

Removal of Heavy Metal Ions from Mixed Solutions via Polymer-Enhanced Ultrafiltration using Starch as a Water-Soluble Biopolymer

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In this study, aqueous solutions containing mixtures of heavy metals namely Zn (II), Pb (II), Cr (III), and Cr (VI) were treated by polymer-enhanced ultrafiltration (PEUF) using unmodified starch as binding biopolymer. The performance of starch in removing these heavy metals was compared with that of polyethylene glycol (PEG) a commonly used polymer in PEUF processes. Rejection coefficients and flux were studied under different values of pH solution and metal ion concentrations maintaining the transmembrane pressure constant at 1.5 bar. At pH 7, and starch concentration of 0.05%, the rejection was the highest at around 90%. As metal ion concentration increased from 10 to 50 mg/L, the rejection of metal ions decreased. It was found that starch gave higher rejection for Zn (II) and Cr (III) at 0.05 g/L of polymer concentration, whereas 1 g/L of PEG concentration gave higher rejection for Cr (VI) at 10 mg/L. The influence of metal ion concentration on Pb (II) rejection is not significant for the two selected polymers. The rejection of these metal ions by starch in this study is found to be influenced by granule structure that generally behaved in a non-ionic manner. © 2014 American Institute of Chemical Engineers Environ Prog, 34: 359–367, 2015

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INTRODUCTION

Wastewater treatment technology is continuously improving in order to enhance the efficiency of hazardous material removal such as heavy metal ions. One reason is that regulatory and legislative requirements have become more stringent and industries, as well as society, are now much more aware of the need for clean processes. Based on the Department of Environment, permissible limits of Zn (II), Pb (II), Cr (III), and Cr (VI) effluents which can be discharged in water bodies in Malaysia are 2.0 mg/L, 0.5 mg/L, 1.0 mg/L, and 0.05 mg/L, respectively [1]. Methods commonly practiced for the removal of organic and inorganic contaminants include coagulation, air floatation, gravity settling or separation via electrostatic and electro-coagulation. Unfortunately, these techniques can lead to sludge management issues as

well as system operations at the end of the process. The treatment of retentate stream is neither cheap nor simple in comparison to conventional treatment; however, lower retentate concentrations are obtained through backwash treatment. This retentate does not produce large volumes of sludge and can be treated by backwash treatment system in the laboratory. Landfill disposal is not required and not costly as it is safely discharged to sewer line. The cost is lower compared with sludge processing or disposal at landfill as it can be treated in laboratory after experimental runs without any additional treatment system requirement.

Membrane technology has emerged as a standard technology for pollutant separation, either independently or for mixtures, to assist conventional removal technologies that are able to remove contaminants at very low concentrations before allowing the wastewater to be discharged to water bodies [2–4]. New ideas to combine ultrafiltration and other physical or chemical processes are reported as an alternative for heavy metal ion removal from aqueous solutions [5].

Complexation of metal ions by binding polymers is used in conjunction with ultrafiltration in a process known as polymer enhanced ultrafiltration (PEUF). PEUF technology is able to reject metal ions bound with polymer while allowing uncomplexed components and water to pass through the membrane. The PEUF system in this study operated in continuous mode investigating the retention and flux efficiency at different operating parameters: pH, metal ion, and polymer concentration. The pH parameter is investigated as the first major parameter before metal ion and polymer concentration are analyzed. The objective of this study is to evaluate the performance of starch as a biopolymer in the recovery of multivalent metal ions namely Zn (II), Pb (II), Cr (III), and Cr (VI) from aqueous solution using a PEUF process. Starch is known as a water soluble biopolymer with excellent binding properties towards metal cations. There has been very little in the way of academic research work done despite its outstanding metal binding properties, and thus starch has not as yet been academically tested and explored in conjunction with PEUF without modification by means of using native starch where no changes are made to its granular structure.

Most researchers are able to use starch by modifying the changes to the properties of unmodified starch and chemical

modification of starches. Alteration of the physicochemical properties allows for comparison with the original starch [6] even in practiced heavy metal removal in combination with filtration process [7]. The performance of starch in the PEUF process is compared with that of Polyethylene Glycol (PEG) a water soluble polymer frequently used in PEUF. Starch has recently been reviewed since it has unique characteristics in terms of form and variety of functions. It is available for use as water binder, emulsion stabilizer and even gelling agents [8]. There is limited research into metal cations binding by unmodified starch especially in membrane process applications.

