

EFFICIENT REMOVAL OF Cr(VI) BY POLYELECTROLYTE-ASSISTED ULTRAFILTRATION AND SUBSEQUENT ELECTROCHEMICAL REDUCTION TO Cr(III)

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ABSTRACT

This work is focused on the removal of Cr(VI) ions from aqueous solution using water-soluble poly(diallyldimethylammonium chloride), PDDA, coupled to an ultrafiltration membrane of regenerated cellulose and subsequent electrochemical reduction of Cr(VI) to Cr(III). The removal of Cr(VI), using the washing mode, was studied as a function of pH, the molar ratio of polymer:Cr(VI), and the presence of interfering ions. The enrichment mode was used to determine the maximum retention capacity of the polymer, and the release of Cr(VI) and regeneration of the polymer were analysed by sorption-desorption process. Subsequently, the electroanalysis of Cr(VI) was conducted by linear sweep voltammetry and full electrolysis at controlled-potential in acidic media and in the presence of PDDA.

The results show an efficient removal of Cr(VI) (95%, 30 mg/L in the feed) using PDDA at pH 9 and a polymer:Cr molar ratio of 20:1. The retention capacity of the polymer was decreased by the presence of sulphate anions.

The maximum retention capacity of PDDA was 33 mg Cr/g polymer at pH 9. Using the sorption-desorption process, the results indicated that this water-soluble polymer can release Cr(VI) and be regenerated. Finally, the electrolysis of Cr(VI) to Cr(III) was performed successfully in the presence of PDDA.

Keywords: Chromium; ion exchange; membrane; water-soluble polymer

1. INTRODUCTION

Chromium is a chemical element of importance to organisms in nature. Chromium is a required component of glucose, some proteins and fat metabolism, but it is also associated with serious problems of environmental pollution and damage to health. Chromium is present in residual waters from electroplating industries, metal finishing, leather tanning, photography, dyes and textile industries.^{1,2}

The predominant species of chromium in aqueous solutions are the hexavalent and trivalent form (oxidation states Cr(VI) and Cr(III), respectively), depending on the pH and concentration. Chromium (VI) is more toxic than chromium (III), highly mobile in the environment, not biodegradable, cumulative, carcinogenic and has a corrosive effect on tissues.³ The human health effects include lung cancer and kidney, liver and stomach damage. The World Health Organization recommends a limit for chromium (VI) in drinking water at the level of 0.05 mg L⁻¹.^{4,5}

Various techniques for removing chromium (VI) in water are currently available, including electrodeposition,⁶ ion exchange,⁷ electrocoagulation,⁸ adsorption,⁹ and membrane filtration.¹⁰ Many of these processes are not widely used due to their disadvantages, which include incomplete metal removal, requirements for expensive equipment and monitoring systems, and generation of toxic sludge or other waste products that require disposal.²

One alternative to remove chromium is the use of water-soluble polymers combined with ultrafiltration membranes. This method separates ionic species from aqueous solution and is called polymer-enhanced ultrafiltration (PEUF), polymer-assisted ultrafiltration or liquid-phase polymer-based retention.¹¹⁻¹⁵ PEUF is a hybrid method that involves interaction of the functional polymer with the chromate ion, forming a new polymer-metal macromolecule whose molecular weight is above the ultrafiltration membrane molar mass cut off; therefore, it is retained by size exclusion.^{11,2} The advantage of the PEUF method is that it is performed in homogeneous media, preventing the phenomenon of diffusion or mass transfer that occurs with heterogeneous media.^{11,16}

The use of different water-soluble polymers (commercial and synthesized in the laboratory) for the removal of different metal cations from aqueous solution has been reported.¹⁶ Recently, PEUF has been used in combination with photocatalysis processes,¹⁷ and electro-oxidation to remove arsenic species.^{18,19} The advantage of the latter was the double use of a polyelectrolyte as a supporting electrolyte in the electro-oxidation and for extracting material-assisted ultrafiltration.

Poly(diallyldimethylammonium chloride) (PDDA) is a water-soluble polymer used in industrial applications and as a model for charged polymer behaviour.²⁰⁻²² PDDA has been used in PEUF for the removal of species in

solution, such as perchlorates,²³ arsenate,²⁴ and chromates.²⁵ Cañazares *et al.* found an interaction between PDDA and the chromate ion. They also studied the chemical regeneration of the polymer using NaCl. However, the conclusion was that NaCl is not a feasible option to perform polymer regeneration because the higher affinity of PDDA to bind chromate than chloride requires a very high concentration of chloride to achieve the complex breakage.²⁵

Studies focused on the electrochemical reduction of Cr(VI) in aqueous solution have been developed mainly for analytical purposes. Compton *et al.* studied the electroreduction of Cr(VI) to Cr(III) using gold electrodes and acid,^{26,27} which could be used to electrochemically transform a toxic Cr(VI) species to its analogue Cr(III), which is less toxic.

