

POLY(4-VINYLBENZYL) TRIMETHYLAMMONIUM CHLORIDE-*CO*-(4-VINYLBENZYL)-N-METHYL-D-GLUCAMINE) COPOLYMER WITH REMOVAL PROPERTIES FOR VANADIUM (V) AND MOLYBDENUM(VI). ADSORPTION ISOTHERM STUDY

D. V. MORALES¹, M. TORREGROSA¹, B. L. RIVAS^{2*} AND M. GONZÁLEZ²

¹Department of Environmental Chemistry, Faculty of Sciences, Universidad Católica de la Santísima Concepción, Concepción, Chile.

²Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile.

ABSTRACT

It was studied the removal properties of poly(4-vinylbenzyl) trimethylammonium chloride-*co*-(4-vinylbenzyl)-N-methyl-D-glucamine P(CIVBTA-*co*-VBNMDG) ion exchange resin towards vanadium (V) and molybdenum (VI), and compared with a commercial resin Amberlite IRA-743 which contains the same functional group. The resin was characterized by FT-IR spectroscopy and SEM. Parameters like water adsorption capacity, effect of the pH, maximum retention capacity of the metal ions, elution, regeneration, selectivity, interferences effect, adsorption time, and adsorption isotherms were studied. All the studies were carried out by batch equilibrium procedure. Thermodynamic parameters such as enthalpy, entropy, and free energy were calculated. The P(CIVBTA-*co*-VBNMDG) resin showed higher capacity to remove V(V) and Mo(VI) from water solution than that Amberlite IRA-743 commercial resin. The higher capacity displayed by P(VBNMDG) resin was attributed to the higher degree of swelling and the stronger active functional groups.

Keywords: Resin, Ion Exchange, Adsorption, Molybdenum, Vanadium.

INTRODUCTION

With the rapid growth of world population, the amount of resources consumed is increasing and inevitably so is the amount of industrial waste generated in order to meet the global demand. These industrial wastes may contain components that still have a good market value, but are not recovered due to technological or economic constraints¹. Furthermore, these wastes present in the industry are heavy metals. Besides, these wastes present in the industry are heavy metals.

Heavy metals contamination has become one of the most serious environmental and human health issues², because, are not biodegradable and tend to accumulate in living organisms, moreover, it is known that many heavy metal ions are toxic or carcinogenic³⁻⁶. Nevertheless, there are several methods to treat and recover these types of metals from wastewater have been extensively studied^{2,7}. These treatment technologies include precipitation^{8,9}, solvent extraction¹⁰⁻¹⁴, adsorption¹⁵⁻¹⁷, liquid membrane separation,¹⁸⁻¹⁹ and ion exchange by resin²⁰⁻²⁴. The most studied methods for the treatment of wastewater containing heavy metals are ion exchange, adsorption, and membrane filtration²⁵. Besides, ion exchange resins have a great advantage, compared with other recovery technologies, such as a high recovery rate²⁴.

Those metals that are of environmental and industrial importance are vanadium and molybdenum. Besides, this kind of metals occur in the earth crust in mean concentrations of approximately 0.0001% and 150 g t⁻¹, respectively.

Therefore, vanadium is the 20th most abundant element in the Earth's crust, and is beneficial or essential for living organisms due to its unique roles in biological structures and functions²⁶⁻²⁷. Furthermore, vanadium and molybdenum are very important in high-end technologies such as aerospace and rockets, respectively, are irreplaceable for their unique properties of high strength, corrosion resistance, and abrasion resistance²⁸⁻²⁹. Moreover, the molybdenum-containing catalysts, which are widely used in the oil refining industry. However, environmental legislation is becoming strict, therefore, the emission of these residues must be drastically reduced.

Molybdenum is a part of the group (VI) of the periodic table of the elements. In addition, it is a transition element with atomic weight of 95.94 and able to form various compounds. The equilibrium in aqueous solutions of molybdenum(VI) has been investigated in detail. The tetrahedral [MoO₄]²⁻ is predominant when molybdenum is found at pH > 6 at concentrations lower than 10⁻³ mol l⁻¹³⁰. Furthermore, molybdate ion is weaker base than [VO₄]³⁻ and protonation starts at pH ≥ 7. When the pH is between 5 and 6, condensation of the polymerization takes place and heptomolybdate (Mo₇O₂₄)⁶⁻ is obtained, while at pH 3-5 the octamolybdate (Mo₈O₂₆)⁴⁻ is generated. Moreover, when MoO₃ is found at a pH of 0.9 it precipitates, and in more acidic solutions, the [MoO₂]²⁺ ion is formed.

Vanadium (V) is a part of the 4th period, Group 5 (VB), of the periodic table of elements. It is a transition element with atomic weight of 50.94 u capable of forming various compounds and functioning as an anion or a cation³¹. It exists in the +2, +3, +4, and +5 oxidation states, mainly in tetravalent and pentavalent form³². Excessive concentration of this metal is harmful to both plants and animals and sometimes it's even threatens human health³³. On the other hand, the chemistry of vanadium is even more complicated than that of molybdenum. Similar to molybdenum, vanadate (V) can be converted into a form of vanadyl (V) cation. In addition, vanadium forms aquo-complexes whose colors are violet [V(H₂O)₆]²⁺, green [V(H₂O)₆]³⁺, blue VO²⁺(aq), and yellow VO₂⁺(aq). Changes in the adsorption of these species could play an essential role in their mutual separations.

