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ORIGINAL PAPER

Removal of zinc and lead ions by polymer-enhanced ultrafiltration using unmodified starch as novel binding polymer

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Abstract The removal of zinc and lead from aqueous dilute solutions by polymer-enhanced ultrafiltration process using unmodified starch as a new binding polymer was studied. Experiments were performed to determine the effects of transmembrane pressure, pH, concentration of metal ions on the retention and permeate flux. The performance of the proposed new binding polymer was compared to that of polyethyleneimine a conventional polymer frequently used in polymer-enhanced ultrafiltration. The retention of zinc and lead ions reached 96 and 66 %, respectively, using 0.05 % unmodified starch at pH 7. Overall unmodified starch showed better retention for zinc ions then polyethyleneimine, whereas polyethyleneimine retention for lead ions was higher. Solution pH was found to have little effect on flux.

Keywords Complexing agents · Metals · Polyethyleneimine · Separation · Water soluble

Introduction

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

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

Two of the metal elements found to be pervasive in water bodies are Zn(II) and Pb(II). Contamination of these two metals comes from industries such as smelting, mining, plating, manufacture of storage batteries, ceramic and glass. Based on the EQA, by the Department of Environment (DOE), the permissible effluent limit for industrial discharge for zinc and lead are 2 and 0.5 mg/l, respectively (DOE 1994).

Removal of metal ions by complexation with water-soluble polymers and ultrafiltration is known as polymer-enhanced ultrafiltration (PEUF). PEUF is known to have great potential for effectively removing metal ions from aqueous solutions (Ozbelge et al. 1997). Formation of metal ion–polymer complex is a crucial aspect for metal ion removal by PEUF process. The metal ions able to bind to polymer are retained by the membrane, whereas unbound metallic ions are allowed to pass through the membrane. Electrostatic attraction or electron coordination is the main contributor to the interaction of electron donors with acceptors that generate the metal ion–polymer bonds for metal ion–polymer complex formation (Khaidar et al.

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2009). Currently, application of PEUF for removal of metal ions has great potential to be explored further by researchers.

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

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

In this study, unmodified starch is proposed as a binding reagent for removal of target metals, namely Zn(II) and Pb(II) ions from aqueous solutions. Investigation of water-soluble starch as a biopolymer is a new application in complexation–ultrafiltration since to the best of our knowledge, there is no research in the open literature about water-soluble unmodified starch as a polymer in PEUF process. Less toxic polymers like unmodified starch could have high potential for metal ion removal from aqueous solution in the PEUF process. Hence, this unmodified starch is suitable as a potential binding reagent which has no adverse effect to the environment, as the sources are plant-based.

The common polymer, PEI, was also selected in this research besides unmodified starch for comparison purpose. In PEUF studies, one of the most important operating parameters is pH. As indicated from previous studies, pH shows significant effects on flux and retention (Aroua et al. 2007). Generally, it is due to competition of hydrogen ions with metal ions, which can be trapped in the polymer structure at low pH. Nevertheless, pH may influence retention by competing with metal ligands, resulting in high retention value for metal ion removal. As described by Hu et al. (2009), pH has great influence. In the study of cadmium removal, it was shown that increasing pH to a certain value can eliminate competing complexing agents that lead to fluctuation of retention and flux (Hu et al. 2009).

This research was carried out between the 21st April 2010 and 30th August 2011 at the Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Malaysia.

Materials and methods

Materials

Chemicals used in this experiment were unmodified starch in powder form and polyethyleneimine (PEI) 50 % (w/v) in water as a binding reagent in the form of solutions (analytical grade) from ACROS Organics, zinc nitrate hexahydrate (MW: 297.46 g/mol) for preparation of Zn(II) solutions, lead nitrate (MW: 331.2 g/mol) for preparation of Pb(II) solutions, besides sodium hydroxide and hydrochloric acid for pH adjustment. Chemicals were used without further treatment. Dilutions and preparation of feed solutions were carried out using deionized water obtained using Millipore water purification system.

The membrane used was polysulfone hollow fibre from GE Healthcare (Model: UFP-10-C-MM06A) with an effective filtration area, A, of 26 cm^2 with a molecular cut-off (MWCO) of 10 kDa and a pure water permeate flux, Jw, of 0.9421 cm/min after 20 min of operation at 1.5 bar. Polysulfone polymer is selected as the material of the membrane which is hydrophilic and generally designed for particulate removal from solutions during filtration. Before starting, each experimental water flux should be measured to ensure not more than 20 % of reduction from the initial water flux reading and thus maintain the membrane performance in the ultrafiltration process.

