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Polymer enhanced membrane filtration of metals: retention of single and mixed species of metal ions based on adsorption isotherms

Fahad Mohammed Almutairi*, Paul M. Williams, Robert W. Lovitt

Centre for Complex Fluids Processing, Multidisciplinary Nanotechnology Centre,
School of Engineering, Swansea University, Swansea SA2 8PP, UK
Tel. +44 7921253487; email: 170662@swan.ac.uk, Fahad4m@aol.com

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ABSTRACT

The binding and retention of single metal ions and mixtures of metal ions with polyethylenimine (PEI) was studied using polymer enhanced ultrafiltration (PEUF). Using a highly branched chain form of PEI (Sigma Aldrich 181979) with an average molecular weight 750,000 and approximately 60,000, ultrafiltration experiments were carried out in the stirred dead-end ultrafiltration mode. The results of the binding studies show that the Langmuir isotherm offers a good description of the binding process. At pH 5.5, the maximum polymer binding (Q_{max}) and binding affinity constant (K_L) were determined according to Langmuir isotherms. It was observed that the maximum amount of metal ions bound to the polymer for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} decreased substantially in solutions containing mixtures of metal ions when compared to the values obtained for single metal ion solutions. For Cr^{6+} and Co^{2+} no significant decrease was seen. These data indicate that the binding capacity of Cr^{6+} and Co^{2+} remain constant in competition while Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} show changes in both binding capacity and equilibrium constant. The effectiveness of the polymer enhanced ultrafiltration (PEUF) process was shown to be heavily dependent on the concentration of competing metal ions, influencing both capacity and selectivity of the polymer. These findings suggest that the effectiveness of metal binding needs to be determined in the specific water to be treated before the PEUF system can be designed.

Keywords: Polymer enhanced ultrafiltration; Metal ions binding; Polyethylenimine; Retention profiles; Langmuir isotherms

1. Introduction

Toxic heavy metals appear in low concentrations in industrial and wastewater discharges. The potential adverse health impact and environmental concerns have resulted in more stringent environmental legislation regarding effluent quality standards [1,2]. Conventional methods which have been successfully used for heavy metals removal include the use of liquid–liquid extraction, ion-exchange, adsorption and precipitation reagents. However, these techniques offer significant disadvantages relating to heterogeneity of absorption process reactions leading to mass transfer limitations, incomplete removal, high energy requirement or chemical consumption and generation of toxic sludge or solid waste that also requires expensive disposal [3–5]. On the other hand, membrane separations are efficient and widely applied separation processes that are comparable to other separation techniques in terms of technical and economical feasibility [6]. Many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial wastes [7].

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*Corresponding author.

The main disadvantage in using membrane processes for treatment of effluents with heavy metals, is the size of the dissolved 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 [5].

Selective separation, recovery and purification of heavy metals with low energy requirements can be achieved by a number of methods that selective bind metals to large polymeric or aggregated materials such as liquid micelles [6], that contain selective ligand groups that can bind the metals and can be used in combination with membrane filtration [5–11]. A number of interactions are possible but one of the most useful is that of chelation. 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 [12]. Polyethylenimine (PEI) is very interesting compound to study. Commercial branched chained PEI has primary secondary and tertiary amino groups in a 1:2:1 ratio. The branched forms are able to form stable complexes with PEI and these properties have been described [13–15]. As well as directly effecting binding by chelation by altering the pH, the nature of the folding of the branched chains may also impact some selectivity by steric hindrance when the polymer is in solution or at the membrane surface.

