# Starch as novel water soluble biopolymer in removal mixtures heavy metal ions via polymer enhanced ultrafiltration

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# Starch as Novel Water Soluble Biopolymer in Removal Mixtures Heavy Metal Ions via Polymer Enhanced Ultrafiltration

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**Abstract.** Four heavy metals Zn (II), Pb (II), Cr (III) and Cr (VI) were selected in this work was tested through a Polymer Enhanced Ultrafiltration (PEUF) system. The effects of pH, polymer concentration and metal ions feed concentration were the main focus and influenced the performance of PEUF system. A conventional water-soluble polymers was selected, namely polyethylene glycol (PEG), and an unmodified starch as 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) and Cr (VI) ions and hydroxides ions ($OH^-$) present in various charged ions, either as anions or cations, at certain pH range. Investigation through experimental works was done using ultrafiltration systems obtained by 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 rejection coefficient conducted at constant pressure and flowrate. Unmodified starch and PEG as binding polymers performed complexation interactions due to physical attraction of metal ions to the polymer on the molecular surface with high possibility of chemical occurrence. Rejection values were high at pH 7 for Zn (II) and Cr (III) ions corresponding to higher rejections with unmodified starch. Pb (II) ions obtained high rejections when tested with PEG whenever carried out in mixed metal ions solutions. 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.

**Key words:** Starch; polyethylene glycol; polymer enhanced ultrafiltration; metal ions; separation

## INTRODUCTION

The growing water stress both in terms of water scarcity and quality deterioration promotes the development of reclaimed water as a new water resource use. However, reclaiming wastewaters contaminated by heavy metal has become a major challenge over the last decades due to the limitation of technologies and cost. Hence, integration of processes can be a promising alternative to the conventional but approaches used by industry. Currently, 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 an

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].

Pairing complexation–ultrafiltration is one of polishing treatments known as polymer-enhanced ultrafiltration (PEUF) process which presents the advantages of being able to separate ions by complexation of polymer and heavy metal ions. 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 n 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 analysed 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 (C6H10O5) 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, Jw, of 0.9421 cm/min after 20 min of operation at 1.5 bar. Polysulfone polymer is selected as the membrane material as it is hydrophobic 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].
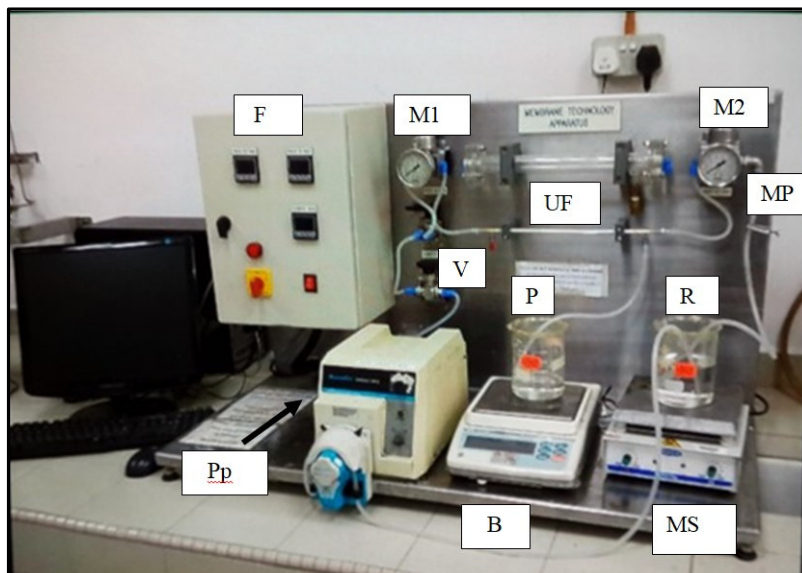
## Apparatus



**FIGURE 1.** Schematic diagram of laboratory-scale ultrafiltration system. (R) – reservoir tank containing 250 ml of feed solution (MS) - magnetic stirrer , (Pp) - peristaltic pump, (V) – valve, (F) – Flowrate and pressure (digital meter), (MP) – manual pressure control using pressure clip, (M1) – pressure meter inlet,  (M2) – pressure meter outlet,  (UF) – ultrafiltration cell (hollow fibre), (P) - permeate solutions, (B) – Electronic balance.