The aim of this research is to evaluate the removal properties of poly(vinylbenzene)trimethylammonium chloride P(CIVBTA-*co*-VBNMDG) ion exchange resin towards vanadium (V) and molybdenum (VI) working under alkaline conditions and compare their performance with their or Amberlite IRA-743 commercial resin.

EXPERIMENTAL

Materials

Poly(4-vinylbenzyl) trimethylammonium chloride-*co*-(4-vinylbenzyl)-N-methyl-D-glucamine) of particle size between 180-250 μm, AmberliteIRA-743 commercial resin purchased from Sigma-Aldrich. The reagents to study the removal properties were ammonium metavanadate (p.a), ammonium heptamolybdate (99%), hydrochloric acid (37%), and nitric acid (65%). All the salts and acid solutions were purchased from Merck.

The structure of the P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 commercial resins used for reference are shown in Figures 1 and 2.

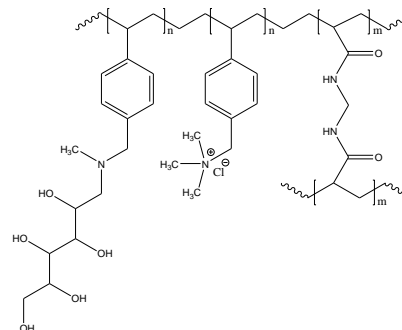


Figure 1. General structure of P(CIVBTA-*co*-VBNMDG) copolymer.

*Corresponding author email: brivas@udec.cl

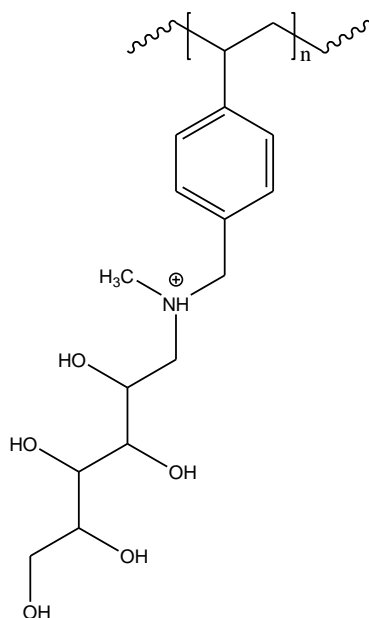


Figure 2. General structure of Amberlite IRA-743 a commercial resin.

Instrumentation

The laboratory equipment used in the experimental stage of this research included: (a) a Shimadzu AUX 220 analytical balance; (b) a Wisebath thermostatic bath; (c) a Memmert heater; (d) a Perkin Elmer PinAAcle 900F atomic absorption spectrometer; (e) a digital pH meter Toledo seven compact; (f) a Magnetic stirrer Wisestir MSH-20*; (g) a scanning electron microscope, Jeol JSM-6380 LV (h) TF-IR spectrometer 550, Magna Nicolet; (i) Thermogravimetric analyzer NETZSCH 209F1 Iris 2020-1.

Characterization

The P(CIVBTA-*co*-VBNMDG) resin was characterized by FT-IR spectroscopy over the range of 400 to 4000 cm^{-1} to identify the typical absorption signals of the ion exchange resin groups, and also by scanning electron microscopy, SEM to observe the morphology of the resin charged with metal ion and alone, at 100, 50, and 5 μm . Finally, it was also analyzed the thermal stability by analysis thermogravimetric, TGA. The profile of decomposition of the resin was running between 0 and 550 $^{\circ}\text{C}$, under N_2 atmosphere and at heating rate of 10 $^{\circ}\text{C min}^{-1}$.

Degree of swelling

The resin swelling was carried out using 100 mg of dry resin and 80 mL of bidistilled water were introduced and kept in a 100-mL beaker over 24 h. For this study was used the particle size between 180 and 250 μm .

Once the residence time was completed, the beaker content was filtered and the wet resin was weighed to obtain the mass of water absorbed per gram of resin (see Eq. 1). The resins were classified as (a) xerogel (0 g $\text{H}_2\text{O/g}$ resin), (b) hydrogel (0-100 g $\text{H}_2\text{O/g}$ resin), and (c) superabsorbent (higher than 100 g $\text{H}_2\text{O/g}$ resin).

$$\text{Degree of Swelling} = \frac{\text{Wet mass of resin}}{\text{Dry mass of resin}} \quad (1)$$

Batch Method

Effect of pH on the removal

To study the pH effect on metal ions removal, solutions of Mo(VI) and V(V) at pH values of 2, 4, 6, 8, 10, and 12 were prepared. The pH values were adjusted with HNO_3 and NaOH . The resins (0.05 g) were contacted with a solution of 50 ppm of metal ion in a water bath at constant agitation of 140 rpm for 60 min and 25 $^{\circ}\text{C}$. Afterward, the solutions were filtered and washed prior to analysis by atomic absorption spectroscopy (AAS). Thus, the optimum pH was determined

and corresponds to the pH at which the resin was capable of retaining the highest amount of the metal ion.

Effect of contact time on the removal

It was contacted 0.05 g of P(CIVBTA-*co*-VBNMDG) resin with 5 mL of metal ion solution at optimal pH and kept at 25 $^{\circ}\text{C}$ with stirring at 140 rpm in a thermodynamic bath. The samples were taken off at 15, 30, 60, and 120 min. The solution was filtered and washed prior to AAS analysis.

Maximum retention capacity

It were contacted 500 mg of P(CIVBTA-*co*-VBNMDG) resin with 10 mL of metal ion solution with a concentration of 1 g L^{-1} at optimum pH during 60 min at 25 $^{\circ}\text{C}$ with stirring at 140 rpm. Finally, the solutions were filtered and washed prior to AAS analysis. The same resin was exposed to a metal ion solution at the same concentration four consecutive times.