The aim of this work is to study Cr(VI) retention by PDDA using the PEUF technique via washing and enrichment with a regenerated cellulose membrane. Using the washing method, we studied the retention of Cr(VI) as a function of the pH, polymer:chromium molar ratio, effect of pressure and presence of interfering ions. Next, under optimum conditions, we investigated the saturation of the water-soluble polymer by the enrichment method. Then, the optimization of the sorption-desorption process and recovery of PDDA using the combined washing (at acidic pH) and enrichment methods (at basic pH) were achieved. Finally, to transform the Cr(VI) previously retained to a less toxic species, the electrochemical reduction of Cr(VI) to Cr(III) was performed in acidic media in the presence of PDDA.

2. EXPERIMENTAL

2.1. Polymer-enhanced ultrafiltration

In this study, the water-soluble poly(diallyldimethylammonium chloride), (PDDA), Mw 400,000-500,000 g/mol, 20 wt. % in H₂O was purchased from Sigma-Aldrich. The main components of the ultrafiltration system were a filtration unit (Amicon 8050 stirred cell of 50 mL volume), an ultrafiltration membrane filter with a 10 kDa molecular weight cut-off (MWCO), a reservoir, and a pressure source, e.g., pressurized nitrogen gas.

2.1.1. Washing Method

In the washing method, a liquid sample containing the water-soluble polymer and chromium to be separated is placed in an ultrafiltration cell at a given pH.¹¹ A solution of 1.15 mmol of polymer was dissolved in water, and a solution containing 57.5 μmol of Cr(VI) (K₂CrO₄ Merck) was added. The solution was brought to a total volume of 20 mL, and the pH was adjusted by the addition of 0.1 mol/L NaOH or 0.1 mol/L HNO₃ (Merck). The experiments were conducted at pH levels of 2, 6, and 9. The period of time needed for the polymer to be in contact with the Cr(VI) ions was 10 min before ultrafiltration. The washing water in the reservoir was at the pH of the cell

solution. Filtration runs were performed under a total pressure between 1 to 3 bars with a regenerated cellulose ultrafiltration membrane with an exclusion range of 10 kDa. The total volume in the cell was kept constant. Fractions of 20 mL were collected by filtration, and the metal concentration was analysed. A blank experiment, without polymer, was also performed. The effect of different interfering ions was studied using the following salts: NaCl (Merck), Na₂SO₄ (Fluka), and KH₂PO₄ (Merck).

To systematically study the polymer interactions with chromium ions in the solution using the PEUF technique via the washing method, two quantities were defined. In equation 1, retention (R %) denotes the fraction of Cr(VI) remaining in the cell, and in equation 2, the filtering factor (Z) denotes the volume exchange ratio in the reservoir.

$$R \% = [\text{Cr}_{\text{cell}}] / [\text{Cr}_{\text{i}}] \quad (1)$$

where $[\text{Cr}_{\text{cell}}]$ is the amount of Cr(VI) that is retained in the cell and $[\text{Cr}_{\text{i}}]$ is the initial amount of Cr(VI). In equation 2, the filtration factor (Z) is the ratio between the total permeate volume (V_p) and the retentate volume (V_r).

$$Z = V_p / V_r \quad (2)$$

Using the experimental data, graph can be drawn (retention profile) in which R % is represented as a function of Z.

2.1.2. Enrichment Method

The second method presented in this work is the enrichment method, which determines the maximum retention capacity (C) of the water-soluble polymer.¹¹ The Cr(VI)-containing solution passed from the reservoir through the ultrafiltration cell filled with the polymer solution. Both cell and reservoir solutions were adjusted to the same values of pH. In this study, the reservoir solution contained 30 mg/L of Cr(VI), and the cell solution also contained 180 mg of water-soluble polymer. The maximum retention capacity of the water-soluble polymer was determined by the enrichment method and is defined as follows (see equation 3):

$$C = (M V) / Pm \quad (3)$$

where Pm is the amount of polymer (g), M is the initial concentration of Cr(VI) (mg/L), and V is the volume of permeate (L) that passes through the membrane. The maximum retention capacity of Cr(VI) was calculated when 200 mL of permeate was collected. The principle of PEUF is shown in Figure 1.

The concentration of chromium (VI) was measured by UV-vis spectrophotometer (Cary 100 Scan) at 350 nm.²⁸ The quantity retained was determined from the difference between the initial and final concentration. The pH was monitored by a pH meter (H. Jurgen and Co., Germany).

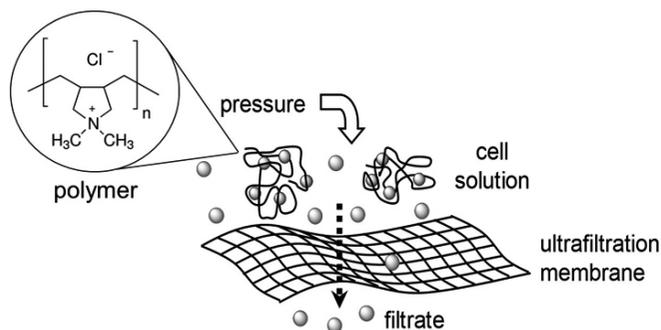


Figure 1. Principle of polymer-enhanced ultrafiltration.