Thus the combination of the two phenomena; binding of metal ions to a water soluble polymer, and ultrafiltration is commonly termed PEUF. This enables the separation of metal ions bound to soluble polymers from non-bound metals by use of an ultrafiltration membrane. This forms a permeate solution almost free of metals and a retentate with a high metal–complex content [5–12,15–18]. 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 associated with multiphase separation processes [16]. The concept of using water-soluble polymers (WSP) to retain small ionic solutes in this way was first discussed by Michaels [19]. There are now reviews on the use of this technology for metal ion separations [20,21] as well as more focused work on the removal of specific ions from solution [22]. There are four distinct advantages of using WSP: (i) The metal bound to the polymer in solution can be easily concentrated by UF; (ii) the metal subsequently released from the WSP can be easily segregated by UF to allow for recycle of the extraction agent and disposal of the metal; (iii) commercially available polymers can be modified to selectively bind the target metal ions [22]; (iv) the kinetics of absorption are rapid as the size of the molecules are relatively small compared to particulate materials such as column absorbents and ion exchange resins, where transport processes are limited by diffusion in the porous materials. PEI is one of the most interesting compounds to use, as the primary interactions between metal cations and the cationic polymer must be through the mechanism of chelation/complexation rather than ionic interaction and should therefore be very selective over a wide range of conditions. This means the polymer does not suffer as badly from interferences such as the ionic strength of the solution, as much as poly acrylic acid for example. The drawback of using the PEUF is that the polymer normally interacts with the membranes. The nature of this interaction is dependent on the solution conditions, particularly ionic strength and most critically the pH, which can alter both the membrane charge and the net charge on the polymer. The overall result of the interaction of the polymer with the membrane is to cause fouling and increased membrane resistance, which results in a reduced flux [28]. The use of a high molecular weight polymer and a relatively small pored membrane means that the fouling layer will only involve concentration polarization and surface adsorption rather than pore blocking as observed elsewhere [28].

In most of the previous PEUF studies, the complexation of single metals with a polymer has been investigated by using batch or semi-continuous ultrafiltration systems [12,18,23–28]. However, in real industrial effluent and waste streams, more than one metal ion will be present and the effect of metals competition should be considered. In addition, other chelating agents and compounds that bind metals can also compete with PEI, reducing performance. In this paper an investigation and comparison of the binding of single metal ions and mixtures of metal ions with PEI is reported. This is done using the retention data from the PEUF process. The data are fitted to the Langmuir isotherm to obtain the key binding characteristics. The effects of the competition between metal ions binding to the polymer and the retention of these metal ions in the PEUF process are also reported.

2. Experimental studies

2.1. Materials

2.1.1. Stock metal solutions

Individual stock metal solutions of 1000 mg/l 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 $3CdSO_4 8H_2O$ all Fisher Scientific chemicals, reagent grade) to a volume of high purity water (conductivity lower than 1 S/cm) obtained from a Millipore Elix 3 unit.

2.1.2. Polyethylenimine solutions

The polychelatogen used was PEI. This 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 and consists of approximately 60,000 subunits.

2.1.3. Metal/polymer solutions for ultrafiltration

Two different types of solution were used in the ultrafiltration experiments: (i) solutions containing a single metal ion, buffer solution (0.01 M KH_2PO_4) and PEI; and (ii) solutions containing mixtures of metal ions, buffer solution (0.01 M KH_2PO_4) and PEI.

The aqueous metal solutions used in ultrafiltration experiments were produced by the addition of the correct amount of stock metal solution to the appropriate amounts of buffer and PEI solutions. The concentrations of each metal in both types of solution before filtration were varied from 2 mg/l to 60 mg/l (metal), whilst the initial concentration of PEI was kept constant at 1 g/l. The mixed metal solution was made up of equal quantities of the metal as their salts. All these solutions were buffered at pH 5.5. The pH of the final solutions was adjusted to the appropriate value by the dropwise addition of 1 M HCl or 1 M KOH.

2.1.4. Membrane

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 a relatively hydrophilic (compared to many other membranes they have low surface tension to water) and thus have 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 PEUF experiments. The membrane has been thoroughly characterized in a previous study [29].

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 maximum operating pressure for the cell is approximately 5 bar, and the cell can hold a membrane disk of 44.5 mm in diameter with an effective membrane area of 13.4 cm². 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 guage (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 and provide homogeneity in the solution inside the cell. A water jacket around the filtration cell body (which was made in the department) was connected to a water bath. The filtration temperature was kept constant at 25 0.1°C.

