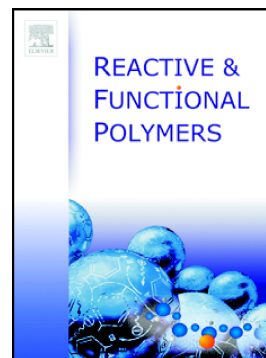


## Accepted Manuscript

Poly(N,N-dimethylaminoethyl methacrylate) for removing chromium (VI) through polymer-enhanced ultrafiltration technique

Julio Sánchez, Carolina Espinosa, Fabian Pooch, Heikki Tenhu, Guadalupe del C. Pizarro, Diego P. Oyarzún



PII: S1381-5148(18)30109-3  
DOI: doi:[10.1016/j.reactfunctpolym.2018.04.002](https://doi.org/10.1016/j.reactfunctpolym.2018.04.002)  
Reference: REACT 4027  
To appear in: *Reactive and Functional Polymers*  
Received date: 26 January 2018  
Revised date: 3 April 2018  
Accepted date: 4 April 2018

Please cite this article as: Julio Sánchez, Carolina Espinosa, Fabian Pooch, Heikki Tenhu, Guadalupe del C. Pizarro, Diego P. Oyarzún , Poly(N,N-dimethylaminoethyl methacrylate) for removing chromium (VI) through polymer-enhanced ultrafiltration technique. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. React(2018), doi:[10.1016/j.reactfunctpolym.2018.04.002](https://doi.org/10.1016/j.reactfunctpolym.2018.04.002)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Poly(N,N-dimethylaminoethyl methacrylate) for removing chromium  
(VI) through polymer-enhanced ultrafiltration technique**

Julio Sánchez<sup>1,\*</sup>, Carolina Espinosa<sup>1</sup>, Fabian Pooch<sup>2</sup>, Heikki Tenhu<sup>2</sup>, Guadalupe del C. Pizarro<sup>3</sup>, Diego P. Oyarzún<sup>4</sup>

<sup>1</sup>*Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, Casilla 40, Correo 33, Santiago, Chile. Email: julio.sanchez@usach.cl*

<sup>2</sup>*Laboratory of Polymer Chemistry, University of Helsinki, Helsinki, Finland.*

<sup>3</sup>*Department of Chemistry, Technological Metropolitan University, J. P. Alessandri 1242. Santiago, Chile.*

<sup>4</sup>*Center of Applied Nanosciences (CANS), Facultad de Ciencias Exactas, Universidad Andrés Bello, Avda. República 275, Santiago, Chile.*

**Abstract**

This work is focused on the removal of Cr(VI) ions from aqueous solution using polymer-enhanced ultrafiltration (PEUF) techniques with water-soluble poly(N,N-dimethylaminoethyl methacrylate), PDMAEMA, used as sorbent.

The polymer was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization at different reaction times, characterized by size exclusion chromatography (SEC) and proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ). The sorption of Cr(VI) was studied by PEUF as a function of pH, the polymer:Cr(VI) molar ratio, and the presence of interfering ions. The PEUF-enrichment mode was used to saturate the polymer and further determine the release of Cr(VI) and regeneration of the polymer using sorption-desorption process.

The RAFT polymerization showed a yield in the range 46% to 79% (determined by  $^1\text{H-NMR}$ ) for polymers with molecular weight ( $M_n$ ) between 28 to 195 kg mol $^{-1}$ . The polydispersity estimated by SEC was between 1.1 and 1.8.

The capacity of PDMAEMA as sorbent of Cr(VI), by the PEUF technique showed an efficient removal of Cr(VI) (100%, 25 mg L $^{-1}$  in the feed) at pH 4 using polymer:Cr molar ratio of 40:1. The presence of interfering ions does not significantly decrease the retention capacity of PDMAEMA. Finally the results indicated that PDMAEMA can release Cr(VI) and be regenerated.

**Keywords:** *chromium; membranes; polymerization; sorption; 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 among others [1, 2].

The predominant species of chromium in aqueous solutions are the hexavalent and trivalent form (oxidation states 6+ and 3+, respectively), depending on the pH and concentration. Chromium (VI) is more toxic than chromium (III), highly mobile in the environment, not biodegradable, cumulative, and carcinogenic, which has a corrosive effect on tissues [3]. The health effects in human include lung cancer and kidney, liver and stomach damage. The World Health Organization (WHO) recommends a limit for chromium (VI) in drinking water at the level of  $0.05 \text{ mg L}^{-1}$  [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 technique separates ionic species from aqueous solution and is called polymer-enhanced ultrafiltration (PEUF), polymer-assisted ultrafiltration or liquid-phase polymer-based retention [11,12]. PEUF is a hybrid methodology that involves interaction of the functional water-soluble polymer with the metal 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 separation [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 [11,12].

Poly(N,N-dimethylaminoethyl methacrylate), PDMAEMA, has been studied in different applications, including its use as functional polymer in the elaboration of sorbent materials. In all these cases, PDMAEMA has been attached or incorporated to a solid matrix to be used in solid-liquid or membrane separations. For example, polypropylene matrix was grafted with PDMAEMA and subsequent used as sorbent of phosphate and nitrate anions [13]. In other studies, PDMAEMA was used in the modification of activated carbon [14], or used for the modification of regenerated cellulose membranes to be applied on copper ions removal [15]. In addition, the sorption of chromate was studied by amphiphilic gels based on 2-(dimethylamino) ethyl methacrylate modified with 1-bromoalkanes [16]. Moreover, the recovery of precious metals can be efficiently performed onto poly(2-(dimethylamino) ethyl methacrylate) gels [17]. According to our knowledge, literature is null for studies related to Cr(VI) removal by PEUF technique using water-soluble PDMAEMA.

The aim of this work is to study the removal of Cr(VI) by PDMAEMA using the PEUF technique with a regenerated cellulose membrane as a filter. PDMAEMA was prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization, the polymer was characterized by proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ), and its molecular weight was measured by size exclusion chromatography (SEC).

Using the PEUF, we studied the retention of Cr(VI) as a function of the pH, polymer:chromium molar ratio and presence of interfering ions. Next, under optimum conditions, we investigated the saturation of the water-soluble polymer by the

enrichment method. Finally, the optimization of the sorption–desorption process and recovery of PDMAEMA was determined.

## 2. Experimental

### 2.1. Materials

The reagents were 2-(dimethylamino) ethyl methacrylate (DMAEMA) (Acros Organics, 99%) was passed through aluminium oxide and then distilled. (4-cyanopentanoic acid)-4-dithiobenzoate (CPA) was synthesized following a literature procedure [18,19]. Azobis(isobutyronitrile) (AIBN) (Fluka, 98%) was recrystallized from methanol. The water used to prepare polymer solution was purified with ELGA purelab ultrapurification system to conductivity of 0.05-0.07  $\mu\text{S}/\text{cm}$ . Acetone, n-hexane (Sigma-Aldrich, HPLC grade), acetonitrile (VWR, HPLC grade), tetrahydrofuran (THF), tetrabutylammonium bromide (TBAB) (Sigma-Aldrich, 99%), HCl, NaOH (FF-Chemicals), NaCl,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  (Sigma-Aldrich) were used as received.