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 cm$^3$ 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 hours.

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˚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 Retention Coefficient

Retention coefficient (%) calculations were determined analytically from the following equation;

$$\text{Retention coefficient; } R = 1 - \frac{C_p}{C_f} \tag{1}$$

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

## Polymer Enhanced Ultrafiltration of Mixed Metal Ion Solutions
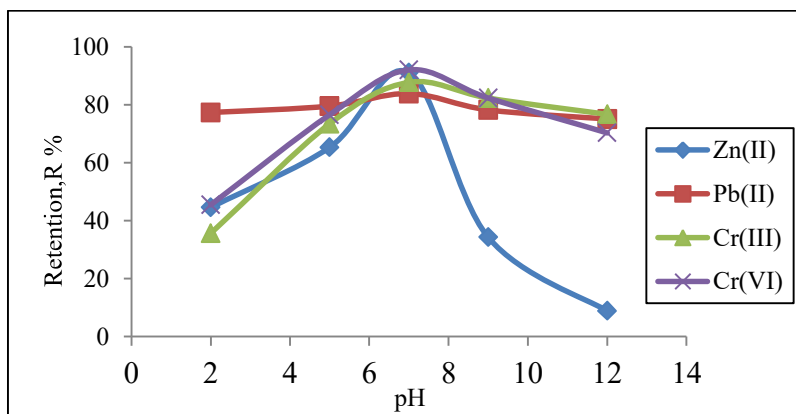### Effect of pH on Retention Using Unmodified Starch



**FIGURE 2**. Effect of pH on a10 mg/l concentration of mixed metal ions ( Zn (II), Pb (II), Cr (III) and Cr (VI)) retentions using 0.05%(w/v) unmodified starch (TMP=1.5 bar, flowrate =115 cm/min)

Figure 2 depicts the influence of feed solution pH on retention in the presence of 0.05% (w/v) starch as polymer at 1.5 bar pressure. The adsorption of selected metal ions by the unmodified starch creates a physical bond and there is a high possibility of ionic interaction.

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

The ability of metal ions to be adsorbed by unmodified starch is influenced by pH. At certain pH levels, the formation of macromolecular complexes decreased since the protonation of carboxyl groups decreased along with the starch. The interaction of binding mechanism between starch and metal ions was lower, which negatively affected retention. Consequently, the retention coefficient decreased. The dissociation of this metal ions-polymer combination can cause the metal ions to pass through the membrane surface, corresponding to less metal ion rejection. Consequently an increase in metal ion retention is found [2].

As pH increased to pH 5, the ability to form macromolecular metal ion-polymer complexes because of increased concentration of deprotonated carboxylic groups increased metal ion rejection [11, 12]. As expected, the retention of the four selected metal ions had the highest retention levels at pH 7, as more hydrogen ions and $CH_2$-CH (COO$^-$) was produced, which increased the binding sites for heavy metal ions in ionic interaction as shown in the following equation:

$$n \{[-CH_2\text{-}CH(COOH)]^-\}_x + xM_e^{n+} \longleftrightarrow \{[-CH_2\text{-}CH(COO^-)]_x\}nM_{ex}^{n+} + n \cdot xH^+ \tag{2}$$

According to Equation 2, the formation of complexes was due to an increase in pH value that caused an increase in metal ion retention.

The Zn (II) cations existed at the initial pH range (pH 1-9) in accordance to Zn (II) speciation species and bonded completely with unmodified starch, but it was replaced by Zn (II) anions species at high pH levels. Thus, repulsion occurred which resulted 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 has a highly branched (70-80%) molecular structure [9] and as a result, has a high possibility of crumpling, losing its structure [13] and allowing metal ions to penetrate surface of the molecules [14].