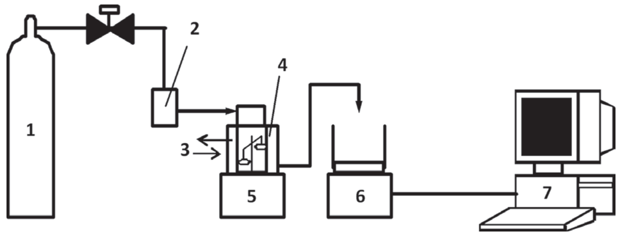

Fig. 1. Schematic diagram of stirred frontal (dead-end) ultrafiltration system. (1) Nitrogen cylinder, (2) pressure gauge, (3) 250 ml reservoir, (4) water jacket, (5) filtration cell, (6) magnetic stirrer, (7) electronic balance, (8) personal computer.

2.2.1. Retention studies

Binding and ultrafiltration studies were carried out in the following manner. A varying amount of each individual metal ion was added to a solution containing PEI and the pH was adjusted to 5.5. The final solution had a PEI concentration of 1 g/l in all cases. The solution was then filtered 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 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). Detailed descriptions of the instrument (Spectro Ciros ICP spectrometer) and operating procedures can be found elsewhere [30]. This was done in order to determine the metal ion content in the permeate.

3. Theory

3.1. Retention of metal ions

The use of ICP analysis of the permeate samples for the relevant metal allows the calculation of the observed retention value (R_i) of each metal ion using:

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

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

3.2. Langmuir isotherms

The use of Langmuir isotherms to describe the complexation process of binding metal ions to the polymer has previously been investigated using the washing and enrichment methods of the PEUF process [23–25]. In this case the assumption that the concentration of metal ions in the permeate, C_{pi}, represents the concentration of metal that is free in the solution, Y_i, is made. This is a simplification of the washing and enrichment methods.

The Langmuir isotherm equation is given by:

$$Q = \frac{Q_{\max} \cdot Y_i}{K_L + Y_i} \tag{2}$$

where Q is the amount of metal bound (mg metal/g polymer). $Q_{\max}$ is the maximum capacity of polymer (mg metal/g polymer). Y_i is the metal-free in solution (mg/l). K_L is the Langmuir equilibrium binding constant (mg/l).

Taking reciprocals of both sides of the Langmuir equation gives a linear form:

$$\frac{1}{Q} = \frac{K_L}{Q_{\max}} \frac{1}{Y_i} + \frac{1}{Q_{\max}} \tag{3}$$

Plots of $1/Q$ versus $1/Y_i$ give a straight line and the values of $Q_{\max}$ and K_L can be calculated from the intercept and slope of the plots, respectively.

The applicability of the Langmuir isotherm to describe the systems investigated was explored. The linear form of the Langmuir equation (Eq. (3)) was fitted to the experimental data using linear regression.

4. Results and discussion

4.1. Study of single metals with PEI binding and filtration

A study of single metal binding was carried out. This was done by adding solutions of individual metals and PEI to the UF filtration apparatus, the permeates were then collected and analyzed for metal content. The filtration was carried out at pH 5.5 as this was determined previously as giving maximum ion retention of Cu^{2+} and Zn^{2+} [31,32]. Fig. 2 shows the linear regression fits of the Langmuir isotherm to the data obtained for single metal ions in solution with PEI at pH 5.5. The Langmuir isotherm fitted the experimental data very well (R^2 values >; 0.98, see Table 1). This shows that the Langmuir isotherm offers a good description of the binding of metal ions to the polymer.

Fitting the Langmuir isotherm to the experimental data also allowed evaluation of the maximum binding capacity, $Q_{\max}$, of the polymer for each metal ion at the given solution conditions. This data is shown in Table 1. The following trend for the $Q_{\max}$ values was found:

Cu^{2+} >; Cr^{6+} >; Zn^{2+} >; Ni^{2+} >; Co^{2+} >; Cd^{2+}

The binding affinity constants are also shown in Table 1. These data show that there is considerable variation in this binding constant and from 22 mg/l with Cu^{2+} to 0.76 mg/l with Co^{2+} and that high affinity is not necessarily related to high capacity. These values can be useful when considering the retention of the metal ions in the ultrafiltration process.