The components of the ultrafiltration system were a filtration unit (Millipore Amicon, model 8050, USA, stirred cell of 50 mL volume), an ultrafiltration membrane filter with a 10 kDa molecular weight cut-off (MWCO) (Millipore), a reservoir, and a nitrogen gas.

### 2.2. RAFT Polymerization

PDMAEMA was synthesized with RAFT polymerization method [20]. The conditions for the preparation of the different polymers are shown in Table 1. Polymers were labeled as PDMAEMA 1, 2, 3 and 4 according to the time of polymerization reaction of 18, 42, 66 and 120 h, respectively. Exemplary for polymer 1, in a flask, 0.0664 g (0.237 mmol) of CPA and 0.0039 g (0.0238 mmol) of AIBN were dissolved to 7.4646 g (47.0 mmol) of DMAEMA. The mixture was bubbled with nitrogen for 1h and immersed to an oil bath preheated at 70 °C. Once the polymerization time is reached, the reaction was stopped by cooling with liquid nitrogen and exposure to the atmosphere, and a

sample was immediately taken to determine the conversion of the reaction. Then, the polymer was purified with three successive precipitations from acetone to hexane, to then be collected with acetonitrile, which was then evaporated to dryness. Finally, the polymer was dissolved in water and isolated by freeze-drying. The procedure is the same for all polymers.

### **2.3. Characterization of PDMAEMA**

#### **2.3.1. Size exclusion chromatography (SEC)**

SEC was conducted using a Waters 515 HPCL pump, Waters Styragel columns, and a Waters 2410 refractive index (RI) detector. To calibrate the system, the poly(methyl methacrylate) standards were used, where the eluent was THF containing 1% TBAB.

#### **2.3.2. Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR)**

The <sup>1</sup>H-NMR spectra were recorded using a 300 MHz Varian Unity INOVA and a Bruker Avance III 500 spectrometers for determining respectively the conversion of the polymerization and verifying the purity of the synthesized polymer.

### **2.4. Polymer-enhanced ultrafiltration (PEUF)**

The PEUF technique consists of separating a liquid sample containing the water-soluble polymer and chromium (VI) at a given conditions (e.g. pH, ionic strength, concentration, pressure) by ultrafiltration (see Figure 1).

PDMAEMA was dissolved in 25 mg/L of Cr(VI) (K<sub>2</sub>CrO<sub>4</sub>). This solution was brought to a total volume of 20 mL, where the pH was adjusted by the addition of 0.1 mol L<sup>-1</sup> of NaOH or HCl, until reaching pH levels of 2, 4, 6, 8 and 10. The time of interaction needed between PDMAEMA and Cr(VI) was 10 min. The filtration tests were performed at a total pressure of 1 bar with a regenerated cellulose ultrafiltration membrane with a MWCO of 10 kDa, keeping the total volume in the cell constant. Fractions of 20 mL were collected by filtration, to measure the Cr(VI) concentration.

Using the PEUF technique, via the washing method, the interaction between the polymer and Cr(VI) was studied, obtaining the retention percentage (% R) which represents the fraction of Cr(VI) remaining in the cell (equation 1 and equation 2).

$$\% R = M_{cell}/M_i \quad (1)$$

$$M_{cell} = M_i - M_p \quad (2)$$

where  $M_{cell}$  is the amount of metal ion that is retained in the cell,  $M_i$  is the initial concentration of metal ion in the feed and  $M_p$  is the concentration of chromium in each permeate volume collected during the filtration.

The filtering factor (Z) represents the volume exchange ratio in the ultrafiltration system (equation 3):

$$Z = V_p/V_r \quad (3)$$

where Z is the ratio between the total permeate volume ( $V_p$ ) and the retentate volume in the cell ( $V_r$ ).

The hydrodynamic flux was estimated by the ratio between the permeate volume (L) and the time (h) to collect the volume by the membrane area ( $m^2$ ), as shown in equation 4:

$$J = L/(h \cdot m^2) \quad (4)$$

The enrichment method (similar to column method) is used to determine the maximum retention capacity of the water-soluble polymer [11,12]. A solution of 28 mg L<sup>-1</sup> of Cr(VI) contained in the reservoir is passed through the ultrafiltration cell, which contains 56 mg of PDMAEMA dissolved in water and adjusted to the same pH. The maximum retention capacity of PDMAEMA (mg Cr(VI)/g PDMAEMA) was calculated by mass balance when 400 mL of permeate was collected.



The pH was monitored by a pH meter (Radiometer Copenhagen model PHM 210, France), and Atomic Absorption Spectroscopy (AAS) (model Unicam Solar 5M Series) was used to measure the concentration of Cr(VI).

### 3. Results and discussion

#### 3.1. Synthesis and characterization of PDMAEMA

PDMAEMA was synthesized by bulk RAFT polymerization using CPA as chain transfer agent [21]. RAFT is a controlled radical polymerization, which makes use of an equilibrium of active and dormant state of the chain end by addition of a chain transfer agent (such as CPA). The aim of the equilibrium is to keep the majority of the chain ends dormant throughout the polymerization to reduce the probability of radical-radical termination reactions [22]. The target molecular weights ( $M_{n,theor}$ , Table 2) of PDMAEMA 1 - 4 were controlled by the [DMAEMA]:[CPA] ratio while keeping the [CPA]:[AIBN] ratio at 10:1. As the polymerization rate depends on the amount of radicals generated through AIBN, increasing the  $M_n$  required longer reaction times (see Table 1 and Table 2). The polymerizations were terminated at conversions ranging from 46 to 79 % and the purified polymers were analyzed by  $^1\text{H-NMR}$  and SEC (see Figure S1 and Figure S2). Theoretical and experimental  $M_{n,s}$  of polymer 1 are in good agreement and the PDI is low (1.14). Achieving higher  $M_{n,s}$  with the applied RAFT protocol turned out problematic as either the theoretical and experimental  $M_{n,s}$  diverge strongly (polymers 2 and 3) or the PDI is similar to that of a conventional free-radical polymerization (polymer 2 and 4). To achieve high conversions, longer reaction times for polymers 2 – 4 were needed. This result in a longer cumulative time of radical chain ends in the active state and increases the probability of termination reactions which broaden the molecular weight distribution. It might be considered to use an initiator

with higher decomposition rate (VA-044) to improve the synthesis of high  $M_n$  PDMAEMA [23]. However,  $^1\text{H-NMR}$  confirmed the purity of all 4 polymers.

### 3.2. Removal of Cr(VI) by PEUF

Preliminary results of Cr(VI) removal using polymers 1, 2, 3 and 4 showed similar behavior towards Cr(VI) removal (see Figure S3). In our experimental conditions, the  $M_n$  of PDMAEMA does not have significant effect on the Cr(VI) removal. The polymer with the highest  $M_n$ , polymer 4, was used to carry out the following tests through the PEUF technique.

