

Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration

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Abstract

This study deals with the removal of chromium species from aqueous dilute solutions using polymer-enhanced ultrafiltration (PEUF) process. Three water soluble polymers, namely chitosan, polyethyleneimine (PEI) and pectin were selected for this study. The ultrafiltration studies were carried out using a laboratory scale ultrafiltration system equipped with 500,000 MWCO polysulfone hollow fiber membrane. The effects of pH and polymer composition on rejection coefficient and permeate flux at constant pressure have been investigated. For Cr(III), high rejections approaching 100% were obtained at pH higher than 7 for the three tested polymers. With chitosan and pectin, Cr(VI) retention showed a slight increase with solution pH and did not exceed a value of 50%. An interesting result was obtained with PEI. The retention of Cr(VI) approached 100% at low pH and decreased when the pH was increased. This behavior is opposite to what one can expect in the polymer-enhanced ultrafiltration of heavy metals. Furthermore, the concentration of polymer was found to have little effect on rejection. Permeate flux remained almost constant around 25% of pure water flux.

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1. Introduction

Chromium is a unique toxic element, regulated with respect to its oxidation stages between Cr(III) and Cr(VI). Chromium(VI) is recognized to be much more toxic than chromium(III). Hexavalent chromium compounds are carcinogenic and corrosive on tissue, and are found to be toxic to bacteria, plant, animals and people. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage. This is the reason why World Health Organization recommends the toxic limits of chromium(VI) in wastewater at the level of 0.005 ppm [1]. Chromium is widely used as an alloying and plating element on metal and plastic substrates for corrosion resistance, chromium-containing stainless steels, protective coating for automotive and equipment accessories, nuclear and high temperature research, and constituent of inorganic pigments.

Thus, stringent quality standards for wastewater containing heavy metals have been enacted. With these more stringent standards, industries, which previously discharged their effluent with minimal pretreatment, are now being required to remove heavy metals down to very low concentrations. Therefore, there is an urgent need for efficient separation techniques, which may reduce the concentration of heavy metals to low values. To enable further processing and achieve recovery of metals, separation should be selective. One separation technique, which can meet this requirement, is polymer-enhanced ultrafiltration (PEUF).

PEUF is the combination of two phenomena; binding of metal ions to a water-soluble polymer, and ultrafiltration. Since pore size of ultrafiltration membranes are not suitable to separate heavy metal ions, water-soluble polymers are used to bind the metals to form macromolecular complexes [2–5]. These large molecules, having a larger molecular weight than the molecular weight cut off of the membrane, will be retained, while the non-complexed ions pass through the membrane. With this method, using different water-soluble polymers or introducing

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new functional groups to the polymer, it is possible to achieve selective separation and recovery of heavy metals with low energy requirements [6–25].

The pH value is a very important factor in most cases of polymeric binding since either protons or hydroxyl anions can compete with metal to be bound to the polymer. Generally, for example, the presence of protons influences the equilibrium of ion-exchange processes and also, of complex equilibria. In the case of metal binding with polybases, like polyethyleneimine (PEI), at lower pH, electron-donating amino groups become positively charged due to protonation and thus unable to form chelates with cations. If several metal ions form macromolecular complexes with different stability constants, it is possible to separate them by varying the pH. A strong pH dependence of the element retention was also observed for the separation and removal of radionuclides [6,7]. The dependence of the interaction species compound stability upon pH was also used for the recovery of metals from their interaction products with the polymer and to recycle the polymer. If the metal is present in the feed solution in an anionic form, the presence of hydroxyl anions may affect the binding due to the possible competition.