The retention profiles of single metal ion/polymer solutions are shown in Fig. 3. At the lowest concentration of metal ions (i.e., 2 mg/l) all the metal ions showed high retention (> 80%). As the concentration of metal ions increased, differing retention profiles were found. For Cu^{2+} and Cr^{6+} ions, the retention profile remains level for all concentrations of metal ions used. This is because the $Q_{\max}$ value for each of these metal ions is relatively high (169.5 mg metal/g_{PEI} for Cu^{2+} ions and 60.6 mg metal/g_{PEI} for Cr^{6+}) in comparison to the maximum concentration of metal ions used i.e., 60 mg/l. For the other ions used as the $Q_{\max}$ value is approached the retention of the metal ions starts to drop as the polymer becomes saturated with metal ions so no more ions can be bound. This results in more free metal ions in the solution which will pass through the membrane into the permeate.

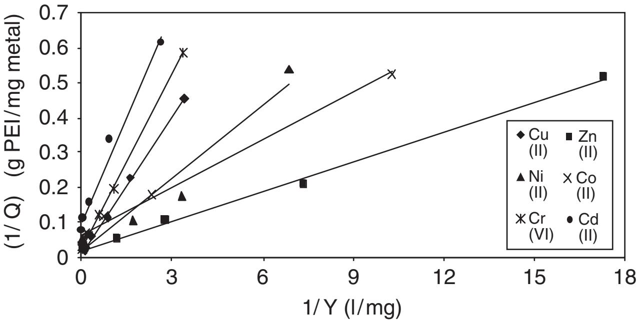

Fig. 2. Langmuir isotherm model fits to the experimental data for binding of single metal ions to PEI at pH 5.5 (polymer concentration = 1 g/l PEI).

Table 1
Values of the constants obtained by linear regression for single metal ions/polymer solutions for the Langmuir isotherms

System	Slope K_L/Q_{max}	Intercept Q_{max}	Q_{max} mg_{me}/g_{PEI} (mmol/g)	K_L mg/ l (mM)	R^2
Cu^{2+}/PEI	0.132	0.0059	169.5 (2.66)	22.3 (0.350)	0.998
Cr^{6+}/PEI	0.169	0.0165	60.6 (1.18)	10.2 (0.203)	0.999
Zn^{2+}/PEI	0.028	0.018	55.2 (0.847)	1.56 (0.021)	0.997
Ni^{2+}/PEI	0.074	0.052	19.2 (0.33)	1.43 (0.024)	0.996
Co^{2+}/PEI	0.046	0.060	16.6 (0.28)	0.76 (0.012)	0.989
Cd^{2+}/PEI	0.201	0.097	10.3 (0.09)	2.08 (0.018)	0.985

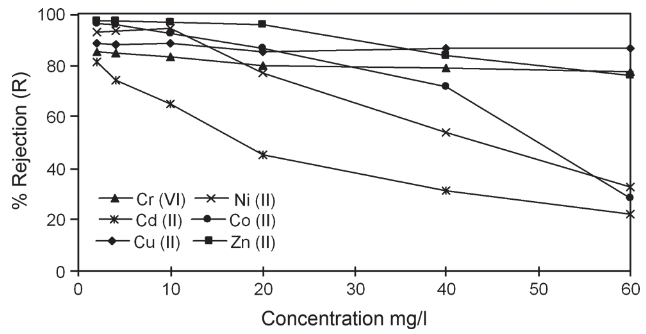

Fig. 3. Retention values of single metal ions at pH 5.5 in the presence of 1 g/l PEI for different feed metal concentrations using batch mode of PEUF.