Unmodified starch used in this research work is derived from natural plant sources which can be found easily in tropical Asian countries. No additional chemical is added to enhance the binding mechanism of starch but unmodified starch still can be bound successfully with metal ions. Availability, relatively inexpensive price and simple handling are the criteria behind the selection of starch as water soluble polymer without modification. The lower feed concentration and final concentration of the sample makes the treated solutions safe for discharge to the environment. In laboratory, retentate solution treatment is commonly supplied to backwash water tank by backwash water pumps. Then, retentate solution in backwash water tank can be treated by using submerged ultrafiltration system and its permeate solution is recycled back to the hollow fiber ultrafiltration inlet system. The PEUF system in this work is geared to treat the resulting retentate solution if the concentration is higher than permissible discharged limits at the end of PEUF process.

In most PEUF systems, a low feed concentration has been applied. In consequence, the retentate solution concentration obtained is not be too high as the maximum concentration is only twice its feed solution concentration (after each run, solution concentration of permeate, and retentate is analyzed by using ICP-oes to check the final solution concentration) to ensure that the discharge standard as set by the DOE, Malaysia, are observed. After the retentate concentration is assured to be within the discharge standard concentration limit, it will be discharged safely to the sewer line system without harm to the environment. In this work, the polymers used are environmental friendly and the only focus is on treating metal solutions such that upon discharge, they are within the discharged standard limit.

METHODS AND MATERIALS

Materials

Different types of chemicals were used in these experiments. These include analytical grade starch in the form of powder and polyethylene glycol (PEG) 50% (w/v) from ACROS organics in water as a binding reagent solution, zinc nitrate hexahydrate 98% extra pure for preparation of Zn (II) solutions, lead nitrate for preparation of Pb (II) solutions, chromium nitrate for preparation of Cr (III) solution, potassium dichromate for preparation of Cr (VI) solution, and sodium hydroxide with hydrochloric acid for pH adjustment. Molecular weight of PEG in this work is 200 g/mol and starch ($C_6H_{10}O_5$) is 162 g/mol used in powder form. All chemicals from ACROS Organics were used without treatment. Ultrapure water obtained using Millipore water purification system was used for dilution and preparation of feed solution.

The membrane used was polysulfone hollow fiber from GE Healthcare (Model: UFP-10-C-MM06A) with an effective filtration area of 26 cm² with a molecular cut-off (MWCO) of 10 kDa and a pure water permeate flux, J_w , of 0.9421 cm³/min after 20 min of operation at 1.5 bar. Polysulfone polymer is selected as the membrane material as it is hydrophobic

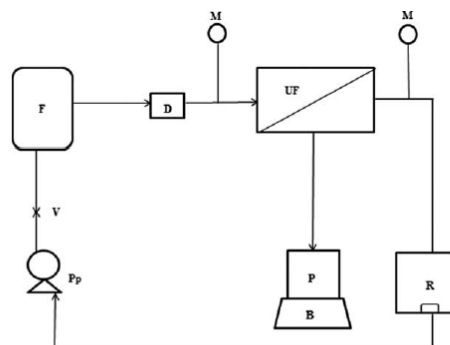


Figure 1. Schematic diagram of laboratory-scale ultrafiltration system. R: Reservoir tank containing 250 mL of feed solutions and magnetic stirrer, Pp: peristaltic pump, V: valve, F: flow rate and pressure (digital meter), D: pressure dampener, M: monometer electronic balance and permeate solutions, UF: ultrafiltration cell (hollow fiber), P: permeate solutions, B: electronic balance.

and generally designed for particulate removal from solutions during filtration. It should be noted that this work is carried out using water soluble polymer employing polysulfone as membrane material as the focus is not on fouling. The work is carried out by frequent backwashing using Millipore water and NaOCl before each run to ensure the pore membranes are not blocked by sample particles. In consequence, water flux is also determined before each run to be not less than 20% of the initial water flux.

A polymer of 0.01% to 1% unmodified starch in water is recommended. Higher concentrations of unmodified starch can form gelatine that can reduce the flux during the ultrafiltration process. Furthermore, it was shown that high concentrations of starch results in reduced adsorptive affinity due to gelatinization [9].

