REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY POLYMER-ENHANCED ULTRAFILTRATION

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ABSTRACT

The effects of pH, polymer concentration and metal ions feed concentration for four selected heavy metals, Zn(II), Pb(II), Cr(III) and Cr(VI), were investigated in this work; these metals were tested through a Polymer Enhanced Ultrafiltration (PEUF) system. Two conventional water-soluble polymers were selected, namely polyethylene glycol (PEG) and polyethyleneimine (PEI), and an unmodified starch as a biopolymer is proposed as an alternative binding reagent for four selected metal ions used for heavy metals' removal from wastewater.

Speciation profiles of Zn(II), Pb(II), Cr(III) and Cr(VI) species were obtained using available software to identify the soluble complexes of Zn(II), Pb(II),Cr(III), Cr(VI) ions and hydroxides ions (OH^-) present in various charged ions, either as anions or cations, at a certain pH range. Potentiometric titration studies were carried out at first to investigate the potential interactions between the selected polymer and metal ions for complexation.

Investigation through experimental works was done using ultrafiltration systems obtained by a laboratory ultrafiltration bench scale equipped with 10 kDa polysulfone hollow fiber membrane. The main operating parameter, namely the effects of pH, polymer composition and metal ions concentrations, were significantly affected by the retention coefficient and permeate flux conducted at constant pressure and flowrate.

Unmodified starch and PEG as binding polymers performed complexation interactions due to non-ionic attraction of metal ions to the polymer on the molecular

surface with a high possibility of chemical occurrence. However, these selected metal ions are mainly complexes by polymer functional groups whenever there is interaction with PEI polymer.

For study of single metal ions solutions, Zn(II) ions retentions approaching over 90% were obtained at pH 7 for each tested polymer. This behavior was similar to Pb(II), Cr(III) and Cr(VI) for which the retentions were obtained at a lower acidic pH and increased at a neutral pH of 7. Different behavior was found by Cr(VI) ions where a high retention was only achieved at an acidic pH region with PEI. Polymer concentration and metal ions concentration are found to have a significant effect on retentions.

For mixed metal ions solutions, the behavior of metal ions retentions was similar to single metal ions solutions for investigation on the effects of pH. Retention values were high at pH 7 for Zn(II) and Cr(III) ions corresponding to higher binding interactions with unmodified starch. Pb(II) ions obtained high retentions when tested with PEG whenever carried out in mixed metal ions solutions. High Cr(VI) ion retention was found with PEI in single and mixed metal ions solutions in a neutral pH range. The retention of these metal ions by starch in this study is found to be influenced by the granule structure that generally behaved in a non-ionic manner.

No significant effects on permeate flux were obtained when tested at different pH ranges, polymer concentrations and metal ions feed either by single or a mixture of metal ions solutions. The Canizares Model was employed as the theoretical model to predict permeate flux and metal ions retention on the study of heavy metal ions removal.

ABSTRAK

Pengkajian berkenaan kesan pH, kepekatan polimer dan kepekatan permulaan bagi ions logam bagi empat logam berat yang dipilih seperti Zn(II), Pb(II), Cr(III) dan Cr(VI) yang dijalankan dalam kerja ini telah diuji menggunakan sistem Ultrapenurasan Ditingkatkan dengan Polymer. Dua polimer perlekatan konvensional berasaskan air dipilih untuk ujikaji iaitu polyethylene glycol (PEG) dan polyethyleneimine (PEI), dan kanji tak diubah biopolimer yang dicadangkan sebagai alternative pelekatan reagent bagi empat ion logam yang dipilih untuk menyingkirkan logam berat daripada sisa air.

Profil spesis ions Zn(II), Pb(II), Cr(III) dan Cr(VI) telah dilakarkan menggunakan perisian yang ada untuk mengenalpasti larutan kompleks Zn(II), Pb(II), Cr(III) dan Cr(VI) ions dan juga ions hidroksida (OH^-) yang hadir dalam pelbagai cas ions, sama ada anion atau kation pada pH tertentu. Pengajian tentang titrat potentiometri dijalankan pada permulaannya untuk mengkaji potensi interaksi di antara ions logam dan polimer untuk menjadi kompleks.

