% of PEI at a range of feed concentrations (10 mg/l to 50 mg/l) at pH 7.

As discussed previously, the behavior of four metal ions species was similar to the behavior exhibited by unmodified starch and PEG. Most metal ions were found to be effectively retained by the membrane via filtration processes at 10 mg/l of feed concentrations applied to the system.

By observing the three polymer performances (unmodified starch, PEG and PEI) on metal ion feeds concentrations, it can be concluded that the retention coefficients of the metal ions were affected by metal ions feed concentrations when concentrations as low as 10mg/l were used in the PEUF study. This concentration was used to reduce the metal hydroxide phenomenon that can cause membrane fouling and influence retention value during the cross-flow filtration processes.

Studies regarding the retention of multivalent solutions containing Zn(II), Pb(II), Cr(III) and Cr(VI) were carried out. It was observed that 10 mg/l of metal ions feed concentration used in a single or mixed solution showed no significant differences in their retention rates, with the exception of Pb(II). The retention rates for the four selected metal ions were successfully achieved using unmodified starch and PEG because the membrane selectivity towards these metal ions was greater for macromolecular complexes of metal ions-polymers than could be retained on the membrane surface, allowing non-complexes ions and water to pass through the membrane in the PEUF system. Investigation of the retention coefficient of aqueous solutions containing Zn(II), Pb(II), Cr(III) and Cr(VI) ions was carried out on single and mixed metal ions solutions (Table 4.2).

To investigate the metal ion concentration parameter, an individual metal ion solution provided better separation than mixed metal ion solutions when studying metal ion-polymer binding in this PEUF study, particularly for Zn(II) and Cr(III) species. Better retention efficiency was observed for single metal ion solutions, and this may be attributed to less competition between metal cations and H^+ to bind with the water-based polymer to form macromolecules. By contrast, Pb(II) and

Cr(VI) prefer to adsorb to unmodified starch by competing with other selected metal ions in mixed metal ion solutions. By comparison, for each metal-polymer the retention of metal ions decreased when the concentration of metal ions increases. This is probably due to partial bonding with selected polymers forming macromolecules, which were smaller than the membrane pores, demonstrating the reduction of retention efficiency.

Less complexation between metal ions solutions of 30 and 50 mg/l with selected polymers compared to 10 mg/l of metal ion solution occurred during the PEUF process. Increasing the initial concentration of the metal ion solution decreased retentions. High concentrations of retentate metal ions solution were found during the ultrafiltration process. This was because more non-complex metal ions were allowed to pass through the membrane surface whenever a higher initial metal ion solution was used during the PEUF process, resulting in a high concentration of the retentate solution.

Compared to the retention values recommended by the DOE, starch could be used as a polymer to remove Zn(II) ions, whereas PEG and PEI can safely remove Zn(II) and Cr(III) ions from metal ions concentrations of 10 mg/l of mixed metal ions solutions.

Table 4.2 The permeate, retentate parameters and retentions coefficients for aqueous solutions containing Zn(II), Pb(II), Cr(III) and Cr(VI) ions in mixed metal ion solutions (pH = 7, TMP = 1.5bar, t = 2 hours, flowrate = 115 ml/min)

Polymer	Metal ions	Unmodified Starch= 0.05g/L			PEG=1 g/L			PEI = 0.01g/L		
Initial metal ion conc. (mg/L)		Permeate conc. mg/l	R (%)	Retente, mg/l	Permeate conc. mg/l	R (%)	Retente, mg/l	Permeate conc. mg/l	R (%)	Retente, mg/l
10	Zn (II)	0.896	91.044	20.353	1.022	89.784	12.829	0.988	90.121	19.233
	Pb (II)	1.614	83.861	11.621	1.412	85.885	19.291	1.158	88.423	12.121
	Cr (III)	1.226	87.739	24.793	0.888	91.125	9.641	0.509	94.912	21.115
	Cr (VI)	0.794	92.064	24.654	0.846	91.536	9.557	0.614	93.864	20.312
30	Zn (II)	8.885	70.382	19.303	4.835	83.885	13.678	22.555	74.451	20.117
	Pb (II)	7.727	74.243	18.012	5.161	82.797	5.664	22.898	71.023	17.224
	Cr (III)	4.470	85.101	20.061	5.795	80.684	17.632	21.206	87.941	21.376
	Cr (VI)	5.884	80.386	19.842	3.260	89.133	17.743	22.423	75.775	19.467
50	Zn (II)	14.925	70.151	19.527	9.158	81.684	21.772	42.480	75.201	19.886
	Pb (II)	14.996	70.009	27.751	11.324	77.353	19.991	43.017	69.831	25.332
	Cr (III)	10.136	79.729	15.393	10.753	78.495	22.712	41.990	80.105	14.472
	Cr (VI)	14.510	70.981	15.442	9.158	81.684	22.612	42.847	71.534	14.376

4.14 Effect of pH on flux

4.14.1 Effect of pH by unmodified starch, PEG and PEI

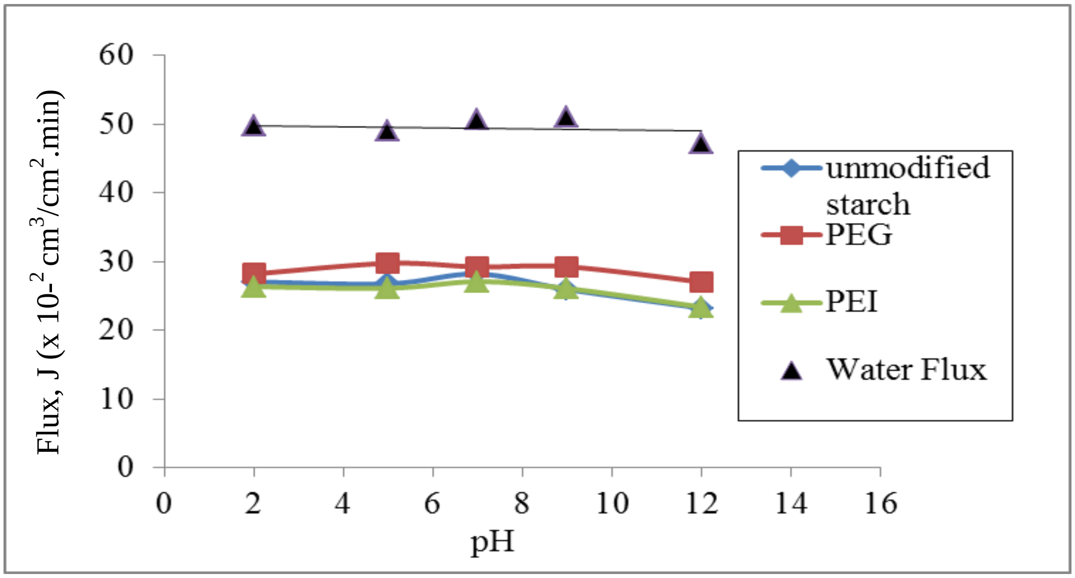


Figure 4.58 The effect of permeate water flux on mixed metal ions solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) and 10 mg/l of each metal ions concentrations at different pH values (TMP= 1.5 bar, flowrate= 115 ml/min)

The investigation into flux based on the study of the effect of pH on the four metal ion species is depicted in Figure 4.57. This study used 0.05% of unmodified starch, 1.0% of PEG and 0.01% of PEI that was tested at different pH values. Flux efficiency values were less affected by pH as seen in Figure 4.58, where flux was obtained in the range of 25-29% for unmodified starch, 27-29 % of PEG, and 23-28 % of PEI.

A few changes in permeate flux values when pH was increased were observed in this study. This behavior indicated that the interaction of metal ions with unmodified starch does not completely form macromolecules complexes and was influenced by the gelatinization behavior of the unmodified starch. This can cause the viscosity of permeate solutions to rise, resulting in decreased flux efficiency. Consequently, unmodified starch provided less flux than PEG over the entire range of pH levels in mixed solutions. PEG bonded with metal ions resists due to the competition for metal ions in the mixed solution.

PEG as a water soluble polymer was able to remove the four selected metal ions species. The results of metal ions uptake by PEG were successful when a PEUF system was used. Since metal hydroxide precipitation was more likely to occur at alkaline pH levels, the flux values were lower at pH levels above 9. The flux values were less significant, and little change was seen for each metal ion tested. By comparison, the behavior of metal ions toward unmodified starch in terms of permeate flux was similar to its behavior towards single solutions. Using a single or mixed solution had little effect on the performance of PEUF. In terms of the overall investigation, the study of how pH affected flux shows that pH has a less significant effect when a PEUF system was used.

The behavior of Zn(II) and Pb(II) ions was found to be similar with single solutions clearly demonstrating that pH was not an important parameter that influenced the permeate flux of Zn(II) and Pb(II) ions in PEUF systems as the value was less than 30%. The flux of metal ions was constant at pH 5-7. Water flux was found to be 47-51% at all pH levels.

The Cr(III) and Cr(VI) permeate flux was at its highest when the pH was alkaline. This was similar to single solution permeate flux behavior, which shows that even with more than one species of metal ion in a solution, there is little significant effect on permeate flux values at the end of the pH regions tested. pH also influences flux efficiency in the presence of unmodified starch, but the effect was minimal compared to PEG. This was because the behavior of unmodified starch interrupted the complexation of metal ions-polymers in the PEUF system but still efficiently removed metal ions from the mixed solution.

It was found that by applying PEI as a water soluble polymer to remove the four metal ions species from a mixed solution, the flux performance at every pH level for three of the polymers was somewhat similar to that of unmodified starch. This behavior was similar when single solutions were used. Pure PEI behavior effectively neutralized anionic species and was not affected by the presence of more than one metal ion species existing in one boot and was able to form macromolecular complexes between metal ion-PEI at pH 2-7. However, the rigidity of the metal ions-polymer solutions was loose whenever the pH became alkaline. By contrast, permeate flux values fell at pH levels greater than 7, indicating that PEUF processes were more or less affected by concentration polarization that caused membrane fouling whenever cross-flow filtration was used in the system.

The pH parameter did not significantly affect permeate flux in the PEUF study for solutions containing the four metal ions species (Zn(II), Pb(II), Cr(III) and Cr(VI)) either as single or mixed metal ions solutions. On the other hand, most of the highest values occurred at pH 7 when a water-soluble polymer (unmodified starch, PEG and PEI) was used. Use of polymers on the removal of the four metal ions species was effective if carried out while using suitable operating parameters during the filtration process.

4.15 Effect of polymer concentration on flux

4.15.1 Effect of unmodified starch, PEG and PEI concentration

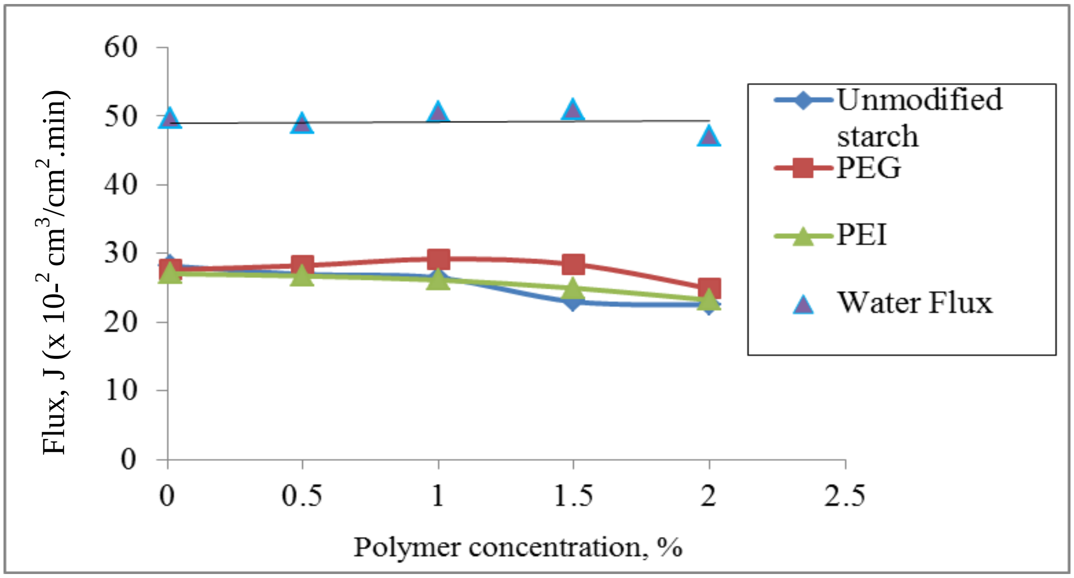


Figure 4.59 The effect of polymer concentration on mixed metal ion solutions Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, each metal ions concentrations= 10 mg/L)

Figure 4.58 revealed the permeate flux value of mixed solutions containing the four selected metal ions species; these values were obtained by using different unmodified starch concentrations. The highest flux efficiency values were achieved when low concentrations of a polymer were 0.05% unmodified starch, 1.0% of

PEG or 0.01% of PEI). Similar trends were found for each metal ions indicating that flux was not affected by the increasing of polymer concentrations.

When polymer concentrations increased, greater access was provided to the medium of interaction allowing metal ions to be adsorbed through a physical or chemical mechanism which was not balanced with the presence of ions in the solutions. This condition contributed to the amount of substances deposited and retained on the surface and inside the membrane pores, leading to a decrease of flux.

This behavior was similar to that exhibited in single solutions exposed to the same operating parameters. The only difference was seen when single solutions were used to test the flux of Cr(III) and Cr(VI) ions. There was a slight increase of unmodified starch concentrations above 1.0 (w/v%) most probably because the single solutions provided the chance for metal hydroxides precipitation to occur due to an abundance of metal ions species in the solutions; they compete between themselves to be adsorbed by excess unmodified starch which can cause deposits on the surface of the membrane.

It was found that flux values were almost constant for each tested metal ions species indicating that there were no significant effects of PEG concentrations on permeate flux.

At 1% (v/v) of PEG concentrations, difference in flux behavior on mixed solutions was most probably due to competition between metal ions in water to be adsorbed by the PEG polymer molecules to form macromolecular complexes. As a result, much lower flux values were obtained at these concentrations compared to a single solution. In terms of overall flux values in the PEUF study, high polymer concentrations contributed to lower flux efficiency in accordance with Uludag et.al (1997). These observations may not be valid for higher polymer concentrations (Uludag et al., 1997).

These results suggest that flux efficiency is likely to be constant in PEI concentrations tested for all three polymers. These values were much different than flux values for single solutions, indicating that the four selected metal ions species present in one solution at the same time and did not compete for adsorption by PEI.

This indicates that PEI was able to provide only weak polyelectrolyte behavior that caused solution viscosity to decrease whenever it was applied to a mixed metal ions solutions, indicating that the interactions between metal ions-PEI were lower. It can be concluded that PEI is the best polymer for removing the four metal ions species from aqueous solutions if obtained through single solutions.

Low polymer concentrations can remove metal ion species from single or mixed metal ions solutions. Different polymers had different effects on flux efficiency when tested using a PEUF system. Some of the polymer successfully interacted with metal ions in a single solution and some were successful in mixed metal ion solutions. Too high polymer concentrations had a negative effect on flux because it caused deposits on the surface and inner membrane in the PEUF system.

4.16 Effect of metal ion feed concentration on PEUF flux

4.16.1 Effect of unmodified starch, PEG and PEI on PEUF flux

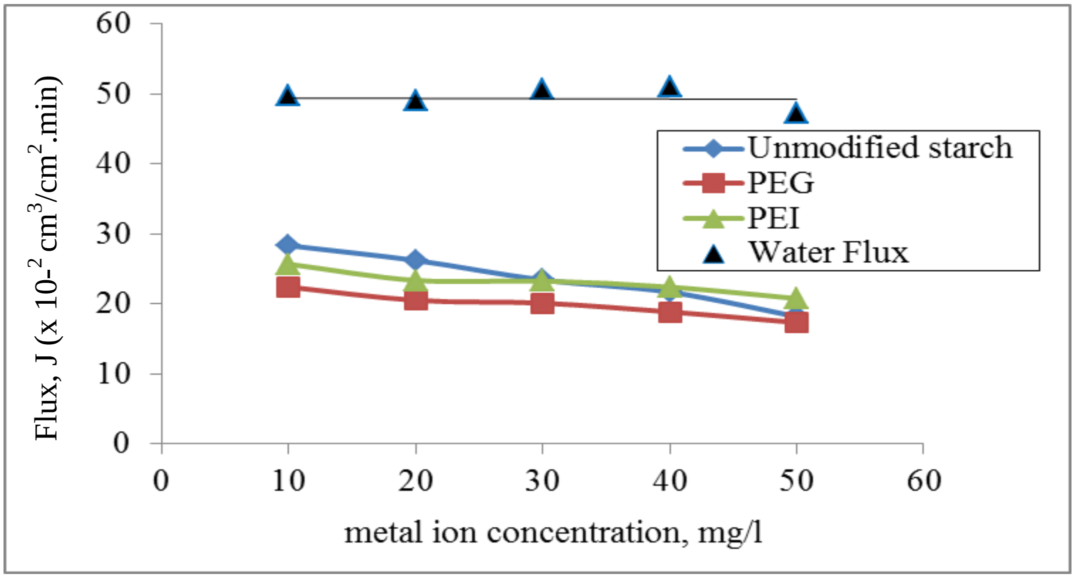


Figure 4.60 The effect of metal ions feed concentration of mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) flux (TMP=1.5 bar, flowrate =115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml), PEG= 1.0% (v/v; ml/ml), PEI= 0.01% (v/v; ml/ml))

Performance of pH on flux was investigated previously, and pH had little effect on flux values for metal ions in both single and mixed metal ion solutions. The behavior of the three selected polymer was the same when studying metal ions feed concentrations on flux as illustrated in Figure 4.60.

Figure 4.59 reveals the flux value of mixed solutions of Zn(II), Pb(II), Cr(III) and Cr(VI) ions by investigating the effects of different metal ions concentrations at pH 7. The pattern of the flux value for the three selected polymers depicted at arrest of tested feed metal ions concentrations indicated that the concentration of metal ions did not significantly influence flux in the ultrafiltration process. Slightly different flux behavior was seen for unmodified starch as feed concentrations of 10 mg/l had the highest flux value before it suddenly dropped when feed concentrations increased to 50 mg/l.

Due to the low feed concentrations, 10 mg/l was able to bond with metal ions species readily, but excess cation species caused by a high feed concentration used in the UF system negatively influences the permeate flux efficiency due to membrane fouling.

It was observed that when 1.0% of PEG was used flux values were almost constant at all feed concentrations. The behavior of feed metal ions concentrations in the study on mixed metal ions solutions was not much different than single solutions. In other words, various metal ions in a solution have a high degree of competition between the metal ions to form macromolecular complexes that do not significantly affect flux. Therefore, 10 mg/l was in for the PEUF system for both single and mixed solutions. The risk of fouling in the cross-flow ultrafiltration system was reduced, and the flux efficiency was at satisfactory levels when lower feed concentrations were used.

For PEI, after the feed concentrations were increased, the flux value was constant due to insignificant metal ion feed concentrations when used in the PEUF system. The performance of flux was not affected by increased feed concentrations.

A 10 mg/l concentration is capable of performing an effective feed concentration for each selected metal ions species when investigating flux efficiency. Employing lower feed concentrations reduces toxic levels discharged at the end of the PEUF system, making it less likely to cause membrane fouling and metal hydroxides precipitation. Whether through single or mixed metal ions metal solutions, it can be concluded that lower initial feed concentration is appropriate for UF systems.

4.17 Model for metal ions removal via PEUF system

a) Mixed metal ion solutions (Canizares et al., 2008):

This model was employed to estimate the results of untested conditions and to better understand the process of metal ions complex with polymers (Llorens et al., 2004; Sabate et al., 2002, 2006). The most important part of these models involves “physical–chemical models” that determine the relationship of polyelectrolytes and ions combined with ultrafiltration results. By considering “macroscopic models”, this model interprets chemical reactions, equilibrium equations, mass balance, as well as a few additional assumptions to express metal retention as a function of different parameters (equilibrium constants, feed concentrations, etc.). These parameters can be determined from ultrafiltration experiments (Volchek, 1993; Juang, 1993) and titration measurements (Morlay et al., 1998, 1999). The following model was based on a previous paper on mixed metal ions component systems (Canizares et al., 2008) that included assumptions and definitions similar to those described in the Canizares et al. paper (Canizares et al., 2008).