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

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

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

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

Extended loose helical chains possess a relatively hydrophobic inner surface that does not hold water well [16] and in consequence metallic cations, namely Zn (II), Pb (II), Cr (III) and Cr (VI), can easily replace these chains. The second component of starch is amylopectin whose behaviour makes it easy to lose viscosity in solution, due to the interaction between amylose chains and the retrogradation process leading to a slimier consistency [17], which influences the possibility of metal ions-starch complexation. This factor caused the adsorptive mechanism between unmodified starch and metal ions to be activated during the ultrafiltration process. Since the molecular structure is weak and these molecules were easily replaced by metal ions, metal ion rejection increased. In addition to the gelatinization behaviour of starch as pH increased, it should be noted that a polarization phenomenon took place that may have interfered with this study. This gelatinization behaviour altered the granular surface of the starch, reducing the ability of the starch polymer to bond with metal cations, hence decreasing retention [14].
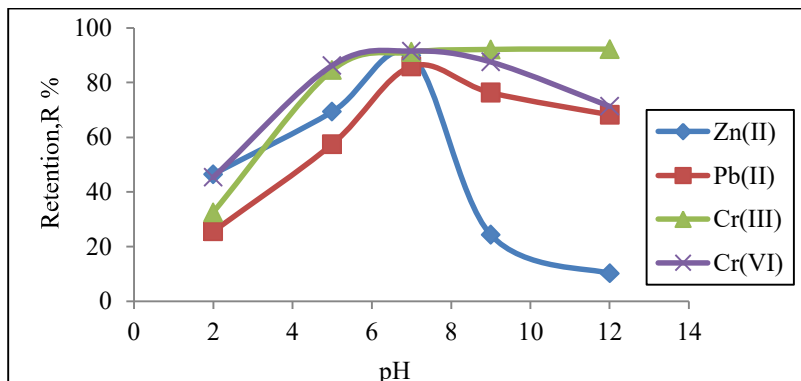
## Effect of pH on Retention by PEG



**FIGURE 3.** The effect of pH on 10mg/l concentration of mixed metal ions solutions (Zn (II), Pb (II), Cr (III) and Cr (VI)) retentions using 1.0% (v/v) PEG (TMP=1.5 bar, flowrate=115 cm/min)

PEG is well known and is frequently used as a water soluble polymer in PEUF systems. Figure 3 shows the retention values caused by the influence of pH on a PEUF system in continuous circulated mode. It is found that the rejection of Zn (II), Pb (II), Cr (III) and Cr (VI) increased with increasing pH levels, especially from pH 2 up to neutral pH. As pH reached 12, Zn (II) rejection decreased drastically; while for Pb (II) and Cr (VI), rejection increased until pH 7 and then decreases until pH 12.

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

Regarding Cr (III) rejection, it was found that a plateau was reached at pH 9. In the case of PEG bonded to Cr (III), the complexation was more dependent on anions than it was on cations [18]. These results were in agreement with the speciation studies of Cr (III), where most anion species were present at pH levels higher than 9 [10], which increased metal ion retention by increasing the macromolecular complexation formation of Cr (III)-PEG. There was evidence that the adsorptive mechanism took place as an electrostatic attraction between metal ions and polymer, and enhanced the formation of complexes at high pH levels (Labanda et al., 2009). At higher pH levels and in the presence of PEG, more hydrogen ions and $HO-(CH_2CH_2O-)$ were produced, increasing the binding sites for heavy metal ions in ionic interaction as shown in Equation 3:

$$n[HO–(CH_2CH_2O)n–H]x + x\ M_e^{n+} \longleftrightarrow \{[HO-(CH_2CH_2O)nO^-]x\}nM_ex^{n+} + n\cdot xH^+ \tag{3}$$

