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Effect of membrane surface charge on filtration of heavy metal ions in the presence and absence of polyethylenimine

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ABSTRACT

Polymer enhanced ultrafiltration (PEUF) was used to study the retention and flux of aqueous solutions of heavy metals. The metal ions investigated were: Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}. For each metal solution, stirred dead-end ultrafiltration experiments were performed in the presence and absence of polyethylenimine (PEI) at different pHs. Addition of PEI significantly affected both the retention of the metal ions and the flux of the filtration process. In the absence of PEI, significant rejection of metals only occurred at higher pH values. This can be attributed to the formation of insoluble metal compounds (hydroxides) at pH 6 or greater. In the presence of PEI the retention was greater than the retention without PEI due to the formation of metal/polymer complexes. This retention was also sensitive to pH with higher values of retention at near neutral or slightly acidic conditions. Although a reduction of flux due to the addition of PEI was anticipated (the flux was reduced by about 50% when compared to the reference solution) the addition of small quantities of metals to the reference solution also significantly affected the flux. Membrane charge properties also play a significant role in the rejection and flux of the metal ion/polymer solutions.

Keywords: Polymer enhanced ultrafiltration; Metal retention; Flux; Membrane charge

1. Introduction

The removal and separation of toxic and environmentally relevant ions is a technological challenge with respect to industrial and environmental applications [1]. Conventional methods which have been successfully used for heavy metals removal include: liquid–liquid extraction, ion-exchange, adsorption and precipitation reagents. However, these methods offer significant disadvantages which may include heterogeneous reactions, incomplete removal, high energy requirement or chemical consumption and generation of toxic sludge or solid waste that may also require expensive disposal [2,3]. Membrane separation processes are efficient and widely applied methods that are comparable to other separation techniques in terms of technical and economical feasibility for the separation of metal ions and complexes from solution [4]. Many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial effluents [5]. The main disadvantage in using membrane processes for treatment of effluents with heavy metals, is the size of the dissolved

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metallic salts. These hydrated ions or low molecular weight complexes, pass easily through most membranes with the exception of reverse osmosis and nanofiltration membranes. However, as these membranes are relatively non selective, all the metallic ions are retained together with alkaline and alkaline-earth ions [6].

Selective separation, recovery and purification of heavy metals with low energy requirements can be achieved by using polymeric reagents containing selective ligand groups, termed "polychelatogens", in combination with membrane filtration [4–9]. The concept of using water-soluble polymers to retain small ionic solutes in this way was first discussed by Michaels [10]. There are now reviews on the use of this technology for metal ion separations [11,12] as well as more focussed work on the removal of specific ions from solution [13].

A soluble polymer reagent with chelating groups is characterized by two main components: the polymer backbone, which provides the solubility and stability of the reagent, and the functional groups, which are necessary for the selective reactivity of the polymer [14]. Polyethylenimine (PEI) is a polyamine with amine functional groups. It has an extremely high cationic charge density owing to the protonation of amine groups as a function of pH. This relationship between pH and charge is useful when PEI forms a complex with metal ions, where the efficiency rises, as amine groups are deprotonated. Nevertheless, this polymer does not interact with alkaline or alkaline–earth metal ions [15,16].

The combination of two phenomena; the binding of metal ions to a water soluble polymer and ultrafiltration, is termed polymer enhanced ultrafiltration (PEUF), and includes complexation of metallic ions with polymers. Separation of metal ions bound to the soluble polymers from non-bound metals is achieved using an ultrafiltration membrane with a resultant permeate solution almost free of selected metal ions and a retentate with high metal content [1,7,9,17,18]. In the PEUF process, complexation of metals with polymers occurs in the homogenous phase, hence avoiding difficulties relating to heterogeneous reactions, interface transfer, and long contact time problems of multiphase separation processes. However, the main parameters affecting metal/polymer complexation are the metal and polymer type, pH, loading ratio and existence of other interacting metal ions in the solution [18]. The charge on the ultrafiltration membrane surface and its pores can also affect the separation of charged solutes and particles [19]. The membrane surface can be characterised by measuring the streaming potential (and thus the zeta potential) since this gives an indication about the charge of the membrane surface [20]. The sign of the membrane charge is also important when considering the optimum process conditions, that is pH and ionic strength.