For this model, multi-component aqueous solutions containing several divalent metal ions were considered under conditions where insoluble hydroxides could not be formed. The following reactions explain the basic relationship between polymers (unmodified starch, PEG and PEI (HL)) and metal ions (Mi) in the solutions:

$$HL \leftrightarrow H + L;\ K_A = \frac{[H][L]}{[HL]} \tag{4.52}$$

$$Mi + L \leftrightarrow MiL;\ K_{i,1} = \frac{[MiL]}{[Mi][L]} \tag{4.53}$$

$$Mi + nL \leftrightarrow MiL_n;\ K_{i,n} = \frac{[MiL_n]}{[Mi][L]^n} \tag{4.54}$$

where n is the average coordination number of polymer ligands bonded to one metal ion. In this global system, polymer and metal ions mass conservation equations can be expressed as:

$$Q_F(t) = Q_P(t) \tag{4.55}$$

$$V_R\frac{d[L]_R}{dt} = -Q_P[L]_P \tag{4.56}$$

$$V_R\frac{d[Mi]_R}{dt} = Q_F[Mi]_F - Q_P[Mi]_P \tag{4.57}$$

By combining Equations 4.56 and 4.57 with the expressions for the retention coefficients of polymer and metal ions, the following relationships were obtained:

$$V_R\frac{d[L]_R}{dt} = -Q_P[L]_R(1 - R_L) \tag{4.58}$$

$$V_R\frac{d[L]_R}{dt} = Q_F[Mi]_F - Q_P[Mi]_R(1 - R_{Mi}) \tag{4.59}$$

a) For total concentration of each metal ion in the reactor solution and in the permeate stream can be expressed in equation:

From Equation 4.21:

$$[Mi]_T = [Mi] + \sum_n [MiL_n] \qquad (4.60)$$

From Equation 4.25:

$$[Mi]_P = [Mi](1 - R_{FMi}) + (1 - R_L)\sum_n [MiL_n] \qquad (4.61)$$

Thus, Equation 4.62a and 4.62b can be obtained by combining Equation 4.60 and 4.61:

$$R_{Mi} = 1 - \frac{[Mi]_P}{[Mi]_T} = 1 - \frac{[Mi](1 - R_{FMi}) + (1 - R_L)_n[MiL_n]}{[Mi] + \sum_n [MiL_n]} \qquad (4.62a)$$

From Equation 4.26b:

$$R_{Mi} = \frac{[Mi]R_{FMi} + R_L \sum_n [MiL_n]}{[Mi] + \sum_n [MiL_n]} \qquad (4.62(b))$$

The retention coefficient of metal ions can be determined by taking into account the stability of constants on complexes between metal ion-polymers:

From Equation 4.29:

$$R_{Mi} = \frac{R_{FMi} + R_L \sum_n K_{i,n}[L]^n}{1 + \sum_n K_{i,n}[L]^n} \qquad (4.63)$$

b) For mass balance of polymer:

In our research, the mass balance of polymer was not included since our proposed model only focused on metal ions balance and retention coefficients using pH as a major factor. All of these equations are based on findings from experimental work and the objectives of study. However, as additional information, Equation 4.63 can be used to calculate an unknown quantity of free ligand concentration [L]:

$$[L]_T = [L] + [HL] + \sum_i \sum_n n[MiL_n] \qquad (4.64)$$

The concentration of polymer ligands in a PEUF system can be explained as concentrations of free ligands, protons and metal ions by using the acid dissociation constant, K_A, and stability constants of complexes, $K_{i,n}$, as demonstrated in the following equations:

$$[L]_T = [L] + \frac{[L][H]}{K_A} + \sum_i \sum_n nK_{i,n}[Mi][L]^n \qquad (4.65)$$

The concentration of free metal ions [Mi] can be obtained from Equations 4.60 and 4.65 and then using the form shown below:

$$[L]_T = [L] + \frac{[L][H]}{K_A} + \sum_i \frac{[Mi]_T \sum_n nK_{i,n}[L]^n}{1 + \sum_n K_{i,n}[L]^n} \qquad (4.66)$$

[L] could be calculated by an iterative procedure, substituting Equation 4.63 to determine the retention coefficient for each metal ion.

For additional information, the volume of a permeate flow can be obtained by integration or as sum of the permeate volumes for each step:

$$V_P(t) = \int_t^0 Q_P(t)dt = \sum Q_P(t)\Delta t \qquad (4.67)$$

This model is a general one, but the initial conditions and metal concentrations in a feed stream are different depending on the stage.

Based on Canizares models, assumed metal concentrations in a feed stream are as follows (Canizares, et al., 2008):

$[Mi]_F \neq 0$ for total retention of metal ions stage (4.68)

$[Mi]_F = 0$ for separation and polymer regeneration stages (4.69)

In the separation and polymer regeneration stages, a typical concept is the metal i retention coefficient:

R_{Mi} (%) (Canizares, et al., 2004):

$$R_{Mi}\ (\%) = \frac{[Mi]_{R,t}}{[Mi]_{R,0}} \times 100 \qquad (4.70)$$

The final stage applied separation factor, α_{12}, which is used to quantitatively express the efficiency of separation between two kinds of metal ions (Muslehiddinoglu, 1998; Juang, 1993; Ahmadi, 1994)

$$\alpha_{12} = \frac{[M_1]_P/[M_2]_P}{[M_1]_R/[M_2]_R} = \frac{1 - R_{M1}}{1 - R_{M2}} \qquad (4.71)$$

The theoretical model developed by Canizares obtained successful correlation with our experimental data since we found similar parameters that dominated all experiments (pH) and also found that retentions were influenced by pH values. Unfortunately, each model has its own weaknesses as in the Canizares mixed model which carries out only two metal ions at a time, but our study used four metal ions in one solution. As a result, the probability equation was used to calculate the separation factor. Some parts of the Canizares model were not applicable in this research, such as polymer regeneration. Consequently, we did not include it in our theoretical calculations. We only conducted metal ions removal concentration based on the objectives of our study. In addition, the correlation between the Canizares model and our experimental data will be carried out in the next section by employing ANOVA design software to calculate the regression coefficient between experimental and theoretical data to check whether our model fit the Canizares models.

4.18 The ANOVA analyses on regression of experimental data and the Canizares theoretical model

a) Mixed metal ion solutions

1) Effects of pH on metal ions retention (R)

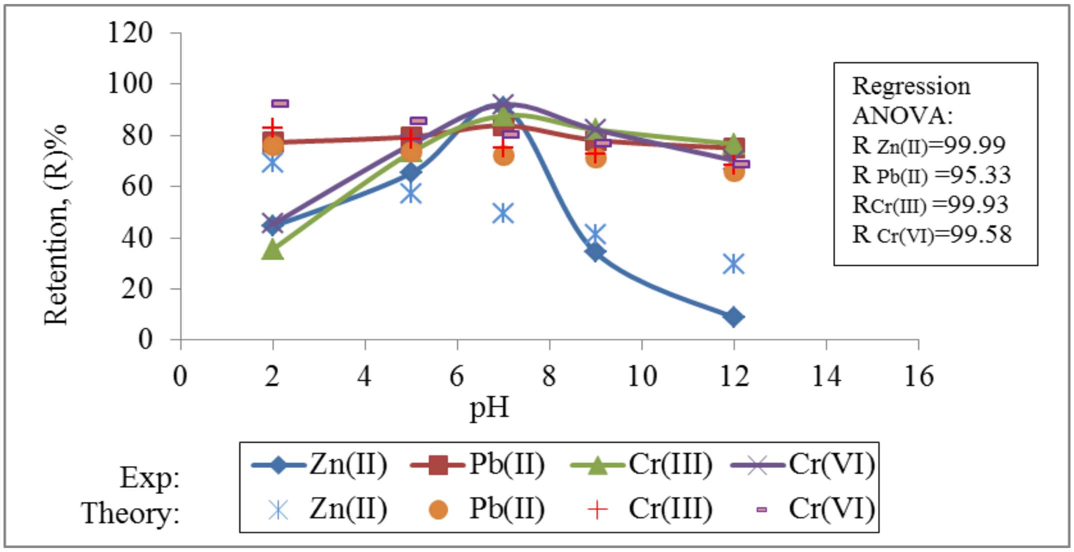


Figure 4.61 Regression coefficient (R^2) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to analyze (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 0.05% (w/v; g/ml) of unmodified starch (TMP=1.5 bar, flowrate=115 ml/min)

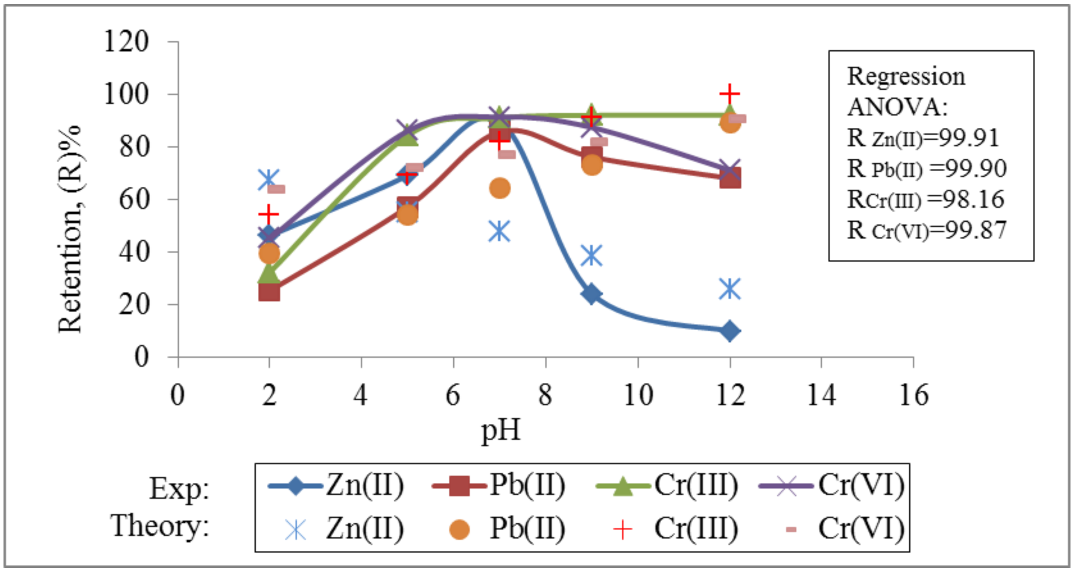


Figure 4.62 Regression coefficient (R^2) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 1.0 %(v/v; ml/ml) of PEG (TMP=1.5 bar, flowrate=115 ml/min)

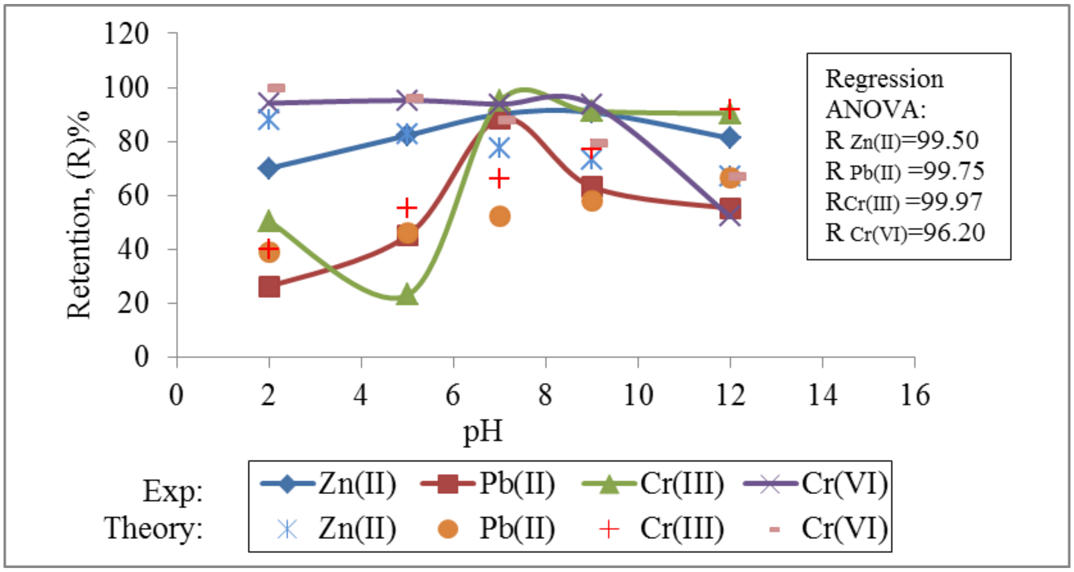


Figure 4.63 Regression coefficient (R^2) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 0.01 %(v/v; ml/ml) of PEI (TMP=1.5 bar, flowrate=115 ml/min)

2) Effects of polymer concentration on metal ions retention (R)

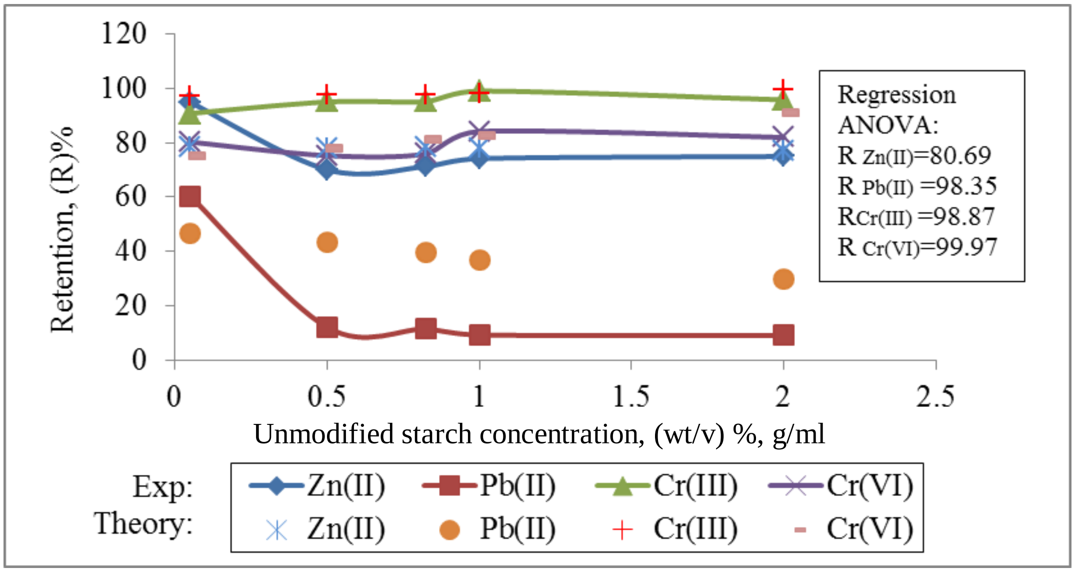


Figure 4.64 Regression coefficient (R^2) of the effect of unmodified starch concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III) and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

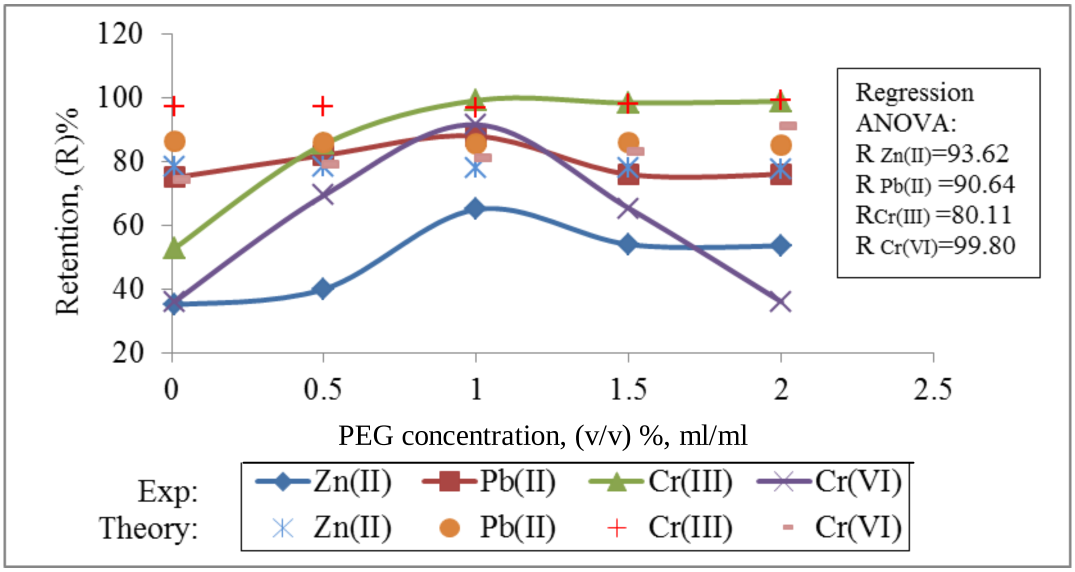


Figure 4.65 Regression coefficient (R^2) of the effect of PEG concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III) and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

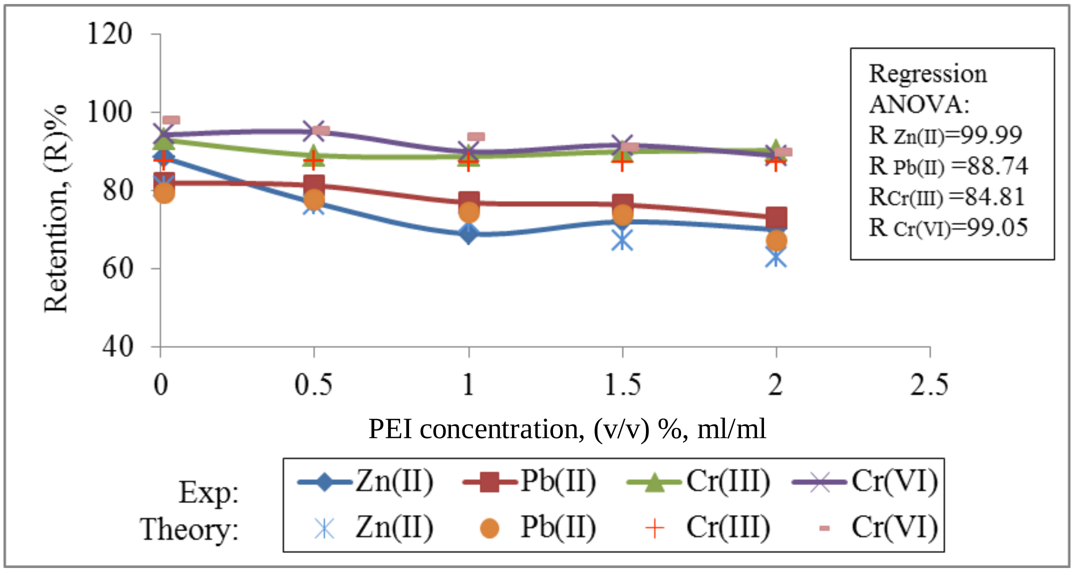


Figure 4.66 Regression coefficient (R^2) of the effect of PEI concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III)

and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)

3) Effects of metal ion concentration on retention (R)

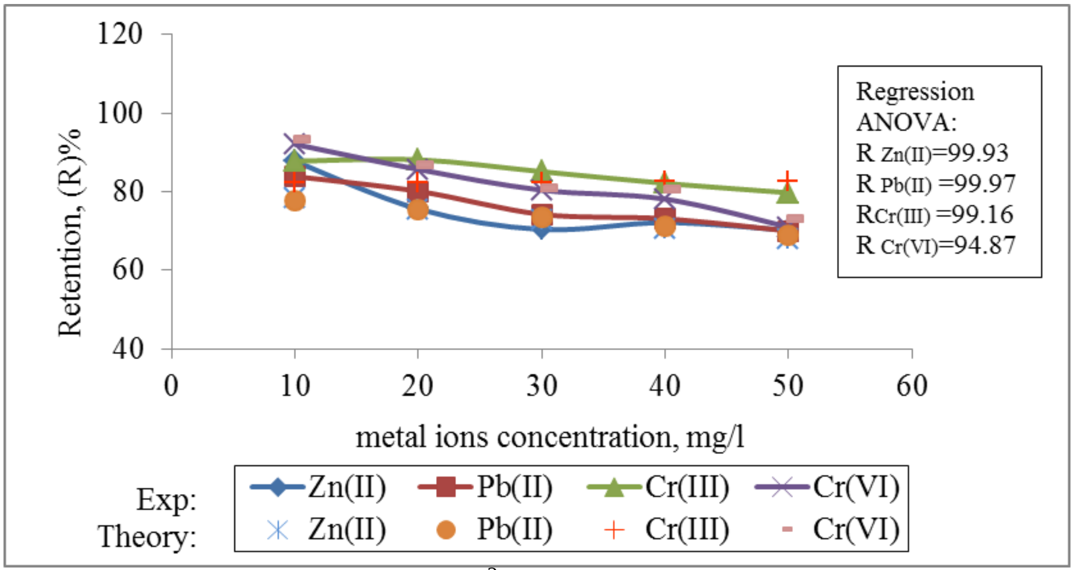


Figure 4.67 Regression coefficient (R^2) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (p=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml))