Apparatus

Cross flow filters were employed in this study by using the membrane bench-scale (Figure 1). The system consists of the feed, retentate and permeate reservoirs with tubing and back-pressure valve, peristaltic pump, pressure transducers, flow meter with a digital panel meter display, stirrer for mixing and a power supply. A Methorm pH meter was used for pH measurements.

Complexation-Ultrafiltration Procedure

The mixed metal ion feed consists of 10 mg/L each of Zn (II), Pb (II), Cr (III), and Cr (VI) solution containing the desired amount of water soluble polymer adjusted to certain pH values using NaOH or HCl. Low concentrations of heavy metal cations were used to avoid metal hydroxide precipitation that can interfere with PEUF process. These can be obviously demonstrated in speciation studies that are explained further in the discussion. For solutions of single metals, 10 mg/L to 50 mg/L concentration of each metal ion was used. Runs with single metal ion solutions were performed prior to those with mixed metal ion solutions. A feed volume of 250 cm³ of metal solutions was prepared and an initial volume of feed solution was dispensed. Feed solution was maintained, stirred and circulated through the peristaltic pump and passed through the hollow membrane fiber within 2 h.

At first, appropriate pH solution and polymer concentrations were determined using single heavy metal solutions at a constant transmembrane pressure of 1.5 bar and constant linear velocity of 0.134 cm/min. All experiments were conducted at room temperature $26 \pm 1^\circ\text{C}$. Before the start of each experiment, water flux should be monitored at not more than 20% of the reduction from the previous initial water flux reading to maintain membrane performance in the ultrafiltration process. The best pH and polymer concentrations were used in the subsequent heavy metal mixture runs. The experiments were done twice and no significant differences between the results of the two runs were observed.

The statistical work was carried out using Design of Experiment (DOE) software Minitab version 3.0 for analysis of the main operating parameters (pH, metal ion concentration, polymer concentration, flow rate, and transmembrane pressure).

Only major operating parameters are considered in the experiments as they have a significant effect on rejection and flux readings.

Determination of Permeate Flux and Retention Coefficient

Flux in $\text{cm}^3/(\text{cm}^2/\text{min})$ and retention coefficient (%) calculations were determined analytically from the following equation:

$$\text{Flux}; F = \frac{\Delta V}{(A, \Delta t)} \quad (1)$$

where ΔV is the volume of the permeate, A is the effective membrane area, and Δt is time.

$$\text{Retention coefficient}, R = 1 - \frac{C_p}{C_f} \quad (2)$$

where C_p is the concentration of metal ion in permeate and C_f is the concentration of metal ion in the feed. C_p in this experiment obtained an average of Zn (II), Pb (II), Cr (III), and Cr (VI) ions throughout the UF system.

Chemical Analysis

Inductively Coupled Plasma (ICP-oes) Optical Emission Spectrometer (Model Optima 7000 DV) from Perkin Elmer is employed for precise analysis of metal concentration in the feed, permeate and retentate solutions. The metal ion concentrations were determined by ICP-OES equipment. The off line method requires calibration which was performed using standard solutions of metal ions.

RESULTS AND DISCUSSION

Effect of Solution pH

Solution pH is a very important parameter in the PEUF process since pH has a tremendous effect on metal complexation. Metal-polymer complexation through polymeric binding with metal ions is found to be significant due to competition between protons, hydroxyl anion groups and metal ion species to be bound to polymer [10]. Charge interaction between metals, polymers, membranes, and metal-polymer complexes may affect the degree of metal cation rejection.

Starch-Multivalent Metal Ion Complexes

Figure 2 depicts the influence of feed solution pH on retention in the presence of 0.05 g/L starch as polymer at 1.5 bar pressure. The adsorption of selected metal ions towards

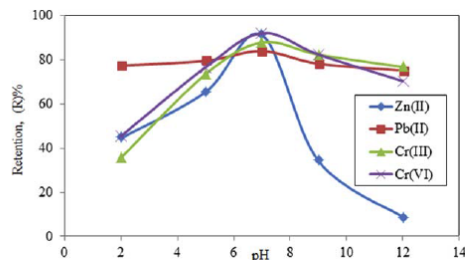
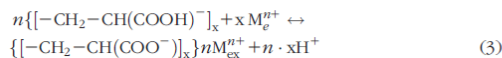


Figure 2. Effect of pH on rejection of mixture solutions of Zn (II), Pb (II), Cr (III) and Cr (VI) from aqueous solutions (unmodified starch = 0.05 g/L, metal ion concentration = 10 mg/L, transmembrane pressure = 1.5 bar, linear velocity = 0.134 cm/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the unmodified starch can be bound physically and there is a high possibility of ionic interaction.