Previous work has investigated PEI-metal interactions and showed that the metals absorb to PEI according to a Langmuir isotherm and in the presence of mixed metal ions, some degree of competition between the metal occurs [21]. The aim of the present study is to investigate and compare the rejection of heavy metal ions and solution flux in the presence and absence of PEI at different pH values. Streaming potential measurements have also been performed at a variety of different pH values in order to characterise the membranes used. This data has then been used to analyse the PEUF performance.

2. Methods

2.1. Materials

Stock metal solutions. Individual stock metal solutions of 1,000 mg l^{-1} were produced by the addition of metal salts ($CuSO_4 \cdot 5H_2O$; $ZnCl_2$; $K_2Cr_2O_7$; $NiCl_2 \cdot 6H_2O$; $CoCl_2 \cdot 6H_2O$; and $3CdSO_4 \cdot 8H_2O$ all Fischer Scientific chemicals, reagent grade) to a volume of high purity water (conductivity lower than 1 µS cm^{-1}) obtained from a Millipore Elix 3 unit.

Polyethylenimine solutions. PEI was received as a 50% by weight solution from Sigma-Aldrich (Cat No: 181978). This was the branched chain form of the polymer with an average molecular weight of 750,000 Da.

Metal solutions for ultrafiltration. Two different types of solution were used in the ultrafiltration experiments: (1) solutions containing metal and buffer solution only and (2) solutions containing metal, buffer solution and PEI. The buffer solution used was 0.01 M KH_2PO_4.

The aqueous metal solutions used in the ultrafiltration experiments were produced by the addition of the correct amount of stock metal solution to the appropriate amounts of buffer solution and PEI solution (when required). The initial concentration of each metal in the solution before filtration was 10 mg l^{-1}, whilst the initial concentration of PEI was 1 g l^{-1}. Individual aqueous solutions of the six metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) were produced over a range of pH values (from pH 2 to 6.5). The pH of the final solutions was adjusted to the appropriate value by the dropwise addition of 1 M HCl or 1 M KOH.

2.2. Ultrafiltration experiments

Filtration experiments were carried out using a stirred frontal (dead-end) ultrafiltration system as shown in Fig. 1.

Ultrafiltration measurements were carried out using a 50 ml capacity filtration cell (Amicon Corp., Model 8050). The cell can hold a membrane disk of 44.5 mm in diameter with an effective membrane area of 13.4 cm^2.

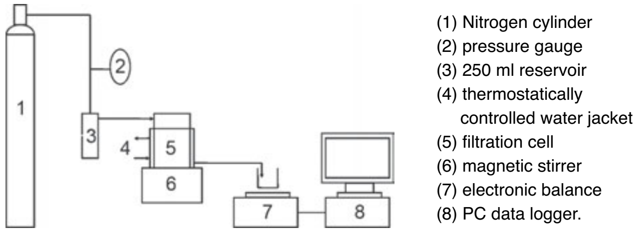

Fig. 1. Schematic diagram of stirred frontal filtration (dead end) ultrafiltration system.

The filtration cell was pressurized via nitrogen gas (oxygen free) out of a nitrogen cylinder, which was controlled by the reducing valve at the gauge of the cylinder. The applied pressure was monitored by an on-line pressure gauge (PSI-Tronix from Cole-Parmer). All experiments were carried out at a constant applied pressure of 3 bar. A magnetic stirrer assembly was mounted inside the body of the cell. Stirring was applied to the contents of the cell at a rate of 300 rpm. This was done to reduce the effects of concentration polarisation near the membrane surface. A water jacket around the filtration cell body was connected to a water bath. The filtration temperature was kept constant at 25 ± 0.1°C. The total filtration time was coupled to the amount of permeate collected with experiments being stopped after 25 ml of permeate was collected. Rates of filtration were determined by continuously weighing the filtrate on an electronic balance connected to a micro-computer. A digital electronic balance, from Mettler-Toledo Limited (PB303 DeltaRange), with an accuracy of 0.001 g was used to continuously measure the weight of the permeate. The balance was connected to a PC for automatic recording of the weight versus time. The average permeate flux through the membrane was calculated using:

$$\text{Average Flux} = \left(\frac{\text{Total volume of permeate (m}^3\text{)}}{\text{Membrane area (m}^2\text{)} \times \text{Total time (hr)}} \right) \tag{1}$$