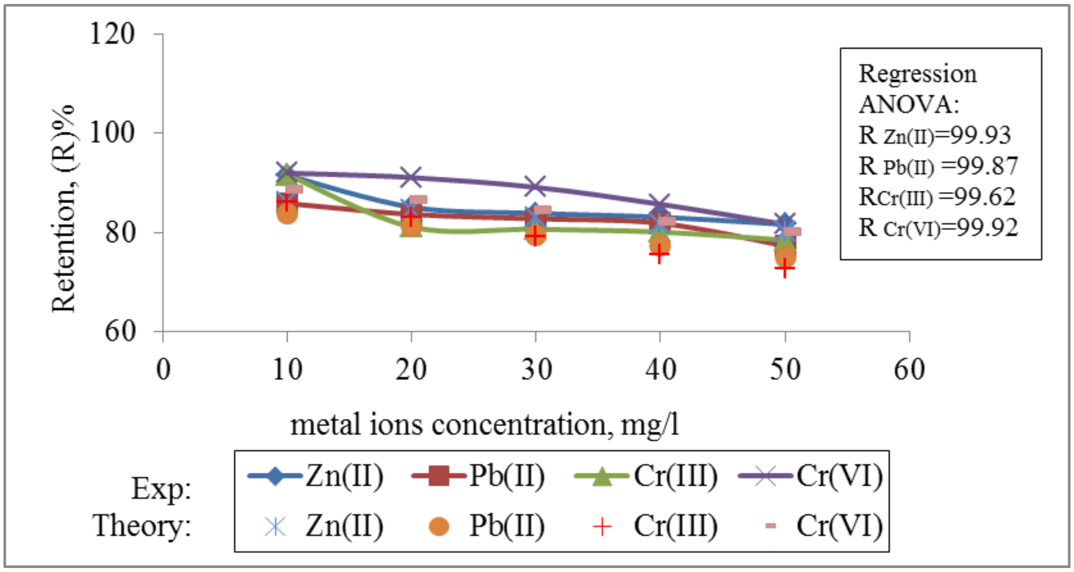


Figure 4.68 Regression coefficient (R^2) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (p=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration = 1.0 % (v/v; ml/ml))

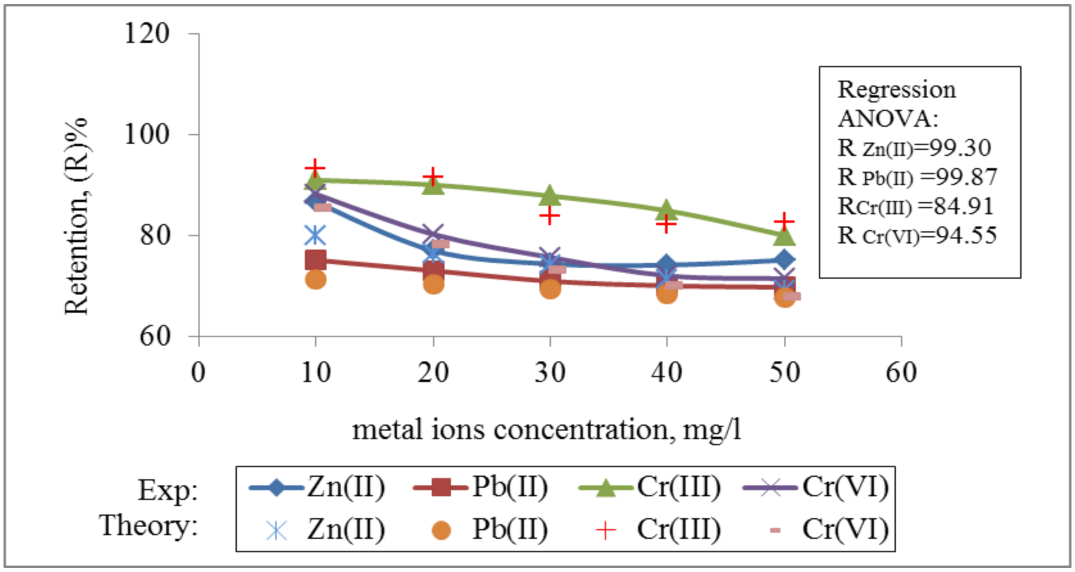


Figure 4.69 Regression coefficient (R^2) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration = 0.01% (v/v; ml/ml))

4.19 Overall conclusions for ANOVA Regression Coefficient Analyses of Retention Coefficient for Single and Mixed Solutions via PEUF System Fitting Canizares Models

The overall regression coefficient analyses using ANOVA to fit the Canizares model for single and mixed metal ions solutions can be seen in Figures 4.39 to Figure 4.47 and Figures 4.60 to Figure 4.68, respectively. The calculations based on retention coefficients can be reviewed in this study as significant effects were caused by three parameters: pH, polymer concentration and metal ions concentrations. The effect of pH was the major parameter as it had the most effect on the retention of metal ions in aqueous solutions via PEUF systems. For overall performance, the calculation fitting Canizares theoretical analyses can be reviewed in Appendix B.

The importance of conducting an analyses using ANOVA software is to determine the P value for each parameter tested and the regression coefficient which will determine if the theoretical calculation was a good fit with the Canizares model. Each of tested metal ions, Zn(II), Pb(II), Cr(III) and Cr(VI), fit well, achieving regression coefficients greater than 90%, but less than 15% of metal ion retention regression coefficients were over 80%. For overall mixed metal ion solutions on regression coefficient (R^2), about 11% of Zn(II) and Pb(II) and 22% of Cr(III) ions achieved greater than 90%. Cr(VI) ions were found to fit well with the Canizares model whenever mixed metal ions solutions were involved.

In conclusion, the overall performance for fitting Canizares Models was in a range of 85-99% for each metal ion tested using single and mixed metal ions solutions. The data has mostly shown that 90% of regression coefficients were achieved, by means most experimental data fitted well to Canizares Model. The ANOVA tested these regression coefficients (R^2), and the results can be reviewed in Appendix C. ANOVA analyses was a good indicator since P value less than 0.05 indicated that our parameters were significant and should be used in these analyses while at the same time fitting the Canizares Model. Appendix C shows that all P value analyzed using ANOVA had P values less than 0.05. Thus, the theoretical data fitting the Canizares Model was significant and has good correlation with the previous experimental data obtained.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

There are several important conclusions in this research:

1) The PEUF study focused on removal of the metal ions Zn(II), Pb(II), Cr(III) and Cr(VI) from aqueous solutions.

2) The proposed new biopolymer; unmodified starch in the PEUF study demonstrated immense potential as a binding polymer as it showed the best performance in terms of removing Zn(II) and Cr(III) and maximizing retention at neutral pH.

3) Unmodified starch was used as a water soluble polymer as it had the ability to adsorb metal cations during an ultrafiltration process without requiring any upgrades on the method of their granular structure (no modifications using additional chemicals or molecular structure readjustments were required corresponding to a less toxic unmodified starch applied via a PEUF system). It corresponds even to other types of starch (e.g. typioca, cassava, or rice) used as water soluble polymers. The metal ions uptake from aqueous solutions can still occur as a result of the dependency on the polysaccharides groups (amylose and amylopectin) contained in starch for metal ions' uptake. This had great influence on the adsorptive mechanism which was probably caused by a physical or chemical mechanism.

4) A high level of retention for metal ions was obtained at pH 7 by employing 0.05% of unmodified starch as a polymer. Zn(II) and Cr(III) ions achieved high retentions at pH 7 in single metal ions solutions whereas Pb(II) and Cr(VI) ions achieved high retentions in mixed metal ion solutions.

5) When tests were conducted using 1.0% of PEG, Zn(II) and Cr(VI), ions had a 99% retention rate in single metal ions solutions. By contrast, the highest retention rate obtained by Pb(II) ions occurred in mixed metal ions solutions. Cr(III) ions achieved high retentions regardless if the solution was a single or a mixed metal ions solution.

6) 0.05 (w/v) % of unmodified starch, 1.0 (v/v) % of PEG and 0.01 (v/v) % of PEI obtained high retentions for Zn(II), Pb(II), Cr(III) and Cr(VI) ions at neutral pH 7 in single metal ion solutions.

7) The effect of pH was found to be significant on the retentions of the four metal ions species selected in this study for both single and mixed solutions. At pH 7, the highest retention for metal ions species in the PEUF study was observed.

8) For single metal ions solutions, about 96% of retentions for the Zn(II) ions species was found with 0.05% unmodified starch. The highest value (99%) of retentions was demonstrated by 1.0% of PEG; this was applied at pH 7 for Zn(II) and Cr(VI). Cr(III) ions retentions were observed to be high when employing 0.05% of unmodified starch at a neutral pH. Pb(II) ions retentions were found to be lower whenever they were tested with the three polymers, namely unmodified starches,

PEG and PEI, which achieved results of only about 62%, 79% and 80% respectively at pH 7.

9) pH had a less significant effect on the flux efficiency of metal ions species when the three water-soluble polymers were used. Unmodified starch, PEG and PEI at 10 mg/l were the optimum metal ions concentrations for the selected metal ions tested at pH 7 in both single and mixed solutions.

10) Retention is found to be lower in single solutions, but different behavior was observed for Pb(II) ions. Pb(II) ions can be removed from mixed metal ions solutions at pH 7 using the three selected polymers. The effect of pH, polymer concentrations and metal ions concentrations were observed to not affect flux performance. The permeate flux of water was in the range of 47- 51 (x10^{-2}) cm^3/cm^2.min compared to the constant value of metal ions flux in this UF study.

11) The ability of Cr(VI) ions to be removed directly without being reduced to Cr(III) was a significant criterion in the selection of unmodified starch and PEG as binding biopolymers.

12) The results of high metal ions retention obtained by use of a low concentration of 0.05 (w/v %) unmodified starch indicated that unmodified starch as a biopolymer can leading to cleaner waste production at the end of the PEUF process..

13) The Canizares model fitted the theoretical data and was used for this study. The regression coefficient (R^2) in this study was calculated by ANOVA, and it approached over 90%. Since the analyses of the experimental works was done using RSM (Response Surface Methodology), the theoretical analyses of the Canizares

Model was chosen as established PEUF theoretical models to fit using the experimental data. ANOVA supported the regression coefficient analyses and results indicating that the theoretical data fitted well with the Canizares Model.

5.2 Recommendations for future work

Applications of new biopolymers to remove metal ions species from aqueous solutions are required to enhance the study of the PEUF system in the future recommendations as follows:

1) The application of new biopolymers can be upgraded by modifying them with chemicals to activate their functional groups so that metal ions can be easily removed. Additionally, the performance of adsorptive mechanism can be compared to unmodified polymers.

2) The effects of a wider range of pressure and temperature can be tested to investigate the performance of polymers used to attract metal ions in the laboratory. Previous studies employed a laboratory bench scale method that did not allow for high pressures and temperatures to be applied during experiments, thus the pilot scale for the PEUF study on the removal of metal ions can be used to analyze the polymer potential to interact with metal ions. Adding high pressures and temperatures results in more realistic conditions and creates better preparations for wastewater treatment.

3) The regeneration process of the selected polymer was recommended to overcome the problems of precipitation in the laboratory scale by recycling retentate metal ions solution back into the PEUF system until the metal ions concentration achieved the discharged standards. When handling real wastewater, a simulation process is

proposed to estimate contact time and larger water volume as well as to scale the PEUF operating parameters, but using the additional chemical is not recommended.

4) Real wastewater can be taken from polluted sites in Malaysia where there are industrial sites and domestic areas. This is because heavy metal is commonly discharged into the water system and mixed in high concentrations and at high temperatures. Future research should replace synthetic wastewater with real wastewater. However, suitable equipment, larger work areas, and more time and funding are necessary for this purpose. Treatments to be used such as Membrane Bioreactor (MBR) can be combined with PEUF systems to remove organic substances in wastewater (considering the use of other potential biopolymers in removing different metal ions species to ensure that less toxic metal solutions are discharged through UF systems and that the end product will not harm the environment).

5) Future models can be developed using software or other mathematical models that involve equilibrium reactions for metal ions-polymer interactions based on other tested parameters, such as pressure and flow-rate. The entire modeling technique should include other tests (t-test, F-test or z-test) via ANOVA or other analyses software, such as SPSS or JMP, which must be relevant to the objective of the study. Modeling is one way to prove that the data is relevant and meets the standards for the removal of metal ions from wastewater.

REFERENCES

Ahmadi, S., Batchelor, B., & Koseoglu, S.S. (1994). The diafiltration method for the study of the binding of macromolecules to heavy metals. *Journal of Membrane Science* 89 (3), 257-265.

Alpatova, A., Verbych, S., Bryk, M., Nigmatullin, R., & Hilal, N. (2004). Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation-ultrafiltration process. *Separation and Purification Technology, 40*(2), 155-162.

Alto, K., Broderius, S., Lloyd, L., & Smith, Jr. (1977). *Toxicity of xanthates to freshwater fish and invertebrates*. Department of Entomology, Fisheries, and Wildlife. State of Minnesota, Environmental Quality Board. Retrieved from: http://www.leg.state.mn.us/lrl/lrl.asp

Amjad, Z. (1993). Reverse Osmosis, Membrane technology, water chemistry, and industrial application. *Science*. New York, NY: *Chapman & Hall, Van Nostrand.*

Anderson, M. (1997). Design of Experiments. *In The Industrial Physicist, American Institute of Physics*, 24-26. Retrieved from http://www.eng.auburn.edu/~drmills/mans486/DOE/Fall09/DOE_advantages_indust_examples.pdf

Aratani, T., Kodukula, P., & Patterson, J.W. (1983). Removal of metals in combined treatment systems. United States Environmental Protection Agency Report, Illinois Institute of Technology Chicago, Illinois.

Aroua, M. K., Fathiah Mohamed Zuki, & Nik Meriam Nik Sulaiman. (2007). Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration. *Journal of Hazardous Materials, 147*(3), 752-758.

Arthanareeswaran, G., Thanikaivelan, P., Jaya, N., Mohan, D., & Raajenthiren, M. (2007). Removal of chromium from aqueous sulfonated poly(ether ether ketone) solution using cellulose acetate and blend ultrafiltration membranes. *Journal of Hazardous Materials, 139*(1), 44-49.

Baharuddin, N. H., Sulaiman, N. M. N & Aroua, M.K. (2014). Unmodified starch as water-soluble binding polymer for chromium ions removal via polymer enhanced ultrafiltration system. *Journal of Environmental Health Science and Engineering, 12*(61), 1.

Barakat, M.A., & Schmidt, E. (2010). Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. *Desalination*, 256 (1-3), 90-93.

Battarbee, R., Anderson, N., Appleby, P., Flower, R.J., Fritz, S., Haworth, E., Higgit, S., Jones, V., Kreiser, A., Munro, M.A., Natkanski, J., Oldfield, F., Patrick, S.T., Richardson, N., Rippey, B., & Stevenson A.C. (1988). Lake Acidification in The United Kingdom, ENSIS, London. Retrieved from: http://www.geog.ucl.ac.uk/~spatrick/f_r_pubs.html

Bednar, B., Trnena, J., Svoboda, P., Vajda, S., Fidler, V., & Prochazka, K. (1991). Time-Resolved Fluorescence Study of Chain Dynamics .1. Poly(Methacrylic Acid) in Dilute Water Solutions. *Macromolecules, 24*(8), 2054-2059.

Bell, C.A. , Smith, S.V., Whittaker, M.R., Whittaker, A. K., Gahan, L. R., & Monteiro, M.J. (2006). Surface-Functionalized Polymer Nanoparticles for Selective Sequestering of Heavy Metals. *Advanced Materials, 18* (5), 582–586.

Bello-Perez, L. A., & Paredes-Lopez, O. (2009). Starches of Some Food Crops, Changes During Processing and Their Nutraceutical Potential. *Food Engineering Reviews, 1*(1), 50-65.

Bertoft, E. (2004). On the nature of categories of chains in amylopectin and their connection to the super helix model. *Carbohydrate Polymers, 57* (2), 211-224.

Bertoft, E., Piyachomkwan, K., Chatakanonda, P., & Sriroth, K. (2008). Internal unit chain composition in amylopectins. *Carbohydrate Polymers, 74*(3), 527–543.

Bertolini, A.C. (2010). Starches: Characterization, Properties, and Applications. Technology & Engineering. *CRC Press*, Taylor & Francis Group.

Bhattacharya, A. K., Mandal, S.N., Das, S.K. (2006). Adsorption of Zn (II) from aqueous solution by using different adsorbents. *Journal of Chemical Engineering123*(1-2), 43-51.

Blume, G., Cevc, G., Crommelin, M. D., Bakker-Woudenberg, I. A., Kluft, C., & Storm, G. (1993). Specific targeting with poly(ethylene glycol)-modified liposomes: coupling of homing devices to the ends of the polymeric chains combines effective target binding with long circulation times. *Biochimica et Biophysica Acta, 1149*(1), 180-4.

Bolto, B. A. (1995). Soluble polymers in water purification. *Progress in Polymer Science 20* (6), 987-1041.

Bosch, X. (2003). Cadmium cuts two ways: The heavy metal mutates DNA,and then prevents cells from repairing the damage. *Science, 609*, 1.

Buleon, A. , Colonna, P., Planchot, V. & Ball. S. (1998). Starch granules: structure and biosynthesis. *International Journal of Biological Macromolecules, 23*(2), 85-112.

Brown, W. H., Poon, T. (2005). *Introduction to organic chemistry* (3rd ed.). Wiley International Edition. John Wiley & Sons Inc Hardcover.

Burrell, D.C. (1974). *Atomic Spectrometric Analysis of Heavy Metal Pollutants in Water*, Ann Arbor Science Publishers, Ann Arbor, Michigan.

Camarillo, R., Llanos, J., Garcia-Fernandez, L., Perez, A., & Canizares, P. (2010). Treatment of copper (II)-loaded aqueous nitrate solutions by polymer enhanced ultrafiltration and electrodeposition. *Separation and Purification Technology, 70*(3), 320-328.

Camarillo, R., Perez, A., Canizares, P., & de Lucas, A. (2012). Removal of heavy metal ions by polymer enhanced ultrafiltration batch process modeling and thermodynamics of complexation reactions. *Desalination, 286*, 193-199.

Canizares, P., de Lucas, A., Perez, A., & Camarillo, R. (2005). Effect of polymer nature and hydrodynamic conditions on a process of polymer enhanced ultrafiltration. *Journal of Membrane Science, 253*(1-2), 149-163.

Canizares, P., Perez, A., & Camarillo, R. (2002). Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters. *Desalination, 144*(1-3), 279-285.

Canizares, P., Perez, A., Camarillo, R., Llanos, J., & Lopez, M. L. (2007). Selective separation of Pb from hard water by a semi-continuous polymer-enhanced ultrafiltration process (PEUF). *Desalination, 206*(1-3), 602-613.

Canizares, P., Perez, A., Camarillo, R., & Linares, J. J. (2004). A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents. *Journal of Membrane Science, 240*(1-2), 197-209.

Canizares, P., Perez, A., Camarillo, R., & Mazarro, R. (2008). Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process. *Journal of Membrane Science, 320*(1-2), 520-527.

Chabot, J. F., & Hood, L.F. (1976). Interaction of iron compounds with starch granules. *Starch 28* (8), 264-267 (in German).

Chang, Y.K., Shih, P.H., Chiang, L.C., Chen, T.C., Lu, H.C., & Chang, J.E. (2007). Removal of heavy metal by insoluble starch xanthate. *Environmental Informatics Archives, 5*, 684-689.

Chen, C. J., Dai, Y. T., Sun, Y. M., Lin, Y. C., & Juang, Y. J. (2007). Evaluation of auditory fatigue in combined noise, heat and workload exposure. *Industrial Health, 45*(4), 527-534.

Chi-Wang, L., Chia-Hsien, C., Kwang-Ho, C. & Wei-Shuen, Y. (2008). Polyelectrolyte enhanced ultrafiltration (PEUF) for the removal of Cd(II): effects of organic ligands and solution pH. *Chemosphere*, 72 (4), 630–635.

Choe, T. B., Masse, P., Verdier, A., & Clifton, M. J. (1986). Membrane Fouling in the Ultrafiltration of Polyelectrolyte Solutions - Polyacrylic-Acid and Bovine Serum-Albumin. *Journal of Membrane Science, 26*(1), 17-30.

Chung, H. J., & Park, T. G. (2009). Self-assembled and nanostructured hydrogels for drug delivery and tissue engineering. *Nano Today, 4*(5), 429-437.

Copeland, L., Blazek, J., Salman, H., & Tang, M. C. (2009). Form and functionality of starch. *Food Hydrocolloids, 23*(6), 1527-1534.

Cotton, A.F., Wilkinson, G., (1989). Advanced Inorganic Chemistry, (5th ed.), *Journal of Chemical Education 66* (3), A104.

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science, 30*(1), 38-70.

Dautzenberg, H. (1994). *Polyelectrolytes.* New York: Hauser Verlag.

Department of Environment. (1994). Environmental Quality Act Report, Ministry of Science, Technology and the Environment. Malaysia.

Department of Environment. (2011). Malaysia Environmental Quality Report, Ministry of Natural Resources and Environment. Malaysia.