Elution

To determine the best eluent was used 0.05 g of P(CIVBTA-*co*-VBNMDG) resin at maximum retention capacity with Mo(VI) or V(V) and eluted with 5 mL of acid solution. It was used hydrochloric and nitric acid at 1 and 4 mol L^{-1} for 60 min at 140 rpm and 25 $^{\circ}\text{C}$. Then, the solutions were filtered, washed, and analyzed by AAS. This procedure was performed separately for each acid with the charged resin.

Regeneration

P(CIVBTA-*co*-VBNMDG) resin and 10 mL of metal ion solution were contacted at the optimum pH for 60 min at 140 rpm and 25 $^{\circ}\text{C}$. Then, the solution was filtered and washed. The resin was further discharged of the metal ions using an acid by stirring during 60 min at 140 rpm and 25 $^{\circ}\text{C}$, and then was filtered and washed. This cycle of charging and discharging the resin was repeated three consecutive times. The obtained solutions were analyzed by AAS after each step.

Removal under competitive conditions. Selectivity

It was prepared a binary solution of Mo(VI) and V(V) of 50 mg L^{-1} of each, at pH 2 and 4. It were contacted 0.04 g of resin with 10 mL of the binary solution, and stirred at 140 rpm, at 25 $^{\circ}\text{C}$ during 1h. After the solutions were filtered and analyzed by AAS.

The selectivity was studied according to equations 2 and 3.³⁴

$$D_i = \frac{M_{i,R}}{M_{i,S}} \times \frac{V_S}{m_R} \quad (2)$$

Where,

D_i : Distribution coefficient for a metal ion,

$M_{i,R}$: Quantity of metal ion in the resin (mmol or mg)

$M_{i,S}$: Quantity of metal ion in solution (mmol or mg)

V_S : Volume of metal ion solution (mL)

m_R : Mass of dry resin (mg)

$$K_{i,j} = \frac{D_i}{D_j} \quad (3)$$

K_{ij} : Selectivity coefficient, which give information about the affinity of the resin for metal ion or other.

Isotherm studies

To obtain more insights about the adsorption equilibrium of the metal ion on the P(CIVBTA-*co*-VBNMDG) surface an adsorption isotherms study was performed varying the concentration of metal ion at constant mass of resin. The experiment was carried out preparing 50-2200 ppm of metal ion, the resin mass (50 mg) and the temperature were kept constant with a stirring at 140 rpm during 24h at 25 $^{\circ}\text{C}$. Then, the solutions were filtered and washed, and subsequently were taken for AAS analysis.

All the data obtained were adjusted to Langmuir and Freundlich isotherms, and thus determine whether the adsorption of the metal ion in the resin corresponds to a physical or chemical adsorption. The equations (4) and (5) show the Langmuir³⁵ and Freundlich linearized isotherms, respectively.

$$\text{Langmuir Equation: } \frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

C_{eq} : Equilibrium concentration (mg L^{-1})

q_e : Amount of metal ion adsorbed per unit weight of the resin ($\text{mg metal ion g}^{-1} \text{ resin}^{-1}$)

q_m : Maximum adsorption capacity ($\text{mg g}^{-1} \text{ resin}^{-1}$)

b : Langmuir constant (L mg^{-1})

$$\text{Freundlich Equation: } \log(q_e) = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

q_e : Amount of metal ion adsorbed per unit weight of the resin ($\text{mg metal ion g}^{-1} \text{ resin}$)

C_{eq} : Equilibrium concentration (mg L^{-1})

K_F : Freundlich constant

n : Dimensionless parameter indicating the preference of the adsorption

RESULTS AND DISCUSSION

Characterization of the resin by FT-IR spectroscopy

The figure 3 shows the FT-IR spectra of P(CIVBTA-*co*-VBNMDG) resin (black square) and Amberlite IRA-743 in red circle where it is possible observe the typical signals of the functional, summarized in table 1.

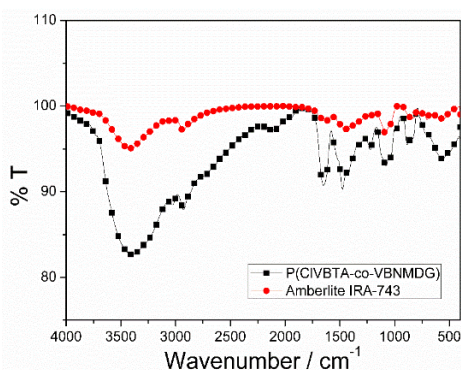


Figure 3. FT-IR spectra of P(CIVBTA-*co*-VBNMDG) copolymer in black square and Amberlite IRA-743 resin in red circle.

Table 1. Main FT-IR absorption bands of P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins

Resin	-NH/cm ⁻¹	-N ⁺ -(CH ₃) ₃ /cm ⁻¹	-CH aromatic/cm ⁻¹	-C=O/cm ⁻¹
P(CIVBTA- <i>co</i> -VBNMDG)	3411.51	1475.40	2942.89	1649.80
IRA-743	3419.29	1429.02	2948.67	1625.72

Scanning Electron Microscopy, SEM

The shape of particles, rugosity of the surface, and porosity were studied by SEM. It is due to the importance to study the surface characteristic for a material that will be used in adsorption process. A resin with a rough surface will have a higher available surface for interact with an adsorbate.