The first 5 ml of permeate was discarded and the following 20 ml was collected for analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). This was done in order to determine the metal ion content in the permeate. Detailed descriptions of the instrument (Spectro Ciros ICP spectrometer) and operating procedures can be found elsewhere [22]. The metal ion analyses were carried out in triplicate and each data point is an average of these three determinations. Results from ICP analysis of the permeate samples for the relevant metal allowed the calculation of the retention value of each metal (R_i) using:

$$R_i = \left(1 - \frac{C_{pi}}{C_{fi}} \right) \times 100 \tag{2}$$

where C_{pi} is the concentration of metal *i* in the permeate; and C_{fi} is the concentration of metal ion *i* in the feed.

2.3. Membrane characterization

NADIR® asymmetric polyethersulphone membranes with a molecular weight cut-off (MWCO) of 30,000 Da (UH030 A) were obtained from MICRODYN-NADIR GmbH (Germany). The NADIR membranes are made from a blend of highly resistant polymers and exhibit high hydrophilicity (having a low tendency towards adsorption), high temperature resistance and excellent chemical resistance (pH 1–14). The NADIR ultrafiltration membranes were thoroughly rinsed and stored in high purity water for at least 24 h prior to any streaming potential or PEUF experiments. The average pure water flux for the membranes used with an applied pressure of 3 bar was found to be 0.096 $m^3\ m^{-2}\ h^{-1}$.

Streaming potential measurements were performed using an electrokinetic analyser (EKA, Anton Paar Gmbh, Graz, Austria-Europe). Streaming potential measurements were used to determine the zeta potential of the membrane surface in a 0.001 M potassium chloride (KCl) solution at different pH values in the range pH 3–10, at 25°C. Detailed descriptions of the instrument, measurement procedure, and zeta potential calculation can be found elsewhere [19,23].

3. Results and discussion

Fig. 2 shows a plot of the zeta potential versus pH for the NADIR polyethersulphone membranes in 0.001 M KCl. This figure shows that the isoelectric point of the

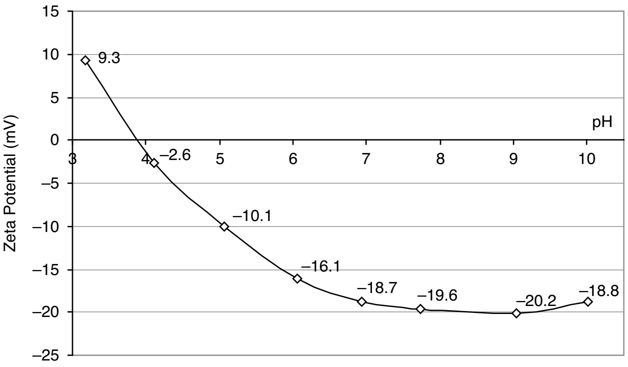

Fig. 2. Zeta potential of the NADIR 30,000 Da MWCO membrane as a function of pH on 0.001 M KCl solution.

membrane, at the given experimental conditions, occurs at approximately pH 3.9. The membrane is negatively charged for pH values above pH 3.9 and positively charged for pH values below pH 3.9.

The membrane zeta potential plateaus out at approximately pH 6.5–7. Once the pH is higher than this no significant increase in zeta potential, and thus membrane charge, is observed. Therefore, the maximum surface charge on the membrane during the ultrafiltration experiments occurs at pH 6.5 and falls as the pH is reduced until it reaches zero at pH 3.9.