Apparatus

In this study, a laboratory bench-scale system of crossflow filters was employed as shown in Fig. 1. The functional ultrafiltration process consists of the reservoir feed, retentate and permeates, which have been connected with tubing and backpressure valves, a peristaltic pump, manual pressure control clips and a flow meter with a digital panel meter/display, a stirrer for mixing and a power supply. For a pH measurement, a Metrohm pH meter was used.

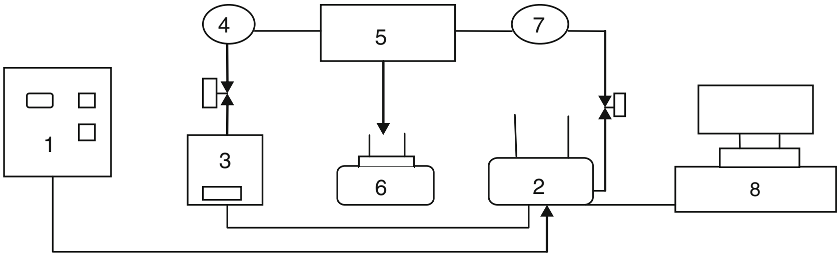


Fig. 1 Schematic diagram of laboratory-scale ultrafiltration system. (1) power supply and digital meter of flow rate, pressure in and out, (2) magnetic stirrer and 250 ml of feed solutions, (*3*) peristaltic pump, (*4*) pressure in, (*5*) hollow fibre filtration cell, (*6*) electronic balance and permeate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

UF experiments

Zn(II) and Pb(II) were prepared as single metal ion solutions containing the desired amount of water-soluble polymer. The pH of the metal feed solutions was adjusted to the desired value by using NaOH or HCl. In this work, low concentrations were used to avoid metal hydroxide precipitation that would influence negatively with the PEUF system. This can be clearly demonstrated in speciation studies that are explained further in the discussions. For mass effect studies, the amount of polymer used was 0.05–2.0 % of starch and 0.01–2.0 % of PEI with an overall concentration at 10 mg/l at a pH of 7. In this study, the PEUF process was employed to find effects of important operating parameters for single metal solutions. All experimental work was conducted at 1.5 bar and 115 ml/min of flow rate at room temperature of 26 ± 1 °C.

A feed volume of 250 cm^3 was prepared. pH, temperature, feed flow rate and pressure differences were monitored to be constant and were observed continuously during the UF process. The feed metal ion solution was kept stirred and circulated continuously through the peristaltic pump and passed through the hollow membrane fibre for 2 h all over the experiments. Although the feed concentration was adjusted for certain concentrations, the evaporation due to sampling from permeate or retentate may cause deviations. Thus, feed concentrations are regularly measured.

Retention values were calculated from the formula:

$$\text{Retention coefficient}, R = 1 - \frac{C_\mathrm{p}}{C_\mathrm{f}} \tag{1}$$

where C_p is the permeate concentration of the metal ion, and C_f is the feed concentration of metal. C_p is the average concentration of Zn(II) and Pb(II) ions in the permeate during the UF experiment.

Permeate flux is determined as follows:

$$\text{Permeate flux} = \frac{\text{Volume of permeate sample through membrane}}{\text{Effective area of membrane filtration} \times \text{time}} \tag{2}$$

At the end of the UF experiments, the membrane was immediately rinsed with ultrapure water obtained using Millipore water purification system and a sequence of 0.1 M of NaOH and 0.1 M NaOCl. Water flux should be continuously monitored to ensure the cleanliness of the membrane.

All experiments were carried out twice, and no significant differences were observed between the 2 runs (Table 1), in consequence, average value is used in this experiment.

Analysis

Inductively coupled plasma (ICP-OES) optical emission spectrometer (Model Optima 7000 DV) from Perkin–Elmer was used in this experiment to determine the concentrations of Zn(II) and Pb(II) in feed, retentate and permeate solutions. Standard metal solutions were prepared before the ICP runs, and average readings were recorded after three readings for each sample tested. The most important part was the calibration using standard solutions, where calibration should be accurate to at least over 95 % for better results.

For speciation studies, Visual MINTEQ software version 3.0 is used to generate the speciation profiles for Zn(II) and Pb(II) ions. The software takes into account the solubility and precipitation equilibria; however, it only plots the speciation curves of soluble species.