The SEM analysis of P(CIVBTA-*co*-VBNMDG) resin was performed with the particle size between 180-250 μm . According with figure 4.a) we can observe homogenous particles, with irregular shape, non-uniform and in figures 4.b) and 4.c) it is possible observe exfoliation and absence of rugosity. Meanwhile for Amberlite IRA-743 commercial resin we can observe in figure 4.d) uniform spheres shape and in figure 4.e) and 4.f) a very rough surface.

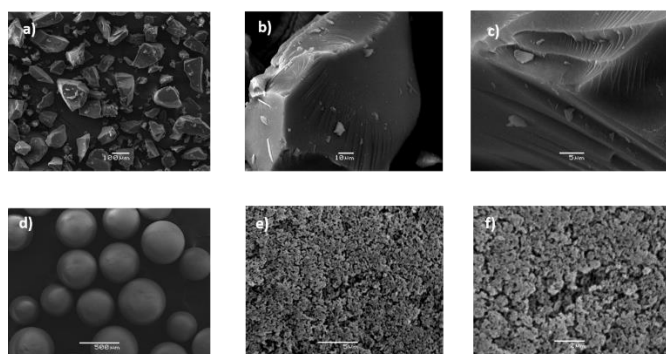


Figure 4. Microphotographs of P(CIVBTA-*co*-VBNMDG) resin at a) 100 μm , b) zoom of 10 μm , and c) zoom of 5 μm , and Amberlite IRA-743 resin at d) 500 μm , e) zoom of 5 μm , and f) zoom of 2 μm .

Thermogravimetric Analysis, TGA

In order to obtain the decomposition profile of P(CIVBTA-*co*-VBNMDG) resin, the resin samples were subjected to control heating. In figure 5 is shown the thermogram of P(CIVBTA-*co*-VBNMDG) resin performed under conditions of inert atmosphere and a heating rate of $10^\circ\text{C min}^{-1}$.

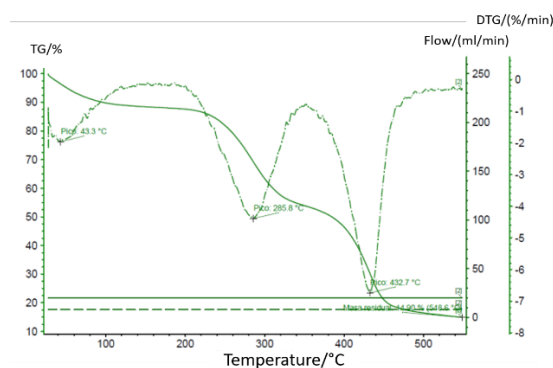


Figure 5. Thermogram of P(CIVBTA-*co*-VBNMDG) resin under nitrogen atmosphere.

There is not a significant decomposition temperature. According to the thermogram P(CIVBTA-*co*-VBNMDG) resin is stable up to 250°C. P(CIVBTA-*co*-VBNMDG) resin don't show an important loss of weight, attributed probably at water molecules. Subsequently it loss weight in two steps, probably due to the ammonium group weight loss.

Degree of swelling

The degree of swelling is the capacity of water absorption that is direct correlation of the available active sites for removal of metal ions. The degree of swelling is the most important property, which in theory allows the metal ions diffuse through the porous crosslinked matrix, favoring the interchange of the metal ions with the functional groups.

The degree of swelling can be influenced by different factors of the polymer matrix structure, like crosslinking degree, concentration, pK of ionizable groups, ionization degree, and hydrophilicity, among others.

According to the degree of swelling, is possible to classify the resins in *Xegorel* ($0 \text{ g H}_2\text{O g}^{-1} \text{ resin}^{-1}$) those resins that are not capable to retain water, *Hydrogel* resins (0 to $100 \text{ g H}_2\text{O g}^{-1} \text{ resin}^{-1}$), are those resins capable to retain water. Exist also the *Super Absorbents* ($100 \text{ g H}_2\text{O g}^{-1} \text{ resin}^{-1}$) that correspond to resins that adsorb higher quantity of water, inhibiting the ion exchange.

Table 2. Degree of swelling for P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins.

Resin	Water absorption /g H ₂ O g ⁻¹ resin ⁻¹
P(CIVBTA- <i>co</i> -VBNMDG)	9.4
IRA-743	4.3

According to table 2, P(CIVBTA-*co*-VBNMDG) resin and Amberlite IRA-743 commercial resin correspond to hydrogels, but P(CIVBTA-*co*-VBNMDG) resin has higher water absorption capacity than the commercial resin Amberlite IRA-743, due to that this resin could have higher available active sites for metal ions removal.

Effect of pH in the absorption

With aim to determinate the optimal adsorption pH were prepared solutions of Mo(VI) and V(V) at different pH: 2, 4, 6, 8, 10 and 12, at 50 mg L⁻¹.

Molybdenum and vanadium have different speciation depending of the pH value, will change the structure. Table 3 shows the speciation in function of pH.

Table 3. Speciation of Molybdenum and Vanadium according to pH.

Molybdenum		Vanadium	
pH	Specie	pH	Specie
> 6.5	MoO ₄ ²⁻	> 13	VO ₄ ³⁻
4	MoO ₂₄ ⁶⁻	9	V ₂ O ₇ ⁴⁻
2	Mo ₈ O ₂₆ ⁴⁻	8.5	VO ₃ ⁻
≤ 1	MoO ₂ ²⁺	6	V ₃ O ₉ ³⁻
0.8	MoO ₃ *2H ₂ O	2	V ₁₀ O ₂₈ ⁶⁻
		< 2	VO ₂ ⁺

For molybdenum, it is possible observe at pH equal or less than 1, the ion has a positive charge which leads to an impossible ion exchange with ammonium quaternary functional groups, but at pH higher than that 2 will be perfectly possible the removal due to the negative charge of the ion as oxyanion specie, which is favored by the resin structure.