#### 3.2.1. Effect of pH

The removal of Cr(VI) from aqueous solutions depends mainly of the pH because it has a strong influence on both the surface binding sites of the functionalized groups of the polymer and hexavalent chromium species.

Figure 2a shows the retention profile of Cr(VI) by PDMAEMA as a function of pH. Here is observed that the removal of Cr(VI) is maximum at pH 4 and 6, while at  $\text{pH} < 4$  or  $\text{pH} > 6$  the retention capacity decreases considerably.

On one hand, this behavior may be explained because PDMAEMA has an apparent  $\text{pK}_a$  of 6.1 [20], which indicates that at this pH value, the polymer is protonated and as the pH decreases, the polymer will be mostly protonated, facilitating the retention of the chromium anions. On the other hand, it is necessary to consider the strong dependence between the pH and the type of chromium (VI) species in solution. At pH values below 1, the predominant species is the chromic acid ( $\text{H}_2\text{CrO}_4$ ) [24]. At pH 2, Cr(VI) can exist in equilibrium with the cation Cr(III) [25]. In addition, in an acid medium with pH values of 2-4, and depending of the concentration (above 0.5 mM), is possible to find  $\text{HCrO}_4^-$  and some  $\text{Cr}_2\text{O}_7^{2-}$  ions. At pH between 4 and 6,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$  ions exist in

equilibrium, and under alkaline conditions, pH 8, it exists predominantly as the chromate anion ( $\text{CrO}_4^{2-}$ ) (see Figure 2b) [2, 25, 26].

In general the retention capacity of Cr(VI) is attributed to the protonation of nitrogen in the amino tertiary group exhibiting a positive charge in the PDMAEMA at pHs  $\leq 6$ , producing an interaction through the protonated form of the PDMAEMA and the chromium anions. At pH 2, the retention of Cr(VI) is 45.02%, probably due to the equilibrium of the chromium species ( $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Cr}^{3+}$ ). At pH values of 4-6, PDMAEMA reach the maximum (100%) chromium retention. PDMAEMA can remove both  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  anions when it is protonated. At pH 8 and 10, the retention reach values of 79.1% and 2.11%, respectively. The chromium retention capacity of PDMAEMA decrease when  $\text{CrO}_4^{2-}$  species are predominant and amine of polymer is less protonated.

Similar results have been found in the literature for Cr(VI) removal using sorbents based on PDMAEMA. One study details the novel 3-D ordered macroporous adsorbent with a cationic PDMAEMA chain tethered on the pore wall, which was prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) and was further used for the removal of toxic Cr(VI) ions from aqueous solution. Results showed the adsorbent has maximum adsorption at around pH 4 to 6 [27]. In another study, DMAEMA-grafted graphene oxide hybrid materials were fabricated using  $\gamma$ -ray irradiation at ambient temperature. The resulting adsorbent with amine groups was highly efficient to remove Cr(VI) from its acidic aqueous solution, but at higher pHs the removal capacity decreased sharply, which is attributed to the lower degree of protonation [28].

The literature reports that X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy techniques have been used to determine the mechanism of

interaction between chromium species and aminated fibers [29]. The study conclude that Cr(III) can be removed by aminated fibers mainly due to the formation of surface complexes between the nitrogen atoms on the fiber and the Cr(III) species. However, the adsorption of Cr(VI) species on the aminated fibers was more likely due through the formation of hydrogen bonds at high solution pH values or through both electrostatic attraction and surface complexation at low solution pH values [29]. In previous work related to Cr(VI) removal by water-soluble polymers containing quaternary ammonium functional groups, it was found that the interaction between the polymer and chromium (VI) was not purely electrostatic, presumably because of the formation of a coordination bond between a partially movable functional group on the polymeric network and one on the oppositely charged chromium anion [2].

To ensure a good interaction between the protonated PDMAEMA and the chromium anions, subsequent experiments in this study were performed at pH 4.

### **3.2.2. Effect of the polymer:Cr(VI) molar ratio on the retention**

The influence of different molar ratios of DMAEMA repeating units-metal ion (P-Cr(VI)) on the retention capacity of Cr(VI) was analyzed. For this experiment, the washing method was used, using a regenerated cellulose membrane as a filter. The molar ratios of P-Cr(VI) were: 10:1, 20:1, 40:1 and 80:1, all at pH 4, where retentions obtained at  $Z = 5$  were of 92%, 98%, 100% and 100% respectively (see Figure 3a). According to the obtained results, the optimum molar ratio P-Cr(VI) to remove the maximum percentage of chromium is 40:1 and 80:1. However, considering the q-values (mg Cr/g polymer), when the amount of polymer increase, the q-values decrease (see Table 3).

This results are consistent with previous studies of Cr(VI) by PEUF using polyelectrolytes containing quaternary ammonium such as poly[2-(acryloyloxy)ethyl]

trimethylammonium chloride and poly[2-(methacryloyloxy) ethyl] trimethylammonium methyl sulfate [30]. In the case of those cationic polyelectrolytes, the capacity of Cr(VI) removal was also limited by the polymer concentration reaching maximum capacities when polymer:Cr(VI) molar ratio was 20:1. It is important to mention that for polyelectrolytes containing quaternary ammonium, when polymer:Cr molar ratios is higher than 50:1, the polymer–metal solution began to precipitate and it was deposited on the ultrafiltration membrane, and therefore, the volumetric flux was decreased dramatically. Polymers in solution can undergo conformational changes depending on the ionic strength, volume of the solution, and pressure of the system [30]. This should be considered in technical applications. For convenience in this study, the 40:1 molar ratio was used in next experiments because a maximum removal of Cr(VI) is obtained with a smaller amount of polymer. In addition, the polymer concentration in the feed was calculated for all polymer:Cr(VI) molar ratios. The values were between 0.695 and 5.564 kg-polymer/m<sup>3</sup> (see Table 3). Using this range of concentration PDMAEMA did not precipitate and the hydrodynamic conditions were adequate to perform the experiments.

### **3.2.3. Effect of volumetric flux in function of polymer concentration**

The permeate flux was studied as a function of the polymer: Cr(VI) molar ratio. As seen in Figure 3 b, the lowest P-Cr(VI) molar ratio are those with the highest average fluxes, being 141.84 (L/hm<sup>2</sup>) for 10:1. As the molar ratio P-Cr(VI) increases, the permeate flux decreases, being 125.99 (L/hm<sup>2</sup>), 122.81 (L/hm<sup>2</sup>) and 98.55 (L/hm<sup>2</sup>) for P-Cr(VI) 20:1, 40:1 and 80:1, respectively. This behavior may be due, in the first place, to the interactions between the polymer and the membrane, which are greater when increasing the amount of polymer present and second, to the fouling effect, despite the fact that the flux keeps constant throughout the course of the test. Fouling is a complex phenomenon

involving sorption on the membrane surface, deposition on the adsorbed layer, compression of the layer, and possible gelation of the deposit [31]. In similar conditions, PDMAEMA showed higher fluxes compared to quaternary ammonium polymers without loss of removal capacity.

