

**APPLICATION OF POLYPYRROLE AND POLYPYRROLE/
POLYETHYLENIMINE FOR THE REMOVAL OF SOME
HEAVY METAL IONS FROM AQUEOUS SOLUTION**

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**DISSERTATION SUBMITTED IN FULFILLMENT OF
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ABSTRAK

Polypyrrole (Ppy) yang disediakan melalui pengoksidaan kimia menggunakan FeCl_3 sebagai oksidan telah mempamerkan 100% kapasiti serapan untuk penyingkiran ion logam berat (Pb, Ni, Cd, Zn dan Cu) daripada larutan akueus. Hasil kajian kumpulan penjerapan menunjukkan bahawa larutan pH mempunyai kesan yang besar terhadap penjerapan logam. 100% penyerapan logam berat didapati pada pH 7. Pada kedua-dua larutan berasid dan beralkali di luar pH 7, kapasiti penjerapan Ppy menurun dengan ketara. Kesan parameter penting yang lain seperti kepekatan awal larutan stok plumbum, masa dan dos penjerap pada pengambilan ion logam juga dikaji untuk mengenalpasti penjerapan optimum. Kajian isothermal produk menunjukkan kebolegunaan persamaan Langmuir dalam kajian ini yang menunjukkan pembentukan polimer multilayer. Keputusan FTIR dan EDX mengesahkan kehadiran plumbum dalam matriks polimer selepas rawatan. Penjerap yang disediakan menunjukkan luas permukaan 5.047 m^2 oleh analisis BET. Mikrograf SEM kelihatan sama bagi kedua-dua penjerapan iaitu selepas dan pra-penjerapan polimer untuk penyingkiran logam berat. Plot penentukuran menunjukkan tindak balas linear dengan pekali korelasi 0.9998. Kaedah ini adalah mudah, cepat dan tepat serta penyingkiran yang lengkap ion plumbum daripada air sisa telah direkodkan.

Kata kunci: polypyrrole, penjerapan, persamaan Langmuir

ABSTRACT

Polypyrrole (Ppy) prepared by chemical oxidation using FeCl_3 as the oxidant has exhibited 100% sorption capacity for the removal of heavy metal ions (Pb, Ni, Cu, Cd and Zn) from aqueous solutions. Batch adsorption results showed that solution pH had a major impact on metal adsorption. 100% heavy metal absorption was found at pH 7. At both acidic and alkaline solutions beyond pH 7, the adsorption capacity of Ppy was substantially lowered. The effects of other important parameters such as initial concentration of lead stock solution, contact time and the sorbent dosage on the uptake of metallic ions were also investigated to identify the optimum adsorption. The isothermal study of product indicated the applicability of Langmuir equation in present study which shows the formation of multilayer polymer. The FTIR and EDX results confirm the presence of heavy metals in polymer matrix after treatment. The prepared adsorbent showed a surface area of 5.047 m^2 by BET analysis. The SEM micrographs of the polymer look similar for both before and after adsorption of heavy metals. The calibration plot shows a linear response with correlation coefficient of 0.9998. This method is simple, fast and precise and the complete removal of lead ions from the wastewater was recorded.

Keywords: polypyrrole, sorption, Langmuir equation

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List of abbreviation

AAS: atomic absorption spectroscopy

AC: activated carbon

BET: Brunauer, Emmett and Teller Adsorption Model

BOD: biochemical oxygen demand

Cd: cadmium

COD: chemical oxygen demand

Cr: chromium

Cu: copper

DOE: Department of Environment

ECH: epichlorohydrin

EDX: Energy-dispersive X-ray spectroscopy

Fe₃O₄: ferric chloride

FESEM: Field Emission Scanning Electron Microscopy

FTIR

HA: humic acid

Hg: Mercury

HMW: High molecular weight

ICPs: intrinsically conducting polymers

Kev: kilo electron volt

LMW: low molecular weight

MW: molecular weight

Ni: nickel

Nm: nanometers

PAC: Poly (acetylene)s

PAni: polyaniline

Pb: lead

PEDOT: poly (3, 4-ethylenedioxythiophene)

PEG: Polyethylene glycol

PEI: polyethyleneimine

PEIMPA: polyethyleneimine methylenephosphonic acid

PEIs: Linear polyethyleneimines

PPM: part per million

PPS: poly (p-phenylene sulfide)

PPV: Poly (p-phenylene vinylene)

Ppy: polypyrrole

PT: poly (thiophene)s

PVA: Polyvinyl alcohol

Py: pyrrole

RPM: revolutions per minute

SD: sawdust

SEM: Scanning Electron Micrograph

SS: suspended solids

WHO: World Health Organization

Zn: zinc

CHAPTER I
INTRODUCTION

CHAPTER I: INTRODUCTION

1.1 Background of Study

High consumption of water is one of the most important environmental concerns in the future of industry. Wastewater generated from various industrial sources such as paper mill containing heavy metals like Cr, Zn, Ni, Cd, Cu and Pb is becoming a grave danger for offering threat to human and animal health and ecological system [1].

Wastewater contains a large amount of pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity and colorants. This may cause bacterial and algal slime growths, thermal impacts, scum formation, color problems and a loss of both biodiversity and aesthetic beauty in the environment [2].

Water-related diseases are one of the leading causes of death all around the world. Millions of people die each year, nearly all from developing countries and some from poor countries. Diseases resulting from contaminated water comprise 80% of the total disease burden. It is estimated that up to half of all hospital beds in the world are occupied by victims of water contamination.

Despite the international attempts to finding the solution for this global concern, waterborne disease is still a major cause of death, particularly in children, and it has also a significant influence on economy in many parts of the world.

Scientific communities from different parts of the entire world have done several various works in removing the toxic material from the wastewater and to make the wastewater clean, pure and drinkable. Activated carbon is one of the well-known adsorbents which were employed for several researches to remove the heavy metal ions from the wastewater.

Impregnation of palm shell activated carbon with polyethylenimine and its effects on Cd²⁺ adsorption was reported in 2007[2]. Removal of, Hg (II), Pb(II), Cd(II), Ni(II), and Cu(II) were studied in 2001 by using activated carbon prepared from an agricultural solid waste [3].The removal of heavy metal cations by natural zeolites were studied by a group of researchers from Turkey in 2004 [4] and in 1990 the removal of heavy metals and other cations from wastewater using zeolite was investigated [5].

Since the discovery of conducting polymers 30 years ago, a large number of research works have been done to remove the heavy metals from wastewater. Conducting polymer can be used as an adsorbent due to its ion exchange property.

According to the related research works, variety of conducting polymers such as polyaniline, poly (acrylic acid), poly (thiophene), polyvinyl alcohol etc, are employed for the removal of heavy metals from wastewater. For example, removal of heavy metals using polyvinyl alcohol semi-IPN poly (acrylic acid)/tourmaline composite optimized with response surface methodology was studied in 2010 by a group of researchers from China [6]. In 2009, polyaniline was used for the removal of mercury from wastewater [7].

Among the wide range of polymers, polypyrrole is one of the well-known polymers owing to its interesting redox ability, high conductivity and stability of the oxidization state. It also has been used several times in different research works as an adsorbent. The removal of some of the heavy metals from wastewater has been reported since two decade ago by using polypyrrole. Although polypyrrole has the ability for the metal uptake from wastewater but the efficiency of this polymer alone is not significant. Thus different research works have shown that the removal of heavy metals by using the additional material in polypyrrole can enhance the power of polypyrrole in metal uptake (Table 1.1).

But little effort has been done to use the polypyrrole alone as an adsorbent for the removal of heavy metals from wastewater.

Thus, the present effort has been done to evaluate polypyrrole as an adsorbent for the removal of lead, copper, zinc, cadmium and nickel from aqueous solution. In addition polypyrrole together with polyethylenimine (PEI) has also been evaluated for the removal of zinc and cadmium from aqueous solution.

1.2 Objectives of the Present Investigation

The objectives of this research work are:

- 1- To prepare polypyrrole by chemical method using FeCl_3 as an oxidant for the removal of heavy metals from aqueous solution.
- 2- To characterize the prepared polypyrrole by FTIR, BET and SEM.
- 3- To study effects of several important factors such as contact time, concentration, pH and dosage of adsorbent on the adsorption of heavy metals.
- 4- To enhance the adsorption capacity of polypyrrole by adding polyethylenimine for the removal of zinc and cadmium which were not completely removed by polypyrrole alone.

Table 1. 1: Polypyrrole-based adsorbent for the removal of heavy metal ions (and Thiocyanate) from wastewater

Polypyrrole-based adsorbent	Ions to remove	References
Hierarchical porous polypyrrole nanoclusters	Chromium	[8]
Poypyrrole and poly(vinyl alcohol) Polypyrrole and poly(ethylene glycol) Polypyrrole and activated carbon Polypyrrole and bentonite	Arsenic	[9]
Polypyrrole- impregnated porous carbon	Lead, mercury and silver	[10]
Polypyrrole and polyaniline	Thiocyanate	[11]
Polypyrrole/ Fe ₃ O ₄ magnetic nano composite	Chromium	[12]
Polypyrrole- sawdust	Silver	[13]
Polypyrrole coated on rice husk ash	Zinc and copper	[14]

1.3 Scope of Research Work

An overview of the development and characteristics of the conducting polymers, polypyrrole and polyethylenimine and their application in wastewater treatment are presented in Chapter 2.

Chapter 3 will discuss the experimental procedures of the preparation of polypyrrole in different ratios and adsorption procedure, in the second part, the removal of 5 heavy metal ions from wastewater were investigated and in the third part, the effect of important parameters such as contact time, dosage of adsorbent, concentration and pH were investigated . This chapter also discusses effect of the addition of polyethylenimine to the structure of polypyrrole such as the adsorption capacity of adsorbent which showed to get the higher efficiency for the removal of Zn and Cd in which polypyrrole alone could not be responsible for the complete removal of these elements. Characterization of the polypyrrole and polypyrrole/ polyethylenimine composite is also explained in this chapter.

Chapter 4 covers the results and discussion obtained from this study. This chapter consists of two main parts. The first part is the verification of the structure of polypyrrole by using FTIR and BET. The second part deals with the isothermal study to find the favorable model that can explain the adsorption behavior of the polypyrrole .

The whole studies will be concluded in Chapter 5. This chapter also reveals the suggestions for further works. The summary of current works is illustrated in Figure 1.1.

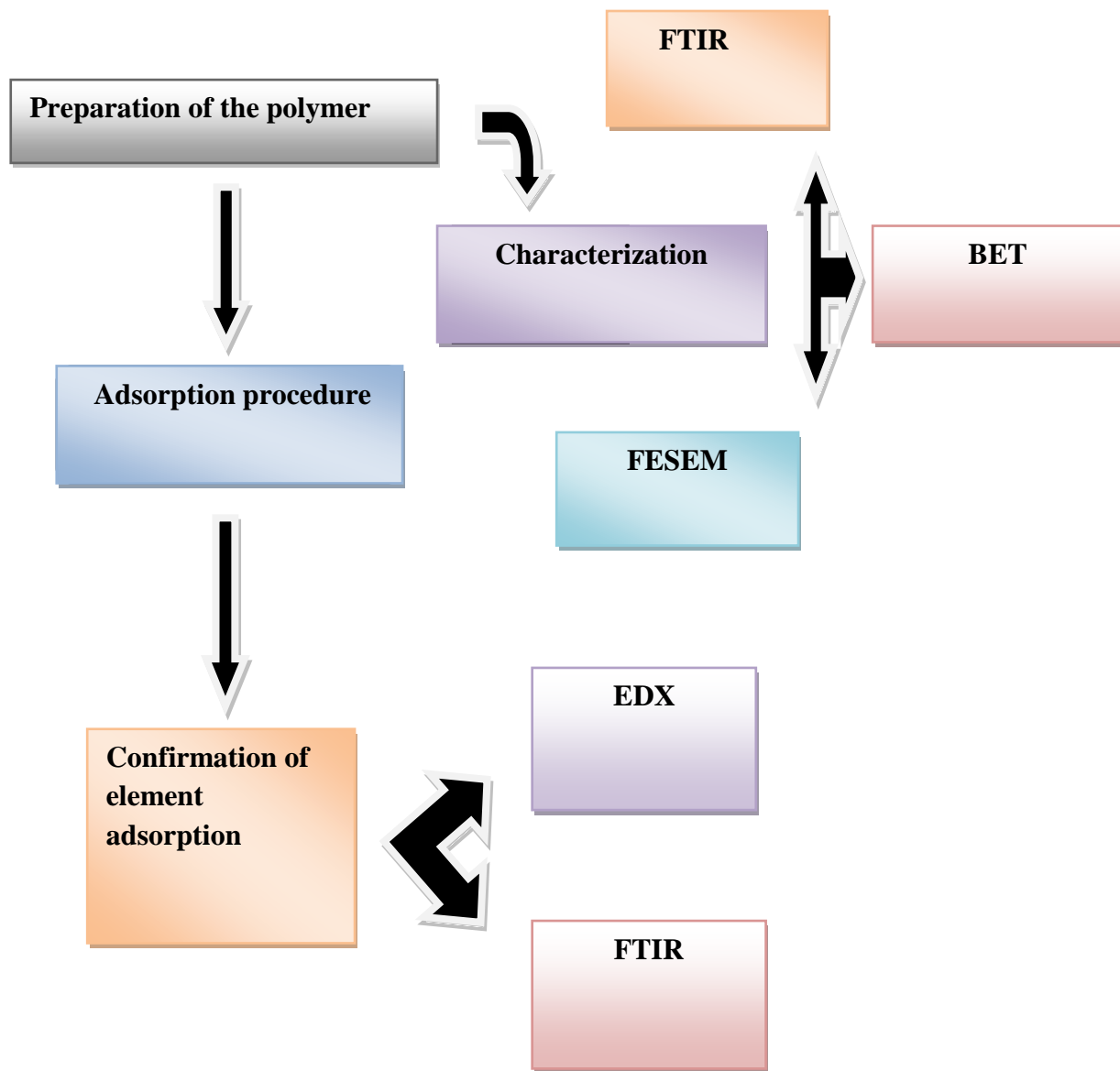


Figure 1. 1: Flow chart of work.

CHAPTER II

LITERATURE REVIEW

CHAPTER II: LITERATURE REVIEW

2. 1 Contaminated Water

Water has always played a prominent role in human civilization. When people first began settling in one place and growing crops for sustenance, it was invariably near water sources like rivers, lakes, or groundwater springs. Water was needed for drinking, preparing food, bathing, cleaning, irrigating crops, and a variety of other tasks, therefore it was important to have ready access to this resource. The water sources used for supplying water were not always clean. Treating drinking water to improve smell, taste, clarity, or to remove disease-causing pathogens has occurred in one form or another throughout recorded history.

Satisfactory disposal of wastewater, whether by surface, subsurface methods or dilution all depends on its treatment prior to disposal. Adequate treatment is necessary to prevent contamination of receiving waters to a degree which might interfere with their best or intended use, whether as water supply, recreation or any other required purpose.

Wastewater treatment consists of applying known technology to improve or upgrade the quality of wastewater. Usually wastewater treatment will involve collecting the wastewater in a central, segregated location and subjecting the wastewater to various treatment processes. Wastewater treatment, however, can also be organized or categorized by the nature of the treatment process operation being used; for example, physical, chemical or biological. A complete treatment system may consist of the application of a number of physical, chemical and biological processes to the wastewater.

2. 1. 1 Treatment methods

As a consequence, a number of global actions have been implemented to reduce the contents of contaminant released from various sources by varied processes including adsorption, ion-exchange, precipitation, phytoextraction, ultrafiltration , reverse osmosis, physical, sedimentation (clarification), screening, aeration, filtration, flotation and skimming, degasification, equalization, chemical, chlorination, ozonation, neutralization, coagulation, adsorption, biological, activated sludge treatment methods, trickling filtration, oxidation ponds, lagoons, aerobic digestion, septic tanks, anaerobic, anaerobic digestion, lagoons and column system.

2. 1. 2 Heavy metals as the dangerous pollutants of water

Among the various pollutants which concern the quality of water, heavy metals group is one of the most dangerous contaminants. In recent years, the removal of heavy metal ions from wastewater has attracted much attention due to the high toxicity of such ions. In this research work, the range of concentration which is chosen to prepare the stock solution consists of the concentration of these elements (Pb, Zn, Cu, Cd and Ni) in environment such as- industrial water, rivers and rain water that is derivative from the DOE (Department of Environment in which the national standard for the drinking water quality prepares by engineering service division Ministry of Health Malaysia). Not only in Malaysia but also in all around the world, the quality of drinking water is under supervision of WHO (World Health Organization) which has different branches in different countries to control the standard level of pollutant inside the drinking water.

2. 2 Conducting polymers

A lot of research has been carried out in the field of conducting polymers since 1977 when the conjugated polymer was discovered to conduct electricity through halogen doping. The Nobel Prize in 2000 in Chemistry recognized the discovery of conducting polymers and over 25 years of progress in this field. In recent years, there has been growing interest in research on the conducting polymer nanostructures since the polymers combine the advantages of organic conductors with low-dimensional systems and therefore create interesting physicochemical properties and potentially useful applications such as adsorption.

Conductive polymers or more precisely intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their process ability, mainly by dispersion. Conductive polymers can offer high electrical conductivity but do not show mechanical properties as other commercial polymers do [16]. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Recently, nanostructure materials have been used for heavy metal removal from water/wastewater and have proven advantageous over traditional adsorbents due to very large surface area and accessible active sites. A nanocomposite acts as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. Appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in a very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler [15].

2. 2. 1 The role of conducting polymer in wastewater treatment

Although the polymers were well understood as an adsorbent, the composite of conducting polymer showed considerable potential in the removal of heavy metals, color and anions from wastewater. The polymer's conductivity can be varied over several orders of magnitude, covering a considerable range that is suitable for adsorption. The ion exchange capacities of some of the conducting polymers such as Ppy were well known and it was found to be dependent on the polymerization conditions, the type and also size of the dopants in polymerization process. Conducting polymers can be used for the treatment of wastewater to remove heavy metal ions.