According to Eqn. 3, an increase in pH enhances the formation of the complexes, increasing metal retention. At low pH levels, PEG has an active carboxylic group of polymer molecules that are unable to completely separate due to the highly flexible C–C bonds in the main chain and the development of cluster configurations by polymer [18] . Alteration of the polymer structure at certain pH levels had a negative effect on metal ion rejection [20-23] as groups of hydrogen bonds developed weak interactions with polymeric molecules and the surface of the membrane, which consequently decreased retention. To reject Cr (VI) ions, PEG without modification can remove Cr (VI) ions without first reducing them to Cr (III) ion thus avoiding precipitation, which occurs during PEUF process.

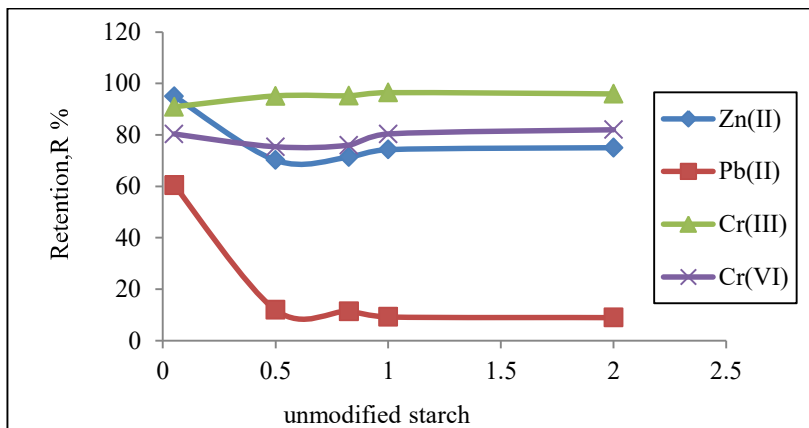# The Effect of Unmodified Starch Concentration



**FIGURE 4.** The effect of unmodified starch concentration on mixed metal ion solutions Zn (II), Pb (II), Cr (III) and Cr (VI) retentions (TMP=1.5 bar, flowrate=115 cm/min, pH=7)

The effect on retention by different unmodified starch concentrations in mixed solutions containing 10 mg/l of the four metal ions species at pH 7 is shown in Figure 4. Most metal ions species had their highest rejection levels at the initial polymer concentration of 0.05% of unmodified starch. This was especially true for Zn (II) and Pb (II) ions that reached 95% and 60% rejections, respectively. This interaction between metal ions and unmodified starch attracted polymers and the low polymer concentration provided enough molecular sites for Zn (II) and Pb (II) ions to be adsorbed by the surface. The behaviour of these metal ions in the mixed metal ion solutions was similar to their behaviour in the single metal ion solution.

For Cr (III) and Cr (VI) ions, the curve demonstrated in Fig. 4 is similar to those presented for single solutions. This is because mixtures of metal ion species were not affected by the presence of quantitative ionic species found in the solutions, but were affected by the polyelectrolyte behaviour of water-soluble polymers.

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

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

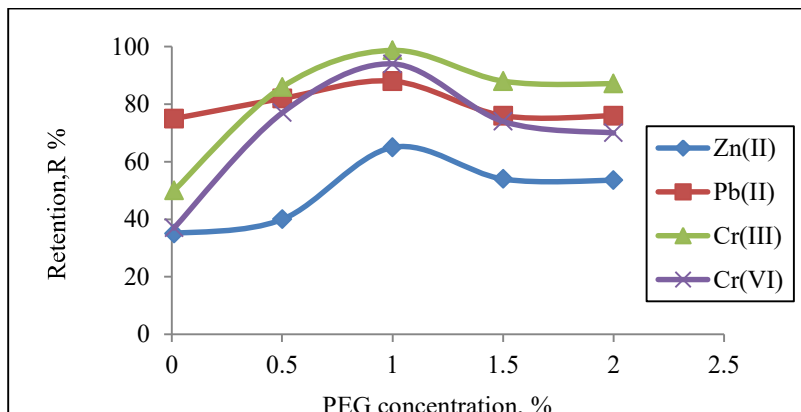## The Effect of PEG Concentration



**FIGURE 5.** The effect of PEG concentrations on mixed metal ion Zn (II), Pb (II), Cr (III) and Cr (VI) retentions (TMP=1.5 bar, flowrate=115 cm/min, pH=7)