Vanadium at pH below 2 is found with positive charge, making impossible the removal by P(CIVBTA-*co*-VBNMDG) resin due to the ammonium quaternary functional groups, but at values above 2, vanadium it is found as oxyanion favoring the ion exchange due to the negative charge.

Effect of pH in the retention

In Tables 4 and 5 are shown the retention of Mo(VI) and V(V) in function of pH for P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins at a 50 mg L⁻¹ of concentration. P(CIVBTA-*co*-VBNMDG) resin shown high percentage of retention at all studied pH from 2 up to 12, over 80%, but the higher retention is at pH 2 with 4.5 mg Mo g⁻¹ resin⁻¹ corresponding to 96%. Meanwhile, Amberlite IRA-743 commercial resin presents a good retention only at pH 2, removing 2 mg Mo g⁻¹ resin⁻¹. Due to that, it was decided work at pH 2 for Mo(VI) removal. Molybdenum at pH 2 it is found as Mo₈O₂₆⁴⁻.

Table 4. Retention of 50 mg L⁻¹ of Mo(VI), in function of pH for P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins.

pH	P(CIVBTA- <i>co</i> -VBNMDG)		IRA-743	
	% Retention	mg Mo g ⁻¹ resin ⁻¹	% Retention	mg Mo g ⁻¹ resin ⁻¹
2	96.7	4.503	84.6	2.067
4	94.5	3.798	34.3	1.031
6	93.3	3.641	30.0	1.037
8	95.7	4.037	30.3	0.864
10	93.7	4.259	20.6	0.545
12	81.7	3.471	0.00	0.000

For the retention from 50 mg L⁻¹ of V(V) by P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins show a good performance. P(CIVBTA-*co*-VBNMDG) resin over 79% at pH between 4-10, with an optimal pH at 4 and 10 retaining 3.7 and 4.7 mg V g⁻¹ resin⁻¹ (83 and 89%), respectively. Amberlite IRA-743 shows a great retention of V(V) in a range of pH 2-10 with an optimal pH of 8, retaining 4.3 mg V g⁻¹ resin⁻¹ (93%). According to that, it was decided to work at pH 4 for V(V) removal, at this pH it is found the specie V₂O₇⁴⁻.

In general, P(CIVBTA-*co*-VBNMDG) resin retain higher amount of Mo(VI) than the commercial resin Amberlite IRA-743, at the optimal pH. For V(V) both retain similar percentage.

Table 5. Retention from 50 mg L⁻¹ of V(V) in function of pH by P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins.

pH	P(CIVBTA- <i>co</i> -VBNMDG)		IRA-743	
	% Retention	mg V g ⁻¹ resin ⁻¹	% Retention	mg V g ⁻¹ resin ⁻¹
2	0.00	0.000	90.0	4.083
4	82.7	3.710	91.5	4.300
6	79.8	3.365	91.2	4.063
8	84.2	3.675	93.1	4.387
10	88.6	4.781	44.4	2.417
12	61.0	3.609	62.4	3.683

Effect of contact time on the removal

In tables 6 and 7 are shown the of retention (%) and (mg) of Mo(VI) and V(V) per g of resin at pH 2 and 4, respectively, by P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins. P(CIVBTA-*co*-VBNMDG) resin reached the equilibrium at around 30 min for both metal ions, with high retentions, 92% and 93% for Mo(VI) and V(V) respectively. On the other hand, Amberlite IRA-743 resin after 120 min couldn't reach the equilibrium with low retention, 25% and 30% for Mo(VI) and V(V), respectively.

Table 6. Removal of Mo(VI) in function of time by P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins at pH 2.

Time (min)	P(CIVBTA- <i>co</i> -VBNMDG)		IRA-743	
	Retention (%)	mg Mo g ⁻¹ resin ⁻¹	Retention (%)	mg Mo g ⁻¹ resin ⁻¹
15	74.1	1.45	4.70	0.08
30	91.8	2.40	11.5	0.30
60	92.1	2.52	9.60	0.25
120	79.6	2.17	24.9	0.63

Table 7. Removal of V(V) in function of time by P(CIVBTA-*co*-VBNMDG) and Amberlite IRA-743 resins at pH 4.

Time (min)	P(CIVBTA- <i>co</i> -VBNMDG)		IRA-743	
	Retention (%)	mg V g ⁻¹ resin ⁻¹	Retention (%)	mg V g ⁻¹ resin ⁻¹
15	62.4	2.74	0.00	0.00
30	92.7	4.18	26.0	1.09
60	87.7	4.01	14.4	0.59
120	89.9	4.16	30.5	1.39

Maximum retention capacity

In table 8 is shown the maximum retention capacity values obtained by successive enrichment of the P(CIVBTA-*co*-VBNMDG) resin at pH 2 and 4, for Mo(VI) and V(V), respectively.

Table 8. Maximum retention capacity of P(CIVBTA-*co*-VBNMDG) resin with Mo(VI) and V(V) ions.