Table 2. 1: Examples of conducting polymers

The main chain contains	Type of the polymers		
	No heteroatom	Nitrogen-containing	Sulfur-containing
Aromatic cycles	<ul style="list-style-type: none"> ▪ Poly(fluorene)s ▪ polyphenylenes ▪ polypyrenes ▪ polyazulenes ▪ polynaphthalenes 	<p>The N is in the aromatic cycle:</p> <ul style="list-style-type: none"> ▪ poly(pyrrole)s (PPY) ▪ polycarbazoles ▪ polyindoles ▪ polyazepines <p>The N is outside the aromatic cycle:</p> <ul style="list-style-type: none"> ▪ Panis (PANI) 	<p>The S is in the aromatic cycle:</p> <ul style="list-style-type: none"> ▪ poly(thiophene)s (PT) ▪ poly(3,4-ethylenedioxythiophene) (PEDOT) <p>The S is outside the aromatic cycle:</p> <ul style="list-style-type: none"> ▪ poly(p-phenylene sulfide) (PPS)
Double bonds	<ul style="list-style-type: none"> ▪ Poly(acetylene)s (PAC) 		
Aromatic cycles and double bonds	<ul style="list-style-type: none"> ▪ Poly(p-phenylene vinylene) (PPV) 		

2. 2. 2 Related past research

Over the years conducting polymers have been a subject to a widespread research in water treatment with the aim of toxicity reduction in water. Conducting polymers can be used for the treatment of wastewater to remove heavy metals due to the ion exchange properties. PANi was used for the removal of mercury from wastewater. It is reported that 58% of mercury ions were removed in pH: 5.5 [7]. Conducting polymer/alumina composites were reported as the viable adsorbent for the removal of fluoride ions from aqueous solution. The effect of chloride, nitrate, sulphate etc as co-ions which led to ~ 3 mg/g removal of fluoride ion from wastewater was investigated in this study [9]. Removal of hexavalent chromium from aqueous solution by Ppy-PANi nanofiber was reported. The maximum adsorption capacity of the Ppy-PANi nanofibers for Cr (VI) was 227 mg/g. Selective adsorption of Cr (VI) from aqueous solution was achieved in the presence of other co-existing ions [12]. Using polyvinyl alcohol semi-IPN poly (acrylic acid)/tourmaline composite was reported for the removal of heavy metals such as Cu and Pb. The adsorption equilibrium was recorded within 30 min with higher adsorption capacity of 3.12 mmol/g for Pb^{2+} ion and 2.98 mmol/g for Cu^{2+} ion [30]. Heavy Metal Detection by Electrochemical Electronic Tongue with Poly(thiophene)-Metal Oxide Nanoparticle Composite Electrodes was studied in 2011 [15]. PEDOT/ PSS Modified glassy carbon electrode were employed for the simultaneous determination of cadmium and lead which are 1.47 and 1.15 $\mu\text{g/ml}$ in PH 4-5, respectively [16].

2. 3 Polypyrrole (Ppy)

Polypyrrole, a chemical compound formed from a number of connected pyrrole ring structures is an inherently conductive polymer due to interchain hopping of electrons.

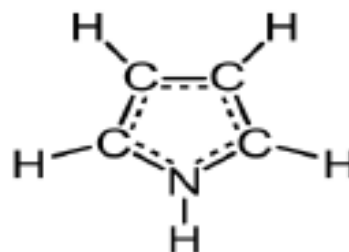
Table 2. 2: Properties of polypyrrole

Table: Properties of Pyrrole

Properties	Descriptions
Appearances	colorless liquid

Molecular formula

C_4H_5N



Molecular weight

67.09 g mol⁻¹

Boiling point

129-131 °C, 402-404 K, 264-268 °F

Melting point

-23 °C, 250 K, -9 °F

Vapor pressure

7 mmHg at 23 °C

Polypyrrole is easy to prepare by electrochemical techniques and its surface charge characteristics can easily be modified by changing the dopant anion (X^-) that is incorporated during synthesis. Polypyrrole was the first of conducting polymers that shows relative high conductivity. It can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. The final form of polypyrrole is a long conjugated backbone of pyrrole monomer.

Since the discovery of conducting polymer three decades ago, various adsorption media have been widely used for heavy metal removal. Ppy is one of the new and well known conducting polymers from a number of connected pyrrole ring structures. Ppy can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. The final form of Ppy is a long conjugated backbone of pyrrole monomer.

Oxidative polymerization of pyrrole to Ppy proceeds are shown in Fig 2.1.

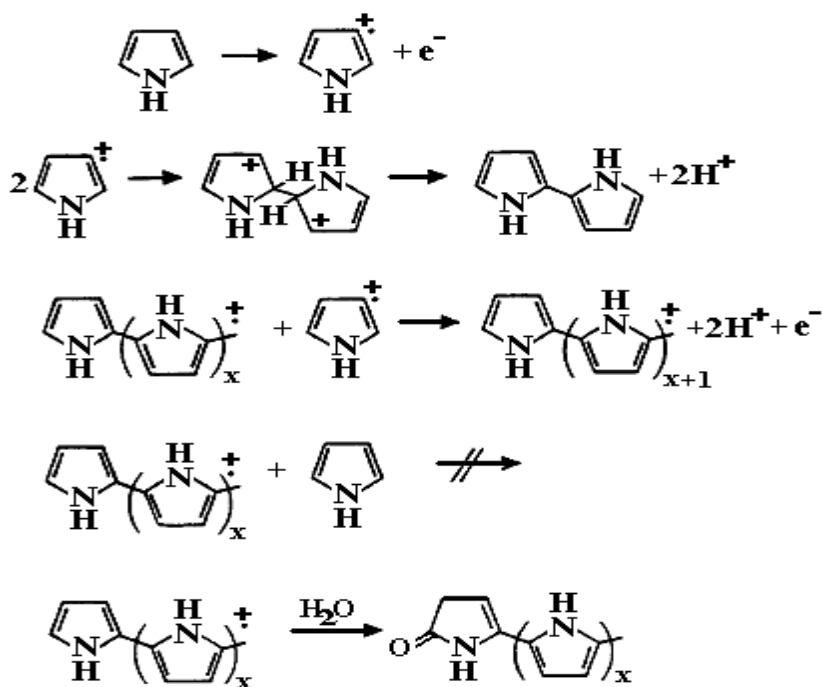


Figure 2. 1: Chemical preparation of polypyrrole via radical cation formation [37].

In this research work, polypyrrole was prepared by chemical polymerization. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as an oxidant and all of the reactions were carried out in an aqueous solution at room temperature.

In a typical experiment, following (1:3) mole ratio of monomer to oxidant which had been previously done by researchers is a common way for the preparation of polypyrrole. Although using this ratio may cause complete formation of polypyrrole but the adsorption experiments have shown lower levels of adsorption capacity for the removal of heavy metal from wastewater. Therefore, all of the ratios were investigated to have comparable results. The different mole ratios of pyrrole monomer to oxidant $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ used in this research were (1:3), (1:2), (1:1), (1:0.5) and (1:0.33). Oxidative polymerization of pyrrole to Ppy proceeds via one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the bipyrrole (Fig 2.1). This process is then repeated to form a longer chain. The final form of Ppy is that of a long conjugated backbone as seen in Fig 2.2.

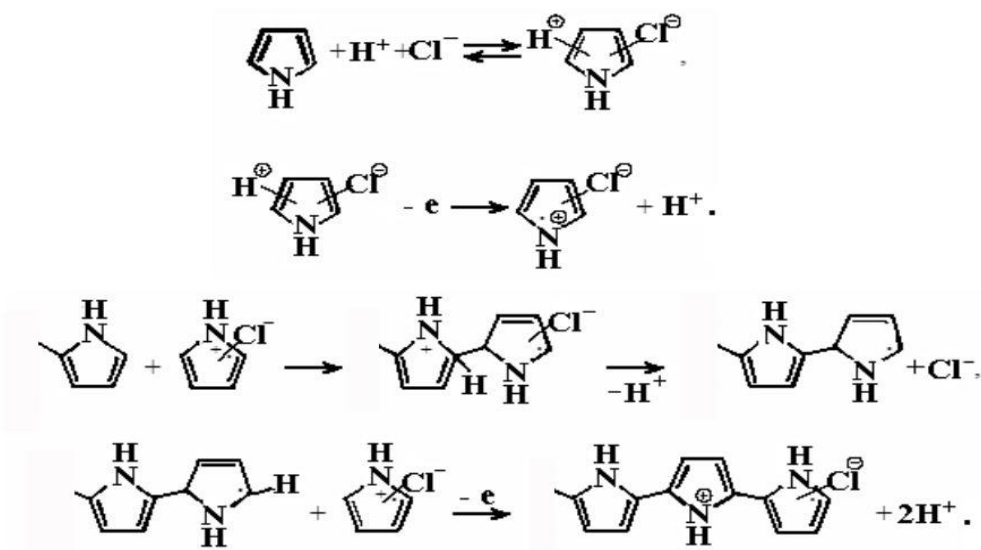


Figure 2. 2: The development of Ppy chains [37].

The polymer has resonance structures that resemble the aromatic or quinoid forms. At the neutral state, the polymer is not conducting but it becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalized over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron). The physical form of Ppy is usually an intractable powder resulting from chemical polymerization and an insoluble film resulting from electropolymerization [6].

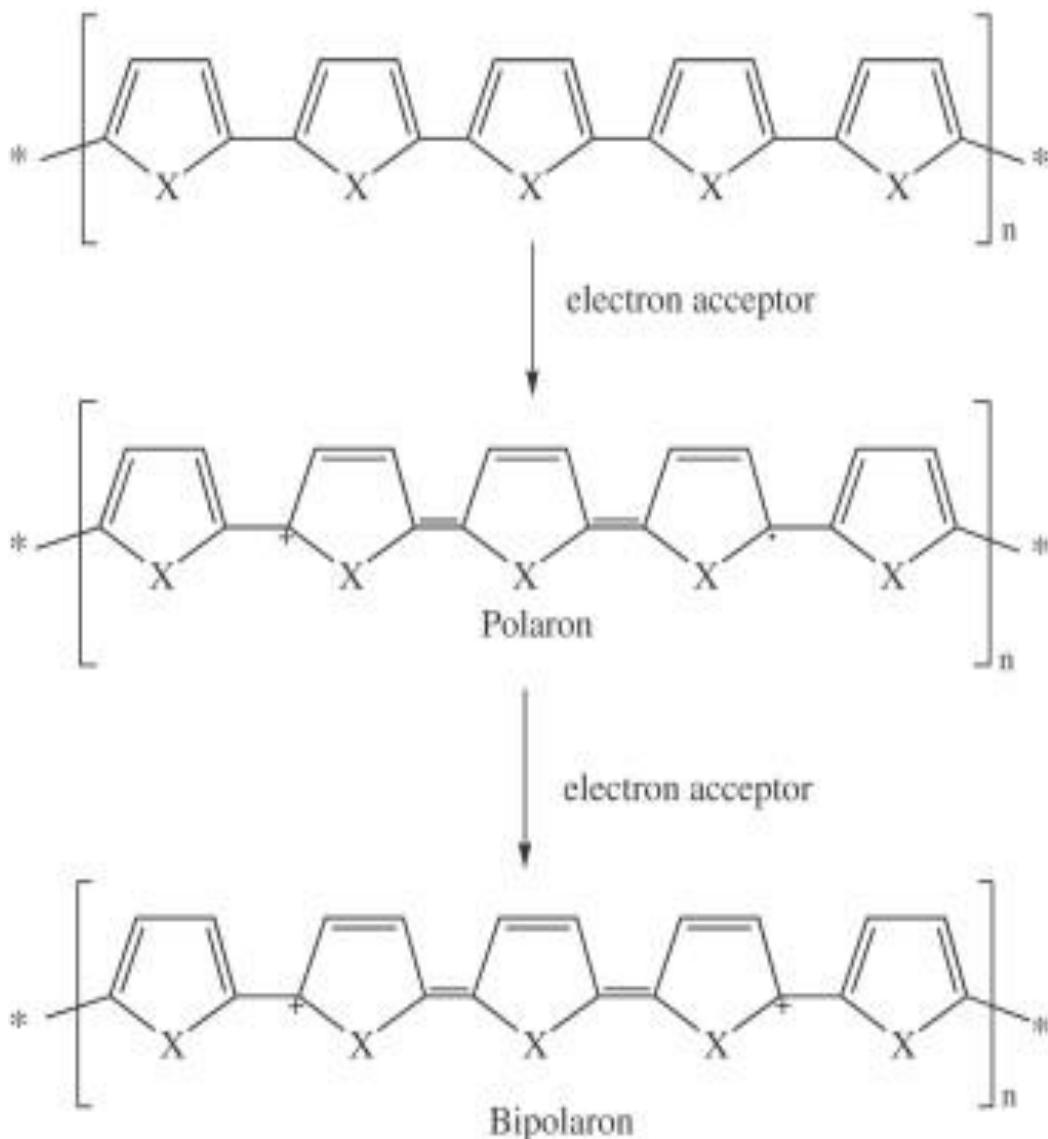


Figure 2. 3: Chemical structures of Ppy in neutral aromatic and in oxidized polaron and bipolaron forms [40].

It is revealed that Ppy synthesized in solutions with small dopants such as Cl^- , ClO_4^- , NO_3^- etc, mainly exhibits anion-exchanger behavior due to the high mobility of these ions in the polymer matrix.

2. 3. 1 Polypyrrole as an adsorbent

Ppy is a conducting polymer that has attractive characteristics for the use as an adsorbent due to its ion exchange property and nitrogen hetero atom in the structure.

2. 3. 2 Related past research

Although Ppy is a well-known polymer with its ion exchange property for the removal of heavy metals like Cr, Zn, Pb, Ni, Co and Cu, but the complete removal (100%) of heavy metals from wastewater is not reported yet. Many efforts have been done so far to increase the efficiency of Ppy as an adsorbent for the removal of heavy metals by adding other materials to the structure of Ppy.

The maximum removal amount of Cr (VI) ions from wastewater using Ppy nanoclusters was 3.47 mmol g/l in aqueous solution at pH = 5.0 [8]. In 2008 the removal of arsenic ions from wastewater using different composites of Ppy were investigated. It is reported that the composites of Ppy with PVA, Ppy with PEG, Ppy with activated carbon and Ppy with bentonite have shown the efficiency of 64.66%, 83.33%, 6.44% and 97.33%, respectively [9]. Ppy coated on wood sawdust (Ppy-SD) for removal of Cr (VI) ion from aqueous solutions has shown ~ 100% metal uptake under acidic or neutral conditions. The application of Ppy and PANi conducting polymers were investigated for the removal of thiocyanate ions from wastewater. The results have shown 40% uptake in pH ~2 using PANi/SD and 90% uptake using Ppy/SD in PH 2-9, respectively [11, 31]. Ppy coated

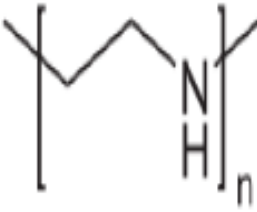
reticulated vitreous carbon electrodes were used for the removal of cadmium from aqueous solution, in these experimental conditions, the highest efficiency value (84%) for cadmium removal is achieved when electrolysis is carried out for 90 min at -3.00 V [33]. Ppy/silica nanocomposites have caused the highest efficiency value (84%) for cadmium removal when electrolysis is carried out for 90 min at -3.00 V [20]. The potentiostatic humic acid/polypyrrole (HA- Ppy) electrode modification made possible complexed Cu (II) extraction from drinking water synthetic samples with an efficiency of up to 72% [21].

But no effort has been done to use the Ppy alone as an adsorbent for the removal of heavy metals from wastewater. Thus, the present effort, in first step, has been made to evaluate Ppy as an adsorbent for the removal of heavy metals from wastewater.

2. 4 Polyethylenimine (PEI)

Linear polyethylenimines (PEIs) contain all secondary amines, in contrast to branched PEIs which contain primary, secondary and tertiary amino groups. The linear PEIs are solids while branched PEIs are liquids. This conducting polymer is soluble in hot water, cold water at low pH, methanol and ethanol. One end of the polymer chain has methyl and on the other end is hydroxyl. PEI possesses quite a number of advantages as polymer chelating agent, such as good water solubility and suitable molecular weights.

Table 2. 3: Properties of PEI**Table: Properties of Pyrrole**

Properties	Descriptions
Appearances	dense and viscous colorless liquid
Molecular formula	$(C_2H_5N)_n$
	
Molecular weight	variable
Boiling point	100°C
Melting point	73-75°C
Vapor pressure	9 mm Hg (20 °C)

2. 4. 1 Polyethylenimine as an adsorbent

Polyethylenimine (PEI) is well known for its metal chelating potential owing to the presence of amino groups. It has been widely used for the retention of metal ions; however to work as a water soluble polymer, it requires additional techniques for effective removal such as membrane support or ultra-filtration.

It has also been used mainly for the removal of single or a few metal ions [22].

2. 4. 2 Related past research

Adsorption of mercury from aqueous solutions by polyethylenimine-modified wool fibers was reported in 1974. It is observed that the adsorptive capacity of wool for mercury (Hg) is substantially increased by polymerization of ethylenimine onto the fibers [23].

In 2003, the decontamination of synthetic Pb(II), Zn(II), Cd(II) and Ni(II) solutions were investigated using silica gels chemically modified with poly (ethylenimine) (PEI) as sorbents [24]. Resins with phosphonemethyl cross linked with branched polyethylenimine (PEI) were used for the study of the uranium recovery from seawater in 2003 [31]. PEI, a positively charged polyelectrolyte was used as an adsorbent for selective separation [25]. Water-soluble polymer, polyethylenimine (PEI) was used for the simultaneous separation and pre concentration of trace Cu and Mn. For this purpose, the sample and the PEI solution were mixed and the metal-bound polymer was precipitated by adding acetone [26]. Highly functionalized polymer (polyethylenimine methylenephosphonic acid (PEIMPA)) possessing phosphonic and amine moieties as chelating groups was studied as a new ion-exchange material [29]. It was investigated that long-chained polymer which consists predominantly of hydrocarbon components with attached with amine groups will be an idealism prenation compound for enhancing metal affinity of activated carbon (AC) and at the same time, enhances its selectivity [28]. Justifications for selecting PEI depends on the

excellent chelating abilities, high content of functional groups, good water solubility and chemical stability [30]. Polyethylenimine (PEI) which is well known for its metal chelating potential was cross-linked by epichlorohydrin (ECH) in order to convert it into a water-insoluble form for direct use as an adsorbent [22].

2. 5 Adsorption systems

Batch method and column method are the most common adsorption systems. In this research, removal of heavy metals from aqueous solution has been done by using the batch method.

2. 5. 1 Column system

Column system is one of the most common ways to treat wastewater which has several types of design and varied materials as an adsorbent. The simple design of such columns is shown in Fig 2.4.