Penyiasatan melalui kerja eksperimen dilakukan melalui sistem ultrapenurasan oleh alat berskala makmal ultapenurasan bersaiz 10 kDa membran fiber geronggang. Parameter operasi utama iaitu kesan pH, komposisi polimer dan kepekatan permulaan logam ion memberi kesan nyata kepada pekali penolakan dan fluks tertapis pada tekanan dan kadar aliran yang tetap.

Kanji tak diubah berserta PEG, sebagai polimer perlekatan menunjukkan interaksi kompleks kemungkinan berlaku berpandukan interaksi bukan ionik pada permukaan

molekul dan juga berkemungkinan berlaku secara kimia. Walaubagaimanapun, utamanya, logam ion yang dipilih dikomplekskan oleh kumpulan berfungsi polimer apabila berinteraksi dengan polimer PEI.

Bagi kajian tentang ion larutan tunggal, penyingkiran Zn(II) ion mencapai lebih 90% pada pH 7 untuk setiap polimer yang dikaji. Ion Pb(II), Cr(III) dan Cr(VI) menunjukkan perlakuan yang sama di mana penyingkiran pada permulaannya rendah pada pH berasid dan meningkat pada pH neutral 7. Perlakuan berbeza ditunjukkan oleh Cr(VI) dengan PEI di mana penyingkiran yang tinggi hanya dicapai pada julat pH berasid. Bagi kedua-dua iaitu kesan ke atas kepekatan polimer dan kepekatan permulaan ion logam, ia menunjukkan kesan nyata terhadap penyingkiran.

Untuk larutan campuran, penyingkiran ion logam yang ditunjukkan sama dengan perlakuannya dengan larutan tunggal dari aspek kesan terhadap pH. Penyingkiran ion Zn(II) dan Cr(III) yang tinggi didapati menunjukkan iaitu interaksi perlekatan yang tinggi dengan kanji tak diubah. Ion Pb(II) mencapai penyingkiran yang tinggi apabila diuji dengan PEG apabila dijalankan pada larutan campuran. Penyingkiran Cr(VI) ion didapati dikaji dengan PEI pada julat pH neutral secara larutan tunggal ataupun larutan campuran serentak. Penyingkiran oleh semua ion logam yang digunakan di dalam kajian ini menunjukkan ianya dipengaruhi oleh struktur granul yang tidak bersifat ionik.

Tiada kesan nyata pada fluk diperolehi apabila dikaji pada perbezaan julat pH, kepekatan polimer dan kepekatan permulaan ion logam sama ada melalui larutan tunggal ataupun campuran serentak. Model Canizares yang digunakan sebagai Model teori bagi menjangka fluks tertapis dan penyingkiran logam ion bagi pengkajian terhadap penyingkiran ion logam berat.

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Nurul Huda Binti Baharuddin

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

%	Percentage
<	Less than
>	More than
Δt	Net increment in time, min or hour
®	Prestal
°C	Degrees Centigrade
°F	Degrees Fahrenheit
C	Carbon units
$CaCl_2$	Calcium (II) chloride
$CaCO_3$	Calcium (II) carbonate
C_e	Final concentration of liquid, mg/L
C_o	Initial concentration of the liquid, mg/L
Cr (III)	Chromium (III)
Cr (VI)	Chromium (VI)
$CuSO_4$	Copper (II) sulfate
H_2SO_4	Sulphuric acid
I_2	Iodine
J_w	permeate water flux
K	Kelvin
K_A	Acid dissociation constant
K_{ads}	Measure of affinity of adsorbate for adsorbent (Langmuir Isotherm)
K_{Ha}	Apparent dissociation constant
$K_{i,n}$	Effective stability constants of complexes
KOH	Potassium hydroxide
M	Molar, mol/liter
Me	Metal
mM	Milimolar, mmol/liter
mg/l	Miligram/liter
mm	Milimeter
MW	Molecular weight, g/mol
n	Freundlich intensity parameter
Na_2CO_3	Sodium carbonate