Results and discussion

Speciation studies

The understanding of speciation profiles is important for investigation of the ionic species reactivity of metal solutions. Interpretation from species studies leads to identification of each ion charge that is present at a certain pH range. In this investigation, Visual MINTEQ software version 3.0 was used to produce species profiles for Zn(II) and Pb(II) both at the concentrations of 10 mg/l.

Table 1 Two set of data on the effect of pH on 10 mg/l concentration of Zn(II) and Pb(II) rejection and flux using 0.05 % (w/v) unmodified starch and 0.01 % (v/v) PEI as water-soluble polymer

Metal ions	Rejection, *R* (%)						Flux, *J* (10^{-2} cm/min)					
	Zn(II)			Pb(II)			Zn(II)			Pb(II)		
	Readings											
pH	1	2	Average	1	2	Average	1	2	Average	1	2	Average
Unmodified starch												
2	84.332	88.630	86.481	58.113	60.373	59.243	11.006	10.438	10.722	18.245	18.899	18.572
5	94.875	95.551	95.213	54.098	54.328	54.213	10.564	9.498	10.031	17.985	18.861	18.423
7	95.167	97.011	96.089	61.567	62.731	62.149	10.074	9.828	9.951	17.698	18.530	18.114
9	89.315	89.115	89.215	53.421	55.483	54.452	9.342	9.702	9.522	15.092	15.792	15.442
12	82.314	79.284	80.799	41.268	44.194	42.731	7.332	7.690	7.511	12.956	13.546	13.251
Mean	89.201	89.918	89.559	53.693	55.422	54.558	9.664	9.431	9.547	16.395	17.126	16.76
Variance, α^2	34.735	49.357	40.235	59.039	51.301	54.895	2.080	1.070	1.481	5.293	5.680	5.483
Standard deviation, SD	5.894	7.025	6.343	7.684	7.162	7.409	1.442	1.034	1.217	2.301	2.383	2.342
PEI												
2	76.648	77.656	76.984	59.004	60.519	59.761	13.221	14.127	13.674	20.896	21.372	21.134
5	74.205	74.533	74.314	73.763	74.863	74.313	14.217	14.829	14.523	20.993	21.257	21.125
7	91.103	90.738	90.981	81.060	80.722	80.891	15.456	16.186	15.821	20.002	23.180	21.591
9	85.680	87.010	86.123	78.675	79.754	79.214	13.227	14.117	13.672	15.976	17.590	16.783
12	83.667	85.005	84.113	83.816	85.016	84.416	10.124	10.146	10.135	15.349	16.343	15.846
Mean	82.260	82.988	82.503	75.263	76.175	75.719	13.249	13.881	13.565	18.643	19.948	19.296
Variance, α^2	47.062	45.056	46.273	96.255	89.623	92.809	3.894	5.070	4.449	7.602	8.186	7.552
Standard deviation, SD	6.860	6.712	6.802	9.811	9.467	9.634	1.973	2.252	2.109	2.757	2.861	2.748

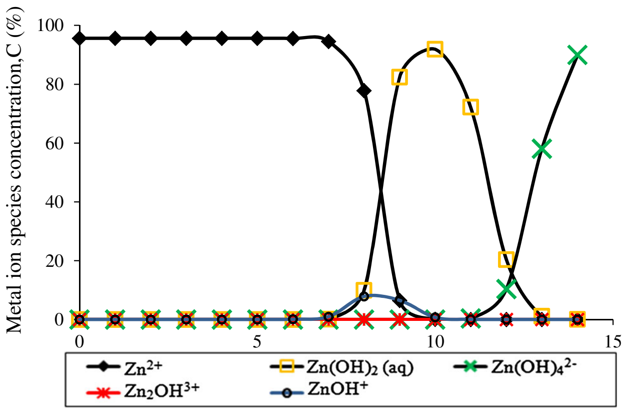


Fig. 2 Speciation profiles of Zn(II) (Zn(II) concentration = 10 mg/l)

Speciation profile of Zn(II)

Figure 2 shows the speciation profile of 10 mg/l concentration for Zn(II). As shown in this figure, five soluble metal species of Zn(II) are identified, and their presence depends on the solution pH. Zn^{2+} appeared as a major species until pH 7 and represents 96 % of the concentration for total zinc. Only $Zn_2 (OH)^{+3}$ cationic species appear at the entire pH 7 range and above. Besides monovalent species, $Zn (OH)^+$ only appears at pH 8 and pH 9. Insoluble $Zn (OH)_2$ becomes the major component when the Zn^{2+} species disappears at pH 10. These species disappear at pH 13, and Zn(II) takes the form of $Zn (OH)_4^{-2}$. $Zn (OH)_4^{-2}$ species become the only species at pH 13 and above.