Studies on the application of PEUF for the removal of chromium species are scarce in the open literature. Furthermore, much of previous studies focused on the use of PEI and chitosan as binding polymers for the removal of heavy metals by ultrafiltration. In this study we are proposing pectin as new binding polymer for the removal of chromium species from aqueous solutions. Pectin was selected because it is a biopolymer with relatively simple structure in which only carboxylic groups are responsible for metal ion complexation. In order to compare the performance of pectin, PEI and chitosan, two frequently used water-soluble polymers were selected for this study. In this case, the nonprotonated amino groups on chitosan and the unshared electron pair on the N atom in PEI, can form donor bonds with coordination-unsaturated transition metals [2,10]. Therefore, the objectives of this research are: (1) to study the effects of pH and polymer concentration on the retention of Cr(III) and Cr(VI), and (2) to compare the performance of pectin as a binding polymer with that of the frequently used polymers, namely chitosan and PEI.

2. Experimental procedures

2.1. Materials

The chemical reagents used in the experiments were pectin powders from citrus fruits with contents of 79% galacturonic acid and 8% of methoxyl from SIGMA, chitosan flakes from crab shell, and polyethyleneimine (PEI) with a MW of 25,000 (50 wt.% aqueous solution) as a polymer binding solutions, chromium nitrate for preparation of Cr(III) solution, potassium dichromate for preparation of Cr(VI) solution, hydrochloric acid, and sodium hydroxide for pH adjustment. All the chemicals were used without treatment. Deionized water obtained from deionization system (Micromeg, Elgastat) was used for dilution and preparation of feed solution. The membrane used was Midgee polysulfone membrane cartridge with effective fil-

tration area of 26 cm² and molecular weight cut-off (MWCO) 50,000 Da and a pure water permeate flux, J_w of 9.8619 m/s after 10 min of operation at 1.2 psig.

2.2. Apparatus

A laboratory scale Midge Cross Flow Filters system was employed in this study. The system consists of the following items: feed, retentate, and permeate reservoirs with tubing and backpressure valve; a peristaltic pump and transformer located on the mounting platform together with the Midgee membrane cartridge; pressure transducers with a digital panel meter/display; stirrer for mixing; and power supply with maximum 20 V dc. A Horiba F-23 pH meter was used for pH measurements.

2.3. UF experiments

The feed consists of a 10 ppm Cr(III) or Cr(VI) solution containing the desired amount of water soluble polymer at a pH adjusted to the desired value using either HCl or NaOH. Such low chromium concentration was used based on the range of application of PEUF process which is known to be useful only for dilute solutions. Furthermore, the use of higher concentrations, especially in the case of Cr(III), may result in metal hydroxide precipitation which will interfere with the PEUF process. In order to study the mass effect, the amount of the polymer was varied from 0.05 to 0.25% keeping the total chromium concentration equal to 10 ppm and solution pH at 8.00.

All experiments were conducted at room temperature and pressure different of 1.2 psig.

In all experiments, the feed volume was 250 cm³ and the first 10 cm³ of permeate were discarded. During the UF runs; solution pH, temperature, feed flow rate and pressure difference were kept constant and monitored continuously. The feed solution was kept stirred at 200 rpm and circulated by means of the pump, then passed through the membrane cartridge. The UF run was stopped when the permeate volume reached 20 cm³. The retentate and permeate streams, and the feed were then analysed for their chromium content. Although feed solution was prepared for certain metal concentration, there were deviations from the prepared concentration due to evaporation and/or taking samples from feed and permeate stream [14]. Therefore, feed streams should also be analyzed. The retention values were calculated from the formula:

$$R = 1 - \frac{C_P}{C_F} \quad (1)$$

where C_P is the concentration of metal ion in permeate and C_F is the concentration of metal ion in feed solution. In this work, the C_P represents the average chromium species concentration throughout the UF run [14–16].

The used membrane was immediately flushed with deionized water after UF, and then, cleaned in sequence by rinsing with 0.1 M NaOH and 100 ppm NaOCl. The water flux was always measured before every UF run in order to assess the cleanness of the membrane.

2.4. Analysis

The concentration of chromium was determined using a Varian Liberty200 ICP-AES equipment. The accuracy of the ICP-AES measurements was evaluated using the feed solutions as standards. Less than 5% deviations were recorded between the ICP readings and the actual feed concentrations.