Low metal rejection at pH 2 is mainly due to competing proton adsorption onto available sites of the polymer. Formation of protonated carboxylate groups decreased the metal ion retention resulting in reduced complexation of metal ions by the polymer. At low pH range, the formation of macromolecular complexes is decreased due to the protonation of carboxyl groups of starch. Thus interaction of binding mechanism between starch and metal ions is lower, which negatively effects retention since free metal ions can pass through the membrane.

As pH increases to pH 5, the ability to form macromolecular metal ion-polymer complexes because of increased concentration of deprotonated carboxylic groups increases metal ion rejection [11,12]. As expected, retention of four selected metal ions obtained the highest retention results at pH 7, as more hydrogen ions and $\text{CH}_2\text{-CH}(\text{COO}^-)$ were produced which increase the binding sites for heavy metal ions in ionic interaction as shown in the following equation:



According to Eq. (3), the formation of complexes due to an increase of pH value causes an increase in metal ion retention.

The Zn (II) cations exist at initial pH range (pH 1–9) in accordance with Zn (II) speciation species and could be bound completely with unmodified starch but replaced by Zn (II) anions species at high pH ranges. Thus, repulsion occurs, which results in low retention. There is a strong possibility that the adsorptive mechanism would occur chemically, where the polymeric binding of starch is generally influenced by two polysaccharide groups, namely amylose and amylopectin. Amylopectin represents a highly branched (70–80%) molecular structure [9] and as a result, has a high possibility crumpling, structure loss [13] and the ability to allow penetration of metal ions onto the surface molecules [14].

Pb (II) exists as cation over the entire pH range, and the competition between H^+ and Pb^{2+} to be bound to starch causes the rejection values to remain constant over all pH ranges. From pH 9 to 12, the rejection of Pb (II) and Cr (III) reaches a plateau at a value of about 80%. It could be found that retention of Pb (II) remained almost constant at a value of 80% over the tested pH range. The results showed the

reduced ability of Pb (II) ions to be bound to the unmodified starch. About 80% of Pb (II) ion retention is obtained throughout the tested pH range. As such the observed retention for Pb (II) is not due to a complexation mechanism but due to formation of a starch gel layer on the surface of the membrane. In this case, the Pb (II) trapped in this gel layer indicates the lower ability of Pb (II) removal using unmodified starch as binding biopolymer. Different divalence of Zn (II) and Pb (II) ions on binding mechanism towards unmodified starch are, at a certain pH range, due to different metal ions charges and the presence of various species in solutions effects the ability of metal ions to be adsorbed by unmodified starch.

In contrast, rejection of Cr (VI) decreases at high pH range due to protonation of chelating groups, namely carboxylic functions. Cr (VI) anions which exist over the entire pH range cannot completely form complexation with unmodified starch. Therefore, since the rejection of metal ions is increased at higher pH ranges using unmodified starch as polymer, there is a high possibility of bonding occurring between unmodified starch and chromium ions via chemical interaction [15]. It is because it is possible for high glucose groups which are contained in starch to be bound effectively via chemical interaction with metal cations.

The adsorptive mechanism is probably due to the formation of a number of pendant hydroxyl (OH) groups capable of forming hydrogen bonds. H+ at position 2-, 3-, and 6- in glucose are able to form donor bonds to be grabbed by metal ions. The retention is constant for Pb (II) but dropped for Zn (II), Cr (III), and Cr (VI) at alkaline pH ranges. This is because the anion species present in alkaline pH ranges for Zn (II), Cr (III) and Cr (VI) [10] which perform the repulsive mechanism are unable to bind with unmodified starch at higher pH ranges. These Cr (VI) anionic species are not expected to be complexed by carboxylic groups [10]. It can be observed that the complexation between Cr (VI) ions and starch occurred due to formation of starch gel layer on the membrane surface, and in consequence, Cr (VI) ions are trapped in this gel layer.