2.2. Electrochemistry

Electrochemical reduction of Cr(VI) was performed using a CHI 660B electrochemical analyser (CH Instruments), using a conventional three-electrode system. The voltages were referenced to an Ag/AgCl in 3 mol/L KCl reference electrode. A platinum wire and a platinum basket were used as the counter electrode in the linear sweep voltammetry and electrolysis, respectively. Gold disc working electrodes (3 mm diameter) were polished with 1 mm diamond for the analytical experiments. Linear sweep voltammograms were recorded at 10 mV/s in the presence of PDDA in acidic HCl media in the range of +0.75 V to -0.1 V. The study of scan rate was carried out at 10, 20, 50,

100, 200 and 500 mV/s.

Electrolysis of Cr(VI) to Cr(III) was performed at controlled potential in air at room temperature and under constant stirring at 1000 rpm on large area gold electrodes (1 cm²). In a typical experiment, the electrolysis cell was filled with 20 mL of solution containing PDDA in acidic media.

3. RESULTS AND DISCUSSION

3.1. Effect of pH on the removal of Cr(VI)

The effect of pH on the removal of Cr(VI) was studied by the washing method. The experiment was performed using a regenerated cellulose ultrafiltration membrane with a MWCO of 10 kDa, and this pore size is much lower than that of the polymer size. PDDA was investigated as an extracting agent. The results of the retention as a function of pH are expressed in Figure 2.

The results indicate that Cr(VI) is more easily retained at basic pH values than at acidic pH values, and this is in accordance with the literature.² The retention of chromium by PDDA was approximately 40%, 50% and 100% at pH 2, 6, and 9, respectively. Chromium (VI) normally exists in the oxy-anionic ($\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- or CrO_4^{2-}) depending on the pH and concentration in the solution. At pH around 1, the predominant species is chromic acid (H_2CrO_4). At pH values between 2 and 4, Cr(VI) exists mostly in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. At pH between 4 and 6, $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- ions exist in equilibrium, and under alkaline conditions it exists predominantly as the chromate anion (CrO_4^{2-}).^{2,29}

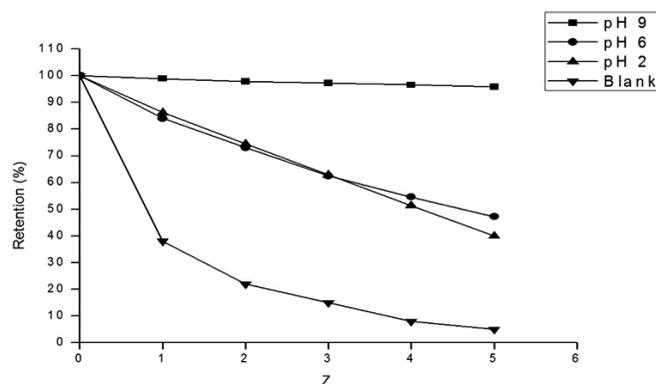


Figure 2. Retention profiles of Cr(VI) using PDDA (400-500 kg/mol) as a polymer and a regenerated cellulose membrane at different pH values, with a polymer:Cr(VI) molar ratio of 20:1, 30 mg/L Cr(VI).

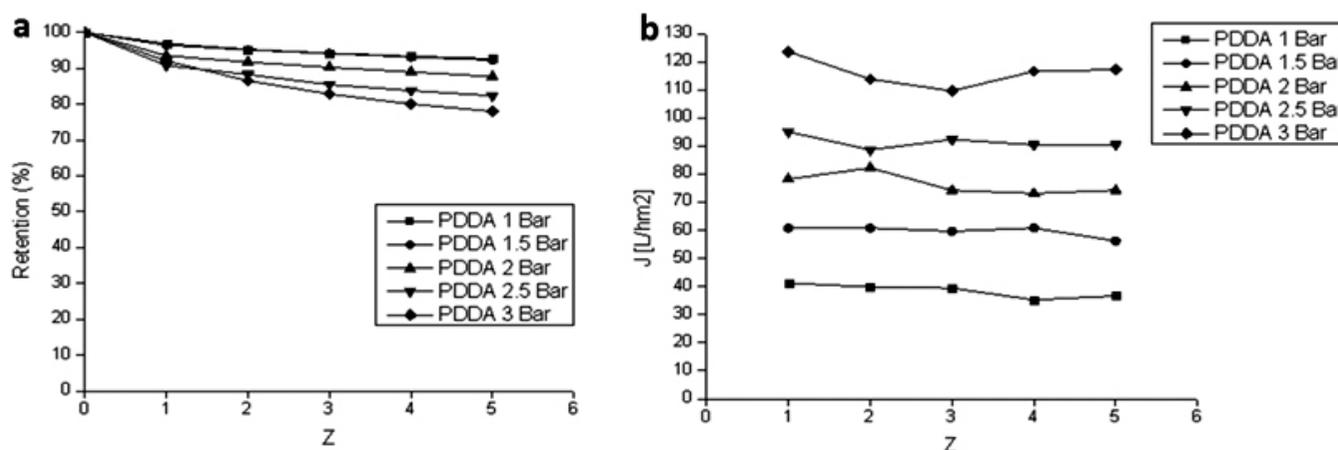
The retention capacity of Cr(VI) is due to the presence of a positively charged quaternary ammonium group in PDDA. The attractive interactions are produced through the anion exchange between the counterion of a quaternary ammonium salt (chloride ions) and the chromium anions, preferably with divalent chromium oxy-anions.²⁵ The higher retention capacity of the polymers at pH 9 is because divalent species (CrO_4^{2-}) are predominant. The chromium removal decreased at pH 6 because $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- ions exist simultaneously in the aqueous solution. Chromium retention was low at pH 2, although the removal of chromium (VI) by the PEUF technique using the washing method with PDDA was suitable over a wide range of pH.