An ion-exchange resin or ion-exchange polymer is an insoluble matrix (or support structure) normally in the form of small (1–2 mm diameter) beads, usually white or yellowish fabricated from an organic polymer substrate. The material has highly developed structure of pores on the surface which can trap and release ions.

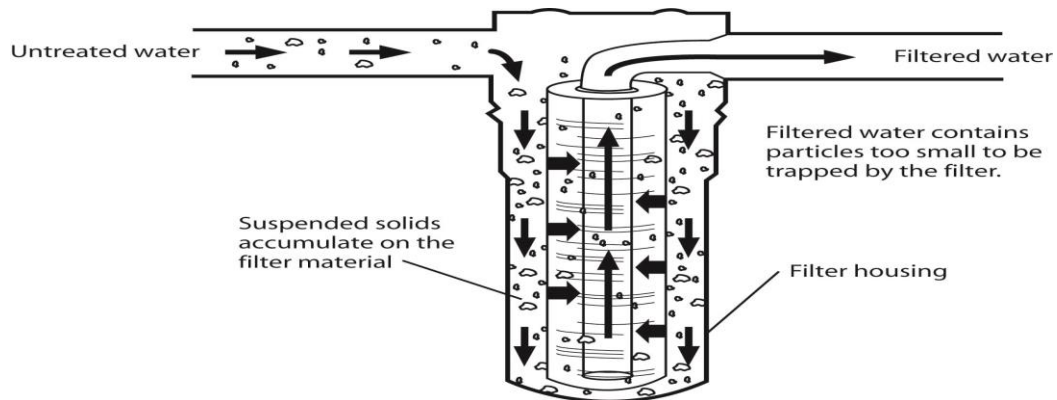


Figure 2. 4: Simple column system.

The trapping of ions takes place only with simultaneous releasing of other ions; thus the process is called ion-exchange. There are multiple different types of ion-exchange resin which are fabricated to select one or several different types of ions.

Ion-exchange resins are widely used in different separation, purification, and decontamination processes. The most common examples are water softening and water purification. In many cases ion-exchange resins were introduced in such processes as a more flexible alternative to the use of natural or artificial zeolites. Ion exchange resins are used in columns, in principle it is similar to those used for sand filters or activated carbon. Pressure vessels, usually made of rubber-lined steel. Small units are made of fiberglass reinforced plastic used in the food industry are often made of stainless steel.

A typical ion exchange column with co-flow regeneration is represented below:

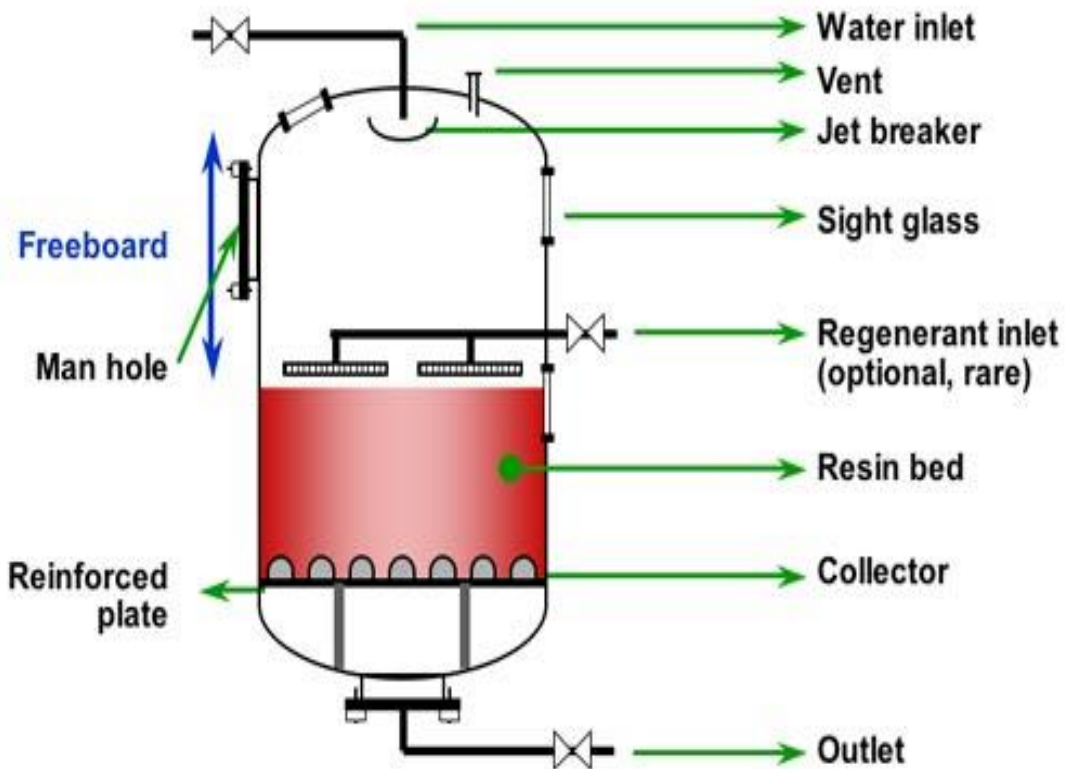


Figure 2. 5: Co-flow regenerated column.

2. 5. 2 Batch method

Batch distillation refers to the use of distillation in batches, meaning that a mixture is distilled to separate it into its component fractions before the distillation still is again charged with more mixture and the process is repeated. This is in contrast with continuous distillation where the feedstock is added and the distillate drawn off without interruption. Batch distillation has always been an important part of the production of seasonal or low capacity and high-purity chemicals. Batch system is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units.

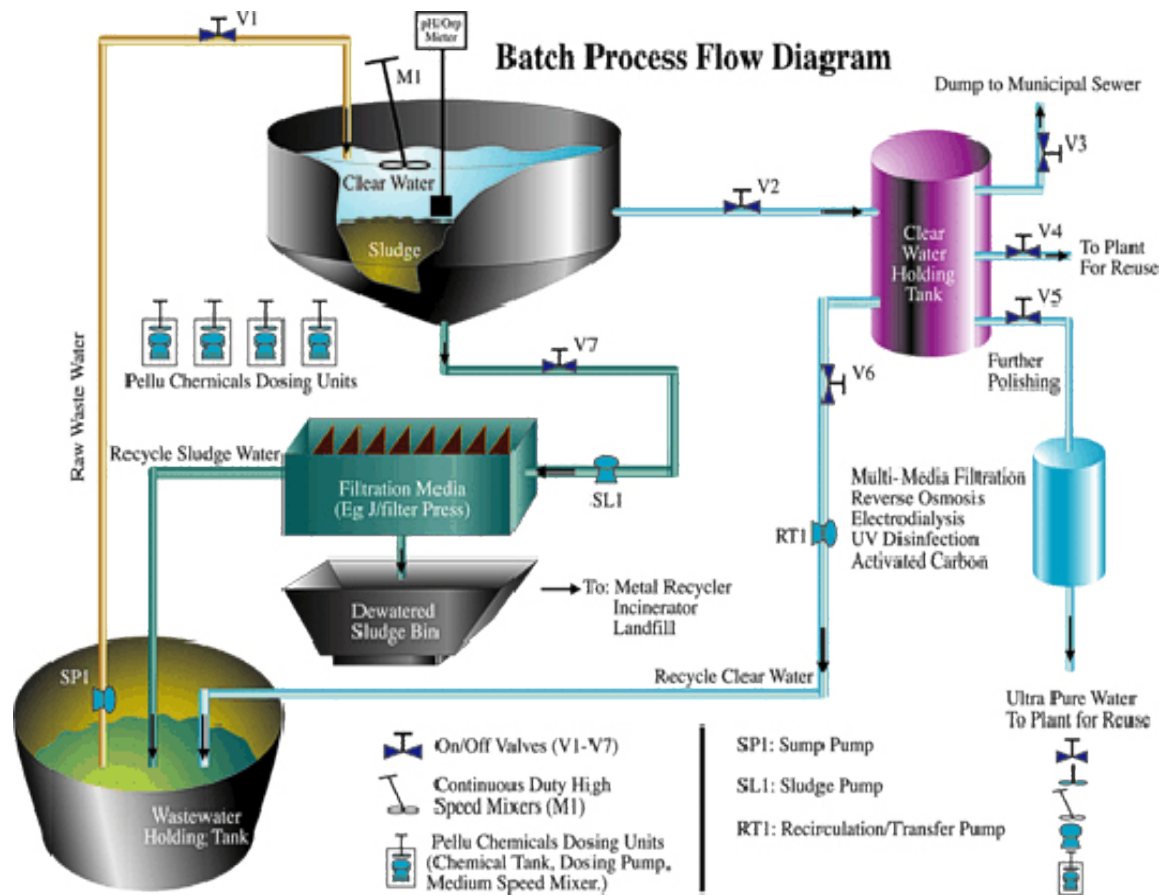


Figure 2. 6: Batch process flow diagram.

2. 6 Characterizations

2. 6. 1 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In an analytical chemistry, the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in a solution or directly in a solid sample. Atomic absorption spectrometry was first used as an analytical technique, and the underlying principles were established in the second half of the 19th century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany.

Principles

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies on Beer-Lambert Law. The electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique of its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a

detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using Beer-Lambert Law.

Instrumentation

In order to analyze a sample for its atomic constituents, the sample has to be atomized. The atomizers most commonly used nowadays are flames and electro thermal (graphite tube) atomizers. The atoms should then be irradiated by the optical radiation and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.

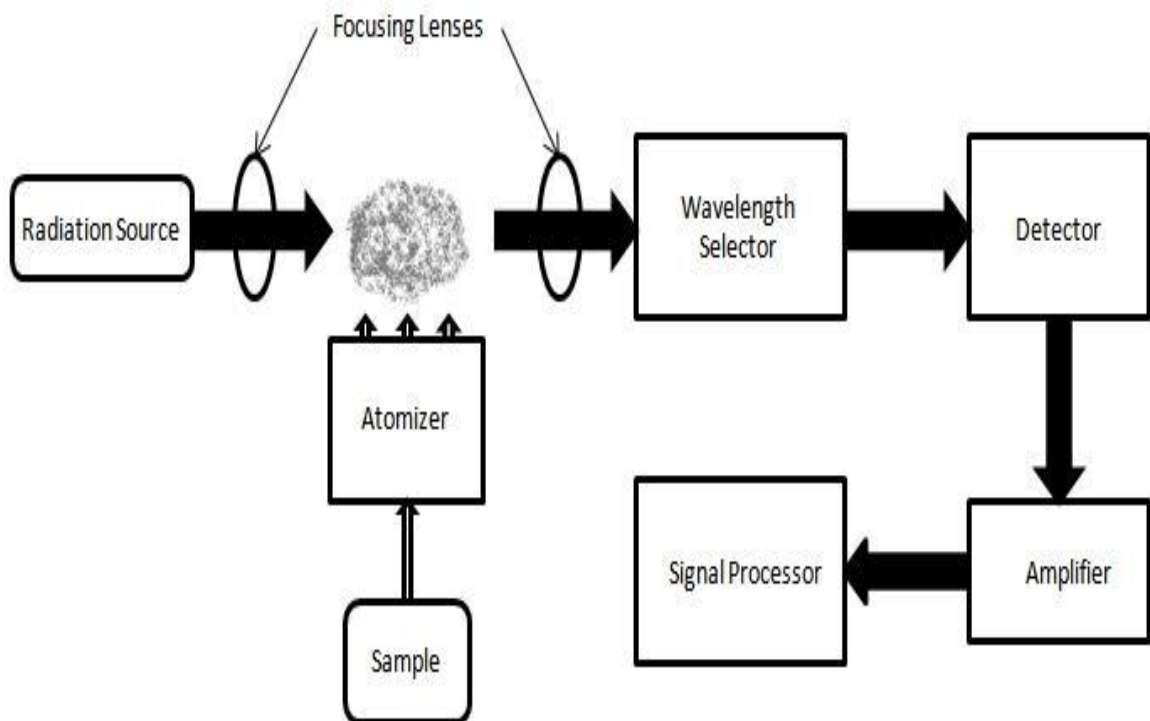


Figure 2. 7: Schematic Atomic Adsorption Spectroscopy.

2. 6. 2 Calibration curve

Calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of a known concentration. A calibration curve is one approach to the problem of instrument calibration. Other approaches may mix the standard into the unknown sample which gives an internal standard.

The calibration curve is a plot of how the instrumental responses, the so-called an analytical signals, changes with the concentration of the analyte (the substance to be measured). The operator prepares a series of standard solution in a range of expected concentrations. The concentrations of the standard samples must be within the working range of the technique (instrumentation) used. Analyzing each of these standard samples using the chosen technique will produce a series of measurements. For the most analyses, a plot of instrument response vs. analyte concentration will show a linear relationship.

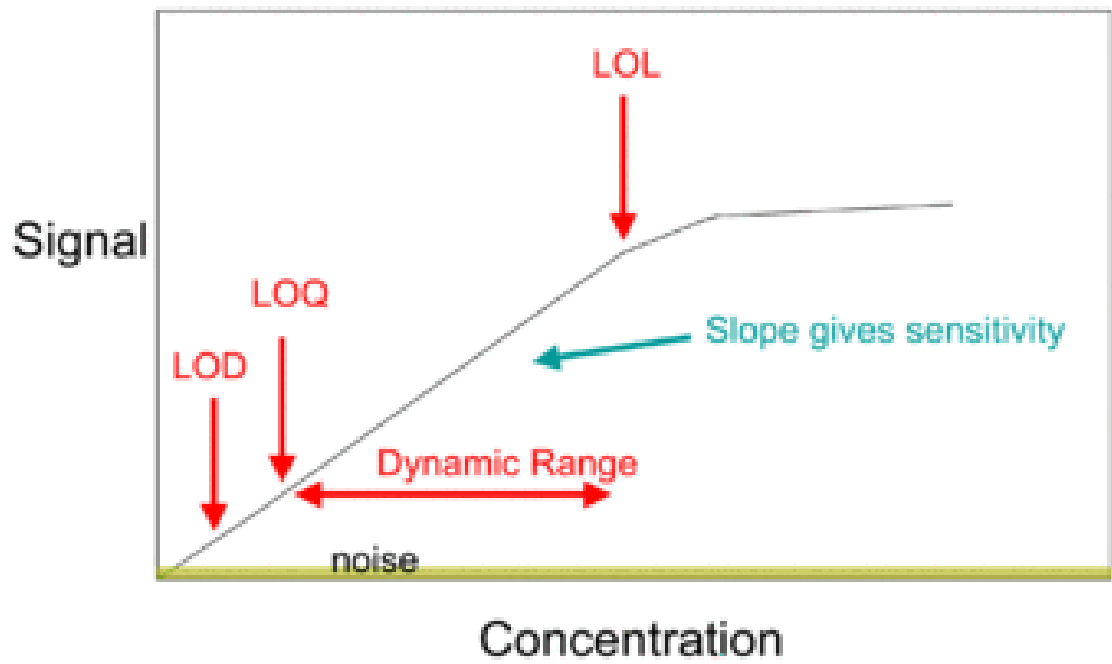


Figure 2. 8: Calibration curve.

2. 6. 3 Fourier Transform Infra-Red (FTIR)

An infrared spectrum can be obtained by passing infrared radiation through a sample of the compound. When a compound is bombarded with radiation of a frequency that exactly matches the frequency of one of its vibrations, the molecule will absorb energy. This allows the bonds to stretch and bend a bit more. Thus, the absorption of energy increases the amplitude of the vibration, but does not change its frequency. By experimentally determining the wave numbers of the energy absorbed by a particular compound, the kind of bond can be ascertained as each stretching and bending vibration of a bond in a molecule occurs with a characteristic frequency. FTIR spectrometer has several advantages as its sensitivity is better because, instead of scanning through the frequencies, it measures all frequencies simultaneously. The spectra of all polymer films were recorded on Spotlight 400 Perkin-Elmer Spectrometer with 15 scanning numbers using attenuated total reflectance (ATR) method. The wavelength was recorded from region 650 to 4000 cm^{-1} at room temperature. FTIR-ATR is a simple, direct, flexible and sensitive in-situ IR technique.

2. 6. 4 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in a high vacuum, a low vacuum and in an environmental SEM, specimens can be observed in wet condition. The types of signals produced by a SEM

include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with the atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic of the three-dimensional appearance useful for understanding the surface structure of a sample.

Sample preparation for SEM analysis

In this study, all of the samples were in a finely powdered form. For the SEM imaging these samples could be used without being coated with gold or titanium. The samples were placed on the carbon tape and the images were taken without using any coatings.

2. 6. 5 Brunauer, Emmett and Teller Adsorption Model (BET)

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett and Edward Teller published an article about the BET theory in a journal for the first time; "BET" consists of the first initials of their family names.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption to multilayer adsorption with the following

hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by (1):

$$\frac{P}{V_{total}(P - P_0)} = \frac{1}{V_{mono}C} + \frac{c-1}{V_{mono}C} \left(\frac{P}{P_0} \right) \quad (1)$$

P and P_0 are the equilibrium and the saturation pressure of adsorbents at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and v_m is the monolayer adsorbed gas quantity. c is the BET constant, which is expressed by (2):

$$c = \exp \left(\frac{E_1 - E_L}{RT} \right) \quad (2)$$

E_1 is the heat of adsorption for the first layer and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

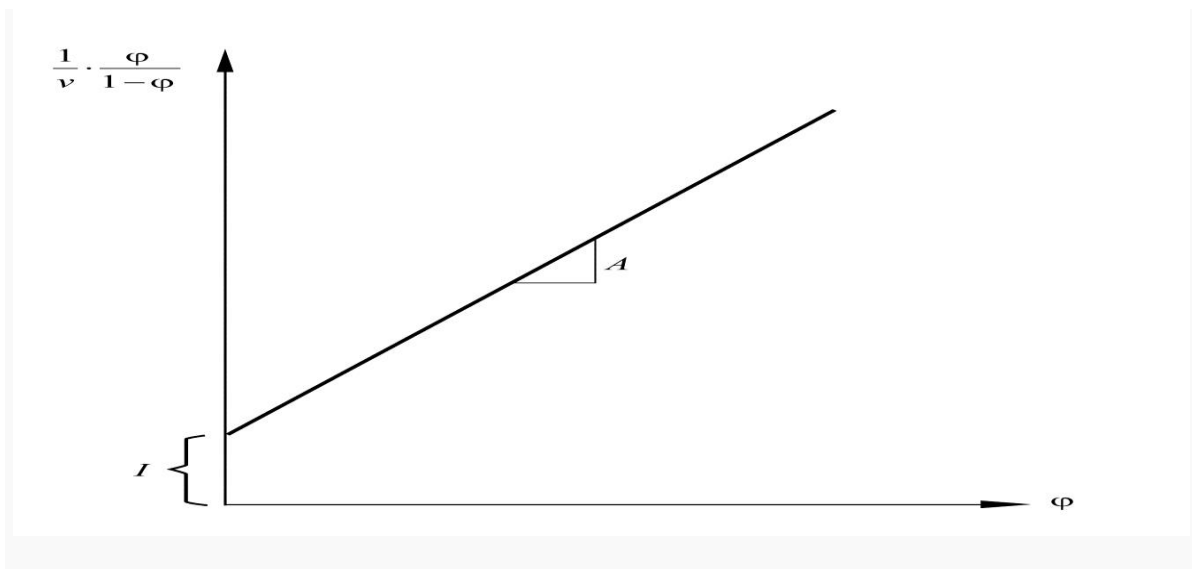


Figure 2. 9: BET plot.