3. Results and discussion

3.1. Speciation studies

Speciation profiles are very important for the interpretation and understanding the reactivity of ionic species in solution. They permit the identification of forms in which ions are present in solution as a function of the pH.

In this investigation, Visual Minteq Software Version 2.25, was used to generate species profiles for Cr(III) and Cr(VI) at total chromium concentration of 10 ppm.

3.1.1. Speciation profiles for Cr(III)

The speciation profiles for Cr(III) are given in Fig. 1. As shown in this figure, Cr(III) exists in solution in seven different soluble species and the proportions of these species vary with the pH.

Up to a pH of 2, the major species is Cr^{3+} , which represents 100% of the total chromium. This species disappears at pH 5, where the soluble complex CrOH^{2+} becomes the major component. CrOH^{2+} species disappears at pH 7 and Cr(III) take the form $\text{Cr}(\text{OH})_3(\text{aq})$, a neutral species and $\text{Cr}(\text{OH})_2^+$ a monovalent cation.

Between pH 8 and 10 the total of Cr(III) is in the form of neutral species $\text{Cr}(\text{OH})_3(\text{aq})$. At pH values higher than 10, the anionic species $\text{Cr}(\text{OH})_4^-$ starts to appear to become the only species at pH 13 and above.

3.1.2. Speciation profile on Cr(VI)

Fig. 2 shows the speciation profile of 10 ppm concentration of Cr(VI). As shown in Fig. 2, Cr(VI) exists in four different soluble species in solution; the proportions of these species vary with pH. Up to pH 6.0, the major species is $\text{Cr}_2\text{O}_7^{2-}$, which represents 96% of the total chromium and disappears at pH 9. A very low

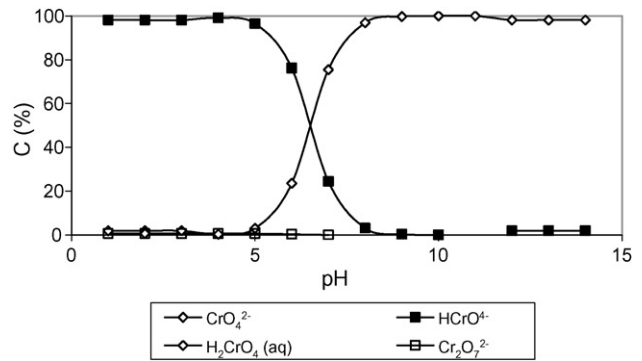


Fig. 2. Speciation profiles of Cr(VI).

concentration of the natural species, $\text{H}_2\text{CrO}_4(\text{aq})$ appears at pH 2.0 and 3.0 only. HCrO_4^- exists in low concentration at pH 1.0–8.0 and disappears at pH 10.0. At pH higher than 8.0, the CrO_4^{2-} species starts to form to become the only species at pH 10 and above. As shown in these profiles, Cr(VI) exists mostly as anionic species over the entire pH range.

3.2. Effect of pH on chromium ion retention by polymer-enhanced ultrafiltration

One of the most important factors in the interaction of metal ion with binding polymer is the pH. The effect of pH may be regarded in several ways, for strong polyelectrolytes, very low pH values are associated to a high ionic strength, and in consequence, competition of H^+ with metal ions to condense on the polymer surface will take place. As described in previous studies [2–4], weak polyelectrolyte containing carboxyl ions are characterized by high retention ability at pH above 3.0, where most carboxylic units are deprotonated.

As pH of solution increases, generally retention of metal cations also increases in the acidic region up to certain pH value. It should be noted that many heavy metals form hydroxides with very low solubility at high pH regions. Since, pH sensitivities of metal–polymer complex formation vary significantly from metal to metal, this can be exploited for their selective separation.

