



Cr(VI) sorption behavior from aqueous solutions onto polymeric microcapsules containing a long-chain quaternary ammonium salt: Kinetics and thermodynamics analysis

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ABSTRACT

This work studies the adsorption of Cr(VI) ions from an aqueous acid solution on hydrophobic polymeric microcapsules containing a long-chain quaternary ammonium salt-type extractant immobilized in their pore structure. The microcapsules were synthesized by adding the extractant Aliquat 336 during the *in situ* radical copolymerization of the monomers styrene (ST) and ethylene glycol dimethacrylate (EGDMA). The microcapsules, which had a spherical shape with a rough surface, behaved as efficient adsorbents for Cr(VI) at the tested temperatures. The results of kinetics experiments carried out at different temperatures showed that the adsorption process fits well to a pseudo-second-order with an activation energy of 82.7 kJ mol^{-1} , confirming that the sorption process is controlled by a chemisorption mechanism. Langmuir's isotherms were found to represent well the experimentally observed sorption data. Thermodynamic parameters, namely, changes in standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), are also calculated. The results indicate that the chemisorption process is spontaneous and exothermic. The entropy change value measured in this study shows that metal adsorbed on microcapsules leads to a less chaotic system than a liquid–liquid extraction system.

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1. Introduction

Chromium is a widely used metal in many industrial applications such as alloying, plating, producing chromium-containing stainless steels, leather tanning, textiles and dyeing, producing pigments, and ceramic manufacturing. From a chemical standpoint, it is a very reactive metal with several oxidation states. However, in most industrial applications, it is present as Cr(VI), a highly toxic ion, exposure to which produces many effects on the biota, including human beings, such as ulcers and dermatitis, effects on the skin, and mutagenic and carcinogenic effects [1]. Therefore, it is compulsory to control the discharge of chromium compounds into aquatic systems in order to prevent severe environmental problems. In fact, Cr(VI)-containing residual industrial waters have to be treated prior to their discharge into fluvial water bodies to decrease their content to below 50 ppb according to Chilean regulations [2].

A number of heavy metals, including chromium, are amphoteric and exhibit a point of minimum solubility. One of the most common and effective methods to remove such metals from wastewaters is

precipitation as hydroxides by addition of lime or caustic to adjust the pH-environment to one of minimum solubility. Cr(VI) has its lowest solubility at pH 7.5 and shows significantly increased concentration in solution above and below this pH-value, making its removal by precipitation very complex and impractical, since the precipitates tend to redissolve. Furthermore, this process requires pretreatment of the wastewaters to remove substances that can interfere with precipitation of the metal. In the particular case of Cr(VI) ions, they must previously be reduced to Cr(III) for treatment with lime. The sludge generated in the process is difficult to handle, which is also a concern.

Other available conventional extraction technologies for heavy metals are the use of ionic exchange solid resins (IX) [3], solvent extraction with liquid extractants (SX) [4,5], solid-supported liquid membranes [6], surfactant liquid membranes [7,8], and biological methods [9]. However, most of them present limitations that prevent their use in many cases. The challenge is finding more efficient and technically and economically feasible alternatives.

The use of natural and synthetic adsorbents is becoming one of the most practical alternatives to uptake pollutants from water, especially in large-scale uses, due to their efficiency and simplicity. Among them, many studies have used biopolymers (i.e., chitosan) [10], active carbon [11], zeolites [12], and graft copolymers [13].

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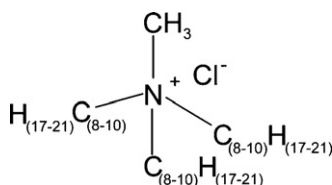


Fig. 1. Structure of the quaternary ammonium salt used as the extractant.

In recent years, the use of polymeric microcapsules (MC) synthesized by an *in situ* radical polymerization method has attracted the attention of some researchers with the aim of applying them to the removal and recovery of heavy metals from aqueous solutions [14–18]. Microcapsules correspond to a porous polymeric matrix that contains an immobilized suitable extractant compound, which is chosen to selectively extract the desired metals. Thus, MCs behave as granular adsorbents appropriate to treat dilute solutions with a high extraction capacity, which can be reused many times after a simple and cheap metal-stripping (back-extraction) process.