Na_2SO_4	Sodium sulfate
$NaNO_3$	Sodium nitrate
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NH_3-N	Ammonical nitrogen
nm	Nanometer, 10^{-9}
Pb (II)	Lead
Pc	Concentrate pressure, bars
Pf	Feed pressure, bars
pKa	Cologarithm of the apparent dissociation constant of polymer
pKw	Negative log of the water ion product , K_w
Q	Flowrate, cm^3/min or L/h
rpm	Revolutions per minute
SS	Suspended solids
T	Temperature, °C
Zn (II)	Zinc
α_a	Dissociation degree
ΔPd	Difference between the feed and concentrate pressures
µm	Micrometer, 10^{-6}

Subscripts

AAS	Atomic Adsorption Spectrometer
ADMI	American Dye Manufactures Institute
BOD	Biological Oxygen Demand
CMC	Carboxymethyl cellulose
DADMAC	Diallyldimethylammonium Chloride
DOE	Department of Environment
EDTA	Ethylenediaminetetraacetic acid
EQA	Environmental Quality Act
ICP-AES	Inductively Coupled Plasma-Atomic Emission
IR spectroscopy	Infrared spectroscopy
LPR	Liquid Phase Polymer-based Retention
MBR	Membrane Bioreactor
mPEG	Methoxypoly(ethylene glycol)
OSHA	Occupational Safety and Health Administration
PAA	Poly(acrylic acid)
PAAS	Polyacrylic acid sodium
PAM-Na	Poly(acrylic acid–maleic anhydride) sodium salt

PEG	Polyethylene Glycol
PEI	Polyethyleneimine
PEO	Polyethylene oxide
PEPEI	Partially ethoxylated polyethylenimine
PEUF	Polymer Enhanced Ultrafiltration
POE	Polyoxyethylene
PVDF	Polymer of vinylidene fluoride
TMP	Transmembrane Pressure
WHO	World Health Organization
WQI	Overall Water Quality Index

Membrane notations

A	Filtration area, cm^2
[L]	Free ligand concentration or polymer concentration
$[L]_{free}$	Concentration of dissociated polyelectrolyte
$[L]_{R,0}$	Initial polymer concentration in reactor
$[L]_{R,t+1}$	Polymer concentration in reactor at time t + 1
$[L]_T$	Total ligand concentration
[M]	Metal concentration
$[M]_0$	Initial metal retention for polymer regeneration process concentration
$[M]_F$	Metal concentration in feed stream
$[M]_P$	Metal concentration in permeate stream
$[M]_{R,0}$	Initial metal retention process concentration in reactor
$[M]_{R,t+1}$	Metal and polymer concentration at time t + 1
C_A	Analytical concentration of polyelectrolyte
Cf	Solute concentration in feed stream
Cp	Solute concentration in permeate stream
CP	Concentration polarization
DOE	Design of Experiments (using computer software)
F	Permeate flux, cm^3/cm^2.min
HL	Represents the polymer used in modelling equations
K	Kilo (x 10^3)
kDa	Kilo Dalton
MF	Microfiltration
Mi	Metal ions
MWCO	Molecular Weight Cut-Off membrane, kDa
n	Empirical constant taking into account the intramolecular electrostatic forces of the

polyelectrolyte (value higher than 1 and usually near 2)

NF	Nanofiltration
NMWL	Nominal molecular weight limit
Qf	Feed flow rate
Q*p*	Permeate stream flow rate
R	Retention coefficient or recovery, %
R_0	Membrane–metal interaction coefficient
RM	Metal retention coefficient in polymer regeneration process, %
R_M	Metal retention coefficient
$R_{M,0}$	Initial metal retention coefficient
RO	Reverse Osmosis
SR	Solutes retention, %
UF	Ultrafiltration
V	Volume, cm^3 or m^3
V_P	Permeate volume, cm^3 or m^3
V_R	Retentate volume, cm^3 or m^3

Greek symbols

ρ	Density, ft^2/ft^3 or m^2/m^3
p	Pressure, psi or kg/m^2 or bar
φ	phi
ψ	psi torsions