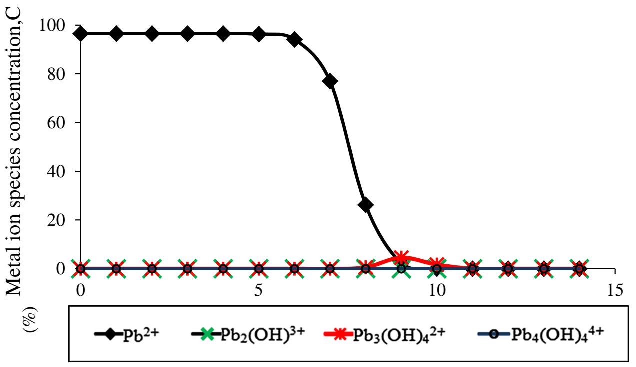


Fig. 3 Speciation profiles of Pb(II) (Pb(II) concentration = 10 mg/l)

Speciation profiles of Pb(II)

Speciation profiles for Pb(II) are given in Fig. 3. As clearly shown in this figure, four soluble species of Pb(II) exist at different pH.

For pH up to 6, about 98 % of Pb(II) exist as Pb^{2+}. This species disappears at pH 9. $Pb_3(OH)_4^{2+}$ concentration is very low at almost the entire pH range with a slightly high

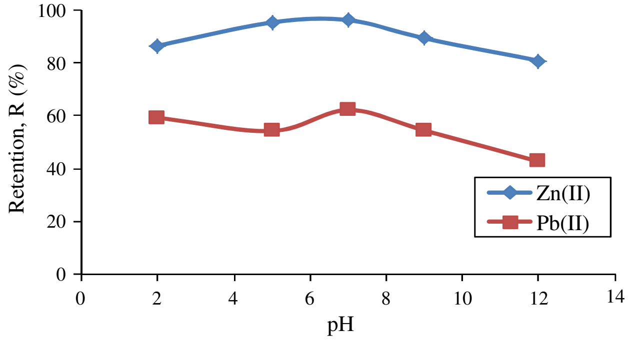


Fig. 4 The effect of pH on 10 mg/l concentration of Zn(II) and Pb(II) rejection using 0.05 % (w/v) unmodified starch

concentration at pH 9. The concentrations of the two other species namely Pb_2 $(OH)^{3+}$ andPb_4 $(OH)_4^{4+}$ are very low and can be considered negligible over the entire range of pH.

Effect of pH on Zn(II) ion retention by polymer-enhanced ultrafiltration

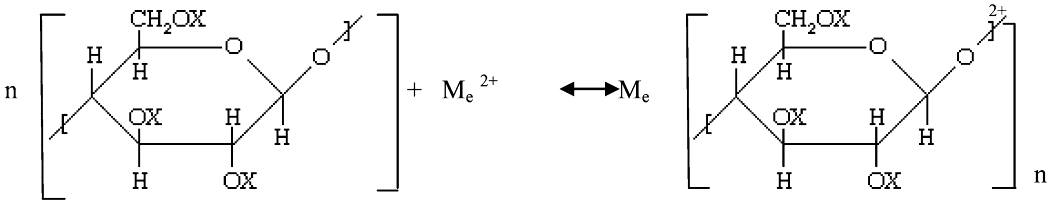
Effect of pH on Zn(II) retention using unmodified starch

Figure 4 shows the effects of pH on rejection of Zn(II) and Pb(II) ions using unmodified starch. The studied pH range was from 2 to 12, and applied pressure was 1.5 bar at room temperature. Almost all rejections of Zn(II) were higher than Pb(II) for entire range of pH tested, but decreased above pH 7. As pH increased, the formation of the complexes is enhanced and eventually increase the Zn(II) retention (Barakat and Schmidt 2010). It is due to an adsorptive mechanism for a metal ion by unmodified starch is most probably caused by a physical mechanism of adsorption, where metal ions are able to bind to the starch surface.

There are high possibilities that the adsorption process is a chemical adsorption. The binding of starch generally influenced by two polysaccharide groups, namely amylose and amylopectin, where amylopectin represents a highly branched (70–80 %) molecular structure (Hoover 2001) in consequence, has a high possibility to be crumpled and lose the structure (Eilers 1936) and able to allow penetration of metal ions onto the surface molecules (Chabot and Hood 1976).