3.2.1. Effect of pH on chromium retention using pectin

The effect of pH on rejection of chromium ions using pectin is shown in Fig. 3. The figure shows clearly that Cr(III) rejection is much higher than that of Cr(VI) over the entire tested pH range. At pH 3, the Cr(III) rejection is low due to the protonation of chelating groups which in this case are carboxylic functions. As expected the retention of Cr(III) increases with increasing pH due to the deprotonation of the carboxylic groups of pectin that results in an increase in Cr(III) complexation. At pH greater than 6, the Cr(III) retention reaches a plateau at a value of 99%. The pH value is evidently a very important factor in most cases of polymeric binding because either protons or hydroxyl anions can compete with the metal component to be bound to the polymer. Therefore, with pectin, at higher pH value, more hydrogen ions and RCOO^- were produced which increases the binding site for

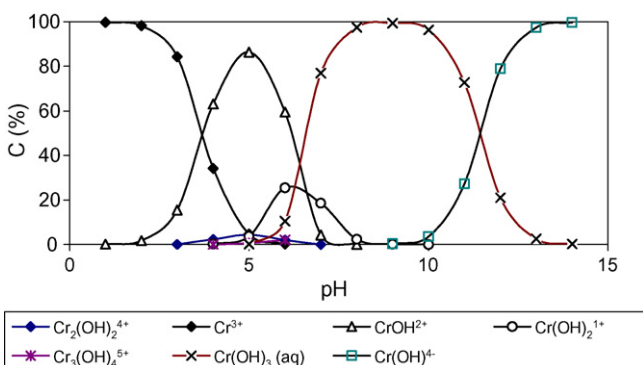


Fig. 1. Speciation profiles of Cr(III).

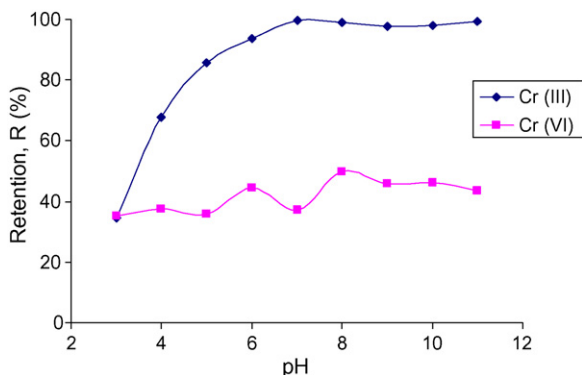
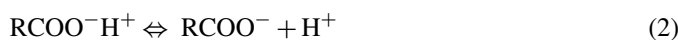


Fig. 3. Effect of pH on Cr(III) and Cr(VI) rejections using 0.05% pectin.

heavy metal ions in ionic interaction as shown in the following equation:



According to Eq. (2), an increase in pH values, enhances the formation of complexes hence increasing metal retention.

The rejection of Cr(VI) is found to be independent of pH. Over the entire investigated pH range, the retention of Cr(VI) remained almost constant around a value of 30%. This result indicates lower ability of Cr(VI) ion to be bound with pectin. This is inline with the Cr(VI) speciation profiles which indicate that Cr(VI) is mainly present as anionic species. These ionic species are not expected to be complexed by carboxylic groups. As such the observed retention for Cr(VI) is not due to a complexation mechanism but is due to the formation of pectin gel layer on the surface of the membrane. In this case, the Cr(VI) are trapped in this gel layer.

3.2.2. Effect of pH on chromium retention using chitosan

Chitosan is the most prominent modified natural polymer as cationic polyelectrolyte. Commercial chitosan is the medium molecular weight and has a charge density, which is pH dependent and can be as high as 80 mol% [8].