Applications of MCs have been studied in many fields, but their potential use in hydrometallurgy is remarkable. Among other advantages, the extractants to be encapsulated are the same commercial compounds widely used in industrial solvent extraction plants, MCs have a large interfacial area compared to other separation systems, and they undergo very simple separation of metal-loaded microspheres from the treated solution by current filtration or sedimentation.

In a previous paper, we reported on the removal of Cd(II) and Cu(II) ions from aqueous solutions by sorption onto microcapsules prepared by copolymerizing styrene (ST) and ethylene glycol dimethacrylate (EGDMA). An acid compound was used as the extractant, reaching a high production of MCs with a suitable hydrophobic character and high effectiveness as adsorbents. The experimental data of chemisorption of metals onto the microcapsules fitted well to an applied pseudo-second-order kinetics model [19].

In this communication, we report the removal of Cr(VI) from acidic aqueous solutions using microcapsules with the same polymeric matrix of ST-EGDMA, but containing a long-chain quaternary ammonium salt as the extractant. The synthesis and characterization of MCs were studied, as well as their behavior in metallurgical sorption tests. Kinetics and thermodynamics information derived from these experimental results is also analyzed and discussed. It is fundamental to know this information to understand the basic principles that govern the sorption process and for scaling it up to a practical system based on continuous columns packed with microcapsules.

2. Experimental procedure

2.1. Reagents and solutions

Aliquat 336, a commercial quaternary ammonium salt, $[\text{C}_{8-10}\text{H}_{17-21}]_3\text{-CH}_3\text{N}^+\text{Cl}^-$, widely used in SX plants, supplied by Cognis-Chile, was used without further purification. Its structure is shown in Fig. 1. This compound, a basic extractant that acts by anion exchange, has a purity of 90% and a mean molecular weight of 435.5 g mol^{-1} . Styrene (C_8H_8 , molecular weight 104.15) and ethylene glycol dimethacrylate ($\text{C}_{10}\text{H}_{14}\text{O}_4$, molecular weight 198.2) (Aldrich) were used as monomers to prepare the microcapsules; their structures have been shown previously [19]. Their purity was higher than 98% and they were used as received. Reagent-grade benzoyl peroxide was used as a polymerization initiator. All other chemicals, including gum arabic and toluene as the solvent for the organic compounds, were of reagent grade.

Stock solutions of Cr(VI) were prepared by dissolving sodium chromate (Merck r.g.) in distilled water. Experimental runs for kinetics were carried out using a 100 mg L^{-1} Cr(VI) feed solution. For equilibrium experiments feed solutions were prepared with metal content varying between 5 and 450 mg L^{-1} . The initial pH of all these aqueous phases was adjusted around a value of 2.0 with a sulfuric acid solution and measured with a pH meter.

2.2. Synthesis and characterization of microcapsules

The synthesis of P(S-co-EGDMA) microcapsules was carried out by *in situ* polymerization in a three-necked round bottom flask equipped with a condenser, a thermometer, N_2 flux, and a stirring system. A solution of 5.4 g of gum arabic and 450 mL of distilled water was heated to 343 K. Once the temperature was stabilized, the organic phase, consisting of 1 g styrene, 7 g ethylene glycol dimethacrylate (EGDMA), 14.5 g of toluene, 6 g of the extractant Aliquat 336, and 2 g of benzoyl peroxide, was added. The polymerization was kept for 3 h at 343 K, with a stirring speed of 500 min^{-1} . The resulting microcapsules were filtered and washed repeatedly with distilled water and left to dry overnight at room temperature.

The amount of extractant retained within the microcapsules was measured by an argentometric method. The microcapsules containing the quaternary ammonium salt-type extractant were observed by scanning electron microscopy (SEM) in a JEOL JSM-25SII apparatus following a typical procedure. The pore diameter, the void fraction, and the surface area were determined by BET porosimetry with a Micromeritics ASAP 2010 porosimeter. Mean particle size was measured using Malvern Mastersizer Hydro 2000 MU equipment.