Depending on the results obtained with PDMAEMA and considering the retention of Cr(VI) and the hydrodynamic flux, it is appropriate to perform the chromium retention tests at a molar ratio P-Cr(VI) of 40:1.

#### **3.2.4. Effect of interfering ions on the retention of Cr(VI)**

The influence of two different interfering anions, such as  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ , on the retention capacity of Cr(VI) was studied. This experiment was performed by the washing method at a 40:1 P-Cr(VI) molar ratio, pH 4, and 1 bar of pressure. In the case of phosphate, it is found as  $\text{H}_2\text{PO}_4^-$  at pH 4. The concentration of both interfering anions in the feed was  $30 \text{ mg L}^{-1}$  and  $100 \text{ mg L}^{-1}$  in separate experiments.

The results showed that the chromium retention decreases slightly from 100% to 93.47% for  $\text{H}_2\text{PO}_4^-$  and from 100% to 93.91% for  $\text{SO}_4^{2-}$  when  $30 \text{ mg/L}$  of salts were used (see Figure 4). Also, the same procedure was analyzed, but at a higher concentration of interfering ions ( $100 \text{ mg/L}$ ), observing that by increasing the concentration of these interfering ions, the retention capacity of Cr(VI) does not decrease dramatically, reaching retention percentages of 92.68% and 96.78% for the  $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$  ions respectively.

Considering the size/charge of interfering anions, both anions ( $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$ ) have similar size to  $\text{HCrO}_4^-$ . Despite of  $\text{SO}_4^{2-}$  has higher negative charge than  $\text{H}_2\text{PO}_4^-$ , both anions affect the Cr(VI) retention behavior similarly.

The results showed that these interfering ions do not compete strongly with chromium (VI) for the active sites of the PDMAEMA. Literature shows different results for

chromium retention by PEUF using water-soluble polymers containing quaternary ammonium groups. In these experiments, the removal of chromium (VI) depends on the type and charge of the interfering ions, since they cause a blockage of the active sites of the polymer, causing a decrease in the retention capacity [30].

### 3.2.5. Maximum retention capacity

The maximum retention capacity was evaluated by the enrichment method (similar to column method), using  $28 \text{ mg L}^{-1}$  of Cr(VI) solution in the feed reservoir at pH 4 and a polymer: metal molar ratio of 40:1 collecting 400 mL total filtrate volume (we collected 20 tubes of 20 mL of filtrate each). To obtain the maximum retention capacity, a test was also carried out without the PDMAEMA (blank), to later be determined from the difference with the concentration of Cr(VI) in the permeate of the experiment in presence of PDMAEMA.

Figure 5 shows the results, where PDMAEMA has a good retention capacity of Cr(VI) in all the permeate volume, maintaining a constant and low concentration, on average less than  $1 \text{ mg L}^{-1}$ , reaching a saturation when 400 mL of permeate volume were collected.

The maximum retention capacity of PDMAEMA in our experimental condition was calculated by mass transport and it reach a value of  $165 \text{ mg Cr(VI) retained/g}$  of PDMAEMA. The polymer can retain and concentrate a higher amount of Cr(VI) in solution being consistent with literature [2]. The maximum retention capacity (q-value) of Cr(VI) obtained in enrichment method (similar to column method) is higher compared to the retention (q-value) of Cr(VI) obtained in washing method (similar to batch method) (see Table 3) mainly due to the difference between both methods. In washing method, the concentration of polymer and chromium is fixed in the feed. However, in enrichment method, the concentration of chromium is increasing constantly

and the retention capacity is also increasing until reach the maximum value of 165 mgCr/g polymer.

Table 4 shows the maximum retention of chromium (VI) (% R and q-values expressed as mg Cr(VI)/g polymer) for different water-soluble polymers. Various water-soluble polymers containing quaternary ammonium groups have been studied for Cr(VI) removal by polymer-enhanced ultrafiltration. These polymers showed good behavior and higher q-values at basic pHs. However, because the sorption of Cr(VI) was higher in a wide range of pH, the sorption-desorption properties were not dominated by changing the pH of the aqueous solution. On the other hand, aminated polymers such as poly(glycidyl methacrylate-N methyl-D-glucamine) and PDMAEMA showed higher Cr(VI) removal at acid than basic pH. It is a key factor to study the regeneration cycles and reutilization of the polymeric sorbent.

### 3.2.6. Sorption-desorption study

The sorption-desorption process was finally studied in six consecutive cycles combining enrichment for sorption and washing for desorption. The objective of this experiment is determine the ability of PDMAEMA to remove the maximum amount of Cr(VI), and then release the Cr(VI) and regenerate its retention capacity. The sorption process was carried out at pH 4, with 28 mg/L of Cr(VI) in the feed at a P:Cr(VI) molar ratio of 40:1, while the desorption process was carried out at pH 10.

Figure 6 a shows the sorption (S) (which is calculated as % R) and desorption (D) (which is calculated as 100 - % R) profile of Cr(VI) by PDMAEMA. The retention percentage of the first sorption (S1) was 98%, of which 100% was released in the first desorption (D1). Then in the next cycle, the second sorption (S2) was 85% of Cr(VI) retention, and releasing 80% of the retained metal ion. After that, the following cycles kept the sorption and desorption around 80% (see Figure 6). These results indicate that



the PDMAEMA lose a bit (~ 20%) of removal capacity compared with the first cycle. However, it is a good sorbent and that it has acceptable capacity for regeneration under the conditions analyzed. Similar results have been reported in the literature for solid polymeric sorbent based on PDMAEMA using solid-liquid separation techniques [27, 35].

The main advantage is the pH-responsive behavior of PDMAEMA. It can be explained by speciation and equilibrium of PDMAEMA and Cr(VI) in solution. At acidic pH, the protonated PDMAEMA is positively charged. The polycation interacts with the Cr(VI) anionic species – allowing its removal. Then changing the pH from acidic to basic, PDMAEMA becomes neutral and Cr(VI) anionic species are released from the polymer to the aqueous solution (see Figure 6 b).

Other studies indicate that, in general, water-soluble polymers have a good regeneration after sorbing/desorbing cycles of metal ions or metalloids such as arsenic with poly(4-vinyl-1-methylpyridinium bromide) [31], chromium (VI) with poly(diallyldimethylammonium chloride) [32], and boron with quaternized hydroxyethyl cellulose ethoxylate [36].

#### 4. Conclusions

The results obtained indicate that using water-soluble PDMAEMA in PEUF technique can efficiently remove chromium (VI) from aqueous solution. The retention capacity of Cr(VI) is mainly attributed to the protonation of nitrogen in the tertiary amino group exhibiting a positive charge in the PDMAEMA at  $\text{pHs} \leq 6$ .

The optimum conditions for the maximum retention percentage of Cr(VI) are pH 4, 40:1 polymer: Cr(VI) molar ratio. The retention of Cr(VI) by PDMAEMA in presence of interfering ions do not decrease significantly.