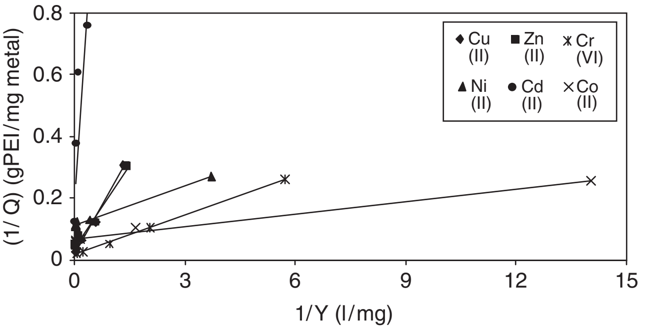

Fig. 4. Langmuir isotherm model fits to the experimental data for binding of mixtures of metal ions to PEI at pH 5.5 (polymer concentration = 1 g/l PEI).

4.2. Study of mixtures of metal ions with PEI binding and filtration

Results from binding studies of single metal ion solutions have shown the ability of achieving a maximum binding of metal ion to the polymer using batch mode PEUF with PEI as a polychelatogen. As an extension to the work carried out on simple aqueous solutions of single metal ions, the competition effect of mixtures of metal ions in batch mode PEUF was investigated. Langmuir isotherms were explored under competitive conditions of mixtures of metal ion solutions with PEI.

Fig. 4 shows the linear regression fits of the Langmuir isotherm to the data for mixtures of metal ions,. As before, the Langmuir isotherm offers a good description of the binding conditions. This is shown in Table 2 where the R^2 values for the Langmuir isotherm are above 0.98 for all ions bar Cd^{2+}.

Again, fitting of the Langmuir isotherm allowed estimation of the maximum capacity of the polymer for metal ions, Q_{max}, under competitive conditions (see Table 2). The following trend for the Q_{max} values was found:

Cu^{2+} >; Cr^{6+} >; Zn^{2+} >; Co^{2+} >; Ni^{2+} >; Cd^{2+}

The positions of Ni^{2+} and Co^{2+} have been switched in this list when comparing to the data for solutions of single metal ions. Comparing the values in Tables 1 and 2, it can be seen that the Q_{max} values for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} decrease substantially (by 50% or greater) under competitive conditions whereas the Q_{max} values for Cr^{6+} and Co^{2+} remain very similar to the values for the single metal ion polymer solutions. Also the binding constant were altered, generally they were lowered substantially with the exception of Zn^{2+} and Cd^{2+}.

This data suggests that Cr^{6+} and Co^{2+} have different binding mechanisms or bind to different sites than the other metal ions and so are not affected by the presence of these ions. However, Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} all seem to be competing for the same binding sites on the polymer and are affected by the presence of other ions.

The retention values with the metal concentrations under competitive conditions are shown in Fig. 5. The retention profile for Cr^{6+} was similar to that obtained for the single metal ion/polymer solutions of these ions

Table 2
Values of the constants obtained by linear regression for mixtures of metal ions/polymer solutions for the Langmuir isotherms

System	Slope K_L/Q_{max}	Intercept Q_{max}	Q_{max} mg_{me}/g_{PEI} (mmol/g)	K_L mg/ l (mM)	R^2
Cu^{2+}/PEI	0.217	0.0147	68.03 (1.07)	14.73 (0.225)	0.991
Cr^{6+}/PEI	0.043	0.0167	59.88 (1.17)	2.56 (0.05)	0.999
Zn^{2+}/PEI	0.179	0.0395	25.32 (0.39)	4.52 (0.07)	0.981
Ni^{2+}/PEI	0.013	0.0693	14.43 (0.27)	0.19 (0.003)	0.989
Co^{2+}/PEI	0.041	0.1143	8.75 (0.149)	0. 36 (0.006)	0.996
Cd^{2+}/PEI	1.611	0.2164	4.62 (0.091)	7.44 (0.006)	0.774