Fig. 4 shows the rejection behavior of Cr(III) and Cr(VI) using chitosan. It is found that the rejection for both chromium increases with increasing pH especially at higher pH started

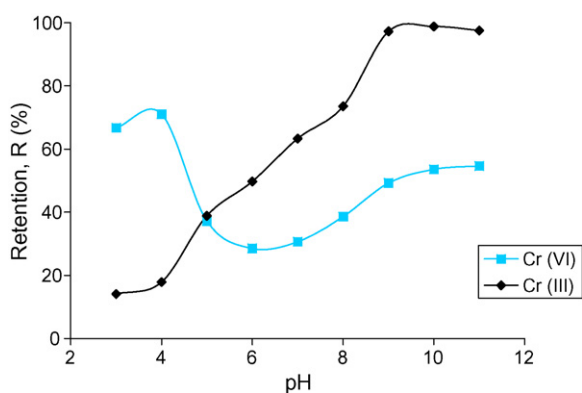
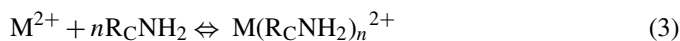


Fig. 4. Effect of pH on Cr(III) and Cr(VI) rejections using 0.05% chitosan.

from neutral pH in the order $R_{\text{Cr(III)}} > R_{\text{Cr(VI)}}$. Cr(III) rejection increases with increasing pH and then reaches plateau at near 1. For Cr(VI), the rejection first decreases with the pH and then gradually increases to reach a plateau starting from pH 9.

It is known that the nonprotonated chitosan, having the unshared electron pair on the nitrogen atom, is capable of forming donor bonds with the coordination-unsaturated transition metals [2,9]. Two –OH groups and one –NH₂ group are grabbed by metals and the fourth site is likely occupied by a water molecule or the –OH group on the third carbon atom. Hence, we have:



where n is the average number of the unprotonated amino group bound to one metal. An increase in rejection by increasing pH can be explained by the following complexation reaction:



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

3.2.3. Effect of pH on chromium retention using polyethyleneimine (PEI)

Fig. 5 demonstrated that Cr(III) rejection with PEI first decreases at low pH values. Then the Cr(III) retention increases very sharply at a pH more than 5 to reach a plateau at pH 7 and above. This behaviour is similar to that of chitosan.

Different behavior is found for Cr(VI) where the rejection values are constant very high near 1 at low pH up to pH 9 and then suddenly it decreases at pH 9 and above. This behaviour is in concordance with the Cr(VI) speciation profiles which show that only anionic species exist in solution. These anionic species can be complexed by the protonated PEI. It is also well known that PEI is very effective for neutralization of excess anionic colloidal charge, especially under acidic and neutral pH conditions [2,11].

3.3. Effect of pH on PEUF flux

Figs. 6–8 show the effect of solution pH on the PEUF flux. As shown in these figures the pH has a little effect on flux with values

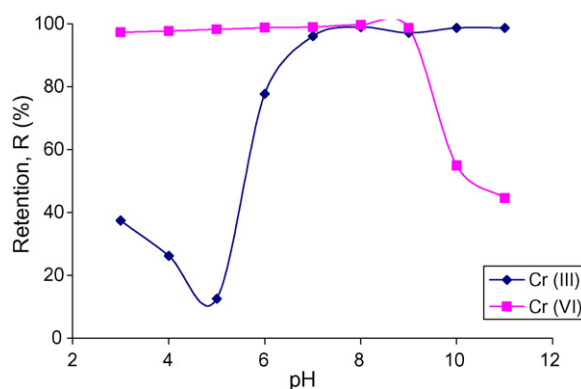


Fig. 5. Effect of pH on Cr(III) and Cr(VI) rejections using 0.05% PEI.

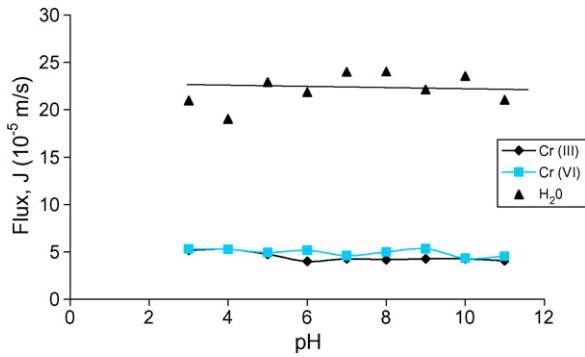


Fig. 6. Permeate flux of water and chromium using 0.05% pectin at different pH value.