Deshmukh, S.P., Li, K. (1998). Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes. *Journal of Membrane Science, 150* (1), 75-85.

De Stefano, C., Gianguzza, A., Piazzese, D., & Sammartano, S. (2003). Quantitative parameters for the sequestering capacity of polyacrylates towards alkaline earth metal ions. *Talanta, 61*(2), 181-194.

Dupler, D. (2001). Heavy metal poisoning: An entry from Thomson Gale's. In the *Gale Encyclopedia of Alternative Medicine*, 23-26.Thompson Gale (digital format). Retrieved from http://www.alldiscountbooks.net/_B000M59HW0_i_.html

Duruibe, J. O., Ogwuegbu, M. O. C., & Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences, 2*(5), 112-118.

Dzul Erosa, M.S., Saucedo Medina, T.I., Navarro Mendoza, R., Avila Rodriguez, M., & Guibal, E. (2001). Cadmium sorption on chitosan sorbents: kinetic and equilibrium studies. *Hydrometallurgy, 61*(3), 157–167.

Eilers, H., (1936). On high polymeric compunds, News: The strong construction structure, About Department of Chemical, (69), 819-848 (in German).

Fatin-Rouge, N., Dupont, A., Vidonne, A., Dejeu, J., Fievet, P., & Foissy, A. (2006). Removal of some divalent cations from water by membrane-filtration assisted with alginate. *Water Research, 40*(6), 1303-9.

French, A.C., Thompson, A.L., & Davis, B.G. (2009). High Purity Discrete PEG Oligomer Crystals Allow Structural Insight. *Angewandte Chemie International Edition* - *Wiley Online Library , 48*(7), 1248-52.

Fu, F., Chen, R., & Xiong, Y. (2006). Application of a novel strategy-coordination polymerization precipitation to the treatment of Cu^{2+}-containing wastewater. *Separation and Purification Technology, 52*(2), 388-393.

Garbarino, J.R., Hayes, H., Roth, D., Antweider, R., Brinton, T.I., & Taylor, H. (1995). Contaminants in the Mississippi River 1987-1992. *U. S. Geological Survey Circular 1133*.

GEA Process Engineering. (2013). Industrial Applications [Electronic version]. *GEA Filtration.*
Retrieved from:http://www.geafiltration.com/applications/industrial_applications.asp

Geckeler, K. E. (2001). Polymer–metal complexes for environmental protection. Chemoremediation in the aqueous homogeneous phase. *Pure and Applied Chemistry,* 73,129-136.

Geckeler, K., Lange, G., Eberhardt, H., & Bayer, E. (1980). Preparation and application of water-soluble polymer-metal complexes. *Pure and Applied Chemistry, 52,*1883-1905.

Geckeler, K.E., Shkinev, V.M. & Ya Spivakov, B. (1987). Interactions of polymer backbones and complexation of polychelatogens with methylthiourea ligands in aqueous solution. *The Applied Macromolecular Chemistry, 155*(1), 151-161.

Geckeler, K.E., Zhou, R., Fink, A., Rivas, B.L. (1996). Synthesis and properties of hydrophilic polymers. III. Ligand effects of the side chain of polyaziridines on metal complexation in aqueous solution. *Journal of Applied Polymer Science, 60* (12), 1291-1298.

Gidley, M. J., Hanashiro, I., Hani, N. M., Hill, S. E., Huber, A., Jane, J-L., Gilbert, R. G. (2010). Reliable measurements of the size distributions of starch molecules in solution: Current dilemmas and recommendations. *Carbohydrate Polymers, 79*(2), 255-261.

Golovanov, V.I., Shkinev, V.M., Ya.Spivakov, B., Geckeler, K.E., & Bayer, E. (1993). Mathematical description of metal retention with water-soluble polymers during membrane filtration. *Separation Science and Technology,* 28 (10), 1887–1898.

Gray, J. A., & BeMiller, J.N. (2004). Development and utilization of reflectance confocal laser scanning microscopy to locate reaction sites in modified starch granules. *Cereal Chemistry, 81*(2), 278-286.

Gray, J. A., & BeMiller, J.N. (2005). Influence of reaction conditions on the location of reactions in waxy maize starch granules reacted with a propylene oxide analog at low substitution levels. *Carbohydrate Polymer, 60*(2), 147-162.

Guzman, J., Saucedo, I., Revilla, J., Navarro, R., & Guibal, E. (2003). Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities. *International Journal of Biological Macromolecules, 33*(1-3), 57–65.

Habashi, F. (1992). Environmental Issues in the Metallurgical Industry –Progress and Problems, Environmental Issues and Waste Management in Energy and Mineral Production, Balkama, Rotherdam, 1143 -1153.

Hamza, A., Pham, V.A., Matsuura, T., Santerre, J.R. (1997). Development of membranes with low surface energy to reduce the fouling in ultrafiltration applications. *Journal of Membrane Science 131*(1-2), 127-227.

Han, J.A., & BeMiller, J.N. (2006). Influence of the reaction conditions on MS values and physical properties of waxy maize starch derivatized by reaction with propylene oxide. *Carbohydrate Polymer, 64(2)*, 158-162.

Hanjun, T., Mitsunaga, T., & Kawamura, Y. (2006). Molecular arrangement in blocklets and starch granule architecture. *Carbohydrate Polymers, 63*(4), 555-560.

Harris, J M. & Zalipsky, S. (1997). *Poly(ethylene glycol)*(Vol. 680)(Chemistry and Biological Applications). America: American Chemical Society Symposium Series.

Hawkes, J.S. (1997). Heavy Metals. *Journal of Chemical Education, 74*(11), 1374.

Hinterdorfer, P., Baumgartner, W., Gruber, H. J., Schilcher, K., & Schindler, H. (1996). Detection and localization of individual antibody-antigen recognition events by atomic force microscopy. *Proceedings of the National Academy of Sciences of the United States of America, 93*(8), 3477–3481.

Hollo, J., Huszar, J., Szejtli, J., & Petho, M. (1962). Investigation of the calcium and magnesium adsorption assets of the starch grains. *Recent contributions to the chemistry of strong fraction, XII, Strength. 14* (10), 343-347(in German).

Holum, J.R. (1983). *Elements of General and Biological Chemistry* (6th ed.). New York, NY*: John Wiley and Sons.*

Hood, L.F., & O'shea, G.K. (1976). Calcium binding by hydroxylpropyl distarch phosphate and unmodified starch. *Cereal Chemistry, 54*(2), 266-271.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: a review. *Carbohydrate Polymers, 45*(3), 253-267.

Huber, K. C., & BeMiller, J.N. (2001). Location of sites of reaction within starch granules. *Cereal Chemistry, 78*(2), 173-180.

Hutton, M., & Symon, C. (1986). The Quantities of Cadmium, Lead, Mercury and Arsenic Entering the U.K. Environment from Human Activities. *Science of The Total Environment, 57,* 129-150.

Hyun-Jung, C., & Qiang, L. (2009). Impact of molecular structure of amylopectin and amylose on amylose chain association during cooling. *Carbohydrate Polymers, 77*(4), 807-815.

Idris, A., Azmin, W. N. W., Soom, M. A. M. & Mamun, A. A. (2005). The importance of sullage (grey-water) treatment in the restoration and conservation of urban streams, International Journal of River Basin Management, 3:3, 223-227, doi: 10.1080/15715124.2005.9635262

Imberty, A., Chanzy, H. & Perez, S. (1988). The double-helical nature of the crystalline part of A-starch. *Journal of Molecular Biology, 201*(2), 365-78.

Isaias, N.P. (2001). Experience in reverse osmosis pretreatment. *Desalination* 139(1-3), 57-64.

Islamoglu, S., & Yilmaz, L. (2006). Effect of ionic strength on the complexation of polyethyleneimine (PEI) with Cd^{2+} and Ni^{2+} in polymer enhanced ultrafiltration (PEUF). *Desalination, 200*(1-3), 288-289.

Jay-lin, J., & Zihua, A. (2007). Characterization and modeling of the A- and B-granule starches of wheat, triticale, and barley. *CarbohydratePolymers, 67*(1), 46-55.

Jen-Yune, L., & An-I, Y. (2001). Relationships between thermal, rheological characteristics and swelling power for various starches. *Journal of Food Engineering, 50*(3), 141-148.

Jianxian, Z., Hongqi, Y., & Zhongyu, H. Z., (2009). Application of the hybrid complexation-ultrafiltration process for metal ion removal from aqueous solutions. *Journal of Hazardous Materials, 161*(2-3), 1491-1498.

Jobling, S. (2004). Improved starch for food and industrial applications. *Current Opinion in Plant Biology, 7*(2), 210-218.

Juang, R. S., & Chen, M. N. (1997). Removal of copper(II) chelates of EDTA and NTA from dilate aqueous solutions by membrane filtration. *Industrial & Engineering Chemistry Research, 36*(1), 179-186.

Juang, R.S., & Liang, J.F. (1993). Equilibrium studies for the interaction of aqueous metal ions and polyacrylic acid by a batch ultrafiltration method. *Journal of Membrane Science, 82* (1-2), 163-174.

Jun, C., Seongbong J., Kinam, P. (1995). Polysaccharide hydrogels for protein drug delivery. *Carbohydrate Polymer 28*(1), 69-76.

Juna, S., Williams, P. A., & Davies, S. (2011). Determination of molecular mass distribution of amylopectin using asymmetrical flow field-flow fractionation. *Carbohydrate Polymers, 83* (3), 1384-1396.

Kadioglu, S. I., Yilmaz, L., & Ozbelge, H. O. (2009). Estimation of Binding Constants of Cd(II), Ni(II) and Zn(II) with Polyethyleneimine (PEI) by Polymer Enhanced Ultrafiltration (PEUF) Technique. *Separation Science and Technology, 44*(11), 2559-2581.

Kim, B.S. & Lim, S.T. (1999). Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. *Carbohydrate Polymers, 39 (3)*, 217–223.

Kojima, H., & Yuan, K.L. (2001). Photosynthetic Microorganisms in Environmental Biotechnology. Hong Kong, HK: *Springer-Verlag Hong Kong Ltd*.

Korus,I., Bodzek, M., & Loska, K. (1999). Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation-ultrafiltration process. *Separation and Purification Technology, 17*(2), 111–116.

Kuncoro, E. P., Roussy, J., & Guibal, E. (2005). Mercury recovery by polymer-enhanced ultrafiltration: Comparison of chitosan and poly(ethylenimine) used as macroligand. *Separation Science and Technology, 40*(1-3), 659-684.

Labanda, J., Khaidar, M. S., & Llorens, J. (2009). Feasibility study on the recovery of chromium (III) by polymer enhanced ultrafiltration. *Desalination, 249*(2), 577-581.

Leach, H.W., Schoch, T.J., & Cheeseman, E.F. (1961). Adsorption of alkaline strong grain. *Starch 13*, 200.

Lenntech. (2014). Lenntech Water Treatment Solutions : Heavy Metals Removal. http://www.lenntech.com/processes/heavy/heavy_metals_removal.html

Lentz, B. R. (1994). Polymer-induced membrane fusion: potential mechanism and relation to cell fusion events. *Chemistry and Physics of Lipids, 73*(1-2), 91–106.

Li, X., Xu, S. M., Pen, Y., & Wang, J. D. (2008). The swelling behaviors and network parameters of cationic starch-g-acrylic acid/poly(dimethyldiallylammonium chloride) semi-interpenetrating polymer networks hydrogels. *Journal of Applied Polymer Science, 110*(3), 1828-1836.

Lim, S., & Seib, P.A. (1993). Location of phosphate esters in a wheat starch by ^{31}P-nuclear magnetic resonance microscopy. *Cereal Chemistry, 70* (2), 145-152.

Llanos, J., Camarillo, R., Perez, A., & Canizares, P. (2010). Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction. *Separation and Purification Technology, 73*(2), 126-134.

Llorens, J., Pujola`, M., & Sabate , J. (2004). Separation of cadmium from aqueous streams by polymer enhanced ultrafiltration: a two-phase model for complexation binding. *Journal of Membrane Science, 239* (2), 173–181.

Lyman, W.J. (1995). Transport and transformation processes, *Fundamentals of Aquatic Toxicology, G. M. Rand (Ed.)*, Taylor & Francis, Washington DC.

Matsuura, H., & Begum, R. (1997). Conformational properties of short poly(oxyethylene) chains in water studied by IR spectroscopy. *Journal of the Chemical Society, Faraday Transactions, 93*, 3839–3848.

Mavrov, V., Erwe, T., Blocher, C., & Chmiel, H. (2003). Study of new integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater. *Desalination, 157* (1-3), 97-104.

Micioi, M., Albu, A., Mateescu, C., Voicu, G., Rusen, E., Marculescu, B., Mutihac, L. (2007). New polymeric structures designed for the removal of Cu(II) ions from aqueous solutions. *Journal Applied Polymer Science, 103*(3), 1397–1405.

Mimoune, S., & Amrani, F. (2007). Experimental study of metal ions removal from aqueous solutions by complexation-ultrafiltration. *Journal of Membrane Science, 298*(1-2), 92–98.

Moreno-Villoslada, I, & Rivas, B. L. (2002). Competition of divalent metal ions with monovalent metal Ions on the adsorption on water-soluble polymer. *The Journal of Physical Chemistry B, 106* (38), 9708-9711.

Morlay, C., Cromer, M., Mouginot, Y., & Vittori, O. (1998). Potentiometric study of Cu(II) and Ni(II)with two high molecular weight poly(acrylic acid). *Talanta 45*(6), 1177.

Morlay, C., Cromer, M., Mouginot, Y., & Vittori, O. (1999). Potentiometric study of Cd(II) and Pb(II)with two highmolecularweight poly(acrylic acid); comparison with Cu(II) and Ni(II). *Talanta 48* (5), 1159-1166.

Muslehiddinoglu, J., Uludag, Y., Ozbelge, H.O., Yilmaz, L. (1998). Effect of operating parameters on selective separations of heavy metals from binary mixtures via polymer enhanced ultrafiltration. *Journal of Membrane Science*, *140*(2), 251-266.

Nriagu, J.O. (1989). A global Assessment of Natural Sources of Atmospheric Trace Metals. *Nature, 338*(6210), 47-49.

Nriagu, J.O., & Pacyna, J. (1988). Quantitative Assessment of Worldwide Contamination of Air, Water and Soil by Trace Metals. *Nature 333*, 134-139.

Owlad, M., Aroua, M. K., & Wan Mohd Ashri Wan Daud. (2010). Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. *Bioresource Technology, 101*(14), 5098-5103.

Palencia, M., Rivas, B. L., & Pereira, E. (2009). Metal ion recovery by polymer-enhanced ultrafiltration using poly(vinyl sulfonic acid): Fouling description and membrane-metal ion interaction. *Journal of Membrane Science, 345*(1-2), 191-200.

Palmer, V., Zhou, R. N., & Geckeler, K. E. (1994). Cetylpyridinium Chloride-Modified Poly(Ethyleneimine) for the Removal and Separation of Inorganic-Ions in Aqueous-Solution. *Applied Macromolecular Chemistry, 215* (1), 175-188.

Pefferkorn, Emile (18 August 2008). Polymer adsorption and interfacial reconformation processes. In *SciTopics*. Retrieved from 26 February 2014, http://www.scitopics.com/Polymer_adsorption_and_interfacial_reconformation_processes.html.

Pinto, C.G., Laespada, M.E.F., Pavon, J.L.P., & Cordero, B.M. (1999). Analytical applications of separation techniques through membranes. *Laboratory Automation & Information Management, 34*(2), 115-130.

Prakasham, R.S., Merrie, J.S., Sheela, R., Saswathi, N., & Ramakrisha, S.V. (1999). Biosorption of chromium (VI) by free and immobilized rhizopus arrhizus. *Environmental Pollution, 104* (3), 421-427.

Puranik, P. R., & Paknikar, K.M. (1999). Biosorption of lead, cadmium, and zinc by citrobacter strain MCM B-181: characterization studies. *Biotechnology Progress 15*(2), 228-237.

Rammika, M. (2010). *An Ion Imprinted Polymer for the Determination of Ni (II) ions from Mine Tailing Samples.* (Rhodes University, South Africa). Retrieved from Rhodes eResearch Repository database.

Rawa-Adkonis, M., Wolska, L., & Namiesnik, J. (2003). Modern Techniques of Extraction of Organic Analytes from Environmental Matrices. *Critical Reviews in Analytical Chemistry, 33*(3), 199-248.

Rayford, W. E., Wing, R. E. & Doane, W. M. (1978). Carboxyl-Containing Starch Graft Polymer: Preparation and Use in Heavy Metal Removal. *Applied Polymer, 24*(1),105-113.

Ring, S. G. , & Parker, R. (2001). Aspects of the physical chemistry of starch. *Journal of Cereal Science, 34*(1), 1-17.

Rivas, B.L, & Geckeler, K.E. (1992). Synthesis and metal complexation of poly(ethylenimine) and derivatives. *Advances in Polymer Science* 102, 171–188.

Rivas, B. L., & Maureira, A. (2007). Poly(2-acrylamido glycolic acid): A water-soluble polymer with ability to interact with metal ions in homogenous phase. *Inorganic Chemistry Communications, 10*(2), 151-154.

Rivas, B.L., Pereira, E., & Maureira, A. (2009). Functional water-soluble polymers: polymer–metal ion removal and biocide properties. *Polymer International, 58*(10), 1093–1114.

Rivas, B.L., Pereira, E. D., & Moreno-Villoslada, I. (2003). Water-soluble polymer–metal ion interactions. *Progress in Polymer Science 28* (2), 173–208.

Roberts, J.R. (1999, June). Metal toxicity in children [Electronic version]. Training Manual on Pediatric Environmental Health. *Children's Environmental Health Network,* 115-132.
Retrieved from: http://www.cehn.org/files/trainingmanual/manual-metal.html

Rouse, J.D., Bjornen , K.K., Taylor, R.W., & Bor-Jier, S. (2004). Surfactant-Based Technologies Applicable to Remediation of Mercury Pollution in the Subsurface. *Cambridge Journals*, *6*(2), 157-164.

Ruey-Shin, J., & Ji- Feng, L. (1993). Removal of copper and zinc fromaqueous sulphate solution with polyacrylic acid by a batch complexation-ultrafiltration process. *Journal of Membrane Science,* 82(1-2), 175-183.

Sabate, J., Pujola, M., & Llorens, J. (2006). Simulation of a continuous metal separation process by polymer enhanced ultrafiltration. *Journal of Membrane Science, 268*(1), 37-47.

Sabate, J., Pujola, M., & Llorens, J. (2002). Two-phases model for calcium removal from aqueous solution by polymer enhanced ultrafiltration. *Journal of Membrane Science, 204*(1-2), 139-152.

Sasaki, K.J., Burnett, S.L., Christian, S.D., Tucker, E.E., Scamehorn, J.F. (1989). Polyelectrolyte ultrafiltration of multivalent ions. Removal of copper ($^{2+}$) by sodium poly(styrenesulfonate), *Langmuir*, 5 , 363-369.

Semiao, A.J.C., & Schafer, A. I. (2010). Xenobiotics Removal by Membrane Technology: An Overview. *Environmental Pollution, 16*, 307-338.

Shah, S., Heinle, S.A., & Glass, J.E. (1985). Water-Soluble Polymer Adsorption From Saline Solutions. Paper presented at SPE Oilfield and Geothermal Chemistry Symposium, Phoenix, Arizona. doi: 10.2118/13561-MS

Stratman, H. (1986). Synthetic membranes and their preparation, P.M. Bungay et al. (eds), *Synthetic Membranes: Science, Engineering and Applications***,** 1-37, Retrieved from : http://link.springer.com/chapter/10.1007%2F978-94-009-4712-2_1#page-1

Tadokoro, H. (1990, February). Structure of Crystalline Polymers. Krieger Pub Co; Revised edition. Retrieved from: http://www.amazon.com/Structure-Crystalline-Polymers-Hiroyuki-Tadokoro/dp/0894643495

Takagishi, T., Okuda, S., Kuroki, N. & Kozuka, H. (1985). Binding of Metal Ions by polyethyleneimine and its derivatives. *Journal of Polymer Science, 23* (8), 2109-2116.

Teck-Yee, L., Chui-Ping, K. & Lee, N. (2012). Spatial and Temporal Variations of Heavy Metals in a Tropical River. *World Applied Sciences Journal*, *16*(4), 550-559.

Teck-Yee, L., Lipan S., & Singh, H. (2010a). Performance of oxidation ponds in removing heavy metals from pig farm wastewater. *Middle-East Journal Scientific Research*, *5*(3), 163-169.

Teck-Yee, L., Srikaran, R., Chui-Ping, & Nyanti, L. (2010b). Organic matter, nutrients and trace metals of Serin River. *World Applied Science Journal*, *8*(4), 496-502.