Equation (1) is an adsorption isotherm and can be plotted as a straight line with $1/v[(p_0/p) - 1]$ on the y-axis and $\phi = p/p_0$ on the x-axis according to

experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of $0.05 < p/p_0 < 0.35$. The value of the slope A and the y-intercept I of the line are used to calculate the monolayer of the adsorbed gas quantity v_m and the BET constant c . The following equations can be used:

$$c = 1 + \frac{A}{I} \quad (4)$$

The BET method is widely used in a surface science to calculate the surface areas of solids by physical adsorption of gas molecules. A total surface area S_{total} and a specific surface area S are evaluated by the following equations:

$$S_{BET, total} = \frac{(v_m N s)}{V} \quad (5)$$

$$S_{BET} = \frac{S_{total}}{a} \quad (6)$$

Where v_m is in units of volume which are also the units of the molar volume of the adsorbate gas.

N : Avogadro's number,

s : adsorption cross section of the adsorbing species

V : molar volume of adsorbate gas

a : mass of adsorbent (in g)

2. 6. 6 Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications of 10 x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy (SEM), field emission SEM (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1/2 nanometers.

Applications include

Semiconductor device cross section analyses for gate widths, gate oxides, film thicknesses, and construction details

Advanced coating thickness and structure uniformity determination

Small contamination feature geometry and elemental composition measurement.

Vacuum

The FESEM can be classified as a high vacuum instrument (less than 1×10^{-7} Pa in the ions pumps 1 and 2). The vacuum allows electron movement along the column without scattering and helps prevent discharges inside the instrument. The vacuum design is a function of the electron source due to its influence on the cathode emitter lifetime.

Field Emission Source

The function of the electron gun is to provide a large and stable current in a small beam.

There are two classes of emission source: thermionic emitter and field emitter. Emitter type is the main difference between the Scanning Electron Microscope (SEM) and the Field Emission Scanning Electron Microscope (FESEM).

Thermionic Emitters use electrical current to heat up a filament; the two most common materials used for filaments are tungsten (W) and lanthanum hexaboride (LaB₆). When the heat is enough to overcome the work function of the filament material, the electrons can escape from the material.

Thermionic sources have relative low brightness, evaporation of cathode material and thermal drift during operation. A field Emission is one way of generating electrons that avoids these problems. A Field Emission Source (FES) also called a cold cathode field emitter, does not heat the filament. The emission is reached by placing the filament in a huge electrical potential gradient. The FES is usually a wire of tungsten (W) fashioned into a sharp point. The significance of the small tip radius (~ 100 nm) is that an electric field can be concentrated to an extreme level, becoming so big that the work function of the material is lowered and electrons can leave the cathode.

FESEM uses Field Emission Source producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM).

Anodes

The FESEM S-800 has two anodes for electrostatic focusing. A voltage (0 ~6.3 KV) between the field emission tip and the first anode, known as the extraction voltage, controls the current emission (1 ~ 20 mA). A voltage (1 ~ 30KV), known as the accelerating voltage, between the cathode and the second anode increases the beam energy and determines the velocity at which the electrons move into the column. This voltage combined with the beam diameter determines the resolution (capacity to resolves two closely spaced point as two separates entities). As a voltage increases, a better point-to-point resolution can be reached.

Electromagnetic lenses

To resolve a feature on the specimen surface, the beam diameter must be smaller than the feature (still containing high current density). Therefore it is necessary to condense the electron beam. To assist in the demagnification of the beam, electromagnetic lenses are employed.

The Table 2.4 shows the cross over diameter, final spot diameter and demagnification for a thermionic and a field emitter. Since the cross over diameter in the Field Emission Source is smaller, a lower level of the beam condensation is necessary to have a probe which is useful for image processing. This makes the FESEM the highest resolution instrument.

Table 2. 4: Demagnification of the beam

Electron source	Cross over diameter	Final spot diameter	Demagnification
Thermionic	(10-50) mm	1 nm - 1mm	10,000-50,000
Field Emission Source	10 nm	1 nm	10

Electron beam and Specimen interaction

The specimen and the electron beam interact in both elastic and inelastic fashion giving different type of signals. Elastic scattering events are those that do not affect the kinetic energy of the electron even when its trajectory had been affected. Inelastic scattering events

are a result of the energy transference from the electron beam to the atoms in the specimen. As a result the electrons have energy loss with a small trajectory deviation. Some of the signals created in this way are secondary electrons (SE), Auger electrons and X-Rays. Each of these signals gets specific information about topography, crystallography, surface characteristics, specimen composition and other properties.

2. 6. 7 Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or the chemical characterization of a sample. It relies on the investigation of an interaction of some sources of X-ray excitation and a sample. Its characterization capabilities are due in large part of the fundamental principle that each element has a unique atomic structure, allowing unique set of peaks on its X-ray spectrum.^[2] To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied. Each atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was before excited. The electron from an outer, higher-energy shell then goes back to the previous level of energy to fill the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is the characteristic of the difference in energy between the two shells and the atomic structure of the element, the elemental composition of the specimen can be determined.

CHAPTER III

EXPERIMENTAL PROCEDURE

CHAPTER III: EXPERIMENTAL PROCEDURE

3. 1 Polypyrrole Adsorbent

The conducting polymer polypyrrole used in this study as an adsorbent for the removal of heavy metals like zinc, copper, nickel, lead and cadmium from wastewater was prepared by chemical method. The prepared polypyrrole adsorbent was characterized for its functional groups by FT-IR, surface area by BET analysis and morphology by SEM. The solution was analyzed by AAS for its metal ion concentration before and after adsorption.

3. 1. 1 Chemicals and Solvents

All the reagents used were from commercially available high purity (Aldrich). Pyrrole was purchased from Sigma–Aldrich. Distilled water was used throughout this work. Stock solutions of zinc, copper, nickel, lead and cadmium were prepared by dissolving the respective heavy metal nitrates (Fulka) in distilled water. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and polyethylenimine (LMW & HMW) were purchased from Sigma Aldrich.

3. 1. 2 Pyrrole distillation

The monomer pyrrole was distilled before polymerization. It was purified by simple distillation. Pyrrole is a monomer with the molecular weight of 67.09 g/mol and the boiling point between 129-131 °C. To prevent from the bumping of the pyrrole during the distillation, some glass beads were added to the pyrrole. The clean and colorless drops of distilled pyrrole were collected at 130 °C.

3. 1. 3 Preparation of polypyrrole

The different mole ratios of pyrrole (monomer) to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (oxidant) used in this study was 1:0.33, 1:0.5, 1:1, 1:2 and 1:3. In each time, 0.33 g of pyrrole was taken in 30 ml of distilled water under stirring condition. Based on the mole ratios, the required amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 ml of distilled water in a separate beaker. Later, this solution was added to the pyrrole solution and the color of the mixture was found to change from green to complete black indicating the formation of polypyrrole product. After 1 hour of polymerization, the black mixture was filtered and washed several times with distilled water to remove the excess oxidant. Finally, it was dried in vacuum oven at 60°C for 24 hours.

3. 2 Polypyrrole modified by polyethylenimine

Polyethylenimine was added to the structure of polypyrrole to enhance its adsorption capacity by modification of the polypyrrole. Polyethylenimine has been known to adsorb heavy metals from aqueous solution.

3. 2. 1 Synthesis of Ppy/ PEI

The preparation condition of modified polypyrrole by using polyethylenimine is shown in Tables 3. 1 and 3. 2.

Table 3. 1 Methods for the preparation of Ppy/ PEI

Methods	Method 1	Method 2	Method 3
Ppy/PEI preparation	<p>1. PEI was added to 10 ml distilled Water for 10 minutes.</p> <p>2. FeCl₃.6H₂O was added to 30 ml distilled water for 15 minutes under stirring condition.</p> <p>3. Mix 1 and 2.</p> <p>4. Monomer Py was added to 10 ml water.</p> <p>5. Mixture 4 was added to mixture 3 and left for 1 hour for polymerization under stirring.</p>	<p>1. PEI was added to 10ml distilled water.</p> <p>2. FeCl₃.6H₂O was added to 30 ml distilled water.</p> <p>3. Mix 1 & 2.</p> <p>4. Add monomer directly to this mixture and stirred for 1 hour.</p>	<p>1. Py was added to 10 ml distilled water.</p> <p>2. PEI was added to distilled water.</p> <p>3. FeCl₃.6H₂O was added to 30 ml distilled water.</p> <p>4. Mixtures 2 & 3 were added at the same time to mixture 1 and left for 1 hour reaction under stirring condition.</p>

After preparation, treatment experiments were carried out, concentrated on these 18 products for the removal of 5 heavy metals (Ni, Cu, Cd, Zn and Pb) from wastewater.

Table 3. 2: Preparation conditions of Ppy/ PEI

Effective parameters	Different conditions				
Preparation technique	Method 1	Method 2		Method 3	
Ratio of the composition (monomer/oxidant)	1:3	1:2	1:1	1:0.5	1:0.33
PEI molecular weight	LMW~2500		HMW~ 25000		
Dosage of PEI, g	0.03	0.06		0.18	
Stirring speed	ON (200rpm)		OFF		

3. 3 Batch adsorption experiments

The batch adsorption was carried out for different concentrations of lead, cadmium, nickel, zinc and copper ions solutions with the polypyrrole adsorbent prepared from various mole ratios of monomer to oxidant. Polypyrrole- polyethylenimine adsorbent was used to increase the efficiency of zinc and cadmium removal. Based on the optimum amount of the adsorbent, the adsorption process was carried out. The adsorption efficiency was determined by measuring the difference between the initial and final concentrations of heavy metals. In this research, the concentrations of heavy metals ions in aqueous samples after treatment were analyzed by Atomic Absorption Spectroscopy (AAS) using a VARIAN Spectra A-10 PLUS in an air-acetylene and nitrous oxide-acetylene flame. By calculating the calibration data, linear through zero curves were determined. The correlation coefficient of the plot was 0.999 which indicated the higher accuracy of the results. By adding 0.08 g of polypyrrole to 25 ml of heavy metal solution, the treatment of wastewater was carried out for 8 hours. The mixture of the stock solution including heavy metal ions and polypyrrole was shaken in a thermostatic shaker at 200 rpm for 8 hours. The pH of stock solution was maintained at 7. After 8 hours, the wastewater was filtered and the treated water was sent for the measurement of the concentration of heavy metal ions by Atomic Absorption Spectroscopy (AAS).

3. 3. 1 Standard solution

Standard solution is a solution containing precisely known concentration of an element or a substance i.e., a known weight of solute is dissolved in to 100 ml of water to make a specific volume as shown in Table 3. 2. Standard solutions are used to determine the concentrations of other substances, such as solutions in titrations. The concentrations of standard solutions are normally expressed in units of moles per liter (mol/L, often

abbreviated to M for molarity), moles per cubic decimeter (mol/dm^3), kilomoles per cubic meter (kmol/m^3) or in a terms related to those used in particular titrations. For determination of the concentration of the stock solution after treatment, at least three standard solutions should be prepared to plot the calibration curve. The concentrations of these standard solutions were determined according to the default condition of the AAS instrument. All standard solutions were prepared in 100 ml volumetric flask. For the ease of preparation the scale was changed from milliliter to the microliter which can be measured using pipetter.

3. 3. 2 Sample preparations for AAS

Solutions containing heavy metals were prepared from 0.3 ppm to 8 ppm. Samples were prepared by following the equation 1 where M_1 is the concentration of the solution and V_1 is the initial volume of the solution while M_2 and V_2 are the finals concentration and volume of the solution, respectively.

$$M_1V_1 = M_2V_2 \quad (1)$$

3. 3. 3 Zinc standard solutions

In order to plot the calibration curve by AAS related to the elements, the concentrations of three standard solutions were prepared i.e., 0.3, 0.5 and 1 ppm. Based on the calibration curve the concentration of the stock solution after adsorption was measured.

Zinc (0.3 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 0.3 \times 100$$

$$M_1 = 0.03 \text{ ml}$$

$$M_1=0.03\times 1000=30\ \mu\text{l}\quad (\text{In } 100\ \text{ml of distilled water})$$

Zinc (0.5 ppm)

$$M_1V_1= M_2V_2$$

$$M_1\times 1000 = 0.5 \times 100$$

$$M_1= 0.05\ \text{ml}$$

$$M_1=0.05\times 1000=50\ \mu\text{l}\quad (\text{In } 100\ \text{ml of distilled water})$$

Zinc (1 ppm)

$$M_1V_1= M_2V_2$$

$$M_1\times 1000 = 1 \times 100$$

$$M_1= 0.1\ \text{ml}$$

$$M_1=0.1\times 1000=100\ \mu\text{l}\quad (\text{In } 100\ \text{ml of distilled water})$$

3. 3. 4 Copper standard solutions

The concentrations of the three standard solutions were prepared i.e., 1.3, 1.6 and 2 ppm.

Copper (1.3 ppm)

$$M_1V_1= M_2V_2$$

$$M_1\times 1000 = 1.3 \times 100$$

$$M_1= 0.13\ \text{ml}$$

$$M_1=0.13\times 1000=130\ \mu\text{l}\quad (\text{In } 100\ \text{ml of distilled water})$$

Copper (1.6 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 1.6 \times 100$$

$$M_1 = 0.16 \text{ ml}$$

$$M_1 = 0.16 \times 1000 = 160 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Copper (2 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 2 \times 100$$

$$M_1 = 0.2 \text{ ml}$$

$$M_1 = 0.2 \times 1000 = 200 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

3. 3. 5 Nickel standard solutions

The concentrations of the three standard solutions were prepared i.e., 1.3, 1.6 and 2 ppm.

By using these standard concentrations, the calibration curve was determined.

Nickel (1 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 1 \times 100$$

$$M_1 = 0.1 \text{ ml}$$

$$M_1 = 0.1 \times 1000 = 100 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Nickel (3 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 3 \times 100$$

$$M_1 = 0.3 \text{ ml}$$

$$M_1 = 0.3 \times 1000 = 300 \text{ } \mu\text{l} \quad (\text{In } 100 \text{ ml of distilled water})$$

Nickel (4 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 4 \times 100$$

$$M_1 = 0.4 \text{ ml}$$

$$M_1 = 0.4 \times 1000 = 400 \text{ } \mu\text{l} \quad (\text{In } 100 \text{ ml of distilled water})$$

3. 3. 6 Cadmium standard solutions

Three standard solutions were prepared with different concentrations such as 0.5, 2 and 4 ppm for determining the calibration curve of cadmium.

Cadmium (0.5 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 0.5 \times 100$$

$$M_1 = 0.05 \text{ ml}$$

$$M_1 = 0.05 \times 1000 = 50 \text{ } \mu\text{l} \quad (\text{In } 100 \text{ ml of distilled water})$$

Cadmium (2 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 2 \times 100$$

$$M_1 = 0.2 \text{ ml}$$

$$M_1 = 0.2 \times 1000 = 200 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Cadmium (4 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 4 \times 100$$

$$M_1 = 4 \text{ ml}$$

$$M_1 = 0.4 \times 1000 = 400 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

3. 3. 7 Lead standard solutions

The concentrations of the three standard solutions were prepared i.e., 4, 6, and 8 ppm.

Lead (4 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 4 \times 100$$

$$M_1 = 4 \text{ ml}$$

$$M_1 = 0.4 \times 1000 = 400 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Lead (6 ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 6 \times 100$$

$$M_1 = 0.6 \text{ ml}$$

$$M_1 = 0.6 \times 1000 = 600 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Lead (8ppm)

$$M_1V_1 = M_2V_2$$

$$M_1 \times 1000 = 8 \times 100$$

$$M_1 = 0.8 \text{ ml}$$

$$M_1 = 0.8 \times 1000 = 800 \text{ } \mu\text{l} \text{ (In 100 ml of distilled water)}$$

Table 3. 3: Standard solutions of the heavy metals

Heavy metals	Concentration (1ppm)	Concentration (2ppm)	Concentration (3ppm)
Zinc	0.3	0.5	1
Copper	1.3	1.6	2
Nickel	1.3	1.6	2
Lead	4	6	8
Cadmium	0.5	2	4

3.3.8 Heavy metal stock solutions

For the removal of heavy metals from wastewater, the stock solutions with different concentrations were prepared by using the same equations and calculations. The Considered concentrations of the stock solution consisting of analyzed metals were 1, 5, 10 and 15 ppm which were prepared by nitrate salts.

3.4 Wastewater treatment

To determining the concentration of heavy metal removal by adsorbents (polypyrrole), 25 ml of heavy metal stock solution was mixed with 0.08g of polypyrrole. Adsorption equilibrium experiments were carried out in a controlled temperature thermostatic shaker operated at 200 rpm for 8 hours. The final concentration of resultant solution was determined by atomic adsorption spectroscopy.

The removal efficiency was determined using Eq. (2).

$$E = \frac{C_0 - C_e}{C_0} \times 100 \% \quad (2)$$

C_0 and C_e are the initial and the equilibrium concentrations (mg/L) of lead respectively.

3.5 Isothermal study

The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether or not adjacent sites are occupied. In this study lead has been chosen as a representative of heavy metal to find the relationship between metal

concentration in solution and the amount of metal sorbed on a specific sorbent at a constant temperature.