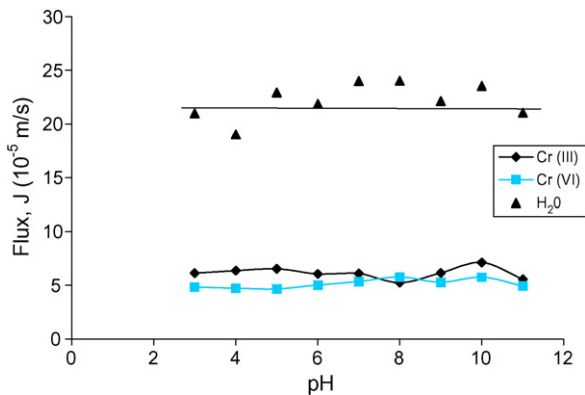


Fig. 7. Permeate flux of water and chromium using 0.05% PEI at different pH values.

fluctuating around 20–25% of the pure water flux. However, the pectin systems showed slightly lower PEUF flux compared to chitosan and PEI. This is expected since pectin is known to form a gel layer that can effect negatively UF flux.

3.4. Effect of polymer concentration on chromium ion retention by polymer-enhanced ultrafiltration

Practically, all water-soluble polymers exhibit typical polyelectrolyte behavior, which decreases in the reduced viscosity

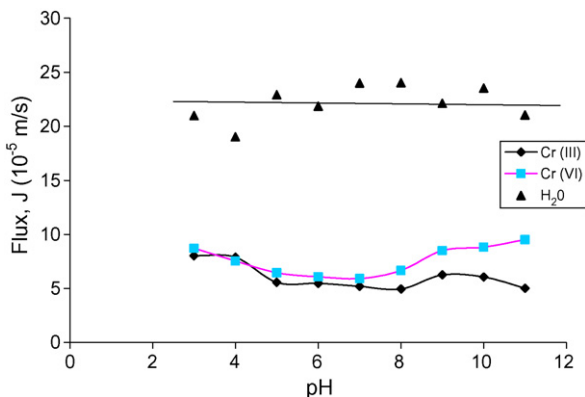


Fig. 8. Permeate flux of water and chromium using 0.05% chitosan at different pH values

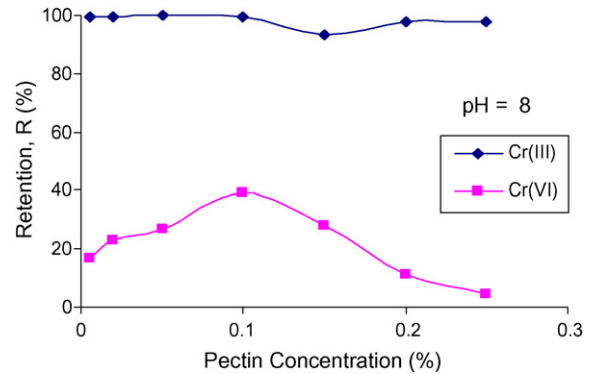


Fig. 9. Effect of pectin concentration on Cr(III) and Cr(VI) rejection.

with an increase in polyelectrolyte concentration. This behavior is due to the fact that as the polyelectrolyte concentration decreases, ionization degree increases and the produced ions forming an ionic atmosphere higher than the diameter of polymeric coil. The repulsion among the ions increases the rigidity of the chain, expanding the polymeric coil with a consequent increase of the viscosity.

3.4.1. The effect of pectin concentration on chromium retention

All the samples of chromium(III) and (VI) with same concentration (10 ppm), at different pectin concentrations were prepared and the effect of pectin concentration on chromium removal were studied. The pH values of these samples were fixed at 8.0. The retention values of Cr(III) and Cr(VI) at different pectin concentration are plotted in Fig. 9.