Tester, R.F., & Xin, Q. (2011). β-limit dextrin - Properties and applications. *Food Hydrocolloids*, *25*(8), 1899-1903.

Trivunac, K., & Stevanovic, S. (2006). Removal of heavy metal ions from water by complexation-assisted ultrafiltration. *Chemosphere, 64* (3), 486-491.

Uludag, Y., Ozbelge, H. O., & Yilmaz, L. (1997). Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration. *Journal of Membrane Science*, *129*(1), 93-99.

UNEP/GPA. (2004). Why The Marine Environment Needs Protection From Heavy Metals, Heavy Metals 2004. *United Nations Environmental Protection/Global Program of Action.*

United States Department of Labor (2004). Occupational Safety and Health Administration (OSHA); Safety and Health Topics: *Toxic Metals*. Retrieved from : https://www.osha.gov/SLTC/metalsheavy/

University of Washington College of Forest Resources and College of Ocean and Fishery Sciences Center for Streamside Studies. (2000). *Environmental Impacts of Mining in Eastern Washington.*Center for Water and Watershed Studies Fact Sheet. Washington, DC: Edmonds, R., & Peplow, D.

Van Warners, A., Stamhuis, E.J., Antonie, A.C. & Beenakers, M. (1994). Kinetics of the hydroxyethylation of starch in alkaline salt-containing aqueous slurries. *Industrial & Engineering Chemistry Research, 33(4)*, 981-992.

Velaa M.C.V. , Blanco,S.A.I., Garcia, J.L., Rodriguez, E.B. (2008). Analysis of membrane pore blocking models applied to the ultrafiltration of PEG. *Separation and Purification Technology, 3*(62), 489–498.

Volchek, K., Krentsel, E., Zhilin, Yu., Shtereva, G., & Dytnersky, Yu. (1993). Polymer binding/ultrafiltration as a method for concentration and separation of metals. *Journal of Membrane Science, 79* (2-3), 253.

Volchek, K., Krentsel, E., Zhilin, Yu, Shtereva, G., & Dytnersky, Yu (1994). Polymer poly(etylenimine) for the removal and separation of inorganic ions in aqueous solution. *The Applied Macromolecular Chemistry, 215*(175)(in German).

Vorwerg, W., Radosta, S., & Leibnitz, E. (2002). Study of a preparative-scale process for the production of amylose. *Carbohydrate Polymer, 47*(2), 181-189.

Vries, W.D., Romkens, P.F.A.M., Leeuwen, T.V. & Bronswijk, J.J.B. (2002). Heavy Metals. In *P.M. Haygarth and S.C. Jarvis. Agriculture, Hydrology and Water Quality.*, New York: CABI Publishing, 207-239.

Wagner, J. (2001). Membrane Filtration Handbook (2nd Edition) - Practical Tips and Hints. *GE Osmonics Inc.*

Wan,L.K., Chen, J.P., Hung, Y., & Shammas, N.K. (2011). Membrane and Desalination Technologies, Springer, New York.

Wang, Z. K., Fu, Z., & Ye, C. L. (2009). Pre-concentration and separation of copper with water-soluble poly(vinyl alcohol) and acetone system prior to its spectrophotometric determination. *Microchimica Acta, 165*(1-2), 103-107.

Wan Ngah, W.S., Endud, C.S., & Mayanar, R. (2002). Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *Reactive and Functional Polymers 50* (2), 181-190.

Weinberg, N.L., Genders, J.D. (1992). Electrochemistry for a Cleaner Environment. Science. *The Electrosynthesis Co.*

Wettstein, F., Neukom, H., & Deuel, H. (1961). Cation exchange on starch phosphate. 17 communication on ion-exchangers. *Helvetica Chimica Acta 44*(7),1949-1956 (in German).

Williams, M. E. (2003). A Brief Review of Reverse Osmosis Membrane Technology. Williams Engineering Services Company, Inc.

Williams, P.A. (2007). *Handbook of Industrial Water Soluble Polymers : Convergence*. Blackwell Publishing. EET Corporation and Williams Engineering Services Company.
Retrieved from: http://www.eetcorp.com/heepm/RO_ReviewE.pdf

Wing, R. E., Doane, W. M., & Russell, C. R. (1975). Insoluble Starch Xanthate: Use in Heavy Metal Removal. *Journal of Applied Polymer Science*, *19*(3), 847-854.

Wu, Y., & Seib, P. (1990). Acetylated and hydroxyprpoylated distarch phosphates from waxy barley: paste properties and freeze-thaw stability. *Cereal Chemistry, 67*, 202-208.

Xinsheng. Z., & Kuang-Ho., C. (2008). A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane. . *Colloids and Surfaces A: Physiochemical and Engineering Aspects* (312), 231.

Yarlagadda, P.S., Matsumoto, M.R., Van Benschoten, J.E. & Kathuria, A. (1995). Characteristics of heavy metals in contaminated soils. *Journal of Environmental Engineering, 121*(4), 276-286.

Zachara, J.M., Ainsworth, C.C., Cowan, C.E., Resch, C.T. (1989). Adsorption of chromate by subsurface soil horizons. *Soil Science Society of America Journal, 53*(2), 418-428.

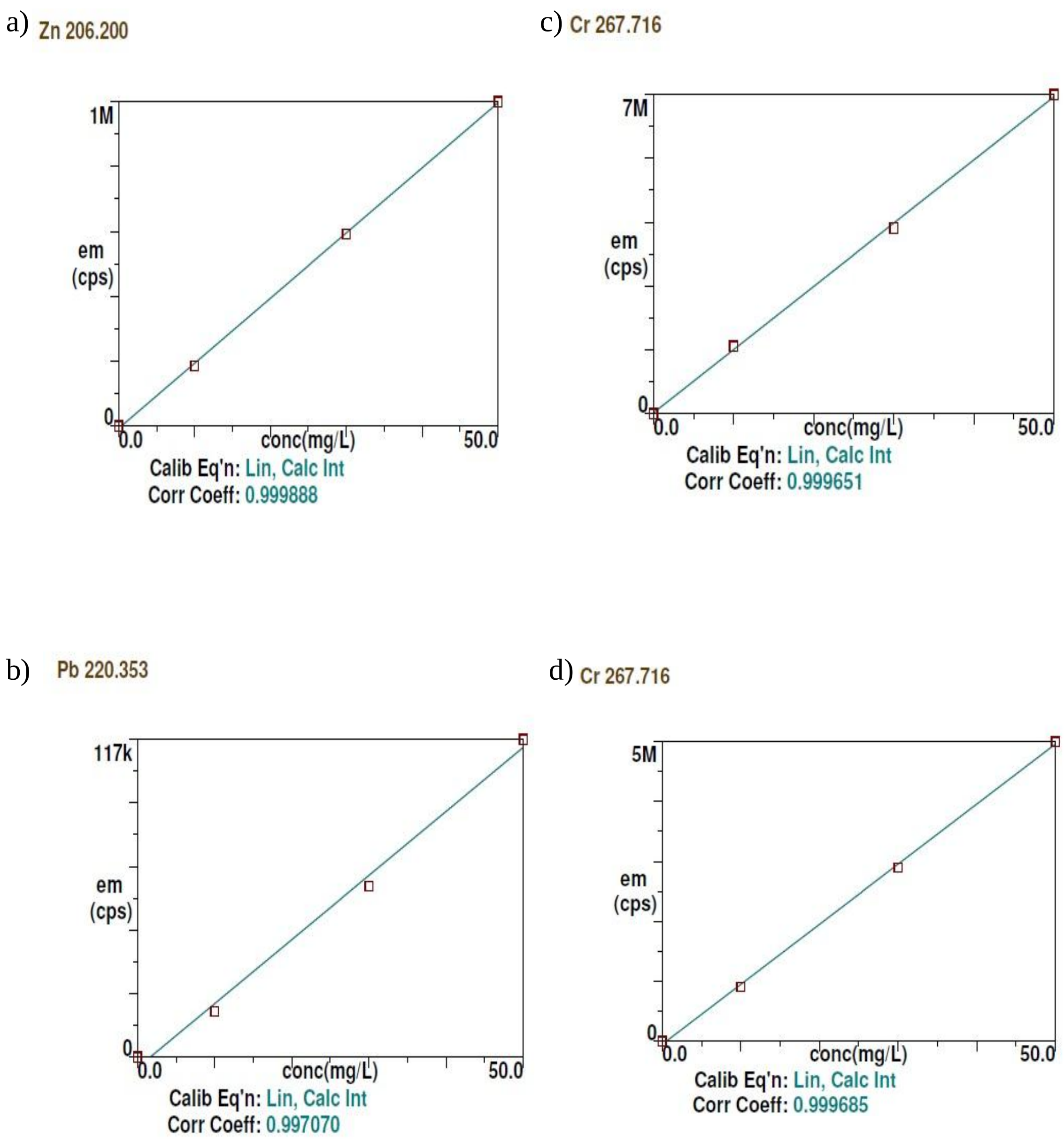
Zalloum, R. M., & Mubarak, M. S. (2008). Chelation properties of poly(2- hydroxy-4-acryloyloxybenzophenone) resins toward some divalent metal ions. *Journal of Applied Polymer Science*, 109, 3180-3184.

Zamora, A. (2012). Carbohydrates - Chemical Structure. In *Scientific Physic*. Retrieved from: http://www.scientificpsychic.com/fitness/carbohydrates.html

Zander, N. E. (2009). Chelating Polymers and Environmental Remediation. *Army Research Laboratory*. Dynamic Science, Inc

APPENDIX A

CALBRATION CURVES FOR SELECTED METAL IONS STANDARD USING ICP(-OES)



a), b), c), and d) are the figures of Zn(II), Pb(II), Cr(III) and Cr(VI) ions calibration curves carried out by ICP-OES, respectively.

APPENDIX B

CALCULATION DATA FOR THEORETICAL ANALYSES USING CANIZARES MODELS SINGLE AND MIXED METAL ION SOLUTIONS

Single metal ion solutions (Fitting Canizares Models)

1) Effects of retention Vs pH (unmodified starch=0.05%, metal ion concentration=10mg/l, flowrate=115ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
2		0.965	38.960	28.960	3.896	37.608	0.965	0.965	4.726	96.530
5		0.963	12.973	2.973	1.297	12.494	0.963	0.963	2.213	96.310
7		0.936	6.082	-3.918	0.608	5.691	0.936	0.936	1.505	93.570
9		0.941	18.187	8.187	1.819	17.109	0.941	0.941	2.652	94.070
12		0.909	21.123	11.123	2.112	19.203	0.909	0.909	2.829	90.910
pH	Pb(II)									
2		0.593	10.021	0.021	1.002	5.946	0.593	0.593	1.188	59.330
5		0.557	10.324	0.324	1.032	5.745	0.557	0.557	1.131	55.650
7		0.522	7.914	-2.086	0.791	4.129	0.522	0.522	0.935	52.170
9		0.496	9.032	-0.968	0.903	4.477	0.496	0.496	0.943	49.570
12		0.461	10.615	0.615	1.062	4.888	0.461	0.461	0.949	46.050
pH	Cr(III)									
2		0.398	9.274	-0.726	0.927	3.688	0.398	0.398	0.767	39.770
5		0.635	9.161	-0.839	0.916	5.820	0.635	0.635	1.217	63.529
7		0.935	8.463	-1.537	0.846	7.913	0.935	0.935	1.726	93.500
9		0.992	41.080	31.080	4.108	40.762	0.992	0.992	5.068	99.227
12		1.000	339.500	329.500	33.950	339.432	1.000	1.000	34.943	99.980
pH	Cr(VI)									
2		0.717	16.357	6.357	1.636	11.725	0.717	0.717	1.889	71.680
5		0.759	9.815	-0.185	0.981	7.447	0.759	0.759	1.504	75.880
7		0.806	7.722	-2.278	0.772	6.221	0.806	0.806	1.428	80.560

12		0.836	17.461	7.461	1.746	14.589	0.836	0.836	2.294	83.550

To identify RL and Rm1*, we need 2 equations to solve it:

For example:

For Zn(II) at pH 2,

a) $$Rm1=\frac{Rm1[M] + RL \sum n\, [MLn]}{[M] + \sum n\, [MLn]}$$

$37.608= 10\, Rm1+28.96RL$

$Rm1= 3.761-2.896RL \quad (1)$

$RL=1.299-0.345Rm1 \quad (2)$

Substitute RL in Eqn. (1)

b) $$Rm= \frac{Rm1+ RL \sum n\, Kn\, [L]^{n}}{1+ \sum n\, Kn\, [L]^{n}}$$

$$0.965 = \frac{Rm1 + (1.299-0.345Rm1)\,(3.896)}{1+ 3.896}$$

$4.72 =Rm1+ 5.061-1.344Rm1$

$3.14-5.061=-0.344Rm1$

$Rm1= 0.965$

$RL=0.965$

Theorethical results				
pH	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
2	96.53	59.33	39.77	71.68
5	96.31	55.65	63.53	75.88
7	93.57	52.17	93.50	80.56
9	94.07	49.57	99.23	81.04
12	90.91	46.05	99.98	83.55

2) Effects of retention Vs pH (PEG=1.0%, metal ion concentration=10mg/l, flowrate=115ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
2		0.859	42.641	32.641	4.264	36.633	0.859	0.859	4.522	85.910
5		0.854	28.147	18.147	2.815	24.040	0.854	0.854	3.258	85.410
7		0.847	0.068	-9.932	0.007	0.057	0.847	0.847	0.852	84.650
9		0.850	4.489	-5.511	0.449	3.814	0.850	0.850	1.231	84.980
12		0.842	10.174	0.174	1.017	8.563	0.842	0.842	1.698	84.160
pH	Pb(II)									
2		0.622	3.629	-6.371	0.363	2.257	0.622	0.622	0.848	62.190
5		0.560	5.853	-4.147	0.585	3.276	0.560	0.560	0.887	55.980
7		0.531	4.432	-5.568	0.443	2.352	0.531	0.531	0.766	53.080
9		0.500	8.128	-1.872	0.813	4.062	0.500	0.500	0.906	49.970
12		0.421	6.531	-3.469	0.653	2.751	0.421	0.421	0.696	42.120

pH	Cr(III)									
2		0.520	10.114	0.114	1.011	5.256	0.520	0.520	1.045	51.970
5		0.687	3.756	-6.244	0.376	2.580	0.687	0.687	0.945	68.680
7		0.785	3.903	-6.097	0.390	3.062	0.785	0.785	1.091	78.450
9		0.832	20.443	10.443	2.044	17.011	0.832	0.832	2.533	83.210
12		1.000	30601.500	30591.500	3060.150	30595.380	1.000	1.000	3060.538	99.980
pH	Cr(VI)									
2		0.582	15.794	5.794	1.579	9.198	0.582	0.582	1.502	58.240
5		0.648	10.178	0.178	1.018	6.600	0.648	0.648	1.308	64.840
7		0.680	0.241	-9.759	0.024	0.164	0.680	0.680	0.696	67.980
9		0.724	0.648	-9.352	0.065	0.469	0.724	0.724	0.771	72.420
12		0.782	1.312	-8.688	0.131	1.025	0.782	0.782	0.884	78.160

3) Effects of retention Vs pH (PEI=0.01%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
2		0.762	9.662	-0.338	0.966	7.361	0.762	0.762	1.498	76.180
5		0.727	9.395	-0.605	0.940	6.827	0.727	0.727	1.409	72.660
7		0.710	3.108	-6.892	0.311	2.206	0.710	0.710	0.930	70.980
9		0.672	4.232	-5.768	0.423	2.844	0.672	0.672	0.957	67.210
12		0.625	4.150	-5.850	0.415	2.592	0.625	0.625	0.884	62.450
pH	Pb(II)									
2		0.443	7.227	-2.773	0.723	3.203	0.443	0.443	0.763	44.320
5		0.353	3.971	-6.029	0.397	1.403	0.353	0.353	0.493	35.320
7		0.304	2.746	-7.254	0.275	0.835	0.304	0.304	0.388	30.420
9		0.228	2.692	-7.308	0.269	0.613	0.228	0.228	0.289	22.780

pH	Cr(III)									
2		0.356	8.103	-1.897	0.810	2.888	0.356	0.356	0.645	35.641
5		0.327	9.096	-0.904	0.910	2.972	0.327	0.327	0.624	32.673
7		0.845	4.519	-5.481	0.452	3.816	0.845	0.845	1.226	84.451
9		0.928	6.536	-3.464	0.654	6.064	0.928	0.928	1.534	92.773
12		1.055	-2.895	-12.895	-0.290	-3.054	1.055	1.055	0.749	105.482
pH	Cr(VI)									
2		0.592	0.776	-9.224	0.078	0.460	0.592	0.592	0.638	59.230
5		0.652	1.374	-8.626	0.137	0.896	0.652	0.652	0.742	65.210
7		0.682	1.073	-8.927	0.107	0.732	0.682	0.682	0.755	68.210
9		0.736	2.179	-7.821	0.218	1.603	0.736	0.736	0.896	73.560
12		0.780	33.960	23.960	3.396	26.482	0.780	0.780	3.428	77.980

4) Effects of retention Vs polymer dosages (unmodified starch, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
0.05		0.782	1.795	-8.205	0.179	1.404	0.782	0.782	0.922	78.210
0.5		0.700	13.861	3.861	1.386	9.700	0.700	0.700	1.670	69.980
0.825		0.640	10.975	0.975	1.098	7.020	0.640	0.640	1.342	63.960
1		0.611	9.473	-0.527	0.947	5.789	0.611	0.611	1.190	61.110
2		0.425	6.390	-3.610	0.639	2.712	0.425	0.425	0.696	42.450
dosages	Pb(II)									
0.05		0.525	7.962	-2.038	0.796	4.177	0.525	0.525	0.942	52.460

0.5		0.494	17.679	7.679	1.768	8.735	0.494	0.494	1.368	49.410
0.825		0.483	17.384	7.384	1.738	8.398	0.483	0.483	1.323	48.310
1		0.472	17.108	7.108	1.711	8.076	0.472	0.472	1.280	47.210
2		0.443	16.305	6.305	1.630	7.226	0.443	0.443	1.166	44.320
dosages	Cr(III)									
0.05		0.978	24.891	14.891	2.489	24.341	0.978	0.978	3.412	97.790
0.5		0.983	20.699	10.699	2.070	20.355	0.983	0.983	3.019	98.340
0.825		0.985	14.045	4.045	1.405	13.827	0.985	0.985	2.367	98.450
1		0.982	4.966	-5.034	0.497	4.878	0.982	0.982	1.470	98.210
2		0.995	18.408	8.408	1.841	18.318	0.995	0.995	2.827	99.510
dosages	Cr(VI)									
0.05		0.830	8.820	-1.180	0.882	7.319	0.830	0.830	1.562	82.980
0.5		0.802	8.630	-1.370	0.863	6.922	0.802	0.802	1.494	80.210
0.825		0.791	10.794	0.794	1.079	8.539	0.791	0.791	1.645	79.110
1		0.784	7.308	-2.692	0.731	5.732	0.784	0.784	1.357	78.430
2		0.761	6.233	-3.767	0.623	4.745	0.761	0.761	1.236	76.130

5) Effects of retention Vs polymer dosages (PEG, pH=7, metal ion concentration=10 mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
0.01		0.780	27.237	17.237	2.724	21.250	0.780	0.780	2.905	78.020
0.5		0.699	18.223	8.223	1.822	12.745	0.699	0.699	1.974	69.940
1		0.638	10.692	0.692	1.069	6.817	0.638	0.638	1.319	63.760
1.5		0.592	10.028	0.028	1.003	5.937	0.592	0.592	1.186	59.210
2		0.432	7.182	-2.818	0.718	3.104	0.432	0.432	0.743	43.220

dosages	Pb(II)									
0.01		0.880	17.357	7.357	1.736	15.278	0.880	0.880	2.408	88.020
0.5		0.830	11.032	1.032	1.103	9.155	0.830	0.830	1.745	82.980
1		0.798	6.796	-3.204	0.680	5.424	0.798	0.798	1.340	79.810
1.5		0.769	16.026	6.026	1.603	12.319	0.769	0.769	2.001	76.870
2		0.653	10.906	0.906	1.091	7.126	0.653	0.653	1.366	65.340
dosages	Cr(III)									
0.01		0.850	31.402	21.402	3.140	26.686	0.850	0.850	3.518	84.980
0.5		0.902	14.830	4.830	1.483	13.379	0.902	0.902	2.240	90.210
1		0.933	1.154	-8.846	0.115	1.077	0.933	0.933	1.041	93.320
1.5		0.941	2.681	-7.319	0.268	2.523	0.941	0.941	1.193	94.110
2		0.999	185.333	175.333	18.533	185.222	0.999	0.999	19.522	99.940
dosages	Cr(VI)									
0.01		0.621	16.862	6.862	1.686	10.473	0.621	0.621	1.668	62.110
0.5		0.599	7.617	-2.383	0.762	4.560	0.599	0.599	1.055	59.870
1		0.595	2.079	-7.921	0.208	1.238	0.595	0.595	0.719	59.540
1.5		0.600	8.671	-1.329	0.867	5.205	0.600	0.600	1.121	60.030
2		0.530	13.605	3.605	1.360	7.208	0.530	0.530	1.251	52.980