2.3. Kinetics and equilibrium adsorption experiments

Batch adsorption tests were carried out with the purpose of examining the equilibrium and kinetics behavior of MCs during the extraction of metal from aqueous feed solutions. Microcapsules (0.2 g) containing the extractant and 25 cm^3 of aqueous solution containing chromium ions were contacted in a Polyscience orbital-shaker apparatus. The feed solutions at pH 2.0 containing various metal concentrations according to the experimental design were previously preheated to the desired temperature (303–323 K). The equilibrium sorption runs were carried out over 60 min, long enough for equilibrium to be reached. The kinetics experiments were done by measuring the change of the metal content in the feed solution from 1 to 60 min. In all of the experiments, once the time had elapsed, the suspension was filtered, and the concentration of chromium at equilibrium in the resulting solution was measured by atomic absorption spectrophotometry on a PerkinElmer 3110 apparatus at a wavelength of 357.9 nm. The amount of metal adsorbed onto the microspheres was calculated from the mass balance between the initial and equilibrium metal concentrations in the aqueous solutions.

3. Results and discussion

3.1. Synthesis and characterization of microcapsules

The synthesis of the microcapsules was simple and fairly efficient, with an average yield of 89.7%. The amount of Aliquat 336 retained in the microspheres was 0.82 mmol of extractant per gram of microcapsule, confirming that most of the extractant used in the preparation of the microcapsules was immobilized within and on the surface of the microspheres. Fig. 2 shows SEM micrographs of the synthesized microcapsules. Fig. 2(a) is an image of an entire microcapsule, and Fig. 2(b) shows the detail of its surface structure. The MCs are spherical with a rough surface. The physical properties

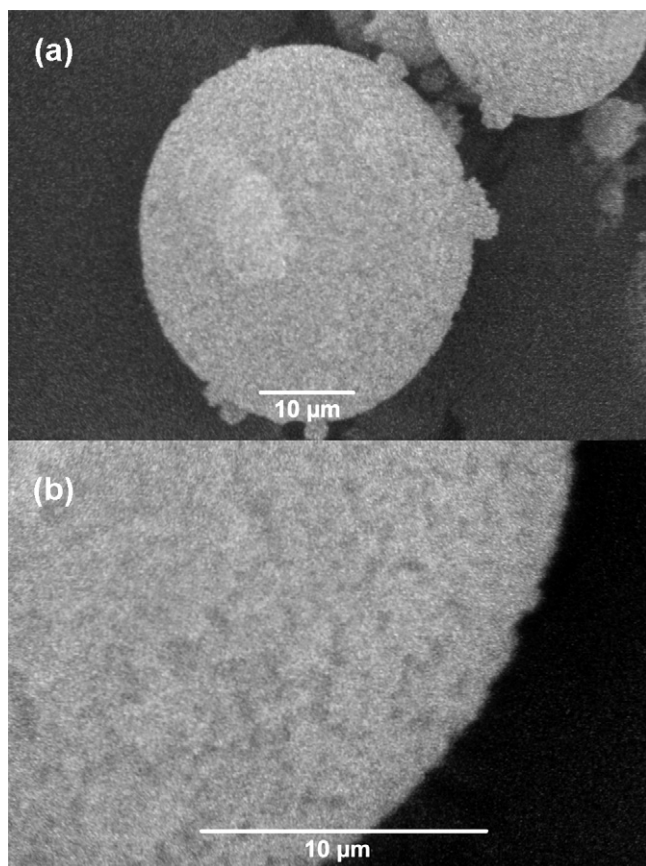


Fig. 2. SEM micrographs of microcapsules: (a) image of the entire microcapsule and (b) surface structure.

Table 1
Physical properties of synthesized microcapsules.

S_{BET} [m^2/g]	18
Pore diameter [nm]	7.2
Pore volume [cm^3/g]	0.0327
Mean particle size [μm]	20

of the microspheres obtained, namely, their surface area, diameter, pore volume, and pore size, are shown in Table 1. The microcapsules had a suitable hydrophobicity, which allowed them to keep the organic extractant in their structure without leakage during the process.