Metal ion	Cycle (Number)	Retained mass (mg)	Mass resin (g)	Mass ret. (mg/g resin)	Retention (%)	Total mass ret.(mg)	Total mass ret.(mg/g resin)
Mo(VI)	1	8.87		17.92	99.5	8.87	17.92
	2	8.88	0.495	17.94	99.6	17.75	35.87
	3	8.90		17.99	99.9	26.66	53.86
	4	8.61		17.40	96.6	35.28	71.27
V(V)	1	9.35		18.29	98.9	9.35	18.29
	2	9.41	0.511	18.42	99.7	18.77	36.71
	3	9.42		18.42	99.7	28.19	55.13
	4	9.42		18.42	99.7	37.61	73.55

*It was used 500 mg of resin with an aliquot of 10 mL of metal ion 1000 mg L⁻¹ of concentration, stirring at 140 rpm, during 1h at 25°C.

Table 8 shows that P(CIVBTA-co-VBNMDG) resin has great retention capacity, retaining up to $71.27 \text{ mg g}^{-1} \text{ resin}^{-1}$ (96.9%) and $73.55 \text{ mg g}^{-1} \text{ resin}^{-1}$ (99.7%), for Mo(VI) and V(V) metal ions, respectively, and do not saturate after 4 consecutive charge cycles. P(CIVBTA-co-VBNMDG) resin could continue being charged with metal ion solution at the optimal pH and contact time. These results suggest that this resin could be used in continuous process as column method.

Elution

In order to recover and reuse the resin, the loaded resin was treated with different acids at two concentrations. Table 9 shows the elution with different acids for P(CIVBTA-co-VBNMDG) resin in contact with Mo(VI) and V(V).

Table 9. Elution of P(CIVBTA-co-VBNMDG) resin with different acids for Mo(VI) and V(V) ions.

Resin	Metal ion	Elution (%)			
		1M HCl	4M HCl	1M HNO ₃	4M HNO ₃
P(CIVBTA-co-VBNMDG)	Mo(VI)	20.2	37.7	22.3	64.8
	V(V)	23.2	40.6	98.0	98.4

According with these results, the best eluent for both metal ions was 4 M HNO₃ solution, removing 65 % of Mo(VI) and 98% of V(V) metal ions.

Regeneration

This study was performed with a solution 1000 mg L^{-1} of metal ion at the optimal pH, 2 and 4 for Mo(VI) and V(V) respectively. It was carried on 3 consecutive cycles of charge-discharge. For the discharge was used the optimal acid for elution, 4 M HNO₃ solution. In table 10 is shown the regeneration for P(CIVBTA-co-VBNMDG) resin. For molybdenum in the first cycle 99.6% was retained, and discharged 64.5%. In the second cycle kept the retention, 99.6%, but start to decrease the regeneration capacity, 52%. In the third cycle the retention decreases to 90.2%, and discharged only 49.4%.

For vanadium it is possible observe that the regeneration is less efficient in comparison with molybdenum. In the first cycle retain 99.7% and discharge 98.4%, in the second cycle this values decrease to 62.6% of charge and 89.7% of discharge. Finally, in the third cycle decreases strongly up to 51.2% of retention and 68.5% of discharge.

The decrease of the regeneration in consecutive cycles could be because not all of the metal ions were removed in earlier cycles, and some amount of metal ions remained trapped inside the pores of the resin.

Table 10. Regeneration of P(CIVBTA-co-VBNMDG) resin with Mo(VI) and V(V) ions at pH 2 and 4 respectively using 4 M HNO₃.

Metal Ion	C ₁		D ₁	C ₂		D ₂	C ₃		D ₃
	mg/g resin	%R	%R	mg/g resin	%R	%R	mg/g resin	%R	%R
Mo(VI)	71.3	99.6	64.8	299.2	99.6	52.0	391.9	90.2	49.4
V(V)	73.6	99.7	98.4	133.1	62.6	89.7	121.8	51.2	68.5

Selectivity

Table 11 shows the selectivity in binary mixtures of Mo(VI)-V(V) ions at pH 2 and 4 for P(CIVBTA-co-VBNMDG) resin. Mo(VI) removal metal ions is higher than that V(V), P(CIVBTA-co-VBNMDG) resin is more selective for Mo(VI) ions in a binary mixture of Mo(VI)-V(V) at pH 2 and 4, which is corroborated by the coefficient of affinity $K_{\text{Mo/V}}$ showing higher affinity for Mo(VI) ions, because the value is above 1. Studies of affinity/ions with N-methyl-D-glucamine group and were performed previously by Alexandratos and col.³⁶

Table 11. Selectivity in binary mix of Mo(VI) -V(V) at pH 2 and 4.

Metal Ion	pH	Mass Retained (mg)	Mass ret. (mg/g resin)	% Retention	$K_{\text{Mo/V}}$
Mo(VI)	2	0.329	8.31	83.7	3.76
V(V)	2	0.088	2.21	25.4	
Mo(VI)	4	0.420	10.36	88.5	3.19
V(V)	4	0.132	3.25	55.2	

Isotherm Studies

Adsorption isotherms give important information about the adsorption process and the interaction between the resins (adsorbent) with the metal ions (adsorbate). It was studied the equilibrium of P(CIVBTA-co-VBNMDG) resin with Mo(VI) and V(V) metal ions and compared with the commercial resin Amberlite IRA-743.

In figure 6 we can observe the adsorption profiles of P(CIVBTA-co-VBNMDG) and Amberlite IRA-743 resins with Mo(VI) at pH 10 at 25°C. P(CIVBTA-co-VBNMDG) resin have higher retention capacity of Mo(VI) (193.0 mg Mo(VI)/g resin) than the commercial resin Amberlite IRA-743 resin (114.8 mg Mo(VI)/g resin) at pH 10. Both resins do not reach the equilibrium and are able to retain higher concentration of Mo(VI) metal ion solution at pH 10 and 25°C.