6) Effects of retention Vs polymer dosages (PEI, pH=7, metal ion concentration=10 mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
0.01		0.821	5.030	-4.970	0.503	4.128	0.821	0.821	1.234	82.07
0.5		0.781	9.052	-0.948	0.905	7.073	0.781	0.781	1.489	78.14

1		0.756	11.851	1.851	1.185	8.958	0.756	0.756	1.652	75.59
1.5		0.750	9.864	-0.136	0.986	7.396	0.750	0.750	1.489	74.98
2		0.680	7.136	-2.864	0.714	4.851	0.680	0.680	1.165	67.98
dosages	Pb(II)									
0.01		0.792	9.191	-0.809	0.919	7.281	0.792	0.792	1.520	79.21
0.5		0.800	8.381	-1.619	0.838	6.703	0.800	0.800	1.470	79.98
1		0.806	6.584	-3.416	0.658	5.304	0.806	0.806	1.336	80.56
1.5		0.810	6.835	-3.165	0.683	5.533	0.810	0.810	1.363	80.96
2		0.826	8.297	-1.703	0.830	6.850	0.826	0.826	1.510	82.55
dosages	Cr(III)									
0.01		0.864	5.170	-4.830	0.517	4.467	0.864	0.864	1.311	86.41
0.5		0.904	8.010	-1.990	0.801	7.244	0.904	0.904	1.629	90.43
1		0.918	10.686	0.686	1.069	9.808	0.918	0.918	1.899	91.79
1.5		0.940	15.977	5.977	1.598	15.021	0.940	0.940	2.442	94.02
2		0.998	388.545	378.545	38.855	387.691	0.998	0.998	39.767	99.78
dosages	Cr(VI)									
0.01		0.964	9.528	-0.472	0.953	9.187	0.964	0.964	1.883	96.42
0.5		0.960	14.065	4.065	1.406	13.498	0.960	0.960	2.309	95.97
1		0.942	10.613	0.613	1.061	10.002	0.942	0.942	1.943	94.24
1.5		0.940	16.643	6.643	1.664	15.641	0.940	0.940	2.504	93.98
2		0.912	12.259	2.259	1.226	11.182	0.912	0.912	2.030	91.21

7) Effects of retention Vs metal ion concentration (unmodified starch=0.05%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)

10		0.982	21.334	11.334	2.133	20.943	0.982	0.982	3.076	98.167
20		0.966	20.182	0.182	1.009	19.504	0.966	0.966	1.942	96.643
30		0.969	18.432	-11.568	0.614	17.854	0.969	0.969	1.564	96.865
40		0.934	19.332	-20.668	0.483	18.065	0.934	0.934	1.386	93.447
50		0.906	18.976	-31.024	0.380	17.198	0.906	0.906	1.250	90.631
metal ion conc.	Pb(II)									
10		0.597	9.388	-0.612	0.939	5.603	0.597	0.597	1.157	59.682
20		0.579	9.201	-10.799	0.460	5.324	0.579	0.579	0.845	57.858
30		0.505	9.228	-20.772	0.308	4.661	0.505	0.505	0.660	50.512
40		0.440	9.263	-30.737	0.232	4.080	0.440	0.440	0.542	44.048
50		0.398	9.259	-40.741	0.185	3.682	0.398	0.398	0.471	39.763
metal ion conc.	Cr(III)									
10		0.968	17.334	7.334	1.733	16.784	0.968	0.968	2.647	96.826
20		0.958	16.234	-3.766	0.812	15.558	0.958	0.958	1.736	95.833
30		0.923	13.663	-16.337	0.455	12.607	0.923	0.923	1.343	92.273
40		0.909	10.822	-29.178	0.271	9.838	0.909	0.909	1.155	90.914
50		0.862	9.957	-40.043	0.199	8.580	0.862	0.862	1.033	86.166
metal ion conc.	Cr(VI)									
10		0.891	13.713	3.713	1.371	12.212	0.891	0.891	2.112	89.053
20		0.807	10.259	-9.741	0.513	8.282	0.807	0.807	1.221	80.727
30		0.737	8.974	-21.026	0.299	6.611	0.737	0.737	0.957	73.674
40		0.639	8.524	-31.476	0.213	5.447	0.639	0.639	0.775	63.896

50		0.490	8.709	-41.291	0.174	4.265	0.490	0.490	0.575	48.967

8) Effects of retention Vs metal ion concentration (PEG=1.0%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
10		0.999	20.671	10.671	2.067	20.661	0.999	0.999	3.066	99.950
20		0.951	11.497	-8.503	0.575	10.930	0.951	0.951	1.497	95.070
30		0.883	10.848	-19.152	0.362	9.582	0.883	0.883	1.203	88.332
40		0.878	11.395	-28.605	0.285	10.007	0.878	0.878	1.128	87.814

metal ion conc.	Pb(II)									
10		0.806	10.714	0.714	1.071	8.635	0.806	0.806	1.669	80.592
20		0.793	9.992	-10.008	0.500	7.926	0.793	0.793	1.189	79.319
30		0.769	9.392	-20.608	0.313	7.225	0.769	0.769	1.010	76.919
40		0.630	9.371	-30.629	0.234	5.904	0.630	0.630	0.778	63.006
50		0.562	9.279	-40.721	0.186	5.211	0.562	0.562	0.666	56.159
metal ion conc.	Cr(III)									
10		0.974	32.601	22.601	3.260	31.760	0.974	0.974	4.150	97.420
20		0.933	6.972	-13.028	0.349	6.506	0.933	0.933	1.258	93.320
30		0.894	2.624	-27.376	0.087	2.347	0.894	0.894	0.973	89.440
40		0.852	1.425	-38.575	0.036	1.214	0.852	0.852	0.882	85.210
50		0.820	1.805	-48.195	0.036	1.480	0.820	0.820	0.850	82.040
metal ion	Cr(VI)									

conc.										
10		0.919	0.951	-9.049	0.095	0.874	0.919	0.919	1.006	91.890
20		0.798	15.318	-4.682	0.766	12.218	0.798	0.798	1.408	79.760
30		0.701	21.340	-8.660	0.711	14.951	0.701	0.701	1.199	70.060
40		0.571	15.050	-24.950	0.376	8.595	0.571	0.571	0.786	57.110
50		0.462	11.947	-38.053	0.239	5.524	0.462	0.462	0.573	46.240

9) Effects of retention Vs metal ion concentration (PEI=0.01%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	MT	∑n [MLn]	∑n Kn [L]^n	Rm1	RM1 *	RL	Rm *(1+ ∑n Kn [L]^n)	Rm(%)
10		0.916	10.744	0.744	1.074	9.842	0.916	0.916	1.900	91.605
20		0.875	8.545	-11.455	0.427	7.478	0.875	0.875	1.249	87.515
30		0.822	7.690	-22.310	0.256	6.324	0.822	0.822	1.033	82.230
40		0.707	9.525	-30.475	0.238	6.737	0.707	0.707	0.876	70.723
50		0.652	9.155	-40.845	0.183	5.966	0.652	0.652	0.771	65.172
metal ion conc.	Pb(II)									
10		0.763	8.064	-1.936	0.806	6.153	0.763	0.763	1.378	76.304
20		0.702	8.301	-11.699	0.415	5.824	0.702	0.702	0.993	70.153
30		0.650	9.047	-20.953	0.302	5.880	0.650	0.650	0.846	64.995
40		0.598	9.369	-30.631	0.234	5.603	0.598	0.598	0.738	59.799
50		0.541	9.180	-40.820	0.184	4.969	0.541	0.541	0.641	54.125
metal ion conc.	Cr(III)									

10		0.934	10.654	0.654	1.065	9.952	0.934	0.934	1.929	93.406
20		0.826	8.453	-11.547	0.423	6.986	0.826	0.826	1.176	82.650
30		0.806	8.091	-21.909	0.270	6.524	0.806	0.806	1.024	80.635
40		0.725	8.572	-31.428	0.214	6.216	0.725	0.725	0.881	72.522
50		0.602	8.711	-41.289	0.174	5.244	0.602	0.602	0.707	60.201
metal ion conc.	Cr(VI)									
10		0.983	20.567	10.567	2.057	20.226	0.983	0.983	3.006	98.342
20		0.973	21.367	1.367	1.068	20.789	0.973	0.973	2.012	97.296
30		0.950	13.511	-16.489	0.450	12.833	0.950	0.950	1.378	94.985
40		0.900	11.606	-28.394	0.290	10.447	0.900	0.900	1.161	90.016
50		0.755	8.429	-41.571	0.169	6.362	0.755	0.755	0.882	75.480

Mixed metal ion solutions (Fitting Canizares Models)

1) i) Effects of retention Vs pH (unmodified starch=0.05%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
2		0.691	17.968	7.968	1.797	12.420	0.691	0.691	1.933	69.120
5		0.574	8.140	-1.860	0.814	4.674	0.574	0.574	1.042	57.420
7		0.495	1.774	-8.226	0.177	0.879	0.495	0.495	0.583	49.520
9		0.415	11.226	1.226	1.123	4.653	0.415	0.415	0.880	41.450
12		0.294	12.920	2.920	1.292	3.801	0.294	0.294	0.674	29.420
pH	Pb(II)									
2		0.761	9.497	-0.503	0.950	7.228	0.761	0.761	1.484	76.110
5		0.737	7.770	-2.230	0.777	5.723	0.737	0.737	1.309	73.650

7		0.723	5.822	-4.178	0.582	4.208	0.723	0.723	1.144	72.280
9		0.710	7.508	-2.492	0.751	5.329	0.710	0.710	1.243	70.980
12		0.660	7.334	-2.666	0.733	4.843	0.660	0.660	1.145	66.030
pH	Cr(III)									
2		0.830	37.814	27.814	3.781	31.374	0.830	0.830	3.967	82.970
5		0.784	12.318	2.318	1.232	9.661	0.784	0.784	1.750	78.430
7		0.752	4.946	-5.054	0.495	3.720	0.752	0.752	1.124	75.210
12		0.681	7.310	-2.690	0.731	4.981	0.681	0.681	1.179	68.140
pH	Cr(VI)									
2		0.927	74.479	64.479	7.448	69.020	0.927	0.927	7.829	92.670
5		0.858	16.491	6.491	1.649	14.148	0.858	0.858	2.273	85.790
7		0.802	4.010	-5.990	0.401	3.217	0.802	0.802	1.124	80.210
9		0.770	7.686	-2.314	0.769	5.921	0.770	0.770	1.362	77.040
12		0.688	9.508	-0.492	0.951	6.538	0.688	0.688	1.341	68.760

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn (II)	Pb (II)	Cr (III)	Cr (VI)
α	1	2	3	4

Zn (II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 1.118 α2,4=1.401 α3,4=1.252
Pb (II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=2.036 α1,4=2.551 α3,4=1.253
Cr (III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 1.821 α1,4=2.551 α2,4=1.401
Cr (VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 1.821 α1,3=2.036 α2,3=1.118

Note: For mixed solutions more than 2 metal ions, used probability for separation factor. For example, Zn (II) represents as 1. Thus, 3 possible relationship were **α2,3, α2,4 and α3,4**. For Zn (II), 3 possibilities are **α2,3**= α2,1 . α1,3, **α2,4**= α2,1 x α1,4 , **α3,4**= α3,1 x α1,4. For Pb (II), **α1,3, α1,4, α3,4.** For Cr (III), **α1,2 , α1,4, α2,4**. For Cr (VI), **α1,2, α1,3, and α 2,3.**

2) i) Effects of retention Vs pH (PEG=1.0%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
2		0.672	16.331	6.331	1.633	10.976	0.672	0.672	1.770	67.210
5		0.553	6.866	-3.134	0.687	3.800	0.553	0.553	0.933	55.340
7		0.478	1.956	-8.044	0.196	0.935	0.478	0.478	0.571	47.780
9		0.386	12.319	2.319	1.232	4.750	0.386	0.386	0.861	38.560
12		0.261	12.158	2.158	1.216	3.170	0.261	0.261	0.578	26.070
pH	Pb(II)									
2		0.397	12.354	2.354	1.235	4.908	0.397	0.397	0.888	39.730
5		0.541	9.276	-0.724	0.928	5.019	0.541	0.541	1.043	54.110
7		0.646	3.983	-6.017	0.398	2.571	0.646	0.646	0.903	64.560
9		0.735	8.928	-1.072	0.893	6.560	0.735	0.735	1.391	73.480

12		0.893	29.760	19.760	2.976	26.582	0.893	0.893	3.551	89.320
pH	Cr(III)									
2		0.545	14.814	4.814	1.481	8.066	0.545	0.545	1.351	54.450
5		0.692	5.009	-4.991	0.501	3.467	0.692	0.692	1.039	69.210
7		0.820	4.925	-5.075	0.493	4.038	0.820	0.820	1.224	81.980
9		0.912	8.976	-1.024	0.898	8.190	0.912	0.912	1.731	91.240
12		1.000	3888.000	3878.000	388.800	887.222	1.000	1.000	389.722	99.980
pH	Cr(VI)									
2		0.641	15.236	5.236	1.524	9.769	0.641	0.641	1.618	64.120
5		0.722	4.953	-5.047	0.495	3.576	0.722	0.722	1.080	72.210
7		0.771	3.690	-6.310	0.369	2.843	0.771	0.771	1.055	77.060
9		0.822	6.965	-3.035	0.697	5.722	0.822	0.822	1.394	82.150
12		0.910	31.937	21.937	3.194	29.069	0.910	0.910	3.817	91.020

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4
Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))			
	α2,3= 1.967 α2,4=1.545 α3,4=0.786			
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))			
	α1,3=2.898 α1,4=2.276 α3,4=0.786			
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))			
	α1,2= 1.473 α1,4=2.276 α2,4=1.545			

Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 1.473 α1,3=2.898 α2,3=1.967

3) i) Effects of retention Vs pH (PEI=0.01%,metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

pH	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
2		0.880	24.989	14.989	2.499	22.000	0.880	0.880	3.080	88.040
5		0.830	10.392	0.392	1.039	8.624	0.830	0.830	1.692	82.980
7		0.773	4.352	-5.648	0.435	3.365	0.773	0.773	1.110	77.320
9		0.731	3.421	-6.579	0.342	2.502	0.731	0.731	0.982	73.140
12		0.671	5.689	-4.311	0.569	3.815	0.671	0.671	1.052	67.070
pH	Pb(II)									
2		0.392	12.116	2.116	1.212	4.751	0.392	0.392	0.867	39.210
5		0.461	10.161	0.161	1.016	4.688	0.461	0.461	0.930	46.140
7		0.521	2.419	-7.581	0.242	1.261	0.521	0.521	0.648	52.140
9		0.579	8.729	-1.271	0.873	5.053	0.579	0.579	1.084	57.890
12		0.665	13.368	3.368	1.337	8.895	0.665	0.665	1.555	66.540
pH	Cr(III)									
2		0.401	8.293	-1.707	0.829	3.327	0.401	0.401	0.734	40.120
5		0.553	17.174	7.174	1.717	9.496	0.553	0.553	1.502	55.290
7		0.663	1.508	-8.492	0.151	0.999	0.663	0.663	0.763	66.270
9		0.771	3.825	-6.175	0.382	2.949	0.771	0.771	1.066	77.090
12		0.920	11.906	1.906	1.191	10.952	0.920	0.920	2.015	91.980
pH	Cr(VI)									
2		1.000	1922.000	1912.000	192.200	1921.423	1.000	1.000	193.142	99.970

5		0.960	12.028	2.028	1.203	11.551	0.960	0.960	2.116	96.040
7		0.879	5.061	-4.939	0.506	4.447	0.879	0.879	1.323	87.870
9		0.795	3.001	-6.999	0.300	2.387	0.895	0.895	1.034	79.540
12		0.672	14.571	4.571	1.457	9.793	0.672	0.672	1.651	67.210

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 1.419 α2,4=3.946 α3,4=2.781
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=0.672 α1,4=1.87 α3,4=2.781
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.474 α1,4=1.87 α2,4=3.946
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.474 α1,3=0.672 α2,3=1.419

4) i) Effects of retention Vs polymer dosages (unmodified starch, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
0.05		0.785	2.319	-7.681	0.232	1.819	0.785	0.785	0.966	78.450
0.5		0.782	13.716	3.716	1.372	10.727	0.782	0.782	1.855	78.210
0.825		0.785	13.309	3.309	1.331	10.442	0.785	0.785	1.829	78.460
1		0.782	11.804	1.804	1.180	9.226	0.782	0.782	1.704	78.160
2		0.772	10.966	0.966	1.097	8.467	0.772	0.772	1.619	77.210
dosages	Pb(II)									
0.05		0.467	7.417	-2.583	0.742	3.462	0.467	0.467	0.813	46.670
0.5		0.431	15.475	5.475	1.548	6.676	0.431	0.431	1.099	43.140
0.825		0.395	14.625	4.625	1.462	5.770	0.395	0.395	0.971	39.450
1		0.368	14.359	4.359	1.436	5.281	0.368	0.368	0.896	36.780
2		0.300	12.996	2.996	1.300	3.896	0.300	0.300	0.689	29.980
dosages	Cr(III)									
0.05		0.970	30.797	20.797	3.080	29.886	0.970	0.970	3.959	97.040
0.5		0.975	19.850	9.850	1.985	19.361	0.975	0.975	2.912	97.540
0.825		0.978	21.527	11.527	2.153	21.049	0.978	0.978	3.083	97.780
1		0.982	5.051	-4.949	0.505	4.962	0.982	0.982	1.479	98.240
2		0.994	72.351	62.351	7.235	71.938	0.994	0.994	8.188	99.430
dosages	Cr(VI)									
0.05		0.752	7.933	-2.067	0.793	5.966	0.752	0.752	1.349	75.210
0.5		0.781	11.285	1.285	1.128	8.818	0.781	0.781	1.663	78.140
0.825		0.813	12.859	2.859	1.286	10.459	0.813	0.813	1.859	81.340
1		0.827	9.086	-0.914	0.909	7.509	0.827	0.827	1.577	82.650

2		0.913	20.733	10.733	2.073	18.933	0.913	0.913	2.807	91.320

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (unmodified starch=0.05%, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 18.017 α2,4=2.151 α3,4=0.119
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=7.28 α1,4=0.869 α3,4=0.508
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.404 α1,4=0.869 α2,4=2.151
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.404 α1,3=7.28 α2,3=18.017

5) i) Effects of retention Vs polymer dosages (PEG, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
0.01		0.785	30.187	20.187	3.019	23.694	0.785	0.785	3.154	78.490
0.5		0.784	27.709	17.709	2.771	21.710	0.784	0.784	2.955	78.350
1		0.780	15.891	5.891	1.589	12.392	0.780	0.780	2.019	77.980
1.5		0.781	21.042	11.042	2.104	16.442	0.781	0.781	2.426	78.140
2		0.775	20.661	10.661	2.066	16.016	0.775	0.775	2.377	77.520
dosages	Pb(II)									
0.01		0.865	18.444	8.444	1.844	15.944	0.865	0.865	2.459	86.450
0.5		0.862	13.012	3.012	1.301	11.212	0.862	0.862	1.983	86.170
1		0.857	8.394	-1.606	0.839	7.194	0.857	0.857	1.577	85.710
1.5		0.861	17.202	7.202	1.720	14.802	0.861	0.861	2.341	86.050
2		0.850	16.013	6.013	1.601	13.612	0.850	0.850	2.211	85.010
dosages	Cr(III)									
0.01		0.972	166.077	156.077	16.608	161.361	0.972	0.972	17.108	97.160
0.5		0.972	52.412	42.412	5.241	50.960	0.972	0.972	6.068	97.230
1		0.970	2.545	-7.455	0.254	2.467	0.970	0.970	1.216	96.970
1.5		0.979	7.531	-2.469	0.753	7.372	0.979	0.979	1.716	97.890
2		0.992	14.063	4.063	1.406	13.952	0.992	0.992	2.387	99.210
dosages	Cr(VI)									
0.01		0.746	25.114	15.114	2.511	18.725	0.746	0.746	2.618	74.560
0.5		0.790	14.563	4.563	1.456	11.506	0.790	0.790	1.941	79.010
1		0.812	4.472	-5.528	0.447	3.630	0.812	0.812	1.175	81.190

2		0.913	73.867	63.867	7.387	67.470	0.913	0.913	7.660	91.340

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (PEG=1.0%, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 4.716 α2,4=0.76 α3,4=0.161
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=7.267 α1,4=1.171 α3,4=0.161
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 1.541 α1,4=1.171 α2,4=0.76
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 1.541 α1,3=7.267 α2,3=4.716