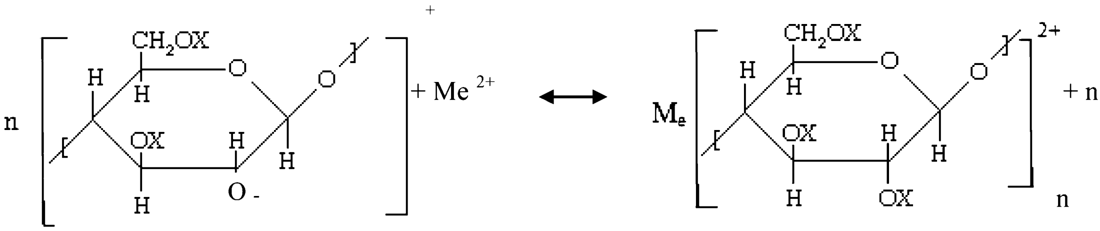
At pH 7 with unmodified starch as binding biopolymer, Zn(II) removal meets permissible limits for the discharged effluent standard of the EQA which is 96 % removal representing 0.4 mg/l by employed PEUF process in metal ions removal.

Unmodified starch uptake of selected metal ions by adsorption is high at certain working conditions are due to chemical adsorption. The metal component is bounded to the unmodified starch because of hydrogen ions forming a number of pendant hydroxyl (OH) groups capable to form hydrogen bonds. H+ at position 2, 3 and 6 in glucose is capable of forming donor bonds to complex metal ions. Hence, there is a high possibility that the adsorption can occur via chemical interactions as expressed in Eqs. 3 and 4: *X* represents hydrogen ions; Me represents metal ion.



(3)

Unmodified starch



(4)

Hydrogen at 2- α glucose

As expected, metal rejection was highly dependent on the solution pH, being lower at low pH range due to the competing protons for available active sites of the macromolecular ligand which causes the loss of the Zn(II) complex stability (Camarillo et al. 2012).

Increase in pH resulted in an increase in the retention up to 96 % at pH 7. This is in concordance with the study of Bertolini who found that the solubility of Zn(II) ions in most types of waters is greater at range 7.0–9.2, in consequent, its ability to be bound to starch is better at this pH range.

When the solution pH is increased above 7, Zn(II) ions retention is decreased. This is might be due to the negative effect of the insoluble metal hydroxides. Furthermore, at such high pH, most probably starch granular reaction takes place and produce heterogeneous granular patterns which reduces the metal ions ability to diffuse into and disperse throughout the granule matrix prior to slow reaction between metal ions–polymer (BeMiller and Huber 2001, BeMiller and Gray 2004). Theoretically, as pH is increased, the reaction efficiency should increase (BeMiller and Gray 2005; BeMiller and Han 2007; Beenakers et al. 1994; Lim and Seib 1993; Seib and Wu 1990), but at certain pH range, the granular reaction pattern of starch to metal ion and species of metal ions exists in solution effect the ability of metal ions in adsorb to starch (Bertolini 2010; Aratani et al. 1983) is decreased.

Unmodified starch has characteristic of long chains and possible as forked and branched structure provides the side group of the macromolecule that can attract each other strongly. The long chains structure can eventually shorten the molecule by physical adsorption. As the structure of molecule would not pack as straighter chain as those cellulose, it has ability to lose the structure to provide chance for solvent to penetrate; results in starch being able to bond, hence increasing its molecular weight and form macromolecules structure in consequence being able to be removed via PEUF, especially at low pH range.

The behaviour demonstrated for Pb(II) is similar to Zn(II) between pH 1 and pH 7, and retention increases then starts to decrease gradually until pH 12. From previous studies, adsorption of metal ions by the polymer increases as pH increases. It is mentioned that at neutral, in this case, Pb^{2+} is present, in concordance to Pb(II) speciation diagram or alkaline pH values interaction of metal ions with polymer can cause precipitation of metal hydroxide, but still metal ions are able to be removed via polymer-assisted ultrafiltration (Alpatova et al. 2004; Barakat and Schmidt 2010). They also concluded that at pH higher than 7, most of Pb(II) species present in metal solutions are in low concentration, but still, the possibility for membrane fouling is high due to metal ion–polymer complexes that are able to completely retain on the membrane which enhances membrane pore blocking (Alpatova et al. 2004). At pH 10, Pb(II) ions retention is decreased due to the presence of three cationic species, namely $Pb_2(OH)_3^+$, $Pb_3(OH)_4^{2+}$ and $Pb_4(OH)_4^{4+}$ (referred to speciation diagram), which cause desorption. This is due to the too low concentration of these three species to be bounded on the available macromolecular starch-PEI site.