3.2. Effect of the polymer:Cr(VI) molar ratio on the retention

Cr(VI) removal was optimized by changing the ratio of PDDA:Cr(VI). Using the washing method with a regenerated cellulose membrane as a filter, we studied the influence of the polymer concentration on the Cr(VI) removal. Solutions with different polymer:Cr(VI) molar ratios, including 5:1, 10:1, 20:1, 40:1 and 100:1, were prepared at pH 9, and the obtained Cr(VI) retentions were 84.3%, 81.1%, 95.0%, 88.8%, and 85.6%, respectively, at Z = 5 for PDDA (see Table 1). With increasing polymer concentration, the permeate flux decreased probably due to the fouling process on the membrane. The same behaviour was previously observed for the same polymer applied on arsenic removal.²⁴ The results indicate an optimum 20:1 (polymer:Cr(VI)) molar ratio for all polymers to reach maximum chromium (VI) removal.

Table 1. Retention of Cr(VI) using different PDDA:Cr(VI) molar ratios and 1.5 bar pressure.

Z	R(%) as function of polymer:Cr(VI) molar ratio				
	5:1	10:1	20:1	40:1	100:1
1	92.9	88.6	98.9	94.5	92.1
2	89.9	86.1	97.9	92.1	90.0
3	87.7	84.3	97.3	90.7	88.2
4	86.0	82.6	96.6	89.7	86.8
5	84.3	81.1	95.0	88.8	85.6

**Figure 3.** (a) Retention profiles of Cr(VI) and (b) permeate flux as a function of pressure using PDDA as a polymer and a regenerated cellulose membrane at pH 9.

3.4. Effect of interfering ions on the retention of Cr(VI)

In the next step, the effect of different interfering ions, such as Cl^- , SO_4^{2-} and PO_4^{3-} , on Cr(VI) removal was investigated. The experiments were conducted separately at pH 9, polymer:Cr(VI) 20:1 and 1.5 bar of pressure. Previous experiments indicated that cationic polyelectrolytes remove chromium species more efficiently under these conditions. The results indicate that when Cl^- and PO_4^{3-} ions are added to the solution in concentration range studied, Cr(VI) retention does not decrease significantly (see Figure 4). However, when the concentration of SO_4^{2-} is 100 mg/L, the retention of chromium begins to decrease. In this case, the retention decreased from 95% to 50%.

The effect of sulphate ions on Cr(VI) binding of the water-soluble polymer is due to the competition between chromate and sulphate anions for binding sites on the polymer. Similar results are reported in the literature for the sorption capacities of chromium (VI) by different polymeric sorbents. Pakade *et al.* studied the selective removal of Cr(VI) from sulphates and other ions using a copolymer prepared from 4-vinylpyridine and styrene. They found that the influence of the investigated co-existing anions on Cr(VI) sorption can be summarised as following the order: $\text{SO}_4^{2-} > \text{F}^- > \text{PO}_4^{3-} > \text{NO}_2^- > \text{NO}_3^- > \text{Cl}^-$. The study indicated that sulphates compete more for binding sites than phosphates and chlorides.³¹ Neagu and Mikhailovsky also studied the removal of hexavalent chromium by new quaternized crosslinked poly(4-vinylpyridines). They also found that the retention of chromium decreased in presence of sulphate ions. The added salts can affect adsorption via two mechanisms: (i) either by screening the coulombic potential between the adsorbing ion and changed adsorbents, or (ii) by adsorbing preferentially on the active site of the adsorbent.³²

3.5. Sorption-desorption process

To study the process of sorption-desorption, the enrichment method was used. The first step of the experiment was the saturation of the polymer through