From Fig. 9, it is found that the retention of Cr(III) stays almost constant at a value very close to one at all pectin concentrations. It is shown that for Cr(III), the rejection is not much affected by the pectin concentration values. Nevertheless, it is obtained that pectin even at very low concentration has the capability to bind with metal to form macromolecular complexes as an effective complexing agent.

This behavior explains that there was the equilibrium between free chromium ions, pectin molecules and complexes formed, and indicates that pectin can be one of the most effective water-soluble polymers to be used for the removal of chromium(III).

Low retention coefficient is obtained in the case of Cr(VI). The retention initially increases until the concentration of pectin becomes 0.1% of pectin then decreases as the concentration of pectin is increased. This result confirm the fact that the interaction between Cr(VI) species and pectin is not a type of complexation mechanism.

3.4.2. The effect of PEI concentration on chromium ion retention

The effect of PEI concentration on chromium ions retention is shown in Fig. 10. It is observed that the rejection of Cr(III) first increases and later remain constant at $R = 1.0$ for all PEI concentrations. It is demonstrated that PEI is also very effective agent for removing Cr(III) from aqueous solution. Cr(VI) rejections obtained are very efficient, where the rejection

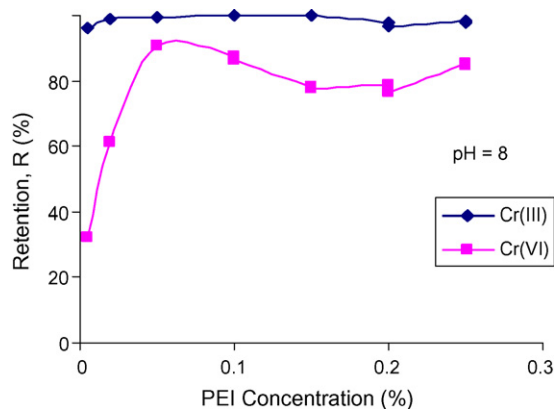


Fig. 10. Effect of PEI concentration on Cr(III) and Cr(VI) rejection.

increases with PEI concentration and achieved highest rejection at 0.05% PEI. However, the rejection is slightly reduced at higher concentration of PEI. This result is due to the typical polyelectrolyte behavior where the retention of both chromium decreases with increasing polymer concentration due to the decreasing of viscosity of the solution. The equilibrium state of protonated and free amino group is strongly dependent on pH and shifted to the free amino group as it increases. Thus, uncharged PEI can be obtained, which allows higher interaction among the backbone segments adopting preferentially a coiled globule-like conformation, and therefore a smaller viscosity [12].

4. Conclusions

This study showed that PEUF is a promising method for the removal of chromium species from dilute aqueous solutions. Pectin, a new polymer introduced in this research, showed better performance for the separation of Cr(III) than chitosan and PEI. Whereas PEI showed better performance for the removal of Cr(VI) compared to the two other polymers.

Solution pH was found to be the major factor which controls the rejection of both chromium species. For Cr(III), high rejections approaching 100% were obtained at pH more than 7 for the three tested polymers. Cr(VI) showed different behavior for each type of polymer. Little effect of pH is obtained for the retention of Cr(VI), which remained almost constant around a value of less than 50% with chitosan and pectin. An interesting result was obtained with PEI where the retention of Cr(VI) approached 100% at low pH and sharply decreased at pH 9 and above. This behavior is opposite to what one can expect in the polymer-enhanced ultrafiltration of heavy metals.

The effect of the pectin and PEI concentrations on the retention of both chromium ions are also investigated. Big impact is obtained on the removal of chromium, especially for Cr(VI) rejection. The rejection increased with change of pectin and PEI concentrations but reduced when the concentration is very high. For Cr(III), rejection was high and not much effected by the change of both pectin and PEI concentrations.

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