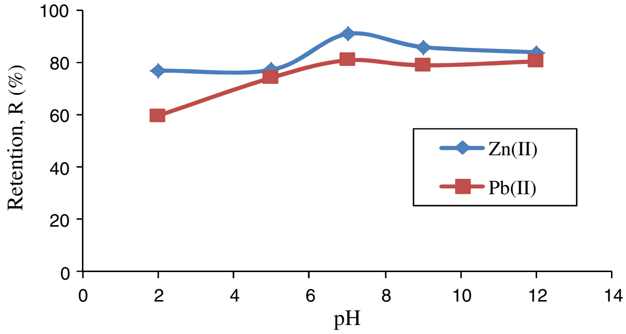


Fig. 5 Effect of pH on 10 mg/l concentration of Zn(II) and Pb(II) rejection using 0.01 % (v/v) PEI

Effect of pH on Zn(II) and Pb(II) retention using PEI

Rejection values for metal ions are shown in Fig. 5 as the effect of pH on selected metal ion removal from aqueous solutions is determined by using PEI. It is clearly shown that the plots of graphs for both Zn(II) and Pb(II) are similar at an acidic pH to neutral pH, but slightly differ at alkaline pH range. As PEI is a cationic polymer able to neutralize excess anionic species, retention achieves the highest rate as it reaches an alkaline pH. This is in accordance with the speciation profile of Zn(II) species, where at a pH over 10, Zn(II) with negatively charged species starts to appear. This contributes towards forming macromolecules by complexation, through interaction of the active amino group of PEI with Zn(II) ions.

The behaviour demonstrated for Pb(II) is slightly similar to that of Zn(II) where at an initial pH of 1 to pH 7, retention is low due to presence of too high concentration Pb(II) ions. Repulsive interaction between PEI and Pb(II) occurs and then starts to reduce as pH reaches 10. The presence of low concentration of Pb(II) species at this pH cause minimum repulsion between PEI and Pb(II). In consequence of, it influences adsorption resulting in an increase in Pb(II) ions uptake by PEI at pH 9 and above. This PEI–Pb(II) interaction is in accordance with Pb(II) speciation profiles, which demonstrates existence of cationic species with low concentration in solution at pH ranges of 9 to pH 14.

These cations cannot be completely complexed by the protonated PEI. Decrease in retention at lower pH

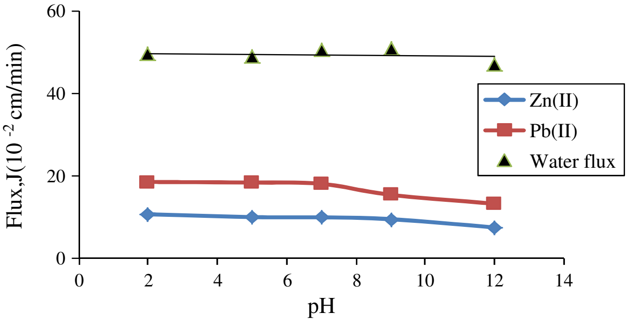


Fig. 6 Permeate water flux, Zn(II) and Pb(II) using 0.05 % (w/v) unmodified starch at different pH values (Zn(II) and Pb(II) concentration = 10 mg/l)

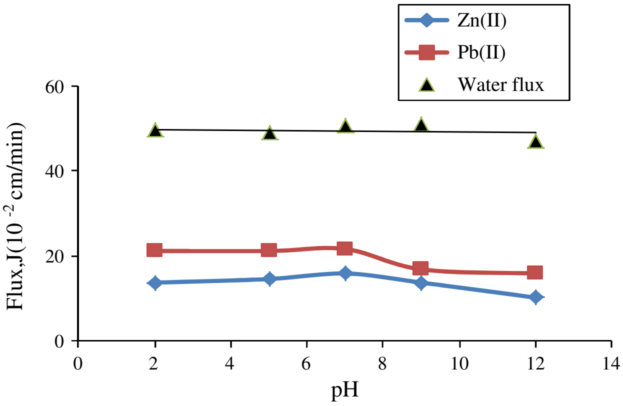


Fig. 7 Permeate water flux, Zn(II) and Pb(II) using 0.01 % (v/v) PEI at different pH values (Zn(II) and Pb(II) concentration = 10 mg/l)

(pH < 7) was connected with competition between H^+ and cationic Pb(II) forms. At acidic values of pH, retention of Pb(II) decreased, but at alkaline pH values Pb(II) retention increased. It is due to lower concentration of cationic Pb(II) present in the solutions, hence low competition of H^+ and cationic Pb(II), resulting in increased retention. According to previous study by Aroua et al., by using PEI as binding polymer, retention increased as pH increased to up to 99 % for Cr(III) ions removal and contrary with Cr(VI), where retention dropped as pH increased up to pH 12 (Aroua et al. 2007).