3.2. Adsorption kinetics

As is well known, a number of adsorption kinetics models have been proposed to explain the experimental results obtained in several studies concerned with the sorption of metals and other adsorbates onto distinct synthetic or natural adsorbents [20–22]. It is important to know the rate at which adsorption is favored, especially for designing a practical industrial sorption system. In particular, when a metal is extracted from aqueous solution by an adsorption process, the overall mechanism includes (a) the diffusion step of metallic ions through the aqueous film close to the surface of the adsorbent, (b) the eventual chemical reaction between the metal and the adsorbent in a mechanism called chemisorption, and (c) the intraparticle diffusion of the metal-extractant species inside the microcapsule [23]. In the synthesis of the microcapsules, during the copolymerization of the monomers with the extractant, the solvent is completely evaporated, leaving

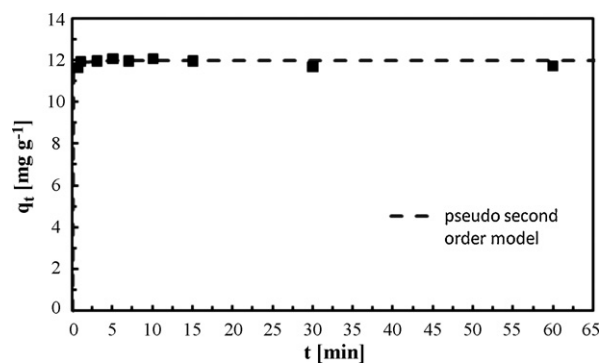
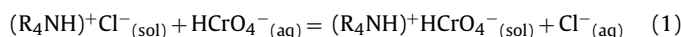


Fig. 3. Cr(VI) adsorption with Aliquat 336 onto microcapsules according to the pseudo-second-order kinetics model.

the practically pure extractant in the microcapsule. Therefore, the concentration of the extractant on the surface and in the pores of the microsphere is high, enabling it to assume pseudo-second-order kinetics, allowing the evaluation of the rate of the chemisorption process by means of the Ho equation [24].

On the surface of the microcapsule loaded with Aliquat 336, the basic extractant $(\text{R}_4\text{N})\text{Cl}$ would react with the anionic chromium species, HCrO_4^- , which is predominant at the pH-value at which these experiments were carried out [25]. The following anion-exchange reaction depicts the extraction process:



where the subscripts (sol) and (aq) denote the solid surface of the microcapsules and the aqueous solution, respectively. The pseudo-second-order kinetics sorption model is based more on the solid's capacity for adsorbing the adsorbents than on the sorbate's concentration in the aqueous solution that contains it. Ho's model, which describes the square of the disappearance of available adsorption sites as a function of time, is expressed as follows:

$$\frac{dq_t}{dt} = -k(q_e - q_t)^2 \quad (2)$$

Integrating and reordering Eq. (2) to its linear form gives the following expression:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (3)$$

where t is the time in minutes, q_t is the amount adsorbed at any time t in mg of metal per gram of microcapsule, q_e is the amount adsorbed at equilibrium in mg g^{-1} , k is the rate constant of Ho's pseudo-second-order model in $\text{g mg}^{-1} \text{min}^{-1}$, and kq_e^2 in $\text{mg g}^{-1} \text{min}^{-1}$ depicts the initial adsorption rate when t tends to 0. Both previous equations indicate that adsorption of metal onto the microcapsule varies with time.

Fig. 3 shows the experimental results of Cr(VI) extraction with the quaternary ammonium salt at 303 K according to the variables of this pseudo-second-order kinetics model.

A high extraction rate is seen for Cr(VI) as acid chromate, the anionic species predominant in aqueous solutions used in these experiments. This result would indicate the existence at the liquid–solid interface of a significant number of available adsorption sites for the chemical reaction between the metal and the extractant retained in the porous structure of the microcapsules. Furthermore, Table 2 lists the values of q_e , k , and kq_e^2 from experiments carried out at 303, 313, and 323 K. These values were obtained by plotting the experimental results according to Eq. (3), and then linearly fitting the data.

At all of the studied temperatures, the microcapsules reached the adsorption equilibrium in less than 5 min. The table shows that the rate constant decreases as the temperature increases. A high

Table 2

Parameters of the kinetics model applied to Cr(VI) adsorption with Aliquat 336 immobilized in P(S-co-EGDMA) microcapsules.