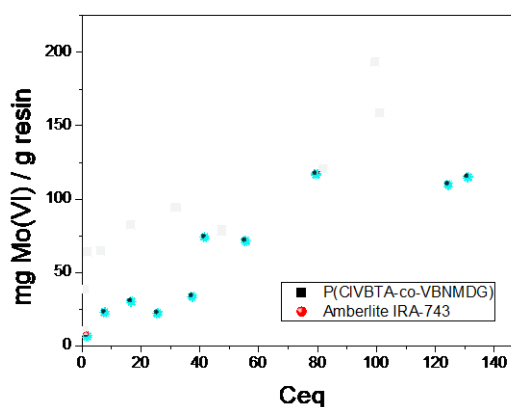


Figure 6. Adsorption isotherm for P(CIVBTA-co-VBNMDG) (black square) and Amberlite IRA-743 (red circle) resins with Mo(VI) at pH 10 and 25°C.

The figure 7 shows the adsorption isotherms of P(CIVBTA-co-VBNMDG) and Amberlite IRA-743 resins at constant temperature (25°C). It is observed that a gradually increase of the concentration of V(V) exist a higher removal at higher concentrations of vanadium at pH 4 and pH 10. At lower concentration there is not a big difference between pH 4 or pH 10.

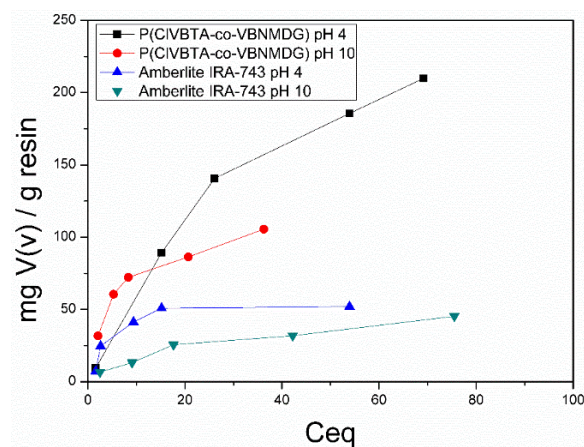


Figure 7. Adsorption isotherm for P(CIVBTA-co-VBNMDG) and Amberlite IRA-743 resins with V(V) at pH 4 and 10 at 25°C.

The isotherms constants are summarized in table 12. Shows a better correlation for Langmuir than Freundlich for Mo(VI) and V(V) ions for P(CIVBTA-co-VBNMDG) resin at pH 10, meanwhile for V(V) at pH 4 follows better Freundlich isotherm. Similar result was found by Dambies and coll. for isotherms of N-methyl-D-glucamine group and As(V) ions.³⁷ In contrast Amberlite IRA-743 commercial resin follows an opposite trend, adjust better a Freundlich isotherm for Mo(VI) and V(V) at pH 10, and to Langmuir for V(V) at pH 4. These results suggest that exists formation of monolayer. The constant has a direct relation with the affinity between resin/metal ion and the maximum retention capacity. P(CIVBTA-co-VBNMDG) resin shown better and higher retentions in comparison with Amberlite IRA-743 commercial resin, with a maximum capacity of retention (125.0 mg Mo/g resin and 384.6 mg V/g resin), suggesting a high affinity resin/metal ion under the experimental conditions at pH 10 for Mo(VI) and V(V), respectively, at 25°C.

Table 12. Langmuir and Freundlich isotherms constants for Mo(VI) at pH 10 and V(V) ions at pH 4 and 10, at 25°C.

Resin	Metal ion	Langmuir			Freundlich		
		qm (mg Mo/g resin)	b (L/mg)	R ²	n	Kr (mg Mo/g resin)	R ²
P(CIVBTA-co-VBNMDG)	Mo(VI), pH 10	125.0	0.183	0.9881	2.62	27.56	0.7251
	V(V), pH 4	384.6	0.018	0.9375	1.19	7.289	0.9743
	V(V), pH 10	169.5	0.073	0.9844	2.76	29.15	0.9496
IRA-743	Mo(VI), pH 10	15.15	0.196	0.9452	1.38	4.380	0.9828
	V(V), pH 4	54.30	0.220	0.9853	2.39	11.35	0.6878
	V(V), pH 10	57.80	0.039	0.9519	1.77	4.089	0.9757

CONCLUSIONS

It was successful synthesized P(CIVBTA-co-VBNMDG) resin with ammonium quaternary groups available for adsorption of anions. P(CIVBTA-co-VBNMDG) resin is a good ion exchange resin for Mo(VI) and V(V) anions at pH 2 and 10, respectively by batch method. P(CIVBTA-co-VBNMDG) resin removed these metal ions fast (before than 1h) by Batch method, and even more efficient than the commercial resin Amberlite IRA-743 with the same functional groups. It is possible regenerate the P(CIVBTA-co-VBNMDG) resin using HNO₃ 4M for both metal ions. P(CIVBTA-co-VBNMDG) resin could be used in a continuous system by Column Method.

Adsorption isotherms demonstrated the adsorption is by monolayer, and P(CIVBTA-co-VBNMDG) resin follows the Langmuir Model for Mo(VI) and V(V) ions meanwhile Amberlite IRA-743 resin follows Freundlich model at pH 10.

ACKNOWLEDGEMENTS

The authors thank to FONDECYT (Grant No 1190469). D.V. Morales thank to Fondecyt Postdoctorate (Grant No 3200467).