Fig. 3 shows the retention of metal ions with and without the addition of the polymer (PEI) for various pH values. In the absence of the polymer all the metal ions showed similar retention characteristics. At low pH values (pH <5) the retention of the metal ions was low (<20%) for all the metal ions considered. For higher pH values (pH >5) the retention of ions climbed

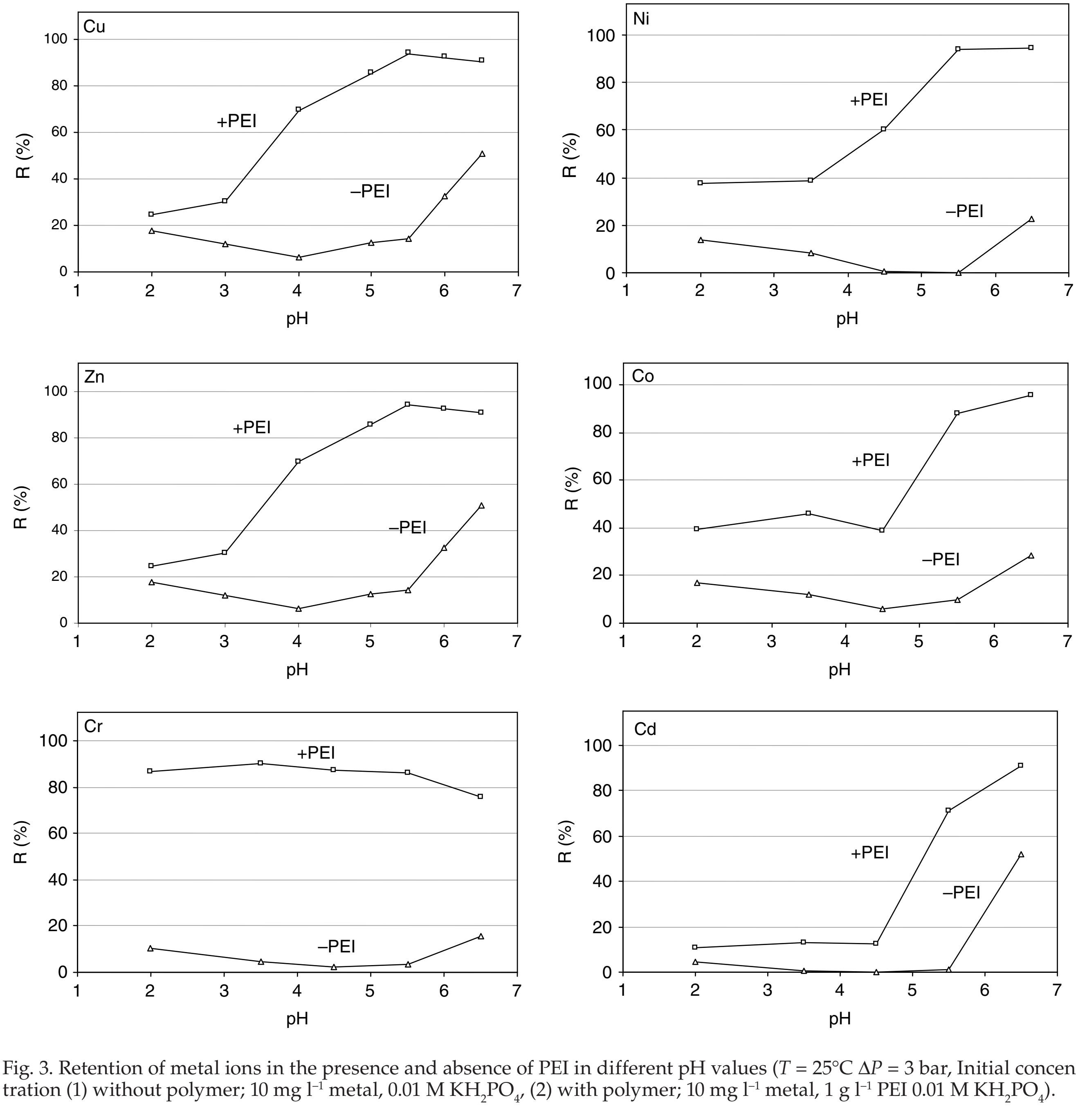

Fig. 3. Retention of metal ions in the presence and absence of PEI in different pH values (T = 25°C ΔP = 3 bar, Initial concentration (1) without polymer; 10 mg l^{-1} metal, 0.01 M KH_2PO_4, (2) with polymer; 10 mg l^{-1} metal, 1 g l^{-1} PEI 0.01 M KH_2PO_4).