Effect of pH on PEUF flux

Permeate flux is one of the important parameters in PEUF process. Figures 6 and 7 show membrane permeability for water, Zn(II) and Pb(II) using unmodified starch and PEI at various pH values. In both figures, the permeate flux is not significantly influenced by pH. It is due to gel layer formation on membrane surface during the PEUF process for entire of tested pH.

Lower permeate flux efficiency of Zn(II) ions indicates that the ability to form complexes with unmodified starch is low due to the starch are able to form gelatinization, of which the starchy formation has resists on flow of metal ions complex solutions, hence negatively influenced on flux efficiency (Bello-Perez and Paredes-Lopez 2009).

From Figs. 6 and 7, it were observed that flux efficiency is slightly similar to Zn(II) and Pb(II) ions at various pH ranges (10–20 % of flux) using starch and PEI. This shows that the behaviour of gelatinization on unmodified starch does not significantly influence the permeate flux in PEUF system. The same results on flux showed by Aroua et.al, where pH has a little effect on flux efficiency in removal of chromium ions (Aroua et al. 2007).

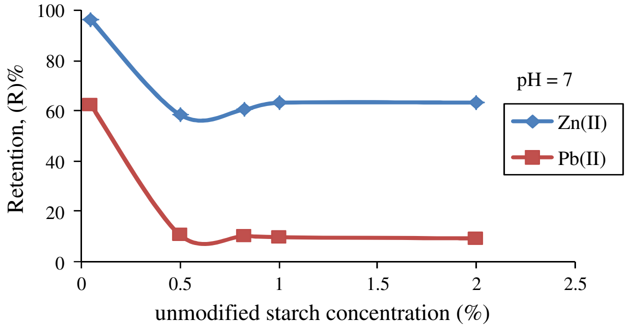


Fig. 8 Effect of unmodified starch concentration on Zn(II) and Pb(II) rejection (Zn(II) and Pb(II) concentration = 10 mg/l)

Effect of polymer concentration on Zn(II) and Pb(II) ion retention by polymer-enhanced ultrafiltration

Effect of unmodified starch concentration on Zn(II) and Pb(II) retention

All the samples of each selected metal solutions were prepared with same concentration (10 mg/l). Starch at different concentrations also prepared, and the effect of unmodified starch concentration on Zn(II) and Pb(II) removal were studied. All pH samples were adjusted at 7.0. From Fig. 8, it is plotted the metal solution retention for both tested metal ions at different starch concentrations.

Similar rejection patterns of Zn(II) and Pb(II) ions are shown in Fig. 8 due to many available complexing sites between polymer and metal ions at low starch concentrations. As polymer concentration increases, the ability of starch to bind with metal ions increases are due to availability of complexing sites is increased. The complexation metal ions and unmodified starch are observed to have great adsorption at lower polymer concentration at the same time can avoid the gelatinization behaviour.

The rejections consistently reach a plateau although starch concentration increases up to 1.0 %. Experimental results support theoretically, whereas higher concentration of polymer is applied, the polyelectrolyte behaviour causes

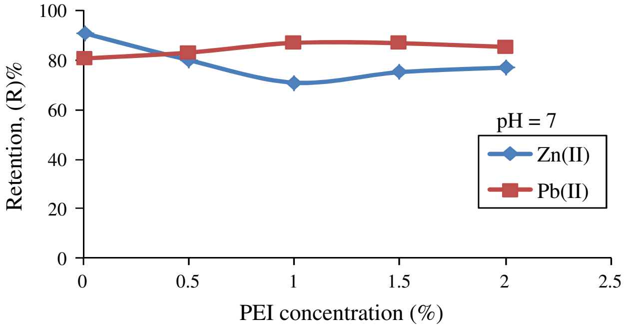


Fig. 9 Effect of PEI concentration on Zn(II) and Pb(II) rejection (Zn(II) and Pb(II) concentration = 10 mg/l)

the decrease in polyelectrolyte concentration. Hence, this phenomenon contributes towards the production of ions caused by low ionic atmosphere compared to diameter of polymeric coil because of the decrease in repulsive ions influencing the decrease in the chain rigidity. Hence, reluctant expand of polymeric coil causes a decrease in solution viscosity (Aroua et al. 2007). The reasons for employing low polymer concentrations are to minimize polymer losses and to have high metal ions retention (Bicak et al. 2013).