Through the sorption-desorption study, the saturation and recovery of PDMAEMA was performed changing the pH values. The sorption of Cr(VI) was at pH 4 and desorption at pH 10 in six cycles. These results are in line with the pH-responsiveness of PDMAEMA. Thus, the developed method allows the regeneration of the polymer.

#### **Acknowledgments**

The authors thank FONDECYT No. 11140324 and Proyecto DICYT código 021741SP, Vicerrectoría de Investigación, Desarrollo e Innovación, Universidad de Santiago de Chile. G del C Pizarro acknowledges the financial assistance for this work by VRAC, Grant Number L216-03 of Universidad Tecnológica Metropolitana (UTEM), Initiative funded by the Initiation R&D Program.

**References**

- [1] J. Wang, K. Pan, Q. He, B. Cao, Polyacrylonitrile/polypyrrole core/shell nanofiber mat for the removal of hexavalent chromium from aqueous solution, *J. Hazard. Mater.* 244 (2013) 121-129.
- [2] J. Sánchez, B.L. Rivas, Cationic hydrophilic polymers coupled to ultrafiltration membranes to remove chromium (VI) from aqueous solution, *Desalination*, 279 (2011) 338-343.
- [3] R. Codd, C.T. Dillon, A. Levina, P.A. Lay, Studies on the genotoxicity of chromium: from the test tube to the cell, *Coord. Chem. Rev.* 216 (2001) 537-582.
- [4] D. Zhao, A.K. SenGupta, L. Stewart, Selective removal of Cr (VI) oxyanions with a new anion exchanger, *Ind. Eng. Chem. Res.* 37 (1998) 4383-4387.
- [5] M.K. Aroua, F.M. Zuki, N.M. Sulaiman, Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration, *J. Hazard. Mater.* 147 (2007) 752-758.
- [6] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, *Water Sci. Technol.* 34 (1996) 109-116.
- [7] L. Alvarado, I.R. Torres, A. Chen, Integration of ion exchange and electrodeionization as a new approach for the continuous treatment of hexavalent chromium wastewater, *Sep. Purif. Technol.* 105 (2013) 55-62.
- [8] M.S. Bhatti, A.S. Reddy, R.K. Kalia, A.K. Thukral, Modeling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium, *Desalination*, 269 (2011) 157-162.
- [9] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste

- materials and activated carbon fabric cloth, *Ind. Eng. Chem. Res.* 44 (2005) 1027-1042.
- [10] C.A. Kozłowski, W. Walkowiak, Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes, *Water Res.* 36 (2002) 4870-4876.
- [11] B.L. Rivas, E.D. Pereira, M. Palencia, J. Sánchez, Water-soluble functional polymers in conjunction with membranes to remove pollutant ions from aqueous solutions, *Prog. Polym. Sci.* 36 (2011) 294-322.
- [12] B.L. Rivas, E.D. Pereira, I. Moreno-Villoslada, Water-soluble polymer–metal ion interactions, *Prog. Polym. Sci.* 28 (2003) 173-208.
- [13] M.F. Abou Taleb, G.A. Mahmoud, S.M. Elsigeny, E.A. Hegazy, Adsorption and desorption of phosphate and nitrate ions using quaternary (polypropylene-g-N,N'-dimethylamino ethylmethacrylate) graft copolymer, *J. Hazard. Mater.* 159 (2008) 372-379.
- [14] S. Zhu, N. Yang, D. Zhang, Poly(N,N-dimethylaminoethyl methacrylate) modification of activated carbon for copper ions removal, *Mater. Chem. Phys.* 113 (2009) 784-789.
- [15] M. Jiang, J. Wang, L. Li, K. Pan, B. Cao, Poly(N,N-dimethylamino ethylmethacrylate) modification of a regenerated cellulose membrane using ATRP method for copper(II) ion removal, *RSC Adv.* 3 (2013) 20625-20632.
- [16] Q. Cheng, C. Li, L. Xu, J. Li, M. Zhai, Adsorption of Cr(VI) ions using the amphiphilic gels based on 2-(dimethylamino) ethyl methacrylate modified with 1-bromoalkanes, *Chem. Eng. J.* 173 (2011) 42-48.
- [17] H. Tokuyama, N. Ishihara, Temperature-swing adsorption of precious metal ions onto poly(2-(dimethylamino) ethyl methacrylate) gel, *React. Funct. Polym.* 70 (2010) 610-615.

- [18] W. G. Weber, J. B. Mc Leary, R. D. Sanderson, *Tetrahedron Lett.* 47 (2006) 4771-4774.
- [19] S.H. Thang, Y.K. Chong, R.T.A. Mayadunne, G. Moad, E. Rizzardo, *Tetrahedron Lett.* 40 (1999) 2435-2438.
- [20] E. Karjalainen, V. Aseyev, H. Tenhu, Influence of hydrophobic anion on solution properties of PDMAEMA, *Macromolecules*, 47 (2014) 2103-2111.
- [21] E. Karjalainen, V. Aseyev, H. Tenhu, Counterion-induced UCST for polycations, *Macromolecules*, 47 (2014) 7581-7587.
- [22] K. Matyjaszewski, M. Möller, *Polymer science: a comprehensive reference*, second ed., Elsevier, Amsterdam, 2012.
- [23] S. Perrier, 50th anniversary perspective: RAFT polymerization—A user guide, *Macromolecules*, 50 (2017) 7433-7447.
- [24] R.T. Kachoosangi, R.G. Compton, Voltammetric determination of Chromium(VI) using a gold film modified carbon composite electrode, *Sensor. Actuat. B-Chem.* 178 (2013) 555-562.
- [25] W. Jin, H. Du, S. Zheng, Y. Zhang, Electrochemical processes for the environmental remediation of toxic Cr(VI): A review, *Electrochim. Acta*, 191 (2016) 1044-1055.
- [26] O. Kebiche-Senhadji, S. Tingry, P. Seta, M. Benamor, Selective extraction of Cr(VI) over metallic species by polymer inclusion membrane (PIM) using anion (Aliquat 336) as carrier, *Desalination*, 258 (2010) 59-65.
- [27] X. Wang, C. Wu, L. Tian, G. Li, X. Zhang, F. Lei, J. Qu, P. Liu, Cationic polymer chain tethered on the pore-wall of 3-D ordered macroporous resin for the removal of hexavalent chromium from aqueous solution, *React. Funct. Polym.* 95 (2015) 55-61.