although this still remained low for most of the metal ions. The highest retention values were seen for Cu^{2+}, Zn^{2+} and Cd^{2+} where the values reached about 55% at pH values greater than pH 6. The higher retention of these ions higher pH values is due to the precipitation of the appropriate metal hydroxide. Hence as solution pH increases the formation of insoluble hydroxides is likely to become the major mechanism responsible for metal ion retention. This observed retention agrees with the results reported by Rivas et al. [24].

As shown in Fig. 3, when the polymer is present the retention of the metal ions increases in all cases above the retention of the metal ions when no polymer is present. For high pH values (pH > 5) the retention of metal ions in the presence of the polymer is greater than 90%. This indicates that the polychelatogen, PEI, had a good affinity for binding to the metal ions especially at higher pH values. Significant increases in the retention of Cu^{2+}, Zn^{2+} and Cr^{6+} is due to strong complexation of these metals with the PEI polymer. However, PEI showed less affinity to form a complex with Ni^{2+}, Co^{2+}, and Cd^{2+} metals especially at low pH where the increasing H^+ concentration favours protonation of the binding sites on the polymer which prevents these metal ions binding at that site. As pH increases, the retention of metal ions increases due to the greater availability of binding sites on the polymer together with the precipitation of metal hydroxides on the membrane surface at pH ≥ 6.

Fig. 3 also shows that at the isoelectric point of the membrane (~pH 3.9) the retention of the metal ions is extremely low when no polymer is added. The retention of metal ions then increased with increasing pH value as the membrane becomes negatively charged and the precipitation of hydroxy-complexes is established. In most cases, the highest retention was observed when the membrane had its highest negative charge, that is at pH > 6. A similar trend was observed when the polymer was added to the solutions. With polymer added, the lowest retention of the metal ions was observed when the membrane was positively charged (pH < 3.9). The exception to this is chromium ions which are retained at any pH in the presence of PEI. This is due to the fact that Cr^{6+} is complex as chromate ions and as such binds to the PEI as a counter ion.

Fig. 4 shows the average flux versus pH for solutions without PEI added. The pure buffer solution flux was used as a reference solution for these experiments. It can be seen that the pure buffer solution flux is similar to the pure water flux (0.096 $m^3\ m^{-2}\ h^{-1}$) for the membrane at low pH values, but decreases away from this value as the pH is increased. The lowest flux for the reference solution is seen to occur when the membrane surface charge is at its highest value, that is at pH 6.5.

This is likely to be due to the electroviscous effect which causes an increase in the fluid viscosity within a charged capillary or pore [25] resulting in a decrease in flux. When metal ions are added to the pure buffer solution (metal concentration 10 mg l^{-1}) some interesting trends are observed. Cu^{2+} and Zn^{2+} ions reduce the flux of the solution in comparison with the pure buffer flux. This corresponds to the data in Fig. 3, as these ions show higher retention values which would result in some concentration polarization at the membrane surface which will reduce the flux (especially at higher pH values.). Cd^{2+} and Cr^{6+} ions had little effect on the flux of the solution as these ions pass relatively easily through the membrane at the conditions investigated. The Cr (IV) ion does not normally exists at as a cation but instead is present as the chromate anion [26] so reducing the interaction with the net negatively membrane surface and pores. The retention of these metal ions is extremely low until the pH exceeds a value of 6. In contrast, Co^{2+} and Ni^{2+} ions actually enhance the flux of the solutions in comparison to the reference solution. Flux enhancement remains to be explained. There is some evidence to suggest that flux may be reduced by interaction of the metal ion with a cellophane membrane [27] but enhancement of flux may also possible. Trivunac and Stevanovic have presented data to show that pure metal salt solutions substantially alter the flux through the membrane (Versapor 200 UF membrane) [28]. The explanation may be that the ions in the buffer interact differently with the metals ions so allowing both reduction and enhancement of the flux over the phosphate buffer control. This would depend on the interaction of the metal ions with phosphate and or the membrane surfaces.