Figure 5 reveals the performance of different PEG concentrations (0.05%, 0.5%, 1.0%, 1.5% and 2.0%) in mixed metal ions solutions by combining 10 mg/l of four metal ions species at pH 7 by cross-flow filtration mode in the PEUF study. As shown in Fig. 5, the behaviour illustrated was similar to behaviour exhibited in single solutions. The tested polymer initially showed fewer rejections due to viscosity of polymer at 0.01% that prevented the rigid PEG chain to bind with the metal ions. Retentions suddenly increased when using a 1.0% concentration of PEG, where Zn (II), Pb (II), Cr (III) and Cr (VI) had the most rejections at 65%, 88%, 99% and 94% respectively, tested in one boot of metal ion solution. It was found that the rejections in single and mixed solutions was similar, which indicates that 1.0% of PEG polymer was able to complex with metal ions and was not affected by polymer concentration.

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

## Effect of Metal Ion Feed Concentration on Retention
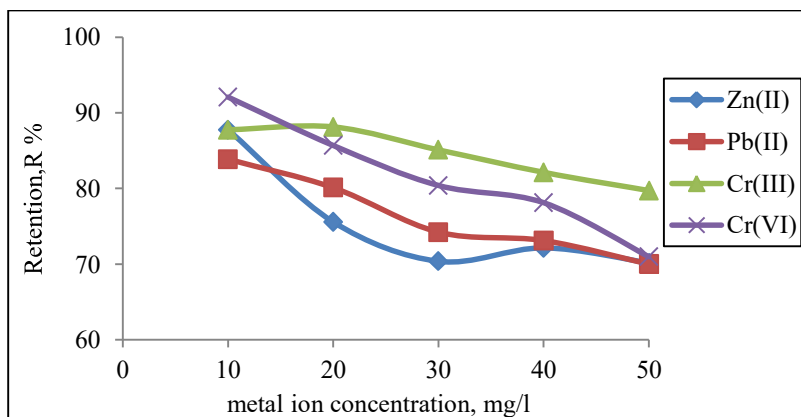## Effect of Metal Ion Feed Concentration by Unmodified Starch



**FIGURE 6.** The effect of metal ion feed concentrations for mixed metal ion solutions on Zn (II), Pb (II), Cr (III) and Cr (VI) retentions (TMP=1.5 bar, flowrate=115 cm/min, pH=7, unmodified starch = 0.05% (w/v))

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

The effects of metal ion concentration on selected metal ion solutions using unmodified starch carried out in mixtures solution is shown in Figure 6. The graph shows that 10 mg/l of metal ions was used for all experiments. For Zn (II), Pb (II), Cr (III) and Cr (VI), the retention amounts were 87.82%, 83.86%, 87.74%, and 92.06% respectively. Unmodified starch was used in low concentrations because its adsorptive affinity is reduced by gelatinization behaviour that occurs at high concentrations [14] and it decreased the rejection coefficients for each tested metal ion species.