3. 5. 1 Langmuir equation

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \quad (3)$$

Where q_e the amount of heavy metal (lead) is adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of metal ions (lead) required forming a monolayer (mg/g). The equilibrium sorption capacity (q_e) of the adsorbent was calculated using Eq. (4)[1].

$$q_e = \left(\frac{c_0 - c_e}{m} \right) V \quad (4)$$

The favorability of an adsorption process can be represented in terms of the dimensionless separation factor R_L , which is defined by the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where C_0 the initial concentration (mg/L) and b is the Langmuir constant (L/mg). The value of R_L represents the adsorption process to be unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $R_L < 1$ and irreversible when $R_L = 0$ [2]. The related calculation is shown in Appendix 2.

3. 5. 2 Freundlich equation

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption on heterogeneous surface can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

k_f and $\frac{1}{n}$ are the Freundlich constant and adsorption intensity, respectively. Equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of $\log q_e$ versus $\log C_e$ based on experimental data.

3. 5. 3 Favorable model

The results of Langmuir isotherm constants for the removal of heavy metal (lead) ions from wastewater are summarized in Table 3. 4.

Table 3. 4: Langmuir isotherm constants for the removal of lead from wastewater

Temperature	q_e	c_e	b	R_L	R^2
25°C	0.25	0.20	0.52	0.60	0.93
35°C	0.21	0.31	7.04	0.12	0.93
45°C	0.19	0.40	3.69	0.21	0.93

Adsorption process was carried out in different temperatures such as 25°C, 35°C and 45°C.

The R_L values were found to be between 0 and 1 which confirms that adsorption process is favorable in Langmuir model and the reaction is endothermic.

The isotherm plot indicates that type I adsorption isotherm is obtained and explains the formation of monolayer.

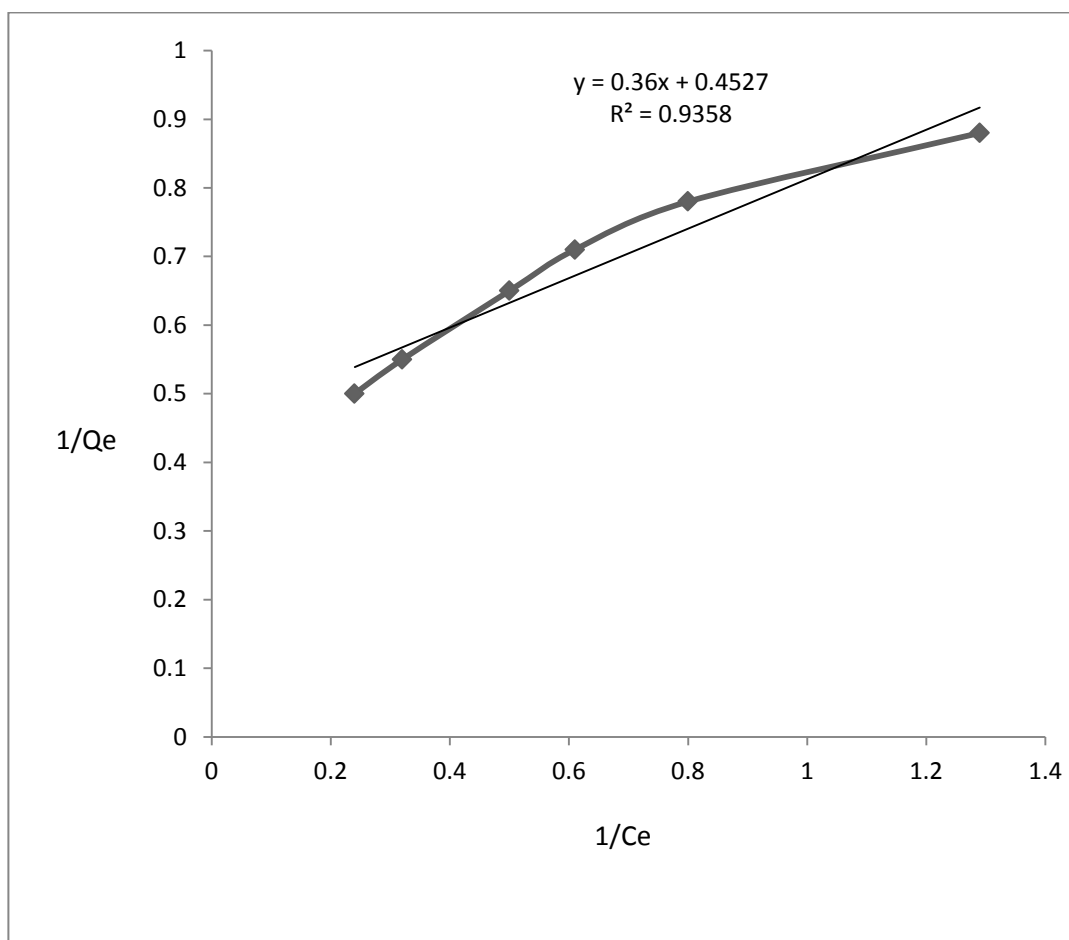


Figure 3. 1: Langmuir adsorption isotherm of polypyrrole for the removal of lead ions.

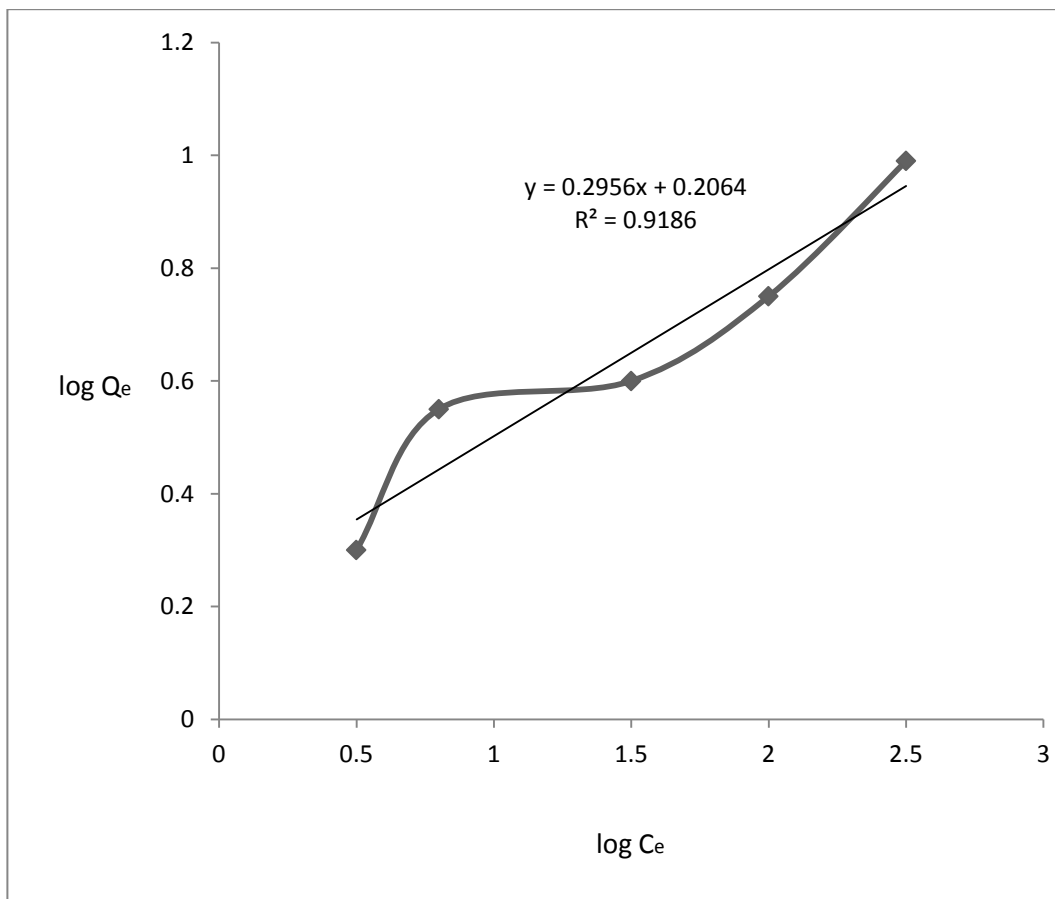


Figure 3. 2: Freundlich adsorption isotherm of polypyrrole for the removal of lead ion.

The correlation coefficient R^2 for Langmuir and Freundlich equation were found to be 0.7635 and 0.7409 respectively which indicate that the equilibrium adsorption data is working well under both equations. However higher value of R^2 indicates Langmuir adsorption model as the favorable model of adsorption.

CHAPTER IV

RESULTS AND DISCUSSION

CHAPTER IV: RESULTS AND DISCUSSION

4. 1 Removal of heavy metal ions

All the ratios of monomer to oxidant for the preparation of polypyrrole adsorbent were investigated to have comparable results (Appendix1). Among the different ratios of monomer to oxidant for the preparation of polypyrrole, the ratio 1:1 has been chosen as the best ratio which has given the best result. Therefore, the rest of the experiments were continued by using the adsorbent polypyrrole prepared from 1:1 monomer to oxidant ratio. The optimum amount of adsorbent was found to be 0.08 g of polypyrrole prepared from 1:1 mole ratio of monomer to oxidant.

Adding PEI to Ppy resulted higher efficiency in the removal of heavy metals from wastewater. It was observed that there is no significant difference in adsorption capacity between preparation with stirring and without stirring condition. The only differences are that the products under stirring condition produced fine powders while the products from without stirring condition are of coarse structures which are hard to make as a fine powder. Furthermore the products under stirring condition have black color while the products without stirring condition are gray. The experiments resulted higher adsorption capacity by using low molecular weight (LMW) polyethylenimine compared to polyethylenimine of high molecular weight (HMW). Furthermore it was observed that the equal amount of oxidant per monomer (or less amount of oxidant per unit mass of monomer) have caused more adsorption while the higher dosage of oxidant per monomer (ratio 1 monomer: 3 oxidant and 1 monomer: 2 oxidant) has caused less adsorption capacity.

4. 1. 1 Batch adsorption of lead ions form aqueous solution

The efficiency of each ratio for the removal of lead ions is reported in Table 10. High adsorption efficiency of polypyrrole (monomer/oxidant 1:1) which can uptake 100% of lead ions from wastewater is due to the less amount of oxidant. The less amount of oxidant may cause a very fine powder polymer with higher active sites while the polymerization with higher dosage of the oxidant produces a very tough polymer with less active sites available for the interaction with metallic ions. Detailed study is required to understand the role of dopins on the adsorption of heavy metals by Ppy. The shorter reaction time also may cause soft powder polymer due to the less polymerization which help to increase adsorption as well. In higher oxidant dosage (1:3) over-oxidation is likely to happen which can led to a less free and active sites of adsorption of the metallic ions although the polymerization will be more in progress. However, very low amount of oxidant ratio 1: 0.5 (monomer/oxidant) and 1:0.33 (monomer/oxidant) caused incomplete polymerization of polypyrrole giving lower percentage of efficiency.

Table 4.1: Adsorption efficiency of polypyrrole with different ratios of monomer to oxidant for the removal of lead ions from aqueous solution

Ratio of monomer/oxidant	1:3	1:2	1:1	1:05	1:0.33
Adsorption efficiency%	21	39	100	87	65

4. 1. 2 Effect of adsorbent dosage

The effect of dose of Ppy on the removal of lead ions is shown in Fig. 4. 1. It was observed that the efficiency increased with a decrease in dose. This increase (80% adsorption (0.05g of adsorbent) – 100% adsorption (0.1g of adsorbent)) in lead ion removal was due to the availability of higher number of lead ions per unit mass of Ppy. Further experiments were carried out using 0.08 g of Ppy per 25 ml of lead stock solution, as it exhibits appreciable removal, for optimization of the adsorption parameters. It was observed that the adsorption capacity decreased with an increase in adsorbent dosages. This decrease (100% adsorption (0.1g of adsorbent) – 50% adsorption (0.2 g of adsorbent)) can be due to over-saturation of the solution.

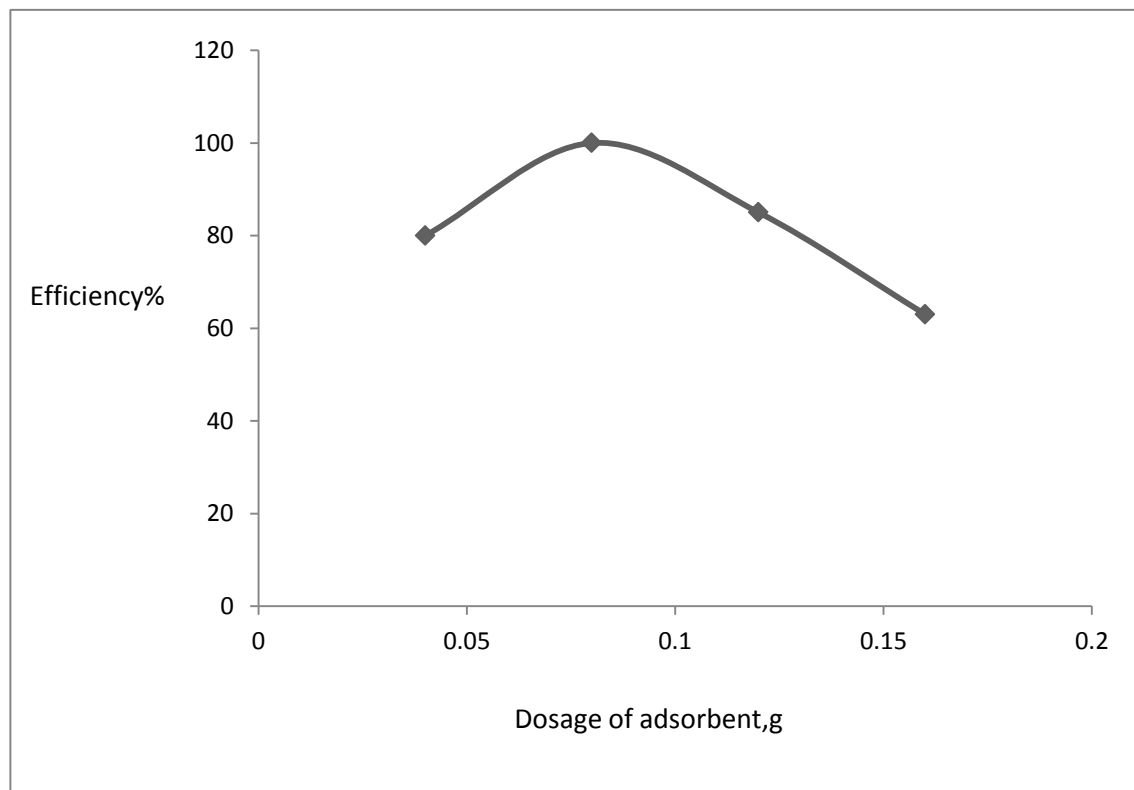


Figure 4. 1: Effect of dosage of adsorbent on the removal of heavy metal (lead) from aqueous solution.

4. 1. 3 Effect of contact time

Adsorption capacity of lead ion was measured as a function of time between 30 min to 24 hours by keeping all the other parameters constant. The effect of contact time on adsorption procedure is shown in Fig. 4. 2. The plot shows that the adsorption capacity increased with the increase of the contact time up to 8 hours beyond which there was no effect of contact time on the efficiency. The maximum level of efficiency thus was found in 8 hours at which the equilibrium was obtained. This is due to the more availability of active sites in primitive hours of adsorption. The favorable time was selected as 8 hours for further experiments.

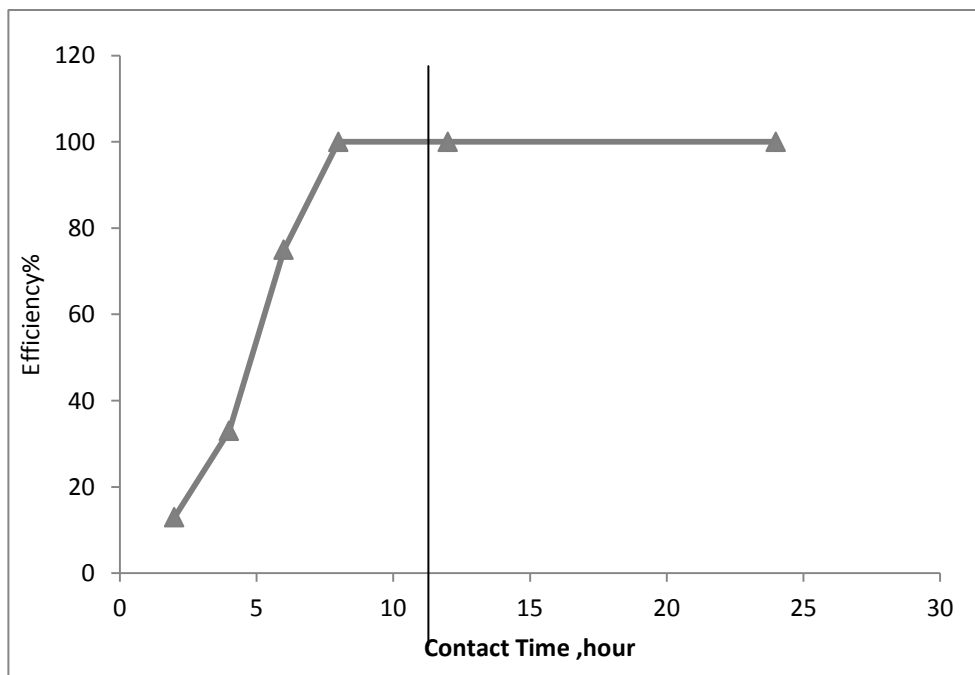


Figure 4. 2: Effect of contact time on the removal of heavy metal (lead) from aqueous solution. (The maximum efficiency was observed on 8 hours).

4. 1. 4 Effect of pH

One of the important controlling parameters in adsorption is pH. The effect of this factor is shown in Fig. 4. 3. It shows that the highest percentage (100%) of heavy metal removal of lead was found at pH=7. In lower level of pH (pH= 2) lower adsorption (~20%) was recorded but with the increase in pH, the efficiency increased up to 100% (pH= 7).The efficiency decreased by increasing the pH in alkaline condition (pH \geq 7).

At lower pH, majority of amine sites in polypyrrole adsorbent are protonated and cannot facilitate the chelating process. With the increase in pH from 2 to 7, protons are released from the amine functional groups of polypyrrole adsorbent which cause more available active amine sites for adsorption of heavy metal ions from aqueous solution. With further increase in pH above 7, the formation of the metal hydroxide renders the low adsorption of heavy metal ions by the adsorbent. Same observation also was reported by Ansari *et al.*, [11, 13 and 31].