3.3. Effect of pressure on the volumetric flux

In previous studies, we analysed the permeate flux in the blank experiment (without water-soluble polymer) and the permeate flux in the presence of water-soluble polymer. As expected, the flux in the blank was higher than the flux in the presence of water-soluble polymers. This finding is attributed mainly to interactions between the polymer and the membrane.³⁰ In this research, we studied the removal of Cr(VI) and the evolution of the permeate flux as a function of different pressures (1 to 3 bar) at a 20:1 polymer:chromium molar ratio. In this experiment, the chromium concentration was 30 mg/L at pH 9. The results show that the retention of chromium decreased slightly from 95 to 80% with increasing pressure from 1 to 3 bar, respectively (see Figure 3 a). However, the permeate flux increased with increasing pressure and was similar at different Z values (see Figure 3 b). Considering the chromium retention and permeate flux as a function of pressure, in our conditions, the optimum pressure is 1.5 bar. At 1.5 bar, the retention is greater than 90%, and the flux is 60 L/hm². These values are in accordance with those reported in the literature.³⁰

the enrichment method using 30 mg/L of Cr(VI) solution at pH 9 and a polymer metal ratio of 20:1 with a 200 mL total filtrate volume. The concentration of Cr(VI) was measured in the filtrate, and the removed concentration was determined from the difference with the initial concentration in the feed. The blank test is the experiment without PDDA in the cell.

The results of the blank experiment showed higher concentrations of Cr(VI) in the first tubes (see Figure 5 a). During the enrichment of the polymer, the same experiment was performed; however, in this case, the polymer in the cell maintained the optimum polymer:Cr(VI) molar ratio. As a result, after performing the experiments, we collected 10 tubes of 20 mL of filtrate and then measured. With the results of the measurements, the profile of Cr(VI) in the filtrate versus volume of filtrate was obtained. When the polymer curve reached a maximum concentration (i.e., chromium concentration was equivalent to the blank) under our experimental conditions, we calculated the maximum retention capacity. After reaching the saturation of the polymer, the Cr(VI) solution retained in the cell was washed with water buffered at pH 2 from the reservoir. The process of sorption-desorption was applied to determine the capacity of Cr(VI) delivery and to regenerate the extraction ability of the water-soluble polymer.

The enrichment process (sorption) reached the maximum retention capacity at pH 9. The value of the maximum retention capacity of the first sorption was 33 mg Cr/g polymer. After the sorption process (see Figure 5 a), desorption was performed by changing the pH from basic to acidic using a HNO_3 . Figure 5 b shows the desorption process of Cr(VI) from the polymer when the polymer-Cr(VI) macromolecule is in contact with the acid solution at pH 2. The polymer released around 40 mg/L in the first tube of filtrate, and then the concentration decreased until reaching 150 mL of filtrate.

Using the enrichment method and the sorption-desorption process, the

recovery of PDDA was performed. The results indicated that this water-soluble polymer can be regenerated (see Figure 5 a). The value of the maximum retention capacity of the second sorption was 30.7 mg Cr/ g polymer. Finally, the second desorption was performed at acidic pH, and the polymer released 24 mg/L in the first tube of filtrate (see Figure 5 b).

In this experiment, the regeneration of PDDA after one sorption-desorption cycle was investigated. Similar results of sorption-desorption of arsenate were obtained for commercial water-soluble P(BrVMP) and arsenic.³³