- [28] H-L. Ma, Y. Zhang, L. Zhang, L. Wang, C. Sun, P. Liu, L. He, X. Zeng, M. Zhai, Radiation-induced graft copolymerization of dimethylaminoethyl methacrylate onto graphene oxide for Cr(VI) removal, *Radiat. Phys. Chem.* 124 (2016) 159–163.
- [29] S. Deng, R. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, *Water Res.* 38 (2004) 2424-2432.
- [30] J. Sánchez, N. Mendoza, B. L. Rivas, L. Basález, J. L. Santiago-García, Preparation and characterization of water-soluble polymers and their utilization in chromium sorption, *J. Appl. Polym. Sci.* (2017) DOI10.1002/app.45355.
- [31] J. Sánchez, A. Bastrzyk, B.L. Rivas, M. Bryjak, N. Kabay, Removal of As(V) using liquid-phase polymer-based retention (LPR) technique with regenerated cellulose membrane as a filter, *Polym. Bull.* 70 (2013) 2633-2644.
- [32] J. Sánchez, B. Butter, L. Basález, B.L. Rivas, M. Ottakam Thotiyil, Efficient removal of Cr(VI) by polyelectrolyte-assisted ultrafiltration and subsequent electrochemical reduction to Cr(III), *J. Chil. Chem. Soc.* 62 (2017) 3647-3652.
- [33] L. Toledo, B.L. Rivas, Quaternised chitosan in conjunction with ultrafiltration membranes to remove arsenate and chromate ions, *Polym. Bull.* 72 (2015) 1365-1377.
- [34] B.L. Rivas, J. Sánchez, Soluble polymer containing an N-methyl-D-glucamine ligand for the removal of pollutant oxy-anions from water, in: H.N. Cheng, C.A. Maryanoff, B.D. Miller, D.G. Schmidt (Eds.), *Stereochemistry and global connectivity: the legacy of Ernest L. Eliel*, American Chemical Society (ACS eBooks), 2017, pp.197-211.

- [35] E.S. Dragana, D. Humelnicu, M.V. Dinu, Design of porous strong base anion exchangers bearing N,N-dialkyl 2-hydroxyethyl ammonium groups with enhanced retention of Cr(VI) ions from aqueous solution, *React. Funct. Polym.* 124 (2018) 55-63.
- [36] J. Sánchez, J. Wolska, E. Yörükoğlu, B. L Rivas, M. Bryjak, N. Kabay, Removal of boron from water through soluble polymer based on N-methyl-D-glucamine and regenerated-cellulose membrane, *Desalin. Water Treat.* 57 (2016) 861-869.

**Figure 1.** Schematic representation of PEUF technique.

**Figure 2.** (a) Retention of Cr(VI) as a function of pH using 25 mg/L of Cr(VI) at 1 bar of pressure, 80:1 polymer- metal ratio and  $Z = 5$ . (b) Fraction of Cr(VI) species versus pH at concentration of 0.5 mM [24].

**Figure 3.** (a) Retention profiles of Cr(VI) at different polymer:metal molar ratios, using 25 mg/L of Cr(VI), pH 4, and 1 bar of pressure. (b) Permeate flux profiles of Cr(VI) at different polymer: metal molar ratios, using 25 mg/L of Cr(VI) , pH 4, and 1 bar of pressure.

**Figure 4.** Retention profiles of Cr(VI) in the presence of interfering ions at P:Cr(VI) of 40:1, using 25 mg L<sup>-1</sup> of Cr(VI) , pH 4, and 1 bar of pressure.

**Figure 5.** Maximum retention profile by PDMAEMA retaining 28 mg L<sup>-1</sup> of metal ions, using a P:Cr(VI) of 40:1, pH 4, and 1 bar of pressure.

**Figure 6.** (a) Sorption-desorption profiles by PDMAEMA with 28 mg L<sup>-1</sup> of Cr(VI), using a P:Cr(VI) of 40:1, pH 4 for the sorption and pH 10 for the desorption , and 1 bar of pressure. (b) pH-responsive behavior of PDMAEMA and ion-exchange in sorption-desorption process.

#### Supplementary material

**Figure S1:** <sup>1</sup>H-NMR (D<sub>2</sub>O) of PDMAEMA 1 with peak assignment.

**Figure S2:** SEC trace of PDMAEMA 1 (THF as eluent).

**Figure S3:** Cr(VI) retention profile using PDMAEMA 1, 2, 3 and 4 at optimum conditions.



**Table 1.** Preparation conditions for the synthesized polymers of PDMAEMA

<b>Polymer</b>	<b>DMAEMA (mmol)</b>	<b>CPA (mmol)</b>	<b>AIBN (mmol)</b>	<b>Time (h)</b>
1	47.0	0.237	$2.38 \times 10^{-2}$	18
2	48.0	0.118	$1.19 \times 10^{-2}$	42
3	47.0	0.0594	$5.98 \times 10^{-3}$	66
4	47.0	0.0396	$3.97 \times 10^{-3}$	120

**Table 2.** Molecular weights, conversion and PDI of synthesized polymers.

<b>Polymer</b>	<b>M<sub>n</sub>SEC (g/mol)</b>	<b>PDI<sub>SEC</sub></b>	<b>Conversion<sub>1H-MNR</sub></b>	<b>M<sub>n</sub> theor<sup>a</sup> (g/mol)</b>
1	28,800	1.14	79 %	24,909
2	142,200	1.86	46 %	29,696
3	142,100	1.45	64 %	79,890
4	195,300	1.79	74 %	138,354

<sup>a</sup>
$$([DMAEMA]/[CPA]) \cdot conv \cdot M(DMAEMA) + M(CPA)$$

**Table 3.** Retention (%) of Cr(VI), q-values at Z=5 and polymer concentration in the feed determined for different polymer:Cr(VI) molar ratios.

<b>P-Cr(VI)</b>	<b>% Retention</b>	<b>q-value (mg Cr/g polymer)</b>	<b>Polymer concentration (kg-polymer/m<sup>3</sup>)</b>
10:1	92	34.40	0.695
20:1	98	18.25	1.391
40:1	100	9.35	2.782
80:1	100	4.67	5.564

**Table 4.** Maximum retention of chromium (VI) (% R and q-values expressed as mg Cr(VI)/g polymer) for different water-soluble polymers

<b>Water-soluble polymer</b>	<b>pH</b>	<b>% R</b>	<b>q-value</b>	<b>[Ref]</b>
poly (ar-vinyl benzyl) trimethylammonium chloride	9	97	164	[2]
poly [3-(acryloylamino) propyl] trimethylammonium chloride	9	96	152	[2]
poly [2-(acryloyloxy) ethyl] trimethylammonium methyl sulfate	9	87	90	[2]
poly(diallyldimethylammonium chloride)	9	95	33	[32]
N,N,N-trimethylchitosan chloride	8	94	48	[33]
poly(glycidyl methacrylate-N methyl-D-glucamine)	3	60	21	[34]
poly(N,N-dimethylaminoethyl methacrylate)	3	100	165	This work