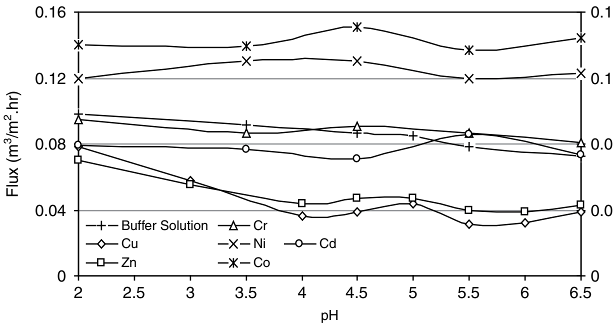

Fig. 4. The effect of pH on the average permeate flux for different metal ions in the absence of PEI. (T = 25°C ΔP = 3 bar, Initial concentration 10 mg l^{-1} metal, 1 g l^{-1} PEI 0.01 M KH_2PO_4).

Fig. 5 shows the average flux versus pH for solutions with 1 g l^{-1} PEI added. In this case the reference solution used was the pure buffer solution with 1 g l^{-1} PEI added. Similar trends to those seen for metal ion buffer solutions without PEI added were observed. However, the fluxes observed in all cases when PEI was added

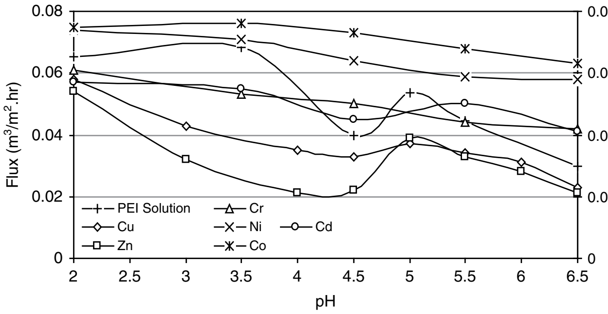

Fig. 5. The effect of pH on the average permeate flux for different meta ions in the presence of PEI (T = 25°C ΔP = 3 bar, Initial concentration 10 mg l^{-1} metal, 1 g l^{-1} PEI 0.01 M KH_2PO_4).

were significantly reduced from the fluxes without PEI (reduced by about 50%). This is due to the metal ion and polymer forming a complex which cannot pass through the membrane resulting in concentration polarization at the membrane surface which reduces the flux.

4. Conclusions

PEUF was used to study the retention and flux of aqueous solutions of heavy metals. These experiments have shown that adding polymer to metal ion solutions significantly increases the retention of the metal ions in the solution to greater than 90% at its best. However, addition of the polymer significantly reduces the flux of the process (by approximately 50%) for equivalent solution conditions. Although reduction of flux was anticipated by the addition of 1 g l^{-1} PEI, the addition of small quantities of metals also significantly affected the flux when comparing these values to the reference phosphate buffer solution. Flux was enhanced by up to 40% by the addition of 10 mg l^{-1} of Co^{2+} and Ni^{2+} to pure buffer solutions. Cr^{6+} and Cd^{2+} had little effect on the flux whilst Zn^{2+} and Cu^{2+} reduced the flux.

The general explanation for these observations is that the metals studied differ significantly in their interaction with the membrane surfaces and pores in the presence of phosphate buffer. The membrane material and its charge pore size are two parameters which can substantially affect membrane surface charge are critical factors to the process performance. Generally the lowest retention of ions with no polymer present occurred at the iso-electric point of the membrane (~pH 3.9). Either side of this pH the retention of metal ions by the membrane increased. As the pH of the solution increased past this point, the retention of metal ions increased both with and without the presence of polymer. In general, the highest retention of metal ions occurred when the membrane had its highest negative charge.

An interesting study to clarify these interactions would be to investigate the metals binding to the membrane surface and possible interactions with suspending buffers. This would not be an easy to study directly as it is the chemistry within the pores of the active membrane that would be critical in these flux phenomena.

Acknowledgements

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