Effect of PEI concentration on Zn(II) and Pb(II) retention

Effect of PEI concentration on Zn(II) and Pb(II) rejection is shown in Fig. 9. It is demonstrated that Zn(II) ions influenced by PEI at low concentration and slight effects were obtained on Pb(II) ions rejection by increasing in PEI concentration to 2.0 %. This behaviour can be interpreted based on the previous finding of an adsorptive mechanism by complexation between several divalent metal cations and PEI (Kozuka et al. 1985). PEI has the ability to become one of the polymers with high complexation behaviour towards metal adsorption because it has an active group PEI of primary, secondary and tertiary imine groups in the ratio of 1:2:1 (Bolto 1995).

In our study, at very low value of PEI concentration, the equilibrium state of free Zn(II) ions with PEI is achieved; hence as PEI concentrations increases, the rejection decreases until a critical ratio, where the most favourable sites for metal ions are filled. A decrease in polymer concentration in consequence increases the solution viscosity, besides interacting with free amino groups and protonated PEI, which increases during optimum pH conditions. Interaction of uncharged PEI with metal ions may cause reduced viscosity because the influence of the backbone structure to form a coiled globule-like conformation (Pereira et al. 2003).

The rejection of Pb(II) ions obtained is almost constant despite an increase in PEI concentration. Number of PEI-Pb(II) ion interaction indicates that the shear force formed by the recirculation feed of low polymer concentration in this study is due to blocking of macromolecules forming on the membrane surface (Ozbelge et al. 1997). From the previous study, rejection is slightly reduced at higher concentration of PEI and obtained the highest at 0.05 % in removal of chromium ions (Aroua et al. 2007). From this investigation, low PEI concentrations can be exploited to achieve the highest rejection of Zn(II) and Pb(II) ions that are the most economical to be applied in wastewater treatment.

Conclusion

This PEUF study comprises removal of divalent metal ions of Zn(II) and Pb(II) in aqueous solutions. Beside the abundance of synthetic polymers available today, unmodified starch demonstrates immense potential as a binding polymer showing the best performance in removal of Zn(II) and Pb(II) over an acidic pH range and maximizing rejection at neutral pH.

In this study, unmodified starch employed as water-soluble polymer has the ability to adsorb metal cations during ultrafiltration process without requiring any upgrade on the method of their molecular structure. No modification by means additional chemicals or molecular structure readjustment is not required in correspond to less toxicity of unmodified starch applied via PEUF system. High rejections of metal ions achieved whenever operated at room temperature. The ability of unmodified starch to reject metal ions is highly dependent on granular structure not the type of starch indicating a possibility of physical interaction not chemical.

Regarding the significant effects of pH as a factor in PEUF systems, results impressively showed that 96 % of Zn(II) ion removal occurred at neutral pH as unmodified starch applied. In contrast, Zn(II) was found almost constantly when tested with synthetic polymer, PEI. For Pb(II), both selected polymers demonstrated little effect on rejection when tested over the entire pH region. Within the range of polymer concentrations tested in this study higher metal ion rejection is obtained low pH, Zn(II) ions reached about 96 % rejection when 0.05 % (w/v) unmodified starch was used, afterwhich this rejection became constant. For Pb(II), rejections with unmodified starch achieved 87 % of Pb(II) at a 1.0 % (v/v) of PEI concentration. Results indicate that unmodified starch could be the best water-soluble biopolymer for Zn(II) and Pb(II) removal from aqueous solutions.

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Nomenclature

MWCO	Molecular weight cut-off (Da)
PEI	Polyethyleneimine
R	Rejection coefficient/retention
A	Membrane area (cm^2)
Cp	Concentration of metal ion in permeate (mg/l)
Cf	Concentration of metal ion in feed (mg/l)
Me	Metal ion
n	Coordination index of ligand L with metal Me
x	Value number of metal molecule coordination
PEUF	Enhanced Ultrafiltration
Jw	Permeate water flux (cm/min)

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