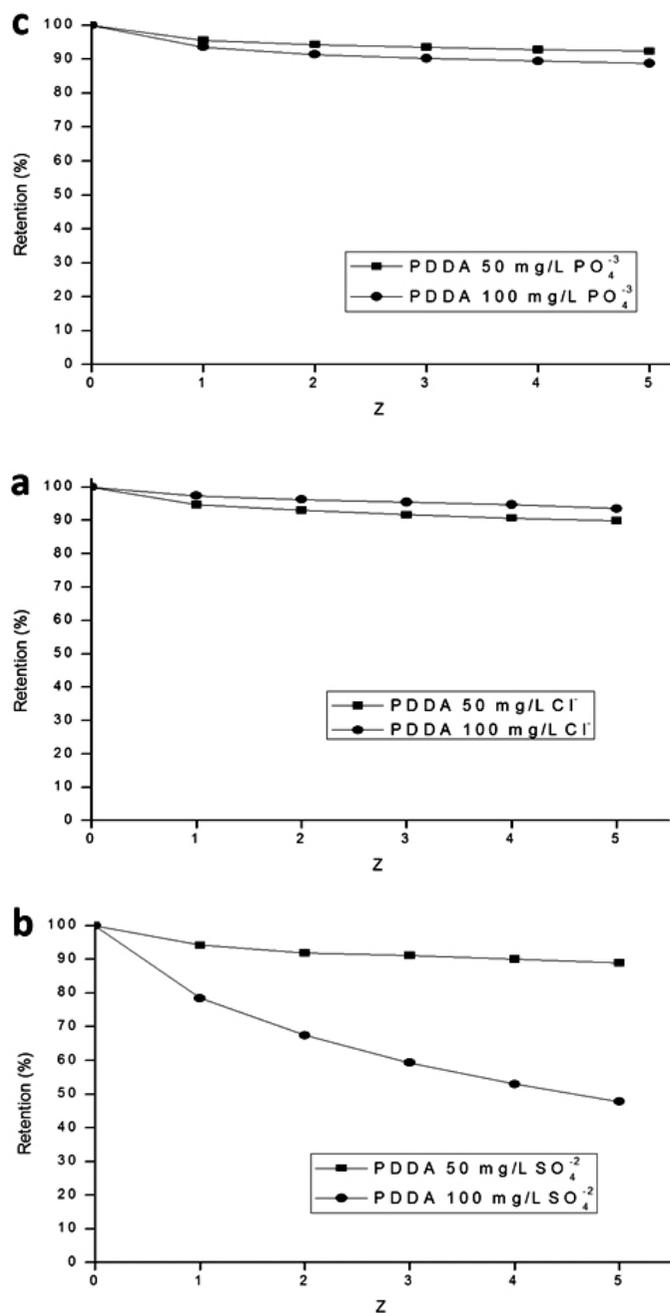


Figure 4. Retention profiles of Cr(VI) in the presence of different concentrations of (a) Cl⁻, b) SO₄²⁻ and c) PO₄³⁻, using PDDA as a polymer and a regenerated cellulose membrane at pH 9 and 1.5 bar of pressure.

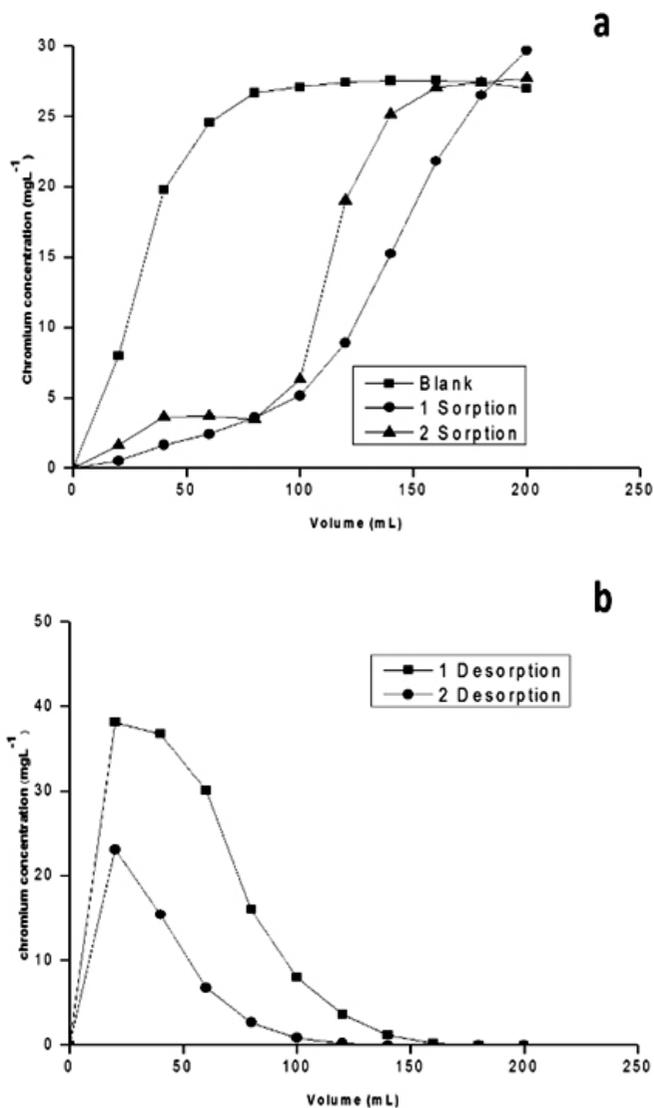


Figure 5. Sorption-desorption process of Cr(VI) ions using PDDA combining (a) enrichment at pH 9 and (b) the washing method at pH 2.

3.6. Electroanalysis of Cr(VI)

An electroanalysis of chromate was performed by linear sweep voltammetry using HCl as the supporting electrolyte in the presence of 0.02 mol/L PDDA. A working electrode of gold, a Ag/AgCl reference electrode and a platinum wire as counter electrode were used. First, a study of pH was conducted; then, at the optimum pH, the calibration curve was created from 5 to 30 mg/L of chromium (VI). Finally, an exhaustive controlled-potential electroreduction was conducted to transform all Cr(VI) (previously retained by PDDA) to Cr(III). The progress of the electrolysis was monitored recording the evolution of applied charge, pH, time and peak current measured by voltammetry.