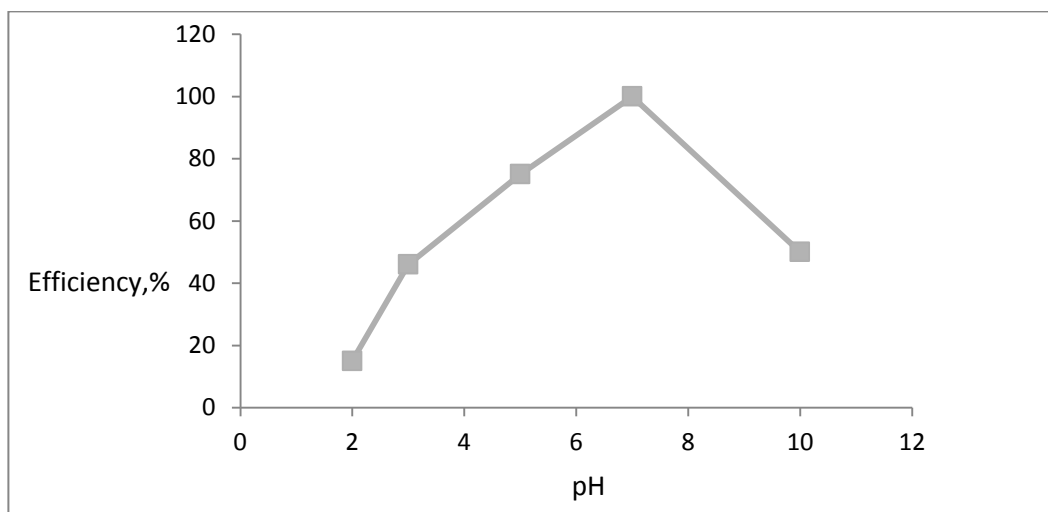


Figure 4. 3: Effect of pH on the removal of heavy metal (lead) from aqueous solution.

4. 1. 5 Effect of initial concentration

The effect of initial metal ion concentration of lead, zinc, copper, nickel and cadmium, on the percentage of their removal from aqueous solution is shown in Table 4. 2. The removal of heavy metal ions gradually decreased with the increase in the initial concentration of stock solution which is due to the higher number of heavy metal ions per unit mass of adsorbent. Similar results were also reported in past research works [13].

According to Table 4.2 it is observed that polypyrrole alone without any additional component has performed a very high efficiency for the removal of lead, nickel and copper with 100%, 100% and 99.99% adsorption, respectively. The higher efficiency of the Ppy/PEI in adsorption of the zinc and cadmium ions may be related to the chelating property of the PEI.

Table 4. 2: Removal of heavy metal ions from aqueous solution

The initial concentration of heavy metals (ppm)	Removal of heavy metal	Efficiency (%)
1	Cd	32.14
5		16.01
10		5.06
15		2.8
1	Cu	99.99
5		99.33
10		99.17
15		90.03
1	Zn	48.15
5		27.90
10		6.80
15		2.5
1	Pb	100
5		92.86
10		34.54
15		29
1	Ni	100
5		91.41
10		88.61
15		83.5

4. 2 Wastewater treatment using Ppy/ PEI as an adsorbent

Since Ppy alone could not exhibit high efficiency for the removal of zinc and cadmium, hence, Ppy adsorbent has been modified with PEI to have the combined effect of these two adsorbents for the removal of zinc and cadmium. The same procedure was carried out for the removal of heavy metal from wastewater using Ppy/PEI. The pH of stock solutions was controlled at pH=7. Water treatments have done by adding 0.08 g of adsorbent to the 25 ml of each stock solution and were shaken in a shaker (200 rpm) for 8 hours.

4. 2. 1 Effect of the mole ratio of monomer to oxidant in Ppy/PEI as an adsorbent

The effect of molar ratio on the adsorption of Zn and Cd is shown in Table 4. 3. The ratio (1:1) of monomer per oxidant was found to be the best.

Table 4. 3: Effect of molar ratio on Zn and Cd adsorption

Molar ratio of (Py/ Oxd) in Ppy/PEI	Removal percentage of Zn	Removal percentage of Cd
1:3	2.5%	6.8%
1:2	16.8%	12.8%
1:1	68%	53.9%
1:0.5	49.5%	32.1%
1:0.33	33%	30%

4. 2. 2 Effect of the concentration of PEI in Ppy/ PEI adsorbent

The effect of PEI concentration on the adsorption efficiency of Ppy/ PEI for the removal of Zn and Cd is shown in Table 4. 4.

Table 4. 4: Effect of PEI dosage on Zn and Cd adsorption

Dosage of PEI, g	0.03	0.06	0.18
Removal percentage of Zn	71%	62.3%	59%
Removal percentage of Cd	64.7%	41.2%	36.6%

The efficiency of the Ppy enhanced by adding the PEI to the structure of the Ppy in order to remove Zn and Cd.

4. 2. 3 Effect of zinc ion concentration

The effect of initial concentration of zinc solution on the adsorption of this element is shown in Table 4. 5.

Table 4. 5: Removal of zinc ions from aqueous solution using Ppy and Ppy/PEI

The initial concentration of zinc	The efficiency of Ppy/PEI
1 ppm	71.3%
5 ppm	49%
10 ppm	15.8%
15 ppm	12.4%

The highest efficiency was observed in 1ppm for the removal of Zn ions from wastewater.

4. 2. 4 Effect of cadmium ion concentration

Effect of initial concentration of cadmium solution on the adsorption of this element has shown in Tables 4. 6.

Table 4. 6: Removal of cadmium ions from aqueous solution using Ppy and Ppy/ PEI

The initial concentration of cadmium	The efficiency of Ppy/PEI
1 ppm	66.6%
5 ppm	37%
10 ppm	19.3%
15 ppm	9%

The highest efficiency for the removal of Cd ions from wastewater was also observed in 1ppm.

4. 2. 5 Wastewater treatment including all of the elements

The real wastewater sources such as industrial water, rain, rivers and etc., contains not only one element but also the pollutants. The mechanism of the competition between the elements to be adsorbed was studied. In this research work and as a final step of experiments, all of these 5 elements were added to the water to prepare the stock solution which is almost similar to the real wastewater.

Table 4. 7: Removal of heavy metal from mixed elements wastewater

Efficiency % Adsorbent	lead	nickel	copper	cadmium	zinc
Ppy	27%	3%	98%	12%	17%
Ppy/ PEI	5%	2%	98%	1%	3%

The same adsorption procedure was followed step by step 0.08 g of adsorbent was added to the 25 ml of wastewater with controlled pH at 7. The mixture was shaken for 8 hours at room temperature and finally was filtered through a filter paper to get the rid of excess .In competitive adsorption, copper shows the higher adsorption i.e., 98% efficiency. In second higher is the lead ions which were adsorbed (27%) and followed by zinc, 17% after treatment. Cadmium and nickel showed little efficiency like 12% and 3% respectively. The outstanding efficiency of Cu comes from the strong chelating agent of Cu than all other heavy metals [40]. This enables Cu to be removed with the highest efficiency of 98%. While copper occupies almost all of the active sites therefore there are less chances for the rest of the elements to be adsorbed.

4.3 Evidence of the formation of polymer

4.3.1 FTIR analysis

The FTIR result of polypyrrole to oxidant ratio (1:1) is shown in Fig 4. 4. The peak at 1520 cm^{-1} is due to C-C and C=C backbone stretching of Ppy and refers to the quinoid formation of polypyrrole. The band at 1432 cm^{-1} corresponds to the C-N stretching of Ppy and refers to the benzenoid form of the polypyrrole. The band at 1276 cm^{-1} is attributed to

C-H and C-N in-plane deformation modes of pyrrole. The band at 1126 cm^{-1} is related to C-C stretching of pyrrole. The band at 1015 cm^{-1} is due to N-H wagging and C-H stretching. The band at 756 cm^{-1} is attributed to C-H wagging vibration. Thus it shows that all the corresponding bands of Ppy are present in the spectrum.

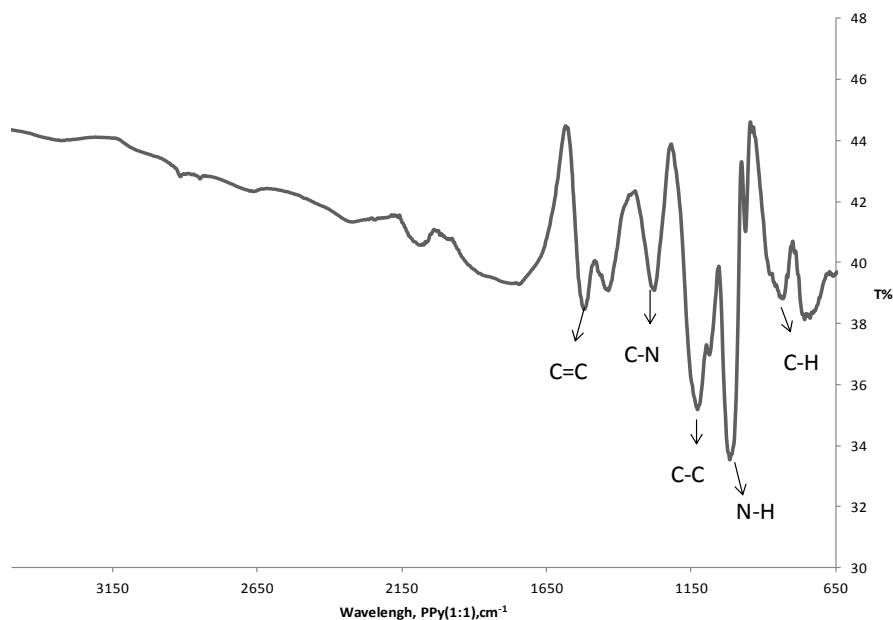


Figure 4. 4 FTIR spectrum of Ppy.

Fourier transforms infrared spectroscopy of the composite of polypyrrole and polyethylenimine is presented in Fig.4.5. The peak at 1135 and 2657 cm^{-1} is due to the C-N and N-H stretching vibration, respectively. The peak at 1523 cm^{-1} corresponds to quinoid formation of polymer and the peak at 1444 cm^{-1} represents the benzioid form of polymer.

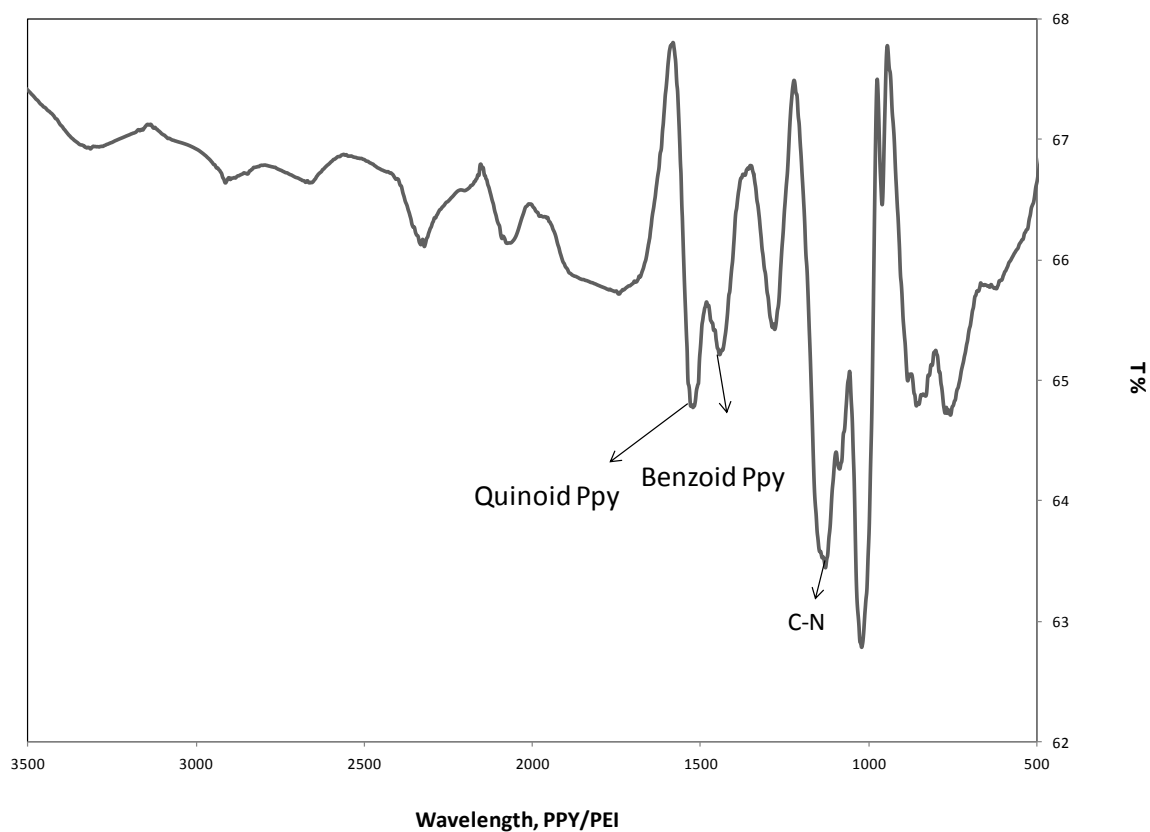


Figure 4. 5: FTIR spectrum of Ppy/PEI.

The FTIR overlapped patterns of Ppy and Ppy/PEI are presented in Fig 4. 6. The band at 1126 cm^{-1} which is related to C-C stretching of pyrrole shifted to the 1129 cm^{-1} and band at 1015 cm^{-1} is due to N-H wagging and C-H stretching shifted to the higher value, 1022 cm^{-1} . The band at 756 cm^{-1} which is attributed to C-H wagging vibration, has shifted to 758 cm^{-1} in the composite form. Interestingly, the peaks at 1434 cm^{-1} and 1518 cm^{-1} which are due to the formation of benzoied and quinoid chain represent the higher value of transmission in Ppy/PEI comparing to Ppy. The peak with the transmission of 39.5% and 38.5% in Ppy shifted to the 65.3% and 64.3% in Ppy/PEI, respectively.

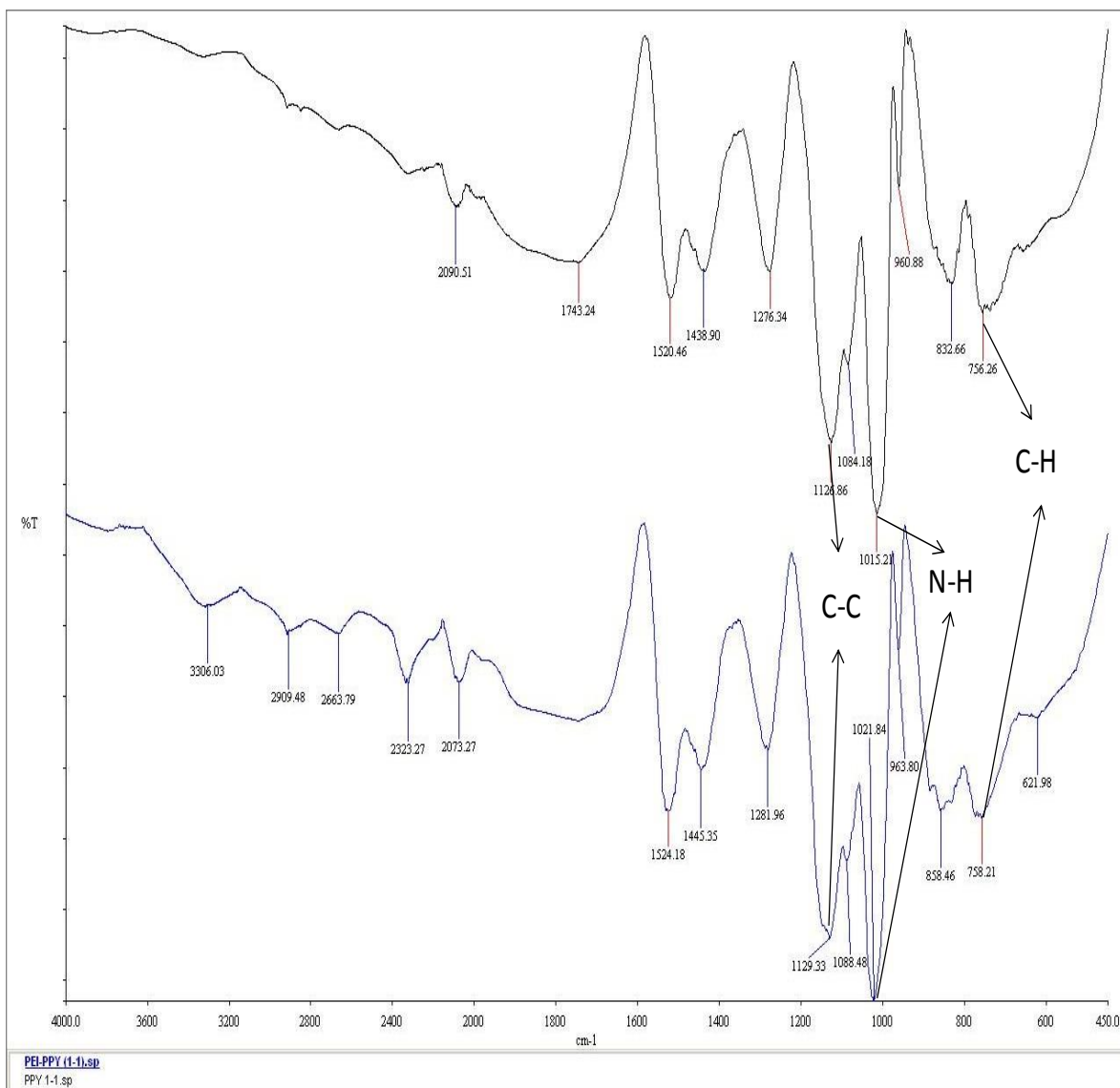


Figure 4. 6: Comparing between FTIR analysis of Ppy and Ppy/PEI.

4.3.2 FTIR analysis and presence of the element after adsorption

The overlapping of all spectrums including polypyrrole before and after adsorption of lead, copper, nickel, cadmium and zinc is shown in Figure 4. 7.