6) i) Effects of retention Vs polymer dosages (PEI, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

dosages	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
0.01		0.810	6.077	-3.923	0.608	4.921	0.810	0.810	1.302	80.980
0.5		0.765	9.802	-0.198	0.980	7.503	0.765	0.765	1.516	76.540
1		0.720	11.062	1.062	1.106	7.962	0.720	0.720	1.516	71.980
1.5		0.675	8.567	-1.433	0.857	5.779	0.675	0.675	1.252	67.450
2		0.629	8.053	-1.947	0.805	5.065	0.629	0.629	1.135	62.890
dosages	Pb(II)									
0.01		0.795	8.769	-1.231	0.877	6.970	0.795	0.795	1.492	79.479
0.5		0.778	8.407	-1.593	0.841	6.540	0.778	0.778	1.432	77.797
1		0.746	9.065	-0.935	0.907	6.766	0.746	0.746	1.423	74.633
1.5		0.739	9.030	-0.970	0.903	6.674	0.739	0.739	1.406	73.909
2		0.672	8.163	-1.837	0.816	5.484	0.672	0.672	1.220	67.189
dosages	Cr(III)									
0.01		0.876	5.628	-4.372	0.563	4.929	0.876	0.876	1.369	87.570
0.5		0.875	8.748	-1.252	0.875	7.653	0.875	0.875	1.640	87.480
1		0.874	8.923	-1.077	0.892	7.800	0.874	0.874	1.654	87.420
1.5		0.874	7.902	-2.098	0.790	6.902	0.874	0.874	1.564	87.350
2		0.874	7.662	-2.338	0.766	6.695	0.874	0.874	1.543	87.380
dosages	Cr(VI)									
0.01		0.980	28.588	18.588	2.859	28.019	0.980	0.980	3.782	98.010
0.5		0.954	10.930	0.930	1.093	10.430	0.954	0.954	1.997	95.430
1		0.937	15.774	5.774	1.577	14.776	0.937	0.937	2.414	93.670
1.5		0.912	9.518	-0.482	0.952	8.683	0.912	0.912	1.781	91.230
2		0.899	10.843	0.843	1.084	9.745	0.899	0.899	1.873	89.870

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (PEI=0.01%, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 1.651 α2,4=3.242 α3,4=6.246
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=1.53 α1,4=9.558 α3,4=6.246
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.9271 α1,4=9.558 α2,4=3.242
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.927 α1,3=1.3 α2,3=1.651

7) i) Effects of retention Vs metal ion concentration (unmodified starch=0.05%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
10		0.782	5.627	-4.373	0.563	4.401	0.782	0.782	1.222	78.210
20		0.754	9.916	-10.084	0.496	7.475	0.754	0.754	1.128	75.380
30		0.729	10.921	-19.079	0.364	7.959	0.729	0.729	0.994	72.880
40		0.704	9.418	-30.582	0.235	6.632	0.704	0.704	0.870	70.420
50		0.679	9.290	-40.710	0.186	6.305	0.679	0.679	0.805	67.870
metal ion conc.	Pb(II)									
10		0.778	7.280	-2.720	0.728	5.666	0.778	0.778	1.345	77.830
20		0.756	8.137	-11.863	0.407	6.149	0.756	0.756	1.063	75.560
30		0.735	9.701	-20.299	0.323	7.126	0.775	0.775	0.972	73.450
40		0.711	9.316	-30.684	0.233	6.627	0.711	0.711	0.877	71.140
50		0.688	9.622	-40.378	0.192	6.623	0.688	0.688	0.821	68.830
metal ion conc.	Cr(III)									
10		0.821	6.865	-3.135	0.687	5.639	0.821	0.821	1.385	82.140
20		0.822	6.686	-13.314	0.334	5.497	0.822	0.822	1.097	82.220
30		0.823	8.422	-21.578	0.281	6.932	0.823	0.823	1.054	82.310
40		0.824	10.184	-29.816	0.255	8.396	0.824	0.824	1.034	82.440
50		0.826	11.617	-38.383	0.232	9.590	0.826	0.826	1.017	82.550
metal ion conc.	Cr(VI)									
10		0.933	11.775	1.775	1.178	10.981	0.933	0.933	2.031	93.260
20		0.868	10.858	-9.142	0.543	9.425	0.868	0.868	1.339	86.797
30		0.809	10.272	-19.728	0.342	8.311	0.809	0.809	1.086	80.906

40		0.807	11.310	-28.690	0.283	9.122	0.807	0.807	1.035	80.652
50		0.732	10.842	-39.158	0.217	7.940	0.732	0.732	0.891	73.234

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (metal ion conc.=10 mg/l, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 1.241 α2,4=3.289 α3,4=2.65
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=1.22 α1,4=3.233 α3,4=2.65
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.983 α1,4=3.233 α2,4=3.289
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.983 α1,3=1.22 α2,3=1.241

8) i) Effects of retention Vs metal ion concentration (PEG=1.0%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
10		0.861	6.098	-3.902	0.610	5.252	0.861	0.861	1.386	86.120
20		0.846	9.650	-10.350	0.483	8.162	0.846	0.846	1.254	84.580
30		0.831	9.558	-20.442	0.319	7.947	0.831	0.831	1.096	83.140

50		0.803	9.307	-40.693	0.186	7.475	0.803	0.803	0.953	80.320
metal ion conc.	Pb(II)									
10		0.838	8.697	-1.303	0.870	7.285	0.838	0.838	1.566	83.770
20		0.813	8.745	-11.255	0.437	7.113	0.813	0.813	1.169	81.340
30		0.794	8.335	-21.665	0.278	6.614	0.794	0.794	1.014	79.360
40		0.773	7.983	-32.017	0.200	6.172	0.773	0.773	0.927	77.310
50		0.750	9.066	-40.934	0.181	6.801	0.750	0.750	0.886	75.020
metal ion conc.	Cr(III)									
10		0.861	5.995	-4.005	0.599	5.163	0.861	0.861	1.377	86.120
20		0.831	11.160	-8.840	0.558	9.272	0.831	0.831	1.294	83.080
30		0.791	9.255	-20.745	0.309	7.324	0.791	0.791	1.035	79.130
40		0.755	8.098	-31.902	0.202	6.110	0.755	0.755	0.907	75.450
50		0.728	7.900	-42.100	0.158	5.750	0.728	0.728	0.843	72.780
metal ion conc.	Cr(VI)									
10		0.888	7.109	-2.891	0.711	6.310	0.888	0.888	1.519	88.760
20		0.866	6.612	-13.388	0.331	5.724	0.866	0.866	1.152	86.560
30		0.845	7.015	-22.985	0.234	5.929	0.845	0.845	1.043	84.510
40		0.822	8.011	-31.989	0.200	6.582	0.822	0.822	0.986	82.170
50		0.803	9.283	-40.717	0.186	7.452	0.803	0.803	0.952	80.270

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (metal ion conc.=10 mg/l, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 1.169 α2,4=1.444 α3,4=1.235
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=1.00 α1,4=1.235 α3,4=1.235
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.855 α1,4=1.235 α2,4=1.444
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.855 α1,3=1.00 α2,3=1.169

9) i) Effects of retention Vs metal ion concentration (PEI=0.01%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

metal ion conc.	Zn(II)	Rm	[M]T	∑n [MiLn]	∑n Ki,n [L]^n	RMi	RFMi *	RL	RMi *(1+ ∑n Ki,n [L]^n)	Rm(%)
10		0.800	6.654	-3.346	0.665	5.326	0.800	0.800	1.333	80.030
20		0.765	9.769	-10.231	0.488	7.477	0.765	0.765	1.139	76.540
30		0.743	9.930	-20.070	0.331	7.375	0.743	0.743	0.989	74.270
40		0.713	8.990	-31.010	0.225	6.413	0.713	0.713	0.874	71.330
50		0.692	8.062	-41.938	0.161	5.582	0.692	0.692	0.804	69.240
metal ion conc.	Pb(II)									
10		0.713	8.633	-1.367	0.863	6.152	0.713	0.713	1.328	71.260
20		0.703	9.056	-10.944	0.453	6.367	0.703	0.703	1.021	70.310

30		0.694	9.465	-20.535	0.315	6.567	0.694	0.694	0.913	69.390
40		0.686	9.514	-30.486	0.238	6.526	0.686	0.686	0.849	68.590
50		0.678	9.353	-40.647	0.187	6.337	0.678	0.678	0.804	67.750
metal ion conc.	Cr(III)									
10		0.933	13.395	3.395	1.339	12.502	0.933	0.933	2.184	93.333
20		0.915	11.679	-8.321	0.584	10.692	0.915	0.915	1.450	91.544
30		0.840	7.533	-22.467	0.251	6.327	0.840	0.840	1.051	83.992
40		0.823	8.452	-31.548	0.211	6.953	0.823	0.823	0.996	82.261
50		0.826	11.438	-38.562	0.229	9.448	0.826	0.826	1.015	82.609
metal ion conc.	Cr(VI)									
10		0.855	8.075	-1.925	0.807	6.902	0.855	0.855	1.545	85.480
20		0.783	9.045	-10.955	0.452	7.078	0.783	0.783	1.136	78.257
30		0.733	9.078	-20.922	0.303	6.655	0.733	0.733	0.955	73.310
40		0.703	9.382	-30.618	0.235	6.593	0.703	0.703	0.868	70.274
50		0.681	8.926	-41.074	0.179	6.079	0.681	0.681	0.803	68.106

ii) Separation factor mixed metal ion solutions (since the metal ions mixed more than 2 metal ions, probability of estimation of separation factor were used) (metal ion conc.=10 mg/l, pH=7, flowrate=115 ml/min, TMP=1.5bar)

separation factor	Zn(II)	Pb(II)	Cr(III)	Cr(VI)
α	1	2	3	4

Zn(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α2,3= 4.31 α2,4=1.979 α3,4=0.459
Pb(II)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,3=2.995 α1,4=1.537 α3,4=0.459
Cr(III)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.695 α1,4=1.375 α2,4=1.979
Cr(VI)	Separation Factor,αi,j ((1-Rmi)/(1-Rmj))
	α1,2= 0.695 α1,3=2.995 α2,3=4.310

APPENDIX C

REGRESSION COEFFICIENT (R^2) OF THEORETICAL & EXPERIMENTAL DATA FITTING CANIZARES MODELS USING ANOVA

For single solutions

1) R^2 for the effects of retention Vs pH using ANOVA (unmodified starch=0.05%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.932
R Square	**0.868**
Adjusted R Square	0.824
Standard Error	0.964
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	18.301	18.301	19.696	0.021
Residual	3	2.788	0.929		
Total	4	21.088			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	98.210	0.985	99.675	0.000002	95.074	101.346	95.074	101.346
pH	-0.562	0.127	-4.438	0.021	-0.965	-0.159	-0.965	-0.159

Note: Small p-value indicates that there is a small chance of getting this data if no real difference existed and therefore you decide that the difference in group expression data is significant. By small we usually mean 0.05. P-value on the other hand, is the probability of obtaining a result at least as extreme as the one that was actually observed, given that the null hypothesis is true.

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.998
R Square	**0.996**
Adjusted R Square	0.994
Standard Error	0.385
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	106.408	106.408	717.432	0.0001
Residual	3	0.445	0.148		
Total	4	106.853			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	62.035	0.394	157.587	0.000001	60.783	63.288	60.783	63.288
pH	-1.354	0.051	-26.785	0.000114	-1.515	-1.194	-1.515	-1.194

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.918
R Square	**0.843**
Adjusted R Square	0.790
Standard Error	12.193
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2391.664	2391.664	16.087	0.028
Residual	3	446.018	148.673		
Total	4	2837.682			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	34.251	12.463	2.748	0.071	-5.414	73.915	-5.414	73.915
pH	6.421	1.601	4.011	0.028	1.326	11.517	1.326	11.517

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.967
R Square	**0.934**
Adjusted R Square	0.913
Standard Error	1.400
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	83.688	83.688	42.715	0.007
Residual	3	5.878	1.959		
Total	4	89.566			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	70.134	1.431	49.019	0.00002	65.580	74.687	65.580	74.687
pH	1.201	0.184	6.536	0.007	0.616	1.786	0.616	1.786

2) R^2 for the effects of retention Vs pH using ANOVA (PEG=1.0%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.935
R Square	**0.874**
Adjusted R Square	0.832
Standard Error	0.277
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.592	1.592	20.769	0.020
Residual	3	0.230	0.077		
Total	4	1.822			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	86.182	0.283	304.500	0.0000001	85.281	87.083	85.281	87.083
pH	-0.166	0.036	-4.557	0.020	-0.281	-0.050	-0.281	-0.050

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.994
R Square	**0.988**
Adjusted R Square	0.984
Standard Error	0.938
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	217.707	217.707	247.405	0.0006
Residual	3	2.640	0.880		
Total	4	220.347			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	66.230	0.959	69.072	0.00001	63.178	69.281	63.178	69.281
pH	-1.937	0.123	-15.729	0.001	-2.329	-1.545	-2.329	-1.545

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.994
R Square	**0.989**
Adjusted R Square	0.985
Standard Error	2.189
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1248.624	1248.624	260.537	0.0005
Residual	3	14.377	4.792		
Total	4	1263.001			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	43.979	2.238	19.654	0.00029	36.858	51.101	36.858	51.101
pH	4.640	0.287	16.141	0.00052	3.725	5.555	3.725	5.555

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.998
Standard Error	0.366
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	227.067	227.067	1698.034	0.00003
Residual	3	0.401	0.134		
Total	4	227.468			

Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*	*Coefficients*
Intercept	54.478	0.374	145.745	0.000001	53.288	55.667	53.288	55.667
pH	1.979	0.048	41.207	0.000031	1.826	2.131	1.826	2.131

3) R^2 for the effects of retention Vs pH using ANOVA (PEI=0.01%,metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.992
R Square	**0.983**
Adjusted R Square	0.978
Standard Error	0.786
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	109.107	109.107	176.550	0.0009
Residual	3	1.854	0.618		
Total	4	110.961			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	79.497	0.804	98.932	0.000002	76.940	82.054	76.940	82.054
pH	-1.372	0.103	-13.287	0.0009	-1.700	-1.043	-1.700	-1.043

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	**0.995**
Adjusted R Square	0.993
Standard Error	1.044
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	596.675	596.675	547.219	0.0002
Residual	3	3.271	1.090		
Total	4	599.946			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	51.446	1.067	48.199	0.00002	48.049	54.843	48.049	54.843
pH	-3.207	0.137	-23.393	0.00017	-3.644	-2.771	-3.644	-2.771

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	**0.993**
Adjusted R Square	0.991
Standard Error	0.686
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	210.331	210.331	446.625	0.0002
Residual	3	1.413	0.471		
Total	4	211.744			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	55.508	0.701	79.132	0.000004	53.275	57.740	53.275	57.740
pH	1.904	0.090	21.134	0.0002	1.618	2.191	1.618	2.191

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	**0.995**
Adjusted R Square	0.993
Standard Error	1.044
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	596.675	596.675	547.219	0.0002
Residual	3	3.271	1.090		
Total	4	599.946			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	51.446	1.067	48.199	0.00002	48.049	54.843	48.049	54.843
pH	-3.207	0.137	-23.393	0.0002	-3.644	-2.771	-3.644	-2.771

4) R^2 for the effects of retention Vs polymer dosages using ANOVA (unmodified starch, pH=7, metal ion concentration=10 mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.9999
R Square	**0.9999**
Adjusted R Square	0.9998
Standard Error	0.1693
Observations	5.0000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	706.674	706.674	24645.854	0.000001
Residual	3	0.086	0.029		
Total	4	706.760			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	79.174	0.127	622.752	0.00000001	78.770	79.579	78.770	79.579
dosages	-18.322	0.117	-156.990	0.0000006	-18.694	-17.951	-18.694	-17.951

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.978
R Square	**0.957**
Adjusted R Square	0.942
Standard Error	0.716
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	34.021	34.021	66.420	0.004
Residual	3	1.537	0.512		
Total	4	35.557			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	51.860	0.537	96.511	0.000002	50.150	53.570	50.150	53.570
dosages	-4.020	0.493	-8.150	0.004	-5.590	-2.450	-5.590	-2.450

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.944
R Square	**0.892**
Adjusted R Square	0.856
Standard Error	0.243
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.452	1.452	24.688	0.016
Residual	3	0.176	0.059		
Total	4	1.628			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	97.733	0.182	536.754	0.00000001	97.154	98.313	97.154	98.313
dosages	0.831	0.167	4.969	0.016	0.299	1.362	0.299	1.362

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.967
R Square	**0.936**
Adjusted R Square	0.914
Standard Error	0.736
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	23.563	23.563	43.545	0.007
Residual	3	1.623	0.541		
Total	4	25.186			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	82.300	0.552	149.011	0.000001	80.542	84.057	80.542	84.057
dosages	-3.346	0.507	-6.599	0.007	-4.959	-1.732	-4.959	-1.732

5) R^2 for the effects of retention Vs polymer dosages using ANOVA (PEG, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.998
R Square	**0.996**
Adjusted R Square	0.995
Standard Error	0.917
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	677.285	677.285	804.901	0.0001
Residual	3	2.524	0.841		
Total	4	679.810			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	78.525	0.689	114.016	0.000001	76.333	80.717	76.333	80.717
dosages	-17.937	0.632	-28.371	0.00010	-19.950	-15.925	-19.950	-15.925

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.998
Standard Error	0.419
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	287.680	287.680	1642.242	0.00003
Residual	3	0.526	0.175		
Total	4	288.205			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	88.833	0.314	282.688	0.0000001	87.833	89.833	87.833	89.833
dosages	-11.690	0.288	-40.525	0.00003	-12.608	-10.772	-12.608	-10.772

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.979
R Square	**0.959**
Adjusted R Square	0.946
Standard Error	1.279
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	115.507	115.507	70.644	0.004
Residual	3	4.905	1.635		
Total	4	120.412			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	86.030	0.960	89.610	0.000003	82.975	89.086	82.975	89.086
dosages	7.408	0.881	8.405	0.004	4.603	10.212	4.603	10.212

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.952
R Square	**0.905**
Adjusted R Square	0.874
Standard Error	1.230
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	43.442	43.442	28.736	0.013
Residual	3	4.535	1.512		
Total	4	47.978			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	62.881	0.923	68.115	0.00001	59.943	65.819	59.943	65.819
dosages	-4.543	0.847	-5.361	0.013	-7.240	-1.846	-7.240	-1.846

6) R^2 for the effects of retention Vs polymer dosages using ANOVA (PEI, pH=7, metal ion concentration=10mg/l, flowrate =115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	**0.994**
Adjusted R Square	0.992
Standard Error	0.453
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	106.031	106.031	517.677	0.0002
Residual	3	0.614	0.205		
Total	4	106.646			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	81.962	0.340	241.210	0.0000002	80.881	83.043	80.881	83.043
dosages	-7.097	0.312	-22.753	0.0002	-8.090	-6.105	-8.090	-6.105

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.998
Standard Error	0.061
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	6.225	6.225	1651.024	0.00003
Residual	3	0.011	0.004		
Total	4	6.237			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	79.147	0.046	1716.720	0.0000000004	79.001	79.294	79.001	79.294
dosages	1.720	0.042	40.633	0.00003	1.585	1.854	1.585	1.854

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.994
R Square	**0.988**
Adjusted R Square	0.984
Standard Error	0.627
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	96.007	96.007	244.509	0.001
Residual	3	1.178	0.393		
Total	4	97.185			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	86.577	0.470	184.021	0.0000004	85.079	88.074	85.079	88.074
dosages	6.753	0.432	15.637	0.001	5.379	8.128	5.379	8.128

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.987
R Square	**0.974**
Adjusted R Square	0.965
Standard Error	0.385
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	16.472	16.472	111.173	0.002
Residual	3	0.445	0.148		
Total	4	16.917			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	96.812	0.289	334.980	0.0000001	95.892	97.731	95.892	97.731
dosages	-2.797	0.265	-10.544	0.002	-3.642	-1.953	-3.642	-1.953

7) R^2 for the effects of retention Vs metal ion concentration using ANOVA (unmodified starch=0.05%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

Regression Statistics	
Multiple R	0.937
R Square	**0.878**
Adjusted R Square	0.817
Standard Error	1.266
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	23.011	23.011	14.349	0.063
Residual	2	3.207	1.604		
Total	3	26.219			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	101.905	2.081	48.973	0.0004	92.952	110.858	92.952	110.858
metal ion conc.	-0.215	0.057	-3.788	0.063	-0.458	0.029	-0.458	0.029

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.993
R Square	**0.987**
Adjusted R Square	0.981
Standard Error	1.102
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	184.522	184.522	152.063	0.007
Residual	2	2.427	1.213		
Total	3	186.949			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	69.307	1.810	38.290	0.001	61.519	77.095	61.519	77.095
metal ion conc.	-0.607	0.049	-12.331	0.007	-0.819	-0.396	-0.819	-0.396