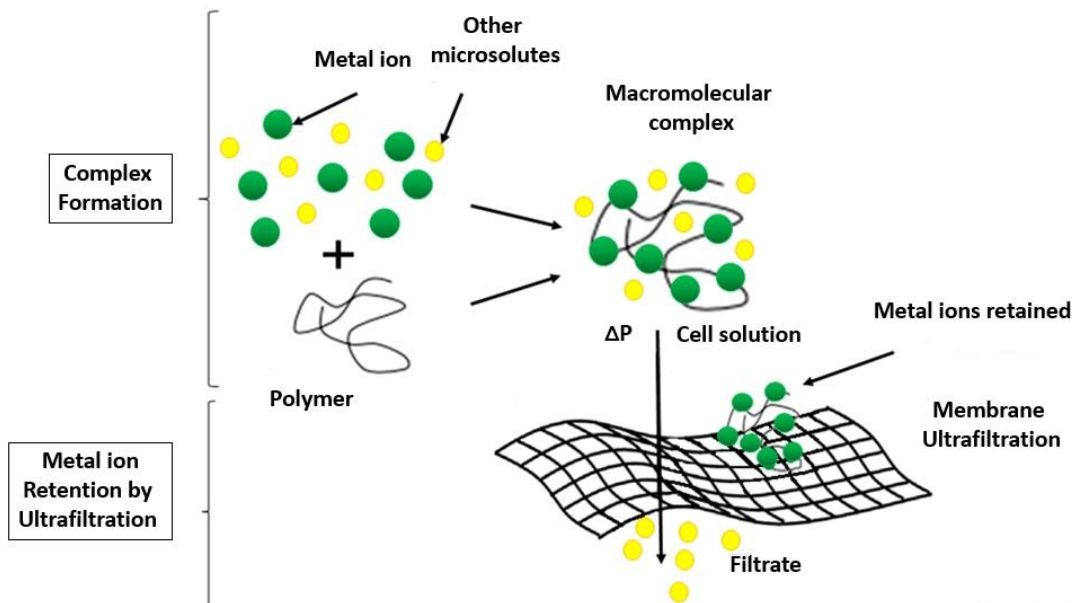


Fig:1

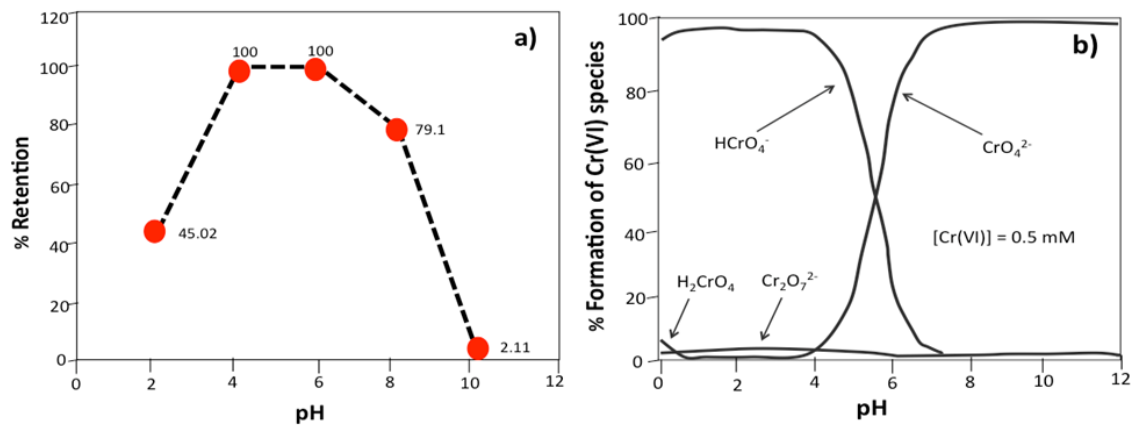


Fig:2

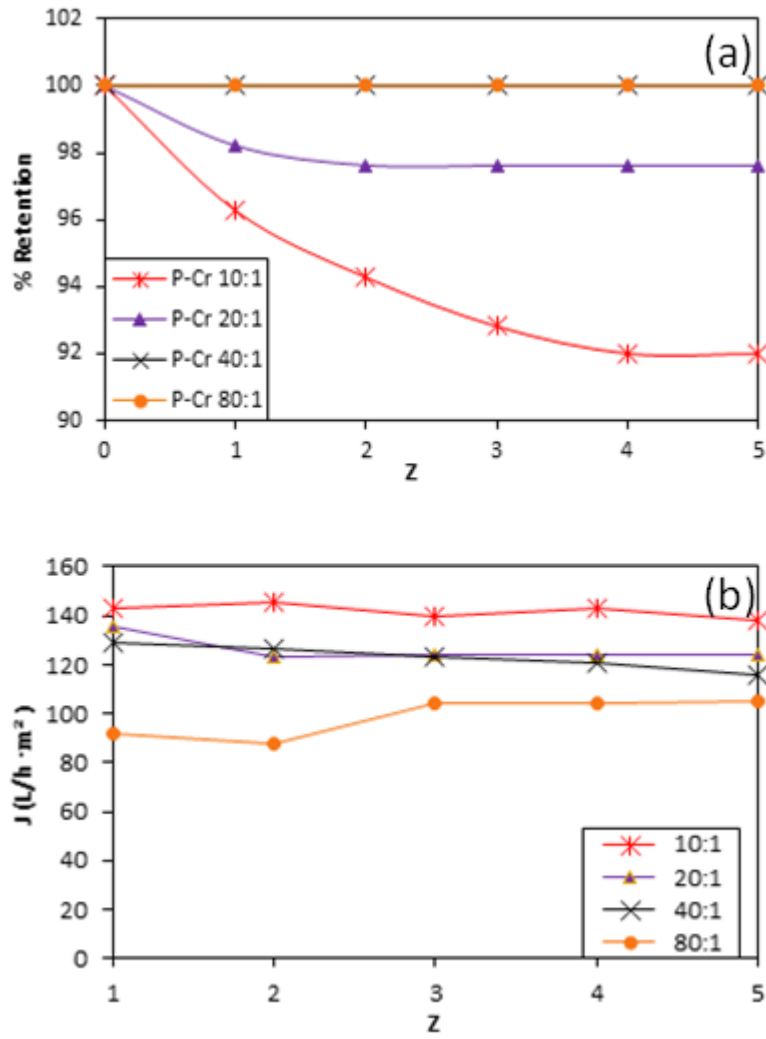


Fig:3