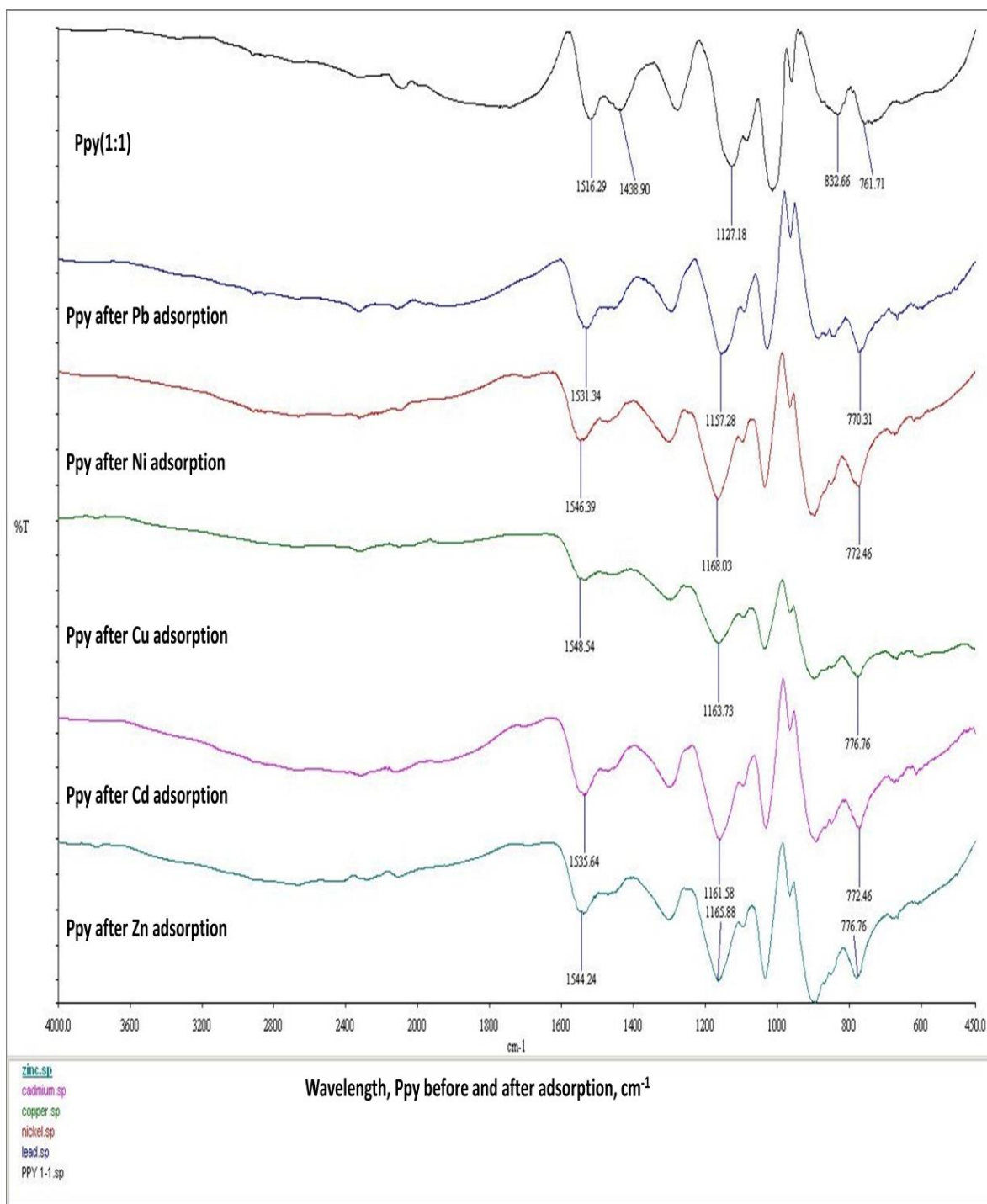


Figure 4.7: Fourier transforms infrared spectra, Ppy (1:1) before and after removal of lead, nickel, copper, cadmium and zinc from wastewater.

FTIR analysis after adsorption of lead ions from wastewater

The entire peak positions observed for Ppy before adsorption have shifted to higher wave numbers in the spectrum of Ppy after adsorption. The bands at 756 cm^{-1} , 1015 cm^{-1} , 1126 cm^{-1} , 1276 cm^{-1} , 1432 cm^{-1} and 1520 cm^{-1} observed in Ppy spectrum before adsorption have shifted to 774 cm^{-1} , 1029 cm^{-1} , 1152 cm^{-1} , 1295 cm^{-1} , 1451 cm^{-1} and 1530 cm^{-1} , respectively after adsorption. The red shift of all these bands in Ppy spectrum after adsorption and the distinct peak observed at 774 cm^{-1} due to metallic bond formation clearly indicates the adsorption of lead ions by Ppy

FTIR analysis after adsorption of nickel ions from wastewater

After removal of nickel from wastewater two additional peaks were observed at 617 cm^{-1} and 602 cm^{-1} . These new peaks are possibly due to the binding between nickel ion and nitrogen group of polypyrrole. The entire peak positions observed for Ppy before adsorption have shifted to higher wave numbers in the spectrum of Ppy after adsorption. The bands at 756 cm^{-1} , 1015 cm^{-1} , 1126 cm^{-1} , 1276 cm^{-1} , 1438 cm^{-1} and 1520 cm^{-1} which were observed in Ppy spectrum before adsorption have shifted to 774 cm^{-1} , 1035 cm^{-1} , 1164 cm^{-1} , 1303 cm^{-1} , 1493 cm^{-1} and 1539 cm^{-1} , respectively after adsorption. All these shifts and the peak observed at 774 cm^{-1} due to presence of metal ions in Ppy clearly indicates the adsorption of nickel ions by Ppy polymer.

FTIR analysis after adsorption of copper ions from wastewater

Only one additional peak was observed at 605.84 cm^{-1} . This new peak is possibly related to the presence of copper ions in the polypyrrole matrix after treatment. Furthermore the

bands at 756 cm^{-1} , 1015 cm^{-1} , 1126 cm^{-1} , 1276 cm^{-1} , 1432 cm^{-1} and 1520 cm^{-1} observed in Ppy spectrum before adsorption have shifted to 770 cm^{-1} , 1055 cm^{-1} , 1164 cm^{-1} , 1301 cm^{-1} , 1453 cm^{-1} and 1539 cm^{-1} , respectively after adsorption. All these shifted bands in Ppy spectrum after adsorption and the peak observed at 780 cm^{-1} due to metallic bond formation clearly indicates the adsorption of copper ions by Ppy polymer.

FTIR analysis after adsorption of zinc ions from wastewater

Intrestingly three new peaks at 609.23 cm^{-1} , 2281.35 cm^{-1} and 2430.50 cm^{-1} were found instead. The entire peak positions observed for Ppy before adsorption have shifted to higher wave numbers in the spectrum of Ppy after adsorption. The bands at 756 cm^{-1} , 1015 cm^{-1} , 1126 cm^{-1} , 1276 cm^{-1} , 1432 cm^{-1} and 1520 cm^{-1} observed in Ppy spectrum before adsorption have shifted to 779 cm^{-1} , 1034 cm^{-1} , 1164 cm^{-1} , 1302 cm^{-1} , 1464 cm^{-1} and the peak in 1539 cm^{-1} , respectively after adsorption. These shifted bands in Ppy spectrum after adsorption and the distinct peak observed at 779 cm^{-1} due to metallic bond formation clearly indicates the adsorption of zinc ions by Ppy conducting polymer.

FTIR analysis after adsorption of cadmium ions from wastewater

FTIR pattern of Ppy after removal of cadmium shows a new peak at 616 cm^{-1} and the disapearing of two peaks at 1799 cm^{-1} and 1742 cm^{-1} . Similar to the other results for the rest of elements, all peaks positions in the first pattern (FTIR before treatment) have shifted towards higher values in the second pattern (FTIR after treatment). The bands at 756 cm^{-1} , 1015 cm^{-1} , 1126 cm^{-1} , 1276 cm^{-1} , 1432 cm^{-1} and 1520 cm^{-1} observed in Ppy spectrum before adsorption have shifted to 772 cm^{-1} , 1031 cm^{-1} , 1160 cm^{-1} , 1298 cm^{-1} , 1471 cm^{-1} and 1538 cm^{-1} , respectively after adsorption. The peaks in Ppy spectrum after adsorption and

the distinct peak observed at 772 cm^{-1} was due to metallic bond formation clearly indicates the adsorption of cadmium ions by Ppy polymer.

The bands at 1015 cm^{-1} due to N-H wagging and 1276 cm^{-1} due to C-N in-plane deformation in polypyrrole before adsorption shifted to 1029 cm^{-1} and 1295 cm^{-1} , respectively after lead ion adsorption, 1035 cm^{-1} and 1303 cm^{-1} after nickel ion adsorption, 1055 cm^{-1} and 1301 cm^{-1} after copper ion adsorption, 1034 cm^{-1} and 1302 cm^{-1} after zinc ion adsorption and 1036 cm^{-1} and 1308 cm^{-1} after cadmium adsorption which also give further evidences of the metallic bond formation with nitrogen of polypyrrole.

Schematic diagram of possible metal ion adsorption on the surface of nitrogen functional groups in polypyrrole conducting polymer is shown in Figure 4. 8.

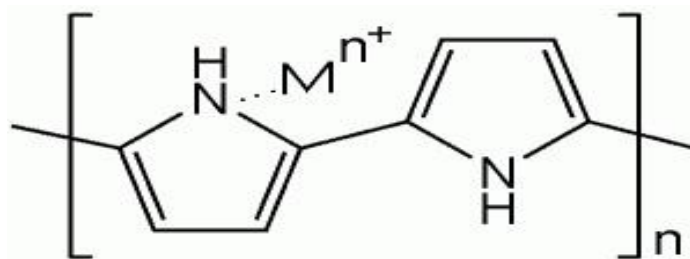


Figure 4. 8: The adsorption scheme of polypyrrole adsorbent for heavy metals (M^{N+}).

4.4 EDX

The Energy-dispersive X-ray spectroscopy has emphasized the presence of metallic ions deposited on the surface of polypyrrole after treatment with heavy metals from aqueous solution. The appearances of the indicative metallic signal are clearly seen.

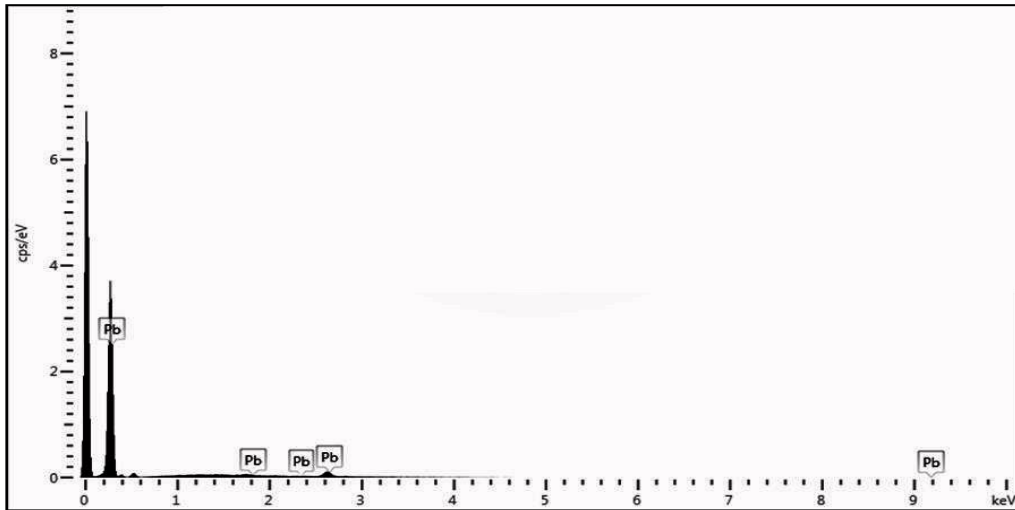


Figure 4. 9: EDX analysis of the constants of lead ion (count per second) per energy (KeV) inside the Ppy after adsorption.

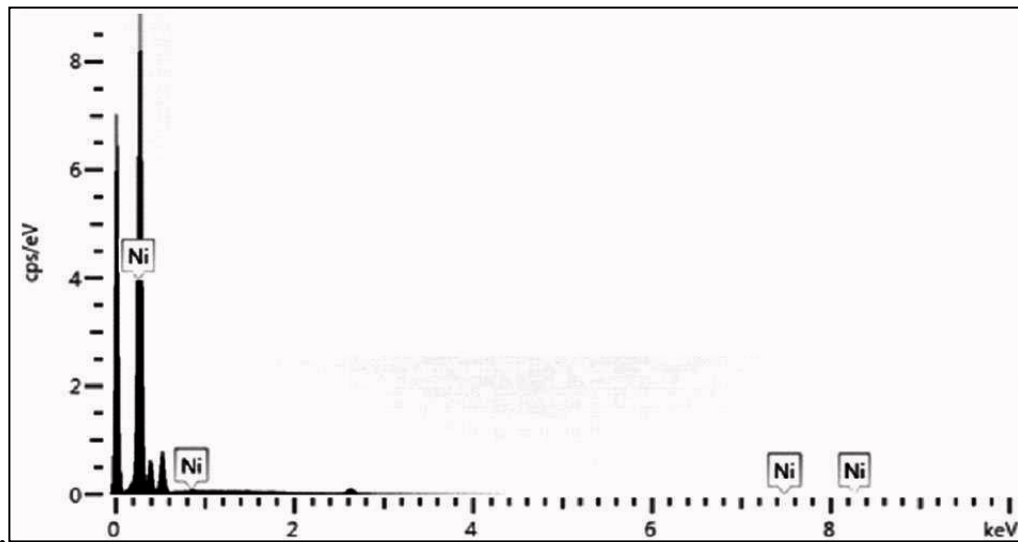


Figure 4. 10: EDX analysis of the constants of nickel ion (count per second) per energy (KeV) inside the Ppy after adsorption.

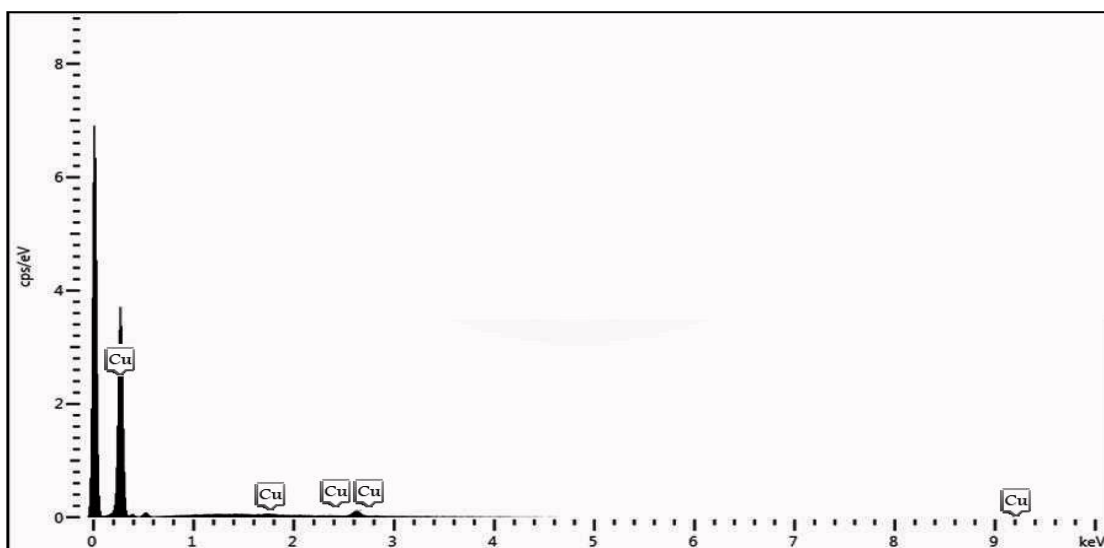


Figure 4. 11: EDX analysis of the constants of copper ion (count per second) per energy (KeV) inside the Ppy after adsorption.

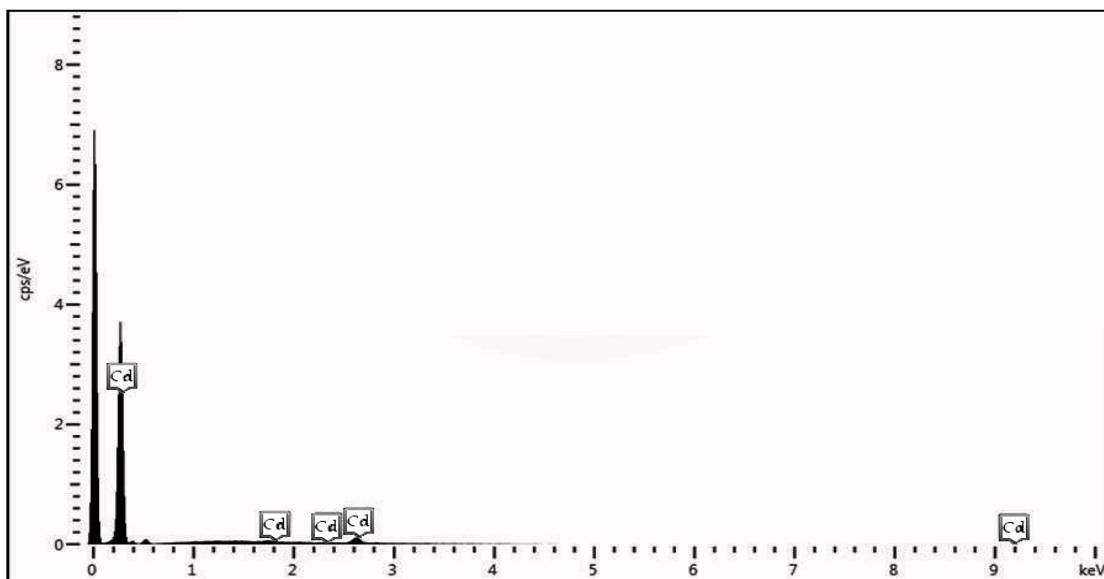


Figure 4. 12: EDX analysis of the constants of cadmium ion (count per second) per energy (KeV) inside the Ppy after adsorption.