3.6.1. Effect of pH on the reduction of Cr(VI) to Cr(III)

The reduction of Cr(VI) was studied at pH 1.5, 2.2, 4.25 and 4.9 (see Figure 6). The results showed that at pH 1.5, the reduction peak was well-defined and increasing the pH reduced the peak size. An increase to pH 2.2 changed the shape of the peak and also decreased its size significantly, and further increases to pH 4.25 and 4.9 resulted in the effective disappearance of the reduction peak. This experiment demonstrates that the pH of the media has a strong effect on the sensitivity, size and the shape of the chromium reduction peak on the gold electrode. A highly acidic solution is required for the successful reduction of chromium, and the presence of a high concentration of protons is essential for the progress of this chromium reduction reaction. These results agree with

those reported by Kachoosangi and Compton, indicating better reduction in acidic pH.²⁷

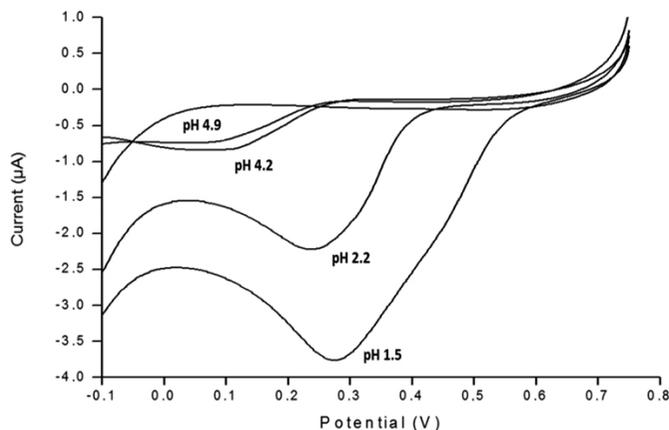


Figure 6. Linear sweep voltammograms for the electroanalysis of 25 mg/L of Cr(VI) in the presence of 0.02 mol/L PDDA as a function of pH (1.5, 2.2, 4.25 and 4.9) at a scan rate of 10 mV/s.

3.6.2. Calibration curve for the reduction of Cr(VI) to Cr(III) in acid medium

In acidic medium (pH 1.5), an increasing concentration of Cr(VI) was consecutively added to the electrochemical cell from 5 to 30 mg/L, and direct linear sweep voltammetry peaks were produced after each addition.

There was an increase in the reduction current at +0.3 V with the increasing concentration of Cr(VI) (see Figure 7). In our conditions, the presence of PDDA did not affect the in situ measurement of the concentration of Cr(VI) via electroreduction to Cr(III). This method is a good approach for the development of new alternatives to measure the in situ chromate concentration in ultrafiltration systems.

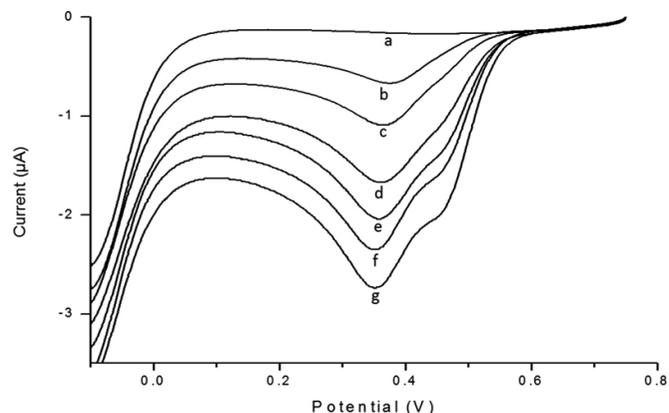


Figure 7. Linear sweep voltammetry for additions of increasing concentrations of Cr(VI) from 5 mg/L to 30 mg/L at a scan rate 10 mV/s at pH 1.0 and in the presence of PDDA.

The curves for a) blank, b) 5 mg/L, c) 10 mg/L, d) 15 mg/L, e) 20 mg/L, f) 25 mg/L, and g) 30 mg/L of Cr(VI).

3.6.3. Study of scan rate

The study of scan rate was carried out at 10, 20, 50, 100, 200 and 500 mV/s in presence of 0.02 mol/L PDDA, 10 mg/L of Cr(VI) and pH 2.0. The results of the voltammetry at different scan rates are shown in Figure 8 a. It is possible to see that when the scan rate increase, the peak current increase as well. In addition, the plot of peak current ($\log I_p$) versus scan rate ($\log V$) shows a linear relationship. The slope of the curve indicates that polymer-Cr(VI) solution presents convenient electro-activity with an approximate value close to 0.54 indicating that the control of the reaction is by diffusion (see Figure 8 b).