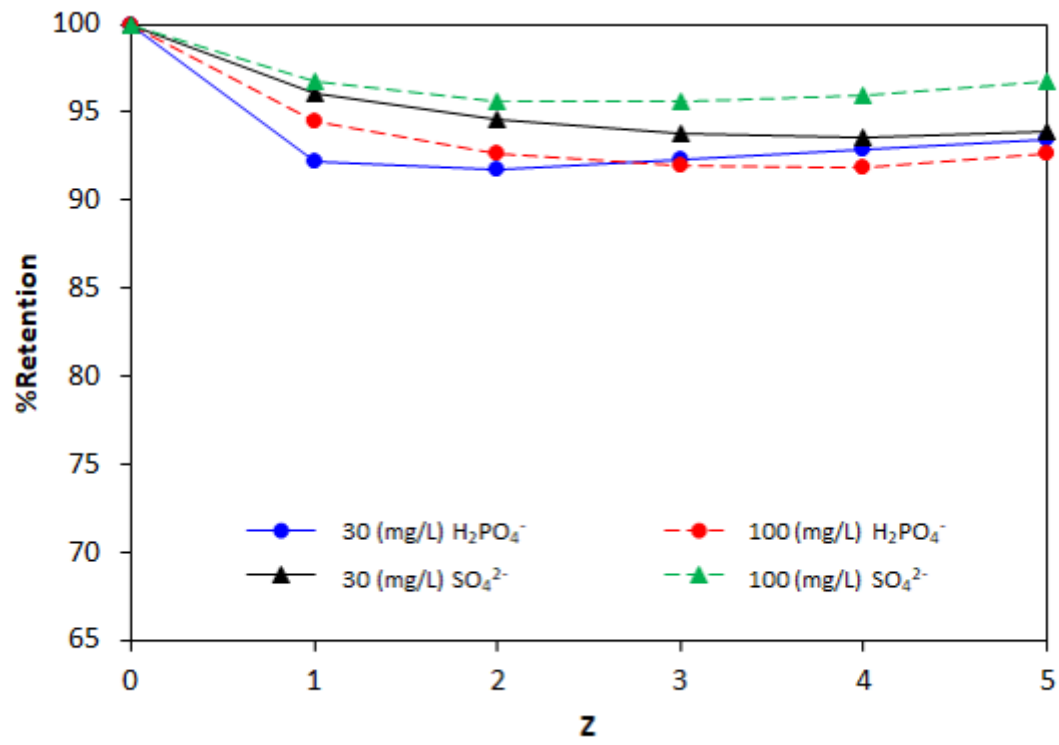


Fig:4



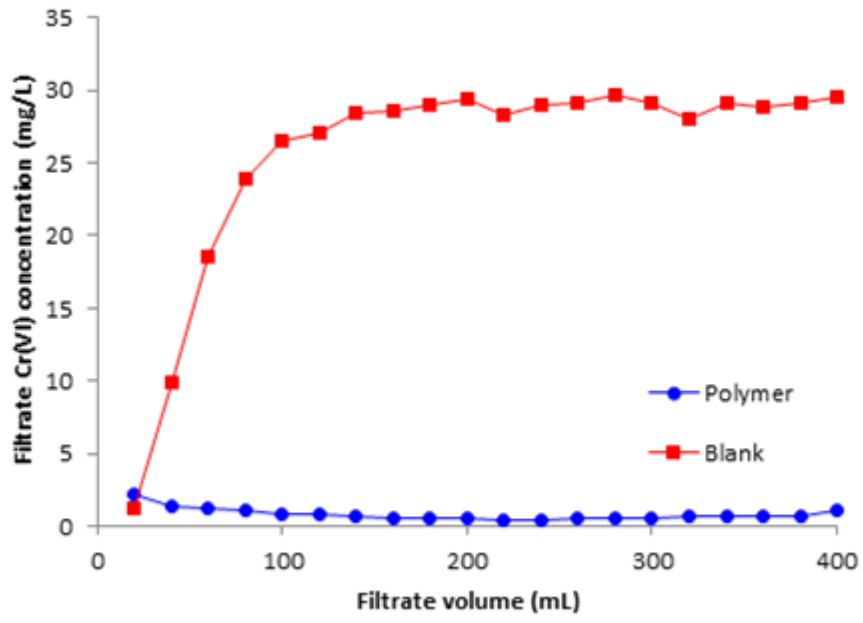


Fig:5

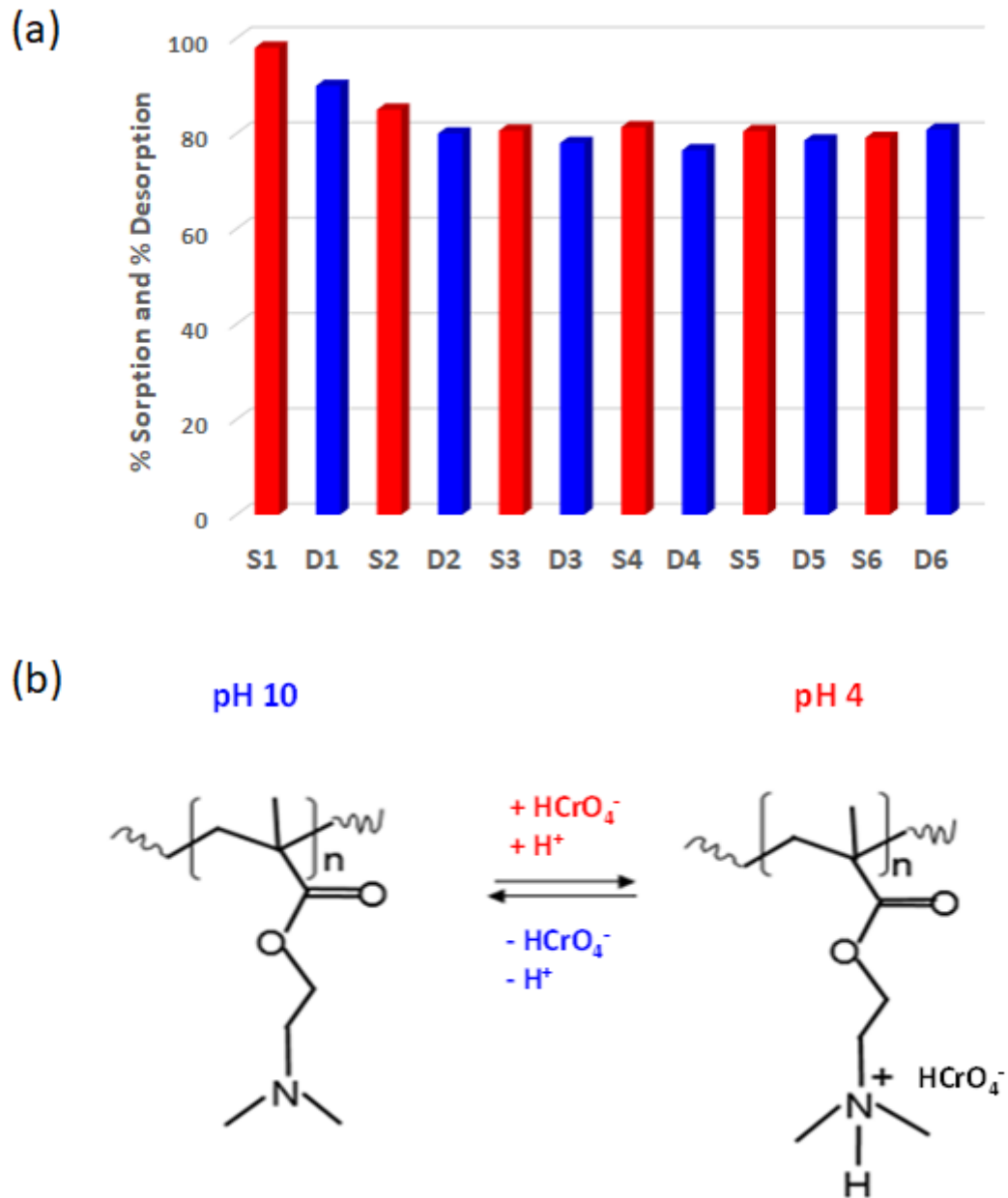


Fig:6