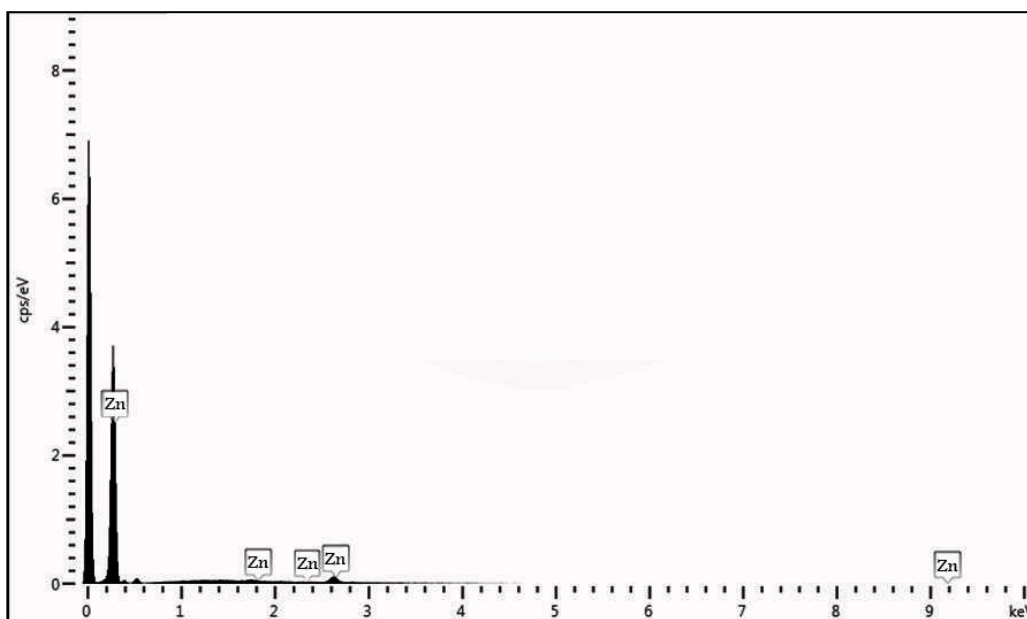


Figure 4. 13: EDX analysis of the constants of zinc ion (count per second) per energy (Kev) inside the Ppy after adsorption.

4.5 BET results

The BET results by comparing both samples have shown the higher pore volume [8.819 cc/g] in Ppy (1:1). According to the BET measurement, it was observed that Ppy (1:1) has smaller pore size [1.49 diameters] compare to Ppy (1:3) [3.12 diameters]. BET results have shown the lower surface area in Ppy (1:1) [5.095 m²/g] compare to Ppy (1:3) [20.36 m²/g]. The surface area does not play the main role in adsorption by polypyrrole since the nitrogen atoms in polypyrrole are only responsible for heavy metal adsorption. The similar results have been reported proving that there is no correlation with the adsorption of cadmium ions with the surface area and pore volume of nitrogen-rich carbon materials [41].

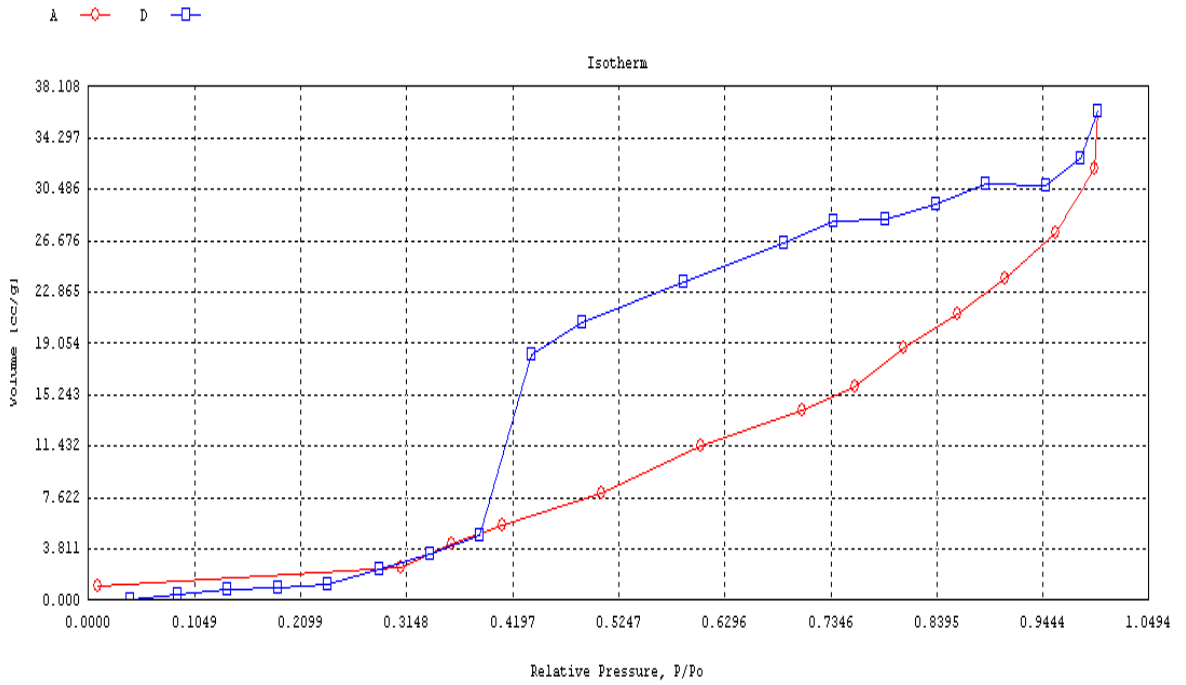


Figure 4.14: BET Isotherm plot, Ppy (1:1).

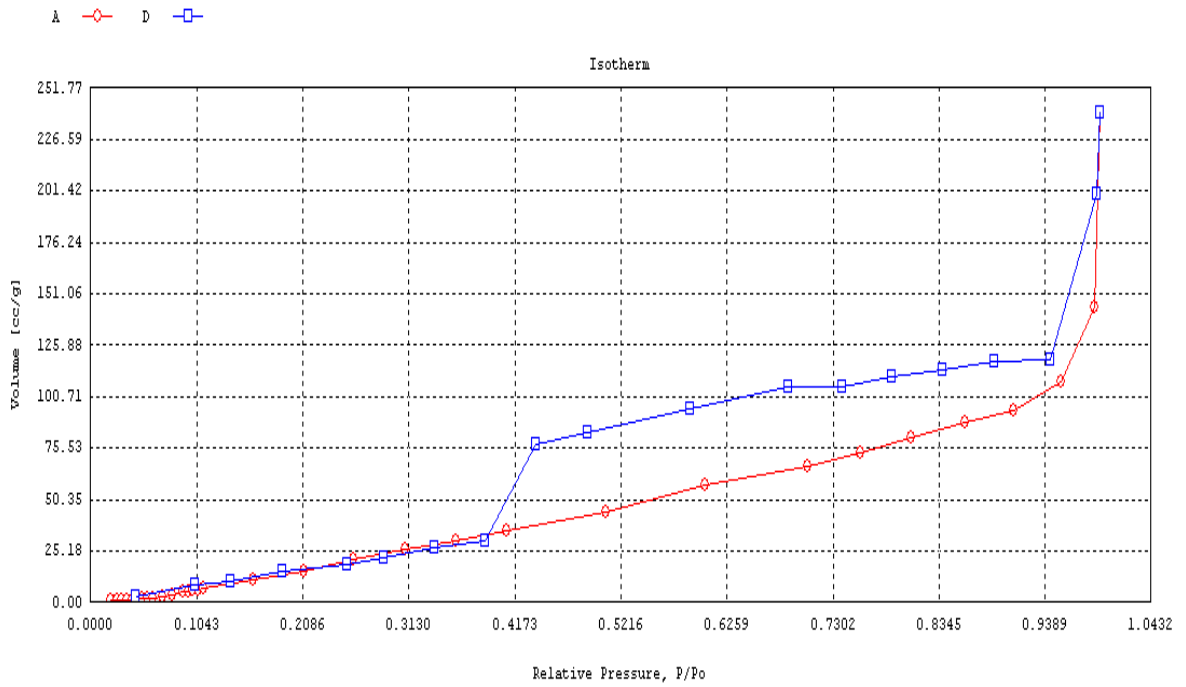


Figure 4.15: BET Isotherm plot, Ppy (1:3).

4.6 Scanning Electron Micrograph (SEM)

The SEM micrographs show the morphologies of Ppy before (a) and after adsorption of lead, nickel, copper, zinc and cadmium ions (b, c, d, e, and f) in Figure 4.16. No significant changes were observed after adsorption of metallic ions.

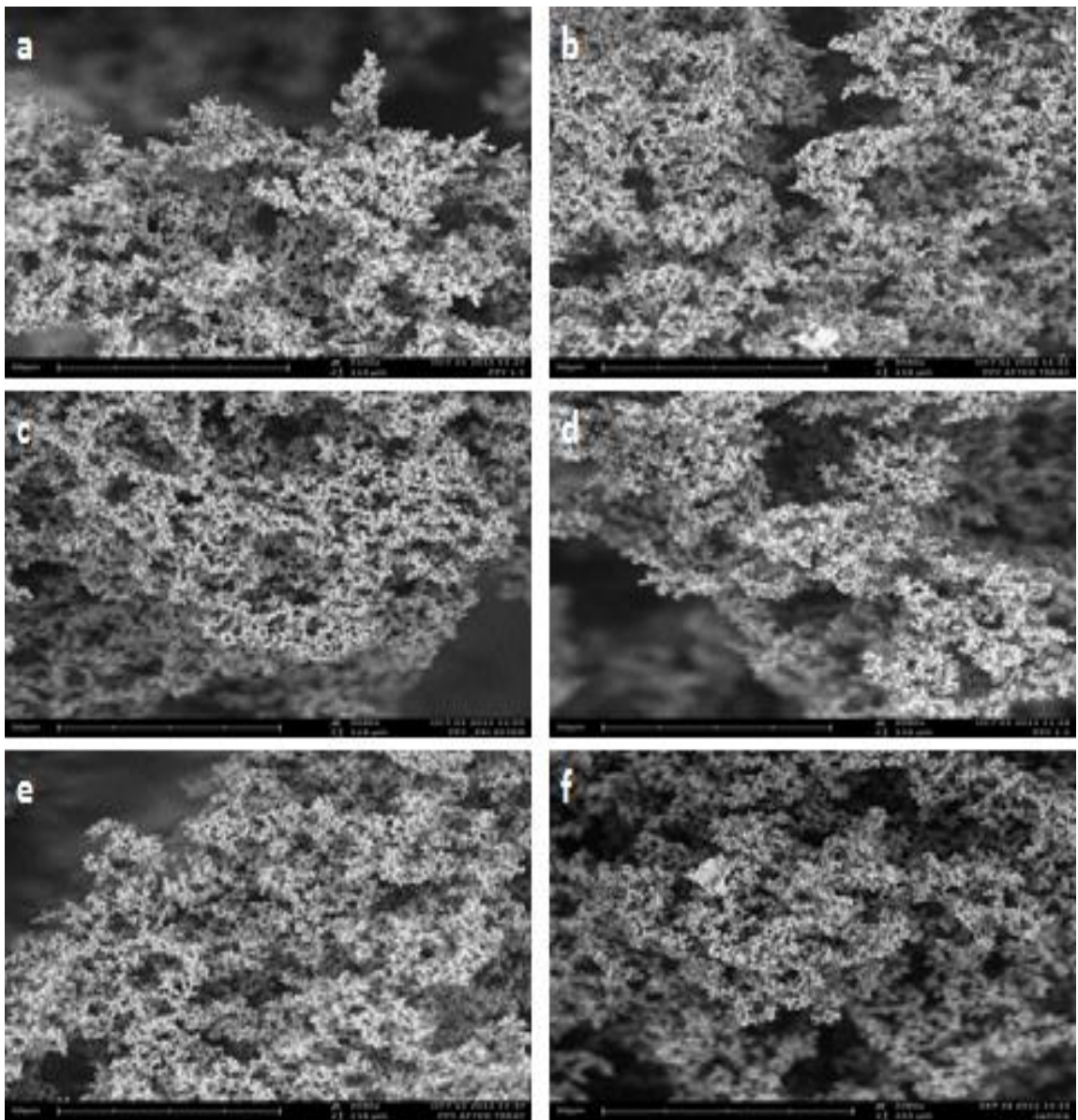


Figure 4.16: Scanning electron micrograph of Ppy a) before and after removal of b) lead, c) nickel, d) copper, e) zinc and f) cadmium.

CHAPTER V

CONCLUSIONS AND

SUGGESTIONS FOR FUTURE

WORK

CHAPTER V: CONCLUSIONS

Polypyrrole was successfully prepared by chemical method using ferric chloride as the oxidant. The higher number of active sites and significant adsorption ability due to the presence of nitrogen functional group in polypyrrole structure made it an effective adsorbent for the removal of lead, copper, nickel, cadmium and zinc ions from aqueous solution. The preparation condition of polypyrrole has a great influence on the adsorption efficiency for the removal of metallic ions from aqueous solution. The characterizations have been done by FTIR, SEM, BET and EDX. It is believed that with the longer process of polymerization and higher amount of oxidant, the available adsorption active sites become hidden as it is evident from the efficiency results. Adsorption experiments have shown that the adsorption procedure is strongly dependent on some of the important parameters such as contact time, adsorbent dosage, pH and initial concentration of metallic ions in aqueous solution. By controlling these essential parameters, the complete removal (100%) of lead, nickel and copper ions from aqueous solution was achieved. It is evident that the adsorption efficiency increased by increasing the pH up to 7 and decreased by increasing the adsorbent dosage. It has been found that adsorption is pH dependent. The adsorption efficiency decreases both at acidic and alkaline. Isothermal study of adsorption shows that the experimental data for the removal of lead ions from aqueous solution fitted well to the Langmuir isotherm. The research findings show that polypyrrole alone without forming any of its composites was capable of removing heavy metal ions like lead, nickel and copper from aqueous solution with 100% efficiency whereas in case of zinc and cadmium removal, polypyrrole was not capable for the complete removal. Polyethylenimine, as a chelating agent was added to the structure of polypyrrole to enhance

the adsorption capacity of these two polymers. The modified polypyrrole using polyethylenimine increased the adsorption efficiency up to 50 % for the removal of zinc and cadmium. Available nitrogen elements in PEI structure are responsible for higher adsorption capacity for the removal of zinc and cadmium from aqueous solution.

SUGGESTIONS

Since this area of research work is very applicable in the field of industry and the main effort in this research has been done to study the application of polypyrrole and Ppy/PEI in order to remove the heavy metals ions from aqueous solution. As a suggestion, the fundamental study of removal of heavy metal ions from aqueous solution would be expanded to

- Investigate the interactions on the surface of adsorbent during the treatment experiments.
- Find out the mechanism of adsorption especially in order to the competition between different elements to be adsorbed on the surface of polymer in real wastewater treatment.
- Concentrate on kinetic study.
- Investigate the regeneration of adsorbent in order to reusability.

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APPENDIX

APPENDIX

Appendix 1

MW of Pyrrole: 67.09 g/mol

67.09g 1000 ml

X 50 ml

$$X = 50 \times 67.09 / 1000$$

$$X = 3.3545 \text{ g (1M)}$$

$$X = 3.3545 / 10 = 0.33 \text{ g (0.1 M)}$$

The same calculation has been done for oxidant ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$):

MW of Iron (III) Chloride: 270.30 g/mol

270.30g 1000 ml

X 50 ml

$$X = 13.5 \text{ g (1M)}$$

$$X = 1.35 \text{ g (0.1M)}$$

Appendix 2

Lead adsorption, 25°C

$$q_e = \left(\frac{c_0 - c_e}{m} \right) V$$

$$C_0 = 1.015 \text{ ppm}$$

$$C_e = 0.205 \text{ ppm}$$

$$V = 0.025 \text{ L}$$

$$m = 0.08 \text{ g}$$

$$q_e = \frac{0.025(1.015 - 0.205)}{0.08} = 0.253125 \text{ mg/g}$$

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m}$$

$$q_m = \left(\frac{c_0 - c_m}{m} \right) V$$

$$q_m = \frac{0.025 \times 1.015}{0.08}$$

$$q_m = 0.31718 \text{ mg/g}$$

$$\frac{0.204}{0.2534} = \frac{1}{0.3178 \times b} + \frac{0.204}{0.31718}$$

$$0.164 \times 0.3178 = \frac{1}{b}$$

$$b = 0.5211$$

$$R_L = \frac{1}{1+bC_0}$$

$$R_L = \frac{1}{1+1.015 \times 0.5211}$$

$$R_L = 0.6$$

$$R^2 = 0.36$$

Lead adsorption, 35°C

$$q_e = \left(\frac{c_0 - c_e}{m} \right) V$$

$$C_e = 1.015 \text{ ppm}$$

$$C_e = 0.318 \text{ ppm}$$

$$V = 0.025 \text{ L}$$

$$m = 0.08$$

$$q_e = \frac{0.025(1.015 - 0.318)}{0.08} = 0.2178125 \text{ mg/g}$$

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m}$$

$$q_m = \left(\frac{c_0 - c_m}{m} \right) V$$

$$q_m = \frac{0.025 \times 1.015}{0.08}$$

$$q_m = 0.31718 \text{ mg/g}$$

$$\frac{0.318}{0.2178125} = \frac{1}{0.3178 \times b} + \frac{0.318}{0.31718}$$

$$1.46 \times 0.3178 = \frac{1}{b}$$

$$b = 7.0422$$

$$R_L = \frac{1}{1+bC_0}$$

$$R_L = \frac{1}{1+1.015 \times 7.0422}$$

$$R_L = 0.1227$$

$$R^2 = 0.015$$

Lead adsorption, 45°C

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V$$

$$C_e = 1.015 \text{ ppm}$$

$$C_e = 0.406 \text{ ppm}$$

$$V = 0.025 \text{ L}$$

$$m = 0.08$$

$$q_e = \frac{0.025(1.015 - 0.406)}{0.08} = 0.1903 \text{ mg/g}$$

$$q_m = \left(\frac{C_0 - C_m}{m} \right) V$$

$$q_m = \frac{0.025 \times 1.015}{0.08}$$

$$q_m = 0.31718 \text{ mg/g}$$

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m}$$

$$\frac{0.406}{0.1903} = \frac{1}{0.3178 \times b} + \frac{0.406}{0.31718}$$

$$0.852 \times 0.3178 = \frac{1}{b}$$

$$b = 3.694$$

$$R_L = \frac{1}{1 + bC_0}$$

$$R_L = \frac{1}{1 + 1.015 \times 3.694}$$

$$R_L = 0.2105$$

$$R^2 = 0.0433$$