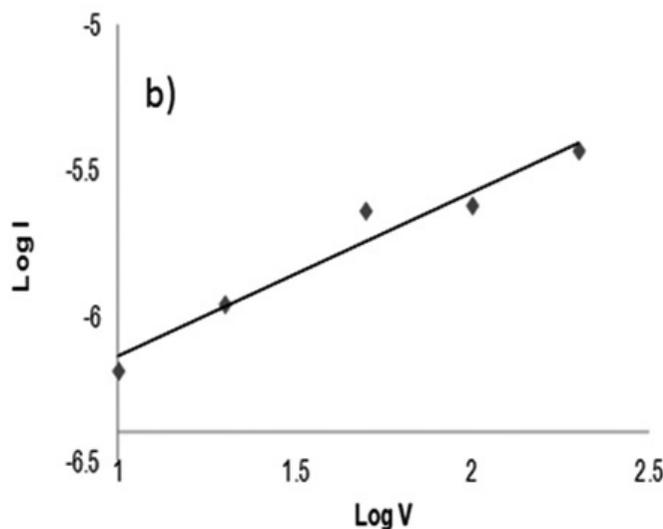
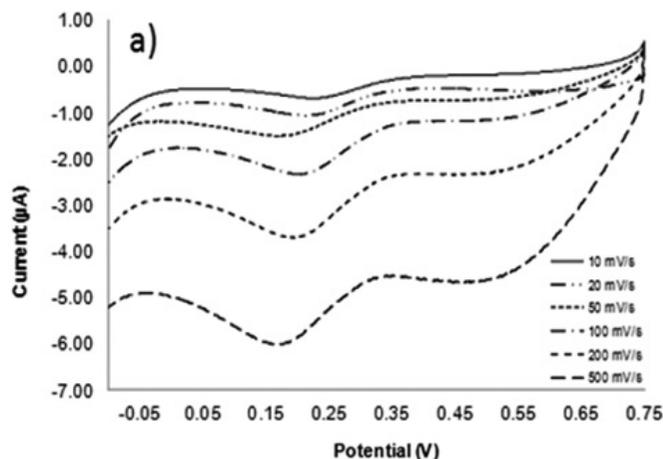


Figure 8. a) Linear sweep voltammetry of Cr(VI) at various scan rates between 10 and 500 mV/s, b) Plot of peak current ($\log I_p$) versus scan rate ($\log V$) for polymer-Cr(VI) solution.

3.7. Electrolysis of Cr(VI) to Cr(III)

The exhaustive electrochemical reduction of Cr(VI) was conducted by electrolysis with coulometry at a controlled potential (+0.25 V) and the evolution of applied charge, pH, time and peak current (measured by voltammetry) at acidic pH in the presence of PDDA was monitored (see Table 2). Previously, the study of scan rate showed that the process is controlled by diffusion. Therefore it is possible to assign the applied charge of the electrolysis to the reduction of Cr(VI) to Cr(III). The applied charge was recorded from the transient i/t obtained during the electrolysis. The results showed that is possible to convert electrochemically Cr(VI) to Cr(III) in 96.5% when the total charge applied was -1.216 C in a total time of 27.3 h. It was not possible to reach the 100% of conversion probably due to the change of pH during the process. Another test that confirm the conversion is the decrement of the peak current recorded by voltammetry.

In addition, the change of colour from a solution containing Cr(VI) and PDDA (yellow) and solutions containing Cr(III) and PDDA (pale green) confirm that electroreduction occurred in the presence of PDDA, which is advantageous because we have shown that it is possible to remove Cr(VI) from solution using PDDA and ultrafiltration membranes. Subsequently, it is possible to reduce the Cr(VI) previously retained by PDDA and to transform into Cr(III).

Table 2. Charge applied, pH, time and peak current measured during the electrolysis of Cr(VI)

Charge (C)	pH	Time (h)	Peak Current (μA)
0	2.15	0	-1.0336
-0.329	2.16	2.9	-0.5861
-0.453	2.41	5.8	-0.4093
-0.278	2.41	5.9	-0.2741
-0.118	2.42	6.8	-0.0905
-0.038	2.43	5.9	-0.0364

4. CONCLUSIONS

The results revealed that using PDDA combined with a regenerated cellulose ultrafiltration membrane can effectively remove Cr(VI) from aqueous solution. The efficient retention of approximately 95% at $Z = 5$ for PDDA was achieved at pH 9, with a 20:1 polymer:Cr(VI) molar ratio, 1.5 bar pressure and 30 mg/L Cr(VI). The presence of SO_4^{2-} competitive ions decreased the retention capacity.

The maximum retention capacity of PDDA determined by the enrichment method was 33 mg Cr/g polymer at pH 9. Using the sorption-desorption process, the recovery of PDDA was performed using changes in pH. The results indicated that this water-soluble polymer can be regenerated.

The electroanalysis of Cr(VI) in presence of PDDA was successful. The results showed that the pH affect the voltammetric response in our experimental conditions. The calibration curve showed a linear behaviour and the scan rate study corroborate a diffusional process. In addition, it is possible to convert by electrolysis Cr(VI) to Cr(III) in 96.5% when the total charge applied was -1.216 C in a total time of 27.3 h.

These results could be of high interest, especially in industry, for the treatment and monitoring of highly contaminated waste water.

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