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.980
R Square	**0.960**
Adjusted R Square	0.940
Standard Error	0.978
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	46.089	46.089	48.156	0.020
Residual	2	1.914	0.957		
Total	3	48.003			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	101.923	1.608	63.404	0.0002	95.006	108.839	95.006	108.839
metal ion conc.	-0.304	0.044	-6.939	0.020	-0.492	-0.115	-0.492	-0.115

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.986
R Square	0.972
Adjusted R Square	0.958
Standard Error	2.811
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	551.852	551.852	69.851	0.014
Residual	2	15.801	7.900		
Total	3	567.653			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	103.586	4.619	22.428	0.002	83.714	123.458	83.714	123.458
metal ion conc.	-1.051	0.126	-8.358	0.014	-1.591	-0.510	-1.591	-0.510

8) R^2 for the effects of retention Vs metal ion concentration using ANOVA (PEG =1.0%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.960
R Square	**0.921**
Adjusted R Square	0.882
Standard Error	1.889
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	83.371	83.371	23.354	0.040
Residual	2	7.140	3.570		
Total	3	90.510			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	102.504	3.105	33.017	0.001	89.145	115.862	89.145	115.862
metal ion conc.	-0.408	0.084	-4.833	0.040	-0.772	-0.045	-0.772	-0.045

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.970
R Square	**0.940**
Adjusted R Square	0.910
Standard Error	3.332
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	347.714	347.714	31.323	0.030
Residual	2	22.202	11.101		
Total	3	369.916			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	98.038	5.475	17.907	0.003	74.482	121.594	74.482	121.594
metal ion conc.	-0.834	0.149	-5.597	0.030	-1.475	-0.193	-1.475	-0.193

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.997
Standard Error	0.311
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	151.088	151.088	1566.054	0.000
Residual	3	0.289	0.096		
Total	4	151.377			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	101.147	0.326	310.488	0.0000001	100.110	102.184	100.110	102.184
metal ion conc.	-0.389	0.010	-39.573	0.00004	-0.420	-0.357	-0.420	-0.357

d) For Cr(VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.999**
Adjusted R Square	0.998
Standard Error	0.771
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1298.460	1298.460	2185.923	0.00002
Residual	3	1.782	0.594		
Total	4	1300.242			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	103.197	0.808	127.666	0.000001	100.625	105.769	100.625	105.769
metal ion conc.	-1.140	0.024	-46.754	0.00002	-1.217	-1.062	-1.217	-1.062

9) R^2 for the effects of retention Vs metal ion concentration using ANOVA (PEI =0.01%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.988
R Square	**0.976**
Adjusted R Square	0.965
Standard Error	1.928
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	308.385	308.385	82.999	0.012
Residual	2	7.431	3.716		
Total	3	315.816			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	103.897	3.167	32.803	0.001	90.269	117.525	90.269	117.525
metal ion conc.	-0.785	0.086	-9.110	0.012	-1.156	-0.414	-1.156	-0.414

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.195
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	141.933	141.933	3732.623	0.0003
Residual	2	0.076	0.038		
Total	3	142.009			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	80.916	0.320	252.532	0.00002	79.537	82.294	79.537	82.294
metal ion conc.	-0.533	0.009	-61.095	0.0003	-0.570	-0.495	-0.570	-0.495

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.956
R Square	**0.914**
Adjusted R Square	0.871
Standard Error	3.656
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	284.693	284.693	21.301	0.044
Residual	2	26.730	13.365		
Total	3	311.423			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	100.412	6.007	16.716	0.004	74.566	126.259	74.566	126.259
metal ion conc.	-0.755	0.163	-4.615	0.044	-1.458	-0.051	-1.458	-0.051

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.928
R Square	**0.862**
	0.793
Adjusted R Square	
Standard Error	4.458
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	247.927	247.927	12.477	0.072
Residual	2	39.742	19.871		
Total	3	287.669			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	114.090	7.325	15.576	0.004	82.574	145.606	82.574	145.606
metal ion conc.	-0.704	0.199	-3.532	0.072	-1.562	0.154	-1.562	0.154

For mixture metal ion solutions

1) R^2 for the effects of retention Vs pH using ANOVA (unmodified starch=0.05%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.0000
R Square	**0.9999**
Adjusted R Square	0.9999
Standard Error	0.1331
Observations	5.0000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	915.562	915.562	51666.942	0.000
Residual	3	0.053	0.018		
Total	4	915.615			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	77.198	0.136	567.342	0.00000001	76.765	77.631	76.765	77.631
pH	-3.973	0.017	-227.304	0.0000002	-4.029	-3.917	-4.029	-3.917

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.976
R Square	**0.953**
Adjusted R Square	0.938
Standard Error	0.936
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	53.568	53.568	61.203	0.004
Residual	3	2.626	0.875		
Total	4	56.194			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	78.537	0.956	82.127	0.000004	75.494	81.581	75.494	81.581
pH	-0.961	0.123	-7.823	0.004	-1.352	-0.570	-1.352	-0.570

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.164
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	127.844	127.844	4773.664	0.00001
Residual	3	0.080	0.027		
Total	4	127.924			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	85.833	0.167	513.117	0.00000002	85.300	86.365	85.300	86.365
pH	-1.485	0.021	-69.092	0.00001	-1.553	-1.416	-1.553	-1.416

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.998
R Square	**0.996**
Adjusted R Square	0.994
Standard Error	0.673
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	323.840	323.840	714.131	0.0001
Residual	3	1.360	0.453		
Total	4	325.200			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	97.435	0.688	141.551	0.000001	95.244	99.625	95.244	99.625
pH	-2.363	0.088	-26.723	0.0001	-2.644	-2.082	-2.644	-2.082

2) R^2 for the effects of retention Vs pH using ANOVA (PEG=1.0%, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.553
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	986.989	986.989	3227.112	0.00001
Residual	3	0.918	0.306		
Total	4	987.906			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	75.868	0.565	134.211	0.000001	74.069	77.667	74.069	77.667
pH	-4.125	0.073	-56.808	0.00001	-4.356	-3.894	-4.356	-3.894

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.501
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1417.089	1417.089	5634.535	0.00001
Residual	3	0.755	0.252		
Total	4	1417.843			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	29.639	0.513	57.820	0.00001	28.008	31.271	28.008	31.271
pH	4.943	0.066	75.064	0.00001	4.733	5.152	4.733	5.152

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.991
R Square	**0.982**
Adjusted R Square	0.975
Standard Error	2.819
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1272.868	1272.868	160.140	0.001
Residual	3	23.845	7.948		
Total	4	1296.713			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	46.579	2.882	16.163	0.001	37.408	55.751	37.408	55.751
pH	4.685	0.370	12.655	0.001	3.507	5.863	3.507	5.863

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.999**
Adjusted R Square	0.998
Standard Error	0.417
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	410.917	410.917	2364.729	0.00002
Residual	3	0.521	0.174		
Total	4	411.438			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	58.680	0.426	137.715	0.000001	57.324	60.036	57.324	60.036
pH	2.662	0.055	48.628	0.00002	2.488	2.836	2.488	2.836

3) R^2 for the effects of retention Vs pH using ANOVA (PEI=0.01%,metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	0.995
Adjusted R Square	0.993
Standard Error	0.672
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	267.374	267.374	592.453	0.0002
Residual	3	1.354	0.451		
Total	4	268.728			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	92.739	0.687	135.055	0.000001	90.554	94.925	90.554	94.925
pH	-2.147	0.088	-24.340	0.0002	-2.428	-1.866	-2.428	-1.866

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.997
Standard Error	0.606
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	442.207	442.207	1203.356	0.0001
Residual	3	1.102	0.367		
Total	4	443.310			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	33.056	0.620	53.347	0.00001	31.084	35.028	31.084	35.028
pH	2.761	0.080	34.689	0.0001	2.508	3.015	2.508	3.015

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.9998
R Square	**0.9997**
Adjusted R Square	0.9996
Standard Error	0.4156
Observations	5.0000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1581.869	1581.869	9156.772	0.000003
Residual	3	0.518	0.173		
Total	4	1582.387			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	29.593	0.425	69.655	0.000007	28.241	30.945	28.241	30.945
pH	5.222	0.055	95.691	0.000003	5.049	5.396	5.049	5.396

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.981
R Square	**0.962**
Adjusted R Square	0.949
Standard Error	2.967
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	667.763	667.763	75.845	0.003
Residual	3	26.413	8.804		
Total	4	694.176			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	109.878	3.033	36.228	0.00005	100.225	119.530	100.225	119.530
pH	-3.393	0.390	-8.709	0.003	-4.633	-2.153	-4.633	-2.153

4) R^2 for the effects of retention Vs polymer dosages using ANOVA (unmodified starch, pH=7, metal ion concentration=10 mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.898
R Square	**0.807**
Adjusted R Square	0.743
Standard Error	0.261
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.855	0.855	12.538	0.038
Residual	3	0.205	0.068		
Total	4	1.060			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	78.656	0.196	401.117	0.00000003	78.032	79.280	78.032	79.280
dosages	-0.637	0.180	-3.541	0.038	-1.210	-0.065	-1.210	-0.065

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.992
R Square	**0.984**
Adjusted R Square	0.978
Standard Error	0.944
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	159.575	159.575	178.881	0.001
Residual	3	2.676	0.892		
Total	4	162.252			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	46.822	0.709	66.027	0.00001	44.566	49.079	44.566	49.079
dosages	-8.707	0.651	-13.375	0.001	-10.779	-6.635	-10.779	-6.635

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.994
R Square	**0.989**
Adjusted R Square	0.985
Standard Error	0.111
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.247	3.247	261.688	0.001
Residual	3	0.037	0.012		
Total	4	3.284			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	96.919	0.084	1158.913	0.000000001	96.653	97.185	96.653	97.185
dosages	1.242	0.077	16.177	0.001	0.998	1.486	0.998	1.486

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.997**
Adjusted R Square	0.996
Standard Error	0.364
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	147.967	147.967	1113.795	0.0001
Residual	3	0.399	0.133		
Total	4	148.365			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	74.396	0.274	271.856	0.0000001	73.525	75.267	73.525	75.267
dosages	8.384	0.251	33.374	0.00006	7.585	9.184	7.585	9.184

5) R^2 for the effects of retention Vs polymer dosages using ANOVA (PEG, pH=7, metal ion concentration=10 mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.968
R Square	**0.936**
Adjusted R Square	0.915
Standard Error	0.110
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.531	0.531	44.034	0.007
Residual	3	0.036	0.012		
Total	4	0.567			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	78.535	0.082	952.750	0.000000003	78.273	78.798	78.273	78.798
dosages	-0.502	0.076	-6.636	0.007	-0.743	-0.261	-0.743	-0.261

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.952
R Square	**0.906**
Adjusted R Square	0.875
Standard Error	0.195
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.109	1.109	29.056	0.013
Residual	3	0.115	0.038		
Total	4	1.224			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	86.513	0.147	589.757	0.00000001	86.046	86.980	86.046	86.980
dosages	-0.726	0.135	-5.390	0.013	-1.154	-0.297	-1.154	-0.297

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.895
R Square	**0.801**
Adjusted R Square	0.735
Standard Error	0.472
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.693	2.693	12.081	0.040
Residual	3	0.669	0.223		
Total	4	3.361			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	96.702	0.354	272.813	0.0000001	95.574	97.830	95.574	97.830
dosages	1.131	0.325	3.476	0.040	0.095	2.167	0.095	2.167

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.998**
Adjusted R Square	0.997
Standard Error	0.316
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	153.018	153.018	1531.737	0.00004
Residual	3	0.300	0.100		
Total	4	153.318			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	74.384	0.237	313.449	0.0000001	73.629	75.139	73.629	75.139
dosages	8.526	0.218	39.137	0.00004	7.833	9.219	7.833	9.219

6) R^2 for the effects of retention Vs polymer dosages using ANOVA (PEI, pH=7, metal ion concentration=10mg/l, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999999
R Square	**0.999999**
Adjusted R Square	0.999998
Standard Error	0.009
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	204.942	204.942	2369432.079	0.000000001
Residual	3	0.000	0.000		
Total	4	204.942			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	81.077	0.007	11209.512	0.000000000002	81.054	81.100	81.054	81.100
dosages	-9.090	0.006	-1539.296	0.000000001	-9.109	-9.072	-9.109	-9.072

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.942
R Square	**0.887**
Adjusted R Square	0.831
Standard Error	1.833
Observations	4.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	52.973	52.973	15.766	0.058
Residual	2	6.720	3.360		
Total	3	59.693			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	81.519	2.245	36.312	0.001	71.860	91.179	71.860	91.179
dosages	-6.510	1.640	-3.971	0.058	-13.564	0.544	-13.564	0.544

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.921
R Square	**0.848**
Adjusted R Square	0.797
Standard Error	0.039
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.026	0.026	16.752	0.026
Residual	3	0.005	0.002		
Total	4	0.031			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	87.542	0.031	2859.849	0.0000000001	87.445	87.640	87.445	87.640
dosages	-0.102	0.025	-4.093	0.026	-0.182	-0.023	-0.182	-0.023

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.995
R Square	**0.990**
Adjusted R Square	0.987
Standard Error	0.366
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	41.9200	41.9200	312.1487	0.0004
Residual	3	0.4029	0.1343		
Total	4	42.3229			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	97.762	0.285	343.022	0.0000001	96.855	98.669	96.855	98.669
dosages	-4.111	0.233	-17.668	0.0004	-4.852	-3.371	-4.852	-3.371

7) R^2 for the effects of retention Vs metal ion concentration using ANOVA (unmodified starch=0.05%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.121
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	65.741	65.741	4511.045	0.00001
Residual	3	0.044	0.015		
Total	4	65.785			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	80.644	0.127	636.937	0.00000001	80.241	81.047	80.241	81.047
metal ion conc.	-0.256	0.004	-67.164	0.00001	-0.269	-0.244	-0.269	-0.244

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.9999
R Square	**0.9997**
Adjusted R Square	0.9997
Standard Error	0.0649
Observations	5.0000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	50.266	50.266	11930.136	0.000002
Residual	3	0.013	0.004		
Total	4	50.278			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	80.088	0.068	1176.409	0.000000001	79.871	80.305	79.871	80.305
metal ion conc.	-0.224	0.002	-109.225	0.000002	-0.231	-0.218	-0.231	-0.218

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.996
R Square	**0.992**
Adjusted R Square	0.989
Standard Error	0.018
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.108	0.108	352.696	0.0003
Residual	3	0.001	0.000		
Total	4	0.109			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	82.020	0.018	4465.706	0.00000000002	81.962	82.078	81.962	82.078
metal ion conc.	0.010	0.001	18.780	0.0003	0.009	0.012	0.009	0.012

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.974
R Square	**0.949**
Adjusted R Square	0.932
Standard Error	1.961
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	213.430	213.430	55.487	0.005
Residual	3	11.539	3.846		
Total	4	224.969			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	96.829	2.057	47.074	0.00002	90.283	103.376	90.283	103.376
metal ion conc.	-0.462	0.062	-7.449	0.005	-0.659	-0.265	-0.659	-0.265

8) R^2 for the effects of retention Vs metal ion concentration using ANOVA (PEG =1.0%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.067
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	20.592	20.592	4599.907	0.00001
Residual	3	0.013	0.004		
Total	4	20.606			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	87.503	0.070	1246.951	0.000000001	87.280	87.726	87.280	87.726
metal ion conc.	-0.144	0.002	-67.823	0.00001	-0.150	-0.137	-0.150	-0.137

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.999**
Adjusted R Square	0.998
Standard Error	0.132
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	46.354	46.354	2648.301	0.00002
Residual	3	0.053	0.018		
Total	4	46.407			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	85.819	0.139	618.482	0.00000001	85.377	86.261	85.377	86.261
metal ion conc.	-0.215	0.004	-51.462	0.00002	-0.229	-0.202	-0.229	-0.202

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.998
R Square	**0.996**
Adjusted R Square	0.995
Standard Error	0.385
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	117.718	117.718	794.906	0.0001
Residual	3	0.444	0.148		
Total	4	118.162			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	89.605	0.404	222.010	0.0000002	88.321	90.889	88.321	90.889
metal ion conc.	-0.343	0.012	-28.194	0.0001	-0.382	-0.304	-0.382	-0.304

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.000
R Square	**0.999**
Adjusted R Square	0.999
Standard Error	0.108
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	45.668	45.668	3933.479	0.00001
Residual	3	0.035	0.012		
Total	4	45.703			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	90.865	0.113	804.052	0.000000004	90.505	91.225	90.505	91.225
metal ion conc.	-0.214	0.003	-62.717	0.00001	-0.225	-0.203	-0.225	-0.203

9) R^2 for the effects of retention Vs metal ion concentration using ANOVA (PEI =0.01%, pH=7, flowrate=115 ml/min, TMP= 1.5 bar)

a) For Zn (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.997
R Square	**0.993**
Adjusted R Square	0.991
Standard Error	0.410
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	71.770	71.770	427.315	0.0002
Residual	3	0.504	0.168		
Total	4	72.274			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	82.319	0.430	191.516	0.0000003	80.951	83.687	80.951	83.687
metal ion conc.	-0.268	0.013	-20.672	0.0002	-0.309	-0.227	-0.309	-0.227

b) For Pb (II),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999
R Square	**0.999**
Adjusted R Square	0.998
Standard Error	0.057
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	7.639	7.639	2377.207	0.00002
Residual	3	0.010	0.003		
Total	4	7.648			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	72.082	0.059	1212.419	0.000000001	71.893	72.271	71.893	72.271
metal ion conc.	-0.087	0.002	-48.757	0.00002	-0.093	-0.082	-0.093	-0.082

c) For Cr (III),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.921
R Square	**0.849**
Adjusted R Square	0.799
Standard Error	2.365
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	94.434	94.434	16.881	0.026
Residual	3	16.782	5.594		
Total	4	111.216			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	95.967	2.481	38.686	0.00004	88.072	103.861	88.072	103.861
metal ion conc.	-0.307	0.075	-4.109	0.026	-0.545	-0.069	-0.545	-0.069

d) For Cr (VI),

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.972
R Square	**0.945**
Adjusted R Square	0.927
Standard Error	1.873
Observations	5.000

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	182.584	182.584	52.034	0.005
Residual	3	10.527	3.509		
Total	4	193.111			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	87.904	1.965	44.743	0.00002	81.652	94.157	81.652	94.157
metal ion conc.	-0.427	0.059	-7.213	0.005	-0.616	-0.239	-0.616	-0.239

APPENDIX D

LIST OF PUBLICATIONS AND PAPERS PRESENTED

List of publication

1) Baharuddin, N.H., Nik Sulaiman, N.M., & Aroua, M.K. (2014). Removal of Zinc and Lead Ions by Polymer Enhanced Ultrafiltration Using Unmodified Starch as Novel Binding Polymer. International Journal of Environmental Science and Technology, 2014, 12 (6). (ISI-Citation, Impact factor: 1.844), DOI: 10.1007/s13762-014-0549-4

2) Baharuddin, N.H., Nik Sulaiman, N.M., & Aroua, M.K. (2014). Removal of Heavy Metal Ions from Mixed Solutions via Polymer-Enhanced Ultrafiltration using Starch as a Water-soluble Biopolymer. Environmental Progress and Sustainability Energy. (ISI-Citation, Impact factor: 1.649), DOI: 10.1002/ep.11995

3) Baharuddin, N.H., Nik Sulaiman, N.M., & Aroua, M.K. (2014). Unmodified starch as water-soluble binding polymer for chromium ions removal via polymer enhanced ultrafiltration system. Journal of Environmental Health Science & Engineering, 2014, 12 (61). (ISI-Citation, Impact factor: 1.230)

List of presented or participate in Paper/ poster

1) Nik Sulaiman, N.M., Baharuddin, N.H., & Aroua, M.K. (2012). Removal of Simultaneous Multivalent Metal Ions via Polymer Enhanced Ultrafiltration by Using Unmodified Starch as Water-Based Polymer. Procedia Engineering SciVerse ScienceDirect, Euromembrane Conference 2012, 44, 2002-2005.

2) The 2nd International Malaysia-Ireland Joint Symposium on Engineering, Science and Business 2012 (IMiEJS2012) organized by Universiti Malaysia Perlis and Athlone Institute of Technology in collaboration with The Ministry of Higher Education (MOHE) Malaysia, Education Malaysia and Malaysia Postgraduates Student Association Ireland (MyPSI), 18th - 19th June 2012 at Putra World Trade Center (PWTC), Kuala Lumpur, Malaysia (http://hdl.handle.net/123456789/30495)

3) 3rd International Congress on Green Process Engineering, KL (6-8 December 2011) – Poster Presenter

4) The 8th International Conference on Membrane Science and Technology, Bandung Indonesia (29 Nov- 1 Dec 2010) – Participant

5) Exhibition Bio- Malaysia, KL (November 2010) - Exhibitor