T [K]	q_e [mg g ⁻¹]	k [g mg ⁻¹ min ⁻¹]	kq_e^2 [mg g ⁻¹ min ⁻¹]	r^2
303	11.98	11.62	1667	1
313	12.20	3.74	556	1
323	12.11	1.36	200	1

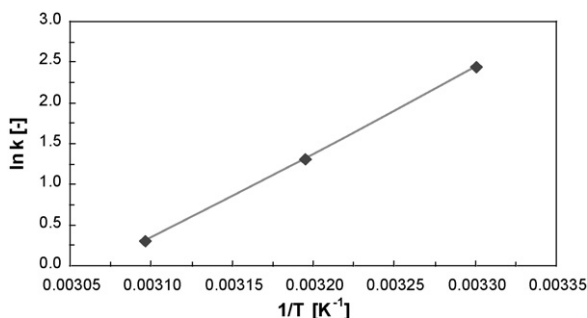


Fig. 4. Plot of $\ln k$ versus $1/T$.

initial adsorption rate kq_e^2 was observed for all tested temperatures, reaching a chromium removal of 1.667 g of Cr(VI) g⁻¹ min⁻¹ at 303 K; i.e., the mass of metal adsorbed per minute was almost twice the mass of porous microcapsules. This high initial adsorption explains why the microcapsules are able to reach the adsorption equilibrium in 1 min, which is mainly due to the small particle size of the microcapsules and to the nature of the adsorption process, which is indeed a liquid–liquid ion-exchange extraction on the surface of microspheres when the liquid organic extractant within the pore and the aqueous metal-containing solution are placed in contact. It is well known that liquid–liquid reactions are much faster than liquid–solid reactions. This aspect would constitute one of the advantages of the use of microcapsules with conventional liquid extractants retained inside: they behave as granular adsorbents, bringing together the properties of the IX solid resins, which are suitable for treating dilute solutions, and the properties of liquid extractants of SX processing, which have a high extraction capacity.

As usual, the activation energy of the sorption process is obtained from the Arrhenius equation [26] as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

where k is the rate constant obtained by applying the pseudo-second-order kinetics model of Ho expressed in g mg⁻¹ min⁻¹, T is the temperature in K, R is the gas constant 8.314 J mol⁻¹ K⁻¹, A is the temperature independent frequency factor in g mg⁻¹ min⁻¹, and E_a is the activation energy of the process. Fig. 4 shows a plot of the experimentally observed results in the temperature range from 303 to 323 K according to Eq. (4). The figure shows that the Arrhenius plot gives a fairly good correlation for the plotted data ($r^2 = 0.998$). Normally, physical adsorption activation energies are in the range of 5–40 kJ mol⁻¹, while chemical adsorption varies between 40 and 800 kJ mol⁻¹ [27]. From the slope and the intercept of the plot of Fig. 4, an activation energy of 82.7 kJ mol⁻¹ was obtained, which is in the range of chemical reaction, confirming the important role played by the chemical reaction between the metal and the extractant on the microcapsule.

3.3. Adsorption equilibrium

To obtain information on the adsorption equilibrium as well as on the sorption capacity and equilibrium constants of the process, the experimental data were modeled using the Langmuir and

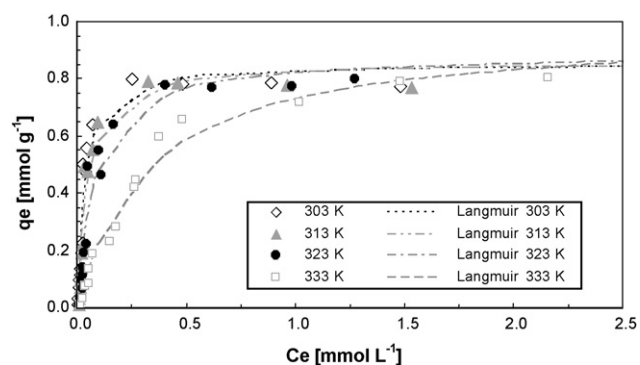


Fig. 5. Langmuir isotherms for Cr(VI) sorption onto microcapsules at different temperatures.

Freundlich isotherms, which enable the analysis of the relative affinity of the adsorbent for the adsorbate and allow the correlation of the experimental results with the surface properties of the microcapsules. Langmuir and Freundlich isotherm data are normally analyzed as linear models; however, this may