Using starch without modification is found to be efficient in the removal of Cr (VI) ions without reducing to Cr (III). As a result, it can also avoid precipitation. The extended loose helical chains possess a relatively hydrophobic inner surface that does not hold water well [16] and in consequence, metallic cations namely Zn (II), Pb (II), Cr (III), and Cr (VI) can replace this easily. The second component of starch is amylopectin whose behavior makes it easy to lose viscosity in solution because of the interaction between amylose chains and the retrogradation process followed by a slimmer consistency [17], which influences the possibility of metal ions-starch complexation. This factor likely causes the activation of the adsorptive mechanism between unmodified starch and metal ions during ultrafiltration process. Since the molecules structure is easily lost and it is easy for these molecules to be replaced by metal ion attachment to starch's molecular surface, metal ion rejection increases. In addition to the gelatinization behavior of starch as pH increases, it should be noted that polarization phenomena takes place which may interfere with this study. This gelatinization behavior alters the granular surface of starch, reducing the ability of starch polymer to bond with metal cations, hence decreasing retention [14].

PEG-Multivalent Metal Ion Complexes

PEG is well known as it is frequently used as water soluble polymer in PEUF system. Figure 3 shows retention values caused by the influence which pH has on operating in a PEUF in continuous circulated mode. It is found that rejection for Zn (II), Pb (II), Cr (III), and Cr (VI) increases with increasing pH, especially at higher pH, from pH 2 up to neutral pH. As pH reaches 12, Zn (II) rejection decreases

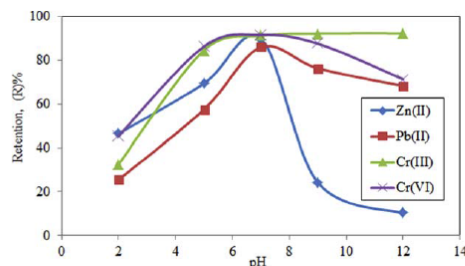
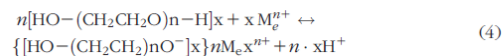


Figure 3. Effect of pH on rejection of mixture solutions of Zn (II), Pb (II), Cr (III), and Cr (VI) from aqueous solutions (PEG = 1 g/L, metal ion concentration = 10 mg/L, trans-membrane pressure = 1.5 bar, linear velocity = 0.134 cm/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

drastically while for Pb (II) and Cr (VI), rejection increases up to pH 7 and then decreases at pH 12.

Speciation analysis shows that Zn^{2+} is the major species from pH 1 to 7, which is then replaced by $Zn(OH)_2$ from pH 7 to 12. $Zn_2(OH)_2^{2+}$ and $ZnOH^+$ are the minor ion species. $Zn(OH)_4^{2-}$ exists at pH 12 and above. From pH 7 to 12, $Zn(OH)_2$ is predominant. Hence, complexation cannot occur since $Zn(OH)_2$ is not a charged species.

For Cr (III) rejection, it was found that a plateau was reached at pH 9. In the case of PEG bound with metal cations Cr (III), the complexation showed greater dependency on anions than cations [18], in agreement with speciation studies of Cr (III) where most anion species present higher than pH 9 [10] which increases metal ion retention caused by an increase of macromolecular complexation formation of Cr (III)-PEG. There is evidence that the adsorptive mechanism takes place as an electrostatic attraction between metal ions and polymer which enhances the formation of complexes at high pH values compared with low pH ranges [19]. At higher pH value, with PEG, more hydrogen ions and $HO-(CH_2CH_2O^-)$ were produced, increasing the binding site for heavy metal ions in ionic interaction as shown in Eq. (4):



According to Eq. (4), an increase in pH enhances the formation of the complexes, hence increasing metal retention.

It is known that at low pH range, PEG has an active carboxylic group of polymer molecules which are unable to separate completely due to highly flexible C-C bonds in the main chain and the development of cluster configurations by polymer [18]. Alteration of polymer structure in certain pH ranges cause negative effects on metal ion rejection [20–23] as groups of hydrogen bonds demonstrate weak interaction between polymeric molecules and the surface of the membrane, which in consequence decreases the retention.

To reject Cr (VI) ions, it should be noted that PEG without modification can remove Cr (VI) ions without first reducing to Cr (III), hence avoiding the precipitation which occurs during PEUF process.

Effect of Metal Ion Concentration

Ultrafiltration of Mixtures and Single Multivalent Solutions by Employing Selected Water-Soluble Polymer

At first, PEUF analysis was carried out to investigate the influence of pH on the rejection of four metal ion species

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