REFERENCES

- A. K. Jain, V. K. Gupta, A. Bhatnagar and Suhas, *J. Hazard. Mater.*, 2003, **101**, 31–42.
- E. Nagy, *desalination*, 2009, **240**, 2–6.
- N. Sarwar, Saifullah, S. S. Malhi, M. H. Zia, A. Naeem, S. Bibia and G. Farida, *J. Sci. Food Agric.*, 2010, **90**, 925–937.
- N. Sarwar, W. Ishaq, G. Farid, M. Rashid, M. Imran, M. Geng and S. Hussain, *Ecotoxicol. Environ. Saf.*, 2015, **122**, 528–536.
- D. E. Rusyniak, A. Arroyo, J. Acciani, B. Froberg, L. Kao and B. Furbee, 1 D. E. Rusyniak, A. Arroyo, J. Acciani, B. Froberg, L. Kao and B. Furbee, *Mol. Clin. Environ. Toxicol.*, 2010, **2**, 365–396.
- B. Barkhordar and M. Ghiasseddin, *Iran. J. Heal. Sci. Eng.*, 2004, **1**, 58–64.
- F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.
- J. Li, Z. Zhao, C. Cao, G. Zhang and G. Huo, *RMHM*, 2012, **30**, 180–184.
- Z. Zhao, C. Cao, X. Chen and G. Huo, *Hydrometallurgy*, 2011, **108**, 229–232.
- K. Park, H. Kim and P. K. Parhi, *Sep. Purif. Technol.*, 2010, **74**, 294–299.
- L. Zeng and C. Yong, *Hydrometallurgy*, 2010, **101**, 141–147.
- E. K. Alamdari, D. Darvishi, D. F. Haghshenas, N. Yousefi and S. K. Sadrnezhad, *Sep. Purif. Technol.*, 2012, **86**, 143–148.
- D. M. Imam, *Hydrometallurgy*, 2018, **180**, 172–179.

- Z. Zhu, K. Tulpatowicz, Y. Pranolo and C. Yong, *Hydrometallurgy*, 2015, **154**, 72–77.
- F. Pagnanelli, F. Ferella, I. De Michelis and F. Vegliò, *Hydrometallurgy*, 2011, **110**, 67–72.
- K. Ho, D. Mohapatra and B. R. Reddy, *J. Hazard. Mater.*, 2006, **138**, 311–316.
- S. Y. Seo, W. S. Choi, T. J. Yang, M. J. Kim and T. Tran, *Hydrometallurgy*, 2012, **129–130**, 145–150.
- A. A. Basualto, Carlos, Jose Marchese, Fernando Valenzuela, *Talanta*, 2003, **59**, 999–1007.
- B. L. Rivas, E. Pereira, *Bol. Soc. Chil. Quím.* 20020, **45**, 165–171.
- Y. Fu, Q. Xiao, Y. Gao, P. Ning, H. Xu and Y. Zhang, *Trans. Nonferrous Met. Soc. China*, 2018, **28**, 1660–1669.
- P. Orrego, J. Hernández and A. Reyes, *Hydrometallurgy*, 2019, **184**, 116–122.
- B. L. Rivas, I. Moreno-Villoslada, *J. Phys. Chem.* 1998, **B 102**, 11024–11028.
- T. H. Nguyen and M. S. Lee, *Hydrometallurgy*, 2013, **136**, 65–70.
- B. L. Rivas, S. Amalia Pooley, G. Canessa, *Polym. Bull.* 1983, **9**, 417–422.
- B. L. Rivas, H. A. Maturana and E. Pereira, *Die Angew. Makromol. Chemie*, 1994, **220**, 61–74.
- D. C. Crans, J. J. Smee, E. Gaidamauskas and L. Yang, *Chem. Rev.* **104**, 849–902
- B. Zhang, C. Tian, Y. Liu, L. Hao, Y. Liu, C. Feng, Y. Liu and Z. Wang, *Bioresour. Technol.*, 2015, **179**, 91–97.
- R. R. Moskalyk and A. M. Alfantazi, *Miner. Eng.*, 2003, **16**, 793–805.
- H. Peng, *J. Environ. Chem. Eng.*, 2019, **7**, 103–313.
- J. J. Cruywagen, *Adv. Inorg. Chem.* 2000, **49**, 127–182
- M. Imtiaz, M. Shahid, S. Xiong, H. Li, M. Ashraf, S. Muhammad, M. Shahzad, M. Rizwan and S. Tu, *Environ. Int.*, 2015, **80**, 79–88.
- A. S. Tracey, G. R. Willsky and E. S. Takeuchi, *Vanadium: Chemistry, Biochemistry, Pharmacological, and Practical Applications*, CRC Press, 1 st ed., 2007, pp 1–2
- J. Rinklebe, V. Antoniadis, S. M. Shaheen, O. Rosche and M. Altermann, *Environ. Int.*, 2019, **126**, 76–88.
- Urbano, B. F. Resinas Nanocompósitos y Su Potencial Aplicación En Procesos de Intercambio Iónico, Universidad de Concepción, 2012.
- Misak, N. Z. Adsorption Isotherms in Ion Exchange Reactions. Further Treatments and Remarks on the Application of the Langmuir Isotherm. *Colloids Surfaces A Physicochem. Eng. Asp.* 1995, **97** (2), 129–140.
- Alexandratos, S. D. New Polymer-Supported Ion-Complexing Agents: Design, Preparation and Metal Ion Affinities of Immobilized Ligands. *J. Hazard. Mater.* 2007, **139** (3), 467–470.
- Dambies, L.; Salinaro, R.; Alexandratos, S. D. Immobilized N-Methyl-D-Glucamine as an Arsenate-Selective Resin. *Environ. Sci. Technol.* 2004, **38** (22), 6139–6146.