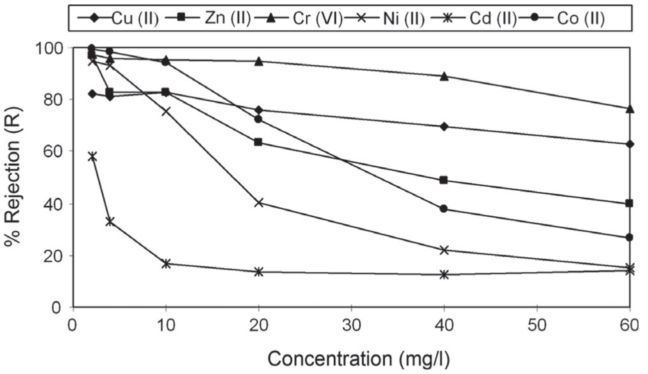

Fig. 5. Retention values of mixtures of metal ions at pH 5.5 in the presence of 1 g/l PEI for different feed metal concentrations using batch mode of PEUF. The individual concentration of metals are given within the mixture.

(Fig. 3), showing no significant impact of metals competition on the retention of these ions. For the other metal ions, the highest retention was observed at low metal concentrations, with a dramatic drop in retention being observed as the concentration of the metal ions increases. The Co retention profile was changed and seems to be more affected by additional concentration of other metal ions reducing this is due to saturation of the polymer binding for this material at high concentrations and hence a rapid decreased rejection (Fig. 5).

5. Conclusions

In an attempt to identify the effect of metal ion competition on binding to PEI, PEUF experiments in the presence of single metal ions and mixtures of metal ions have been carried out. The results have been fitted to the Langmuir isotherms and this gave good fits with the R^2 values near to 1.

Fitting the Langmuir isotherm to the experimental data also allowed evaluation of the maximum binding capacity, Q_{max}, of the polymer for each metal ion. It was observed that the maximum amount of metal ions bound to the polymer, Q_{max}, for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} decreased substantially in solutions containing mixtures of metal ions when compared to the values obtained for single metal ion solutions. However, for Cr^{6+} and Co^{2+} no significant decrease in Q_{max} was seen. These data suggest that the binding sites of Cr^{6+} remain constant in competition, while Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} show changes in both binding capacity and equilibrium constant. Uniquely, Co retains also its binding capacity but as this capacity was low its rejection declines rapidly as polymer becomes saturated (Fig. 5). Chromium (VI) binding has also been investigated with by other workers [33] and this has shown that the ion was retained in PEUF system irrespective of pH [31–33]. The explanation for this is that the Cr (VI) does not exist in a free form but as a series of anionic complexes, the predominate species, at pH 5.5, being dichromate, $Cr_2O_7^{2-}$.

The nature of metal binding to PEI is complex and although the binding mechanism have been discussed elsewhere [13–15], the specific behavior of PEI will be dependent not only on its structure but also environmental factors such as pH and ionic strength that will affect the tertiary structure of this molecule so changing its metal binding characteristics. The binding of a metal may also be changed by interactions with other metals present within the PEI polymer complex, enhancing or reducing binding strength and number of binding sites. The accumulation of the polymer at the membrane surface may also affect its metal binding characteristic and metal rejection by the membrane may also be affected.

The performance and effectiveness of the PEUF process is therefore heavily dependent on the concentration of competing metal ions, influencing both capacity and selectivity of these systems. However, as the kinetics of these processes are relatively fast compared to ion exchange/absorption on to large particles, where diffusion becomes the controlling mechanism for the rate of absorption, then the equilibrium data does represent the absorption capacity and affinity very well.

In practical situations, i.e., multiple metal species in an ill-defined complex mixture of other ions, these inferences have a number of consequences. Firstly, assessing the ability of PEUF systems to recover metals requires study of the specific mixture involved as the characteristics of the binding is dependent on the composition and physical conditions, for example, the selective absorption and purification of metals from land fill leachates or other waste streams. This is a complex relationship and not easily determined from simple fundamental studies using single metal species. A further complication in complex systems, such as wastes or leachates, is also the presence of low molecular weight chelators that may bind metals in competition with PEI, so substantially changing the potential performance of PEUF. Finally, the equilibria determined here also show that it may be possible to select and purify metals from mixtures by a series of absorption stages rather than a single stage process.

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