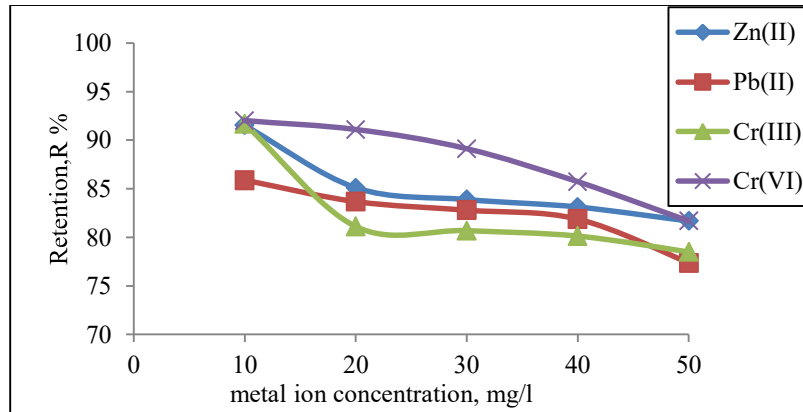## Effect of Metal Ion Feed Concentration by PEG



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

As metal ion concentration increased, excess metal cations failed to bond with the polymer, resulting in diminished metal ion rejection. As shown in Figure 7, the pattern is similar to unmodified starch being replaced with PEG. As metal ion concentrations increased from 10 mg/l to 50 mg/l, metal hydroxide precipitation took place negatively affecting metal ion rejection by increasing the concentration of metal ions. Owlad et al. suggested that the efficiency of Cr (VI) ions removal decreased as feed ions concentrations increased due to the limited active adsorbent sites. In this study, the available polymer sites were replaced by metal ions [25].

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

When four metal ions are present in a solution, their ability to bond freely to starch was limited due to competition between the metal ions. The presence of too many saturated metal ions in the solution resulted in the starch not being able to provide sufficient space for the metal ions. In this case, the polymer deficiency that occurred at this stage caused a free metal ions is able to be found in the permeate stream [2].

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

Similar pattern emerged when PEG was used with Zn (II) and Pb (II), where rejection rates reached only 80.12% and 59.32% respectively at 50 mg/l (Fig. 7). This was likely due to the affinity of metal ions to bind with PEG is

lower at high concentration of metal ion species, in addition to a polarization phenomenon which had a negative effect on rejection coefficients. The behaviour of Cr (III) ions was constant in terms of retention as metal ions concentrations increases. At lower concentrations, 10 mg/l, the highest retention rates were found for each metal ion. Otherwise only small changes in retention were obtained and a plateau phase for both chromium ions was reached when the metal ions concentration increased from 30 to 50 mg/l. There is was a possibility of free metal ions in the solutions containing the four species being successfully bonded at 1 g/l of PEG using this UF process.

In Fig. 7, selected multivalent metallic species were more likely to be removed at pH 7 at a concentration of 10 mg/l in mixed solutions. Generally, this was due to complexation formation between the metal ions-polymer, which was higher when the desired amount of free active forms of these complexes could bind effectively to the polymer present in solutions [26].

## CONCLUSIONS

The adsorption of selected metal ions towards the unmodified starch was found to be bound physically via ionic interaction can reduce the cost of heavy metal removal process. Thus, a viable technique for metal ion rejection via ultrafiltration in combination with selected water soluble polymers including unmodified starch and PEG, known as polymer enhanced ultrafiltration (PEUF), can be applied efficiently to either single or mixture solutions containing Zn (II), Pb (II), Cr (III), and Cr (VI) ions.

Starch without modification, a new polymer introduced in this research, showed better performance in the removal of Cr (III) and Cr (VI) ions from aqueous solutions compared with PEG and no upgrade in their molecular structure method is required, corresponding to less toxicity of unmodified starch used in PEUF system. pH was found to be a major factor which controls the rejection of selected metal ions. The ability of Cr (VI) ions to be removed directly without reduction to Cr (III) can be a significant criterion in the selection of unmodified starch and PEG as a binding biopolymer. The highest rejection of selected metal ions tested for mixtures and single metal ion removal were obtained at an optimum pH of 7. Results indicate that unmodified starch can achieve high rates of metal ion rejection leading to cleaner waste production at the end of the PEUF process. This will render the effluent to be suitable for recycling or to be safely discharged into the water bodies without putting a risk to human health and harming the environment.

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## REFERENCES

1. M. DOE, Malaysia: Environmental Quality Act Report, Ministry of Science, Technology and Environment, 1994.
2. Canizares, P., Perez, A., R. Camarillo, J. Llanos, and M.L. Lopez, M.L. Selective separation of Pb from hard water by a semi-continuous polymer-enhanced ultrafiltration process (PEUF), Desalination, **206**, 602–613 (2007)
3. K. Li, and S.P. Deshmukh. Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes, Journal of Membrane Science, **150**, 75–85 (1998).
4. M. Bodzek, I. Korus, and K. Loska. Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation-ultrafiltration process, Separation and Purification Technology, **17**, 111–116 (1999).
5. J.F. Liang, and R.S. Juang. Equilibrium studies for the interaction of aqueous metal ions and polyacrylic acid by a batch ultrafiltration method, Journal of Membrane Science., **82**, 163 (1993).
6. Q. Azronnizan, D. Rusli, A.G. Maaruf,  I.N.D. Nik and M.I. Bohari. Hydroxypropylation and acetylation of sago starch, Malaysian Journal of Chemistry, **6**, 48–52 (2004).
7. S.T. Lim, and B.S. Kim. Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch, Carbohydrate Polymers, **39**, 217–223 (1999).
8. J. Blazek, L. Copeland, H. Salman, and M.C. Tang. Form and functionality of starch, Food Hydrocolloid, **23**, 1527–1534 (2009).
9. R. Hoover. Composition, molecular structure, and physicochemical properties of tuber and root starches: A review, Carbohydrate Polymer, **45**, 253–267 (2001).

10. M.K. Aroua, F.M. Zuki, and N.M. Sulaiman. Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration, Journal of Hazardous Materials, **147**, 752–758 (2007).

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

12. X. Zhu, and K.H. Choo. A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane, Colloids and Surfaces A, **312**, 231–237 (2008).

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

14. J.F.Chabot, J. F. and L.F. Hood. Interaction of iron compounds with starch granules, Starch, **28**, 264–267 (1976).

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

16. J.Y. Li, and A.I. Yeh. Relationships between thermal, rheological characteristics and swelling power for various starches, Journal of Food Engineering, **50**, 141–148 (2001).

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

18. B. Bednar, J. Trnena, P. Svoboda, S. Vajda, V. Fidler and K. Prochazka. Time-resolved fluorescence study of chain dynamics .1. Poly(methacrylic acid) in dilute water solutions, Macromolecules, **24**, 2054–2059 (1991).

19. J. Labanda, M.S. Khaidar, and J. Llorens. Feasibility study on the recovery of chromium (III) by polymer enhanced ultrafiltration, Desalination, **249,** 577–581 (2009).

20. E. Krentsel, K. Volchek, Y. Zhilin, G. Shtereva, and Y. Dytnersky. Polymer binding/ultrafiltration as a method for concentration and separation of metals, Journal of Membrane Science., **79**, 253–272 (1993).

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

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

23. T.B. Choe, P. Masse, A. Verdier, and M.J. Clifton. Membrane fouling in the ultrafiltration of polyelectrolyte solutions—Polyacrylic-acid and bovine serum-albumin, Journal of Membrane Science, **26**, 17–30 (1986).

24. G.K. O'shea, and L.F. Hood. Calcium binding by hydroxylpropyl distarch phosphate and unmodified starch, Cereal Chemistry, **54**, 266–271 (1976).

25. M. Owlad, M.K. Aroua, W.M.A.W. Daud. Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. Bioresource Technology, **101**, 5098–5103 (2010).

26. J. Llanos, R. Camarillo, A. Perez and P. Canizares. Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction, Seperation and Purification Technology, **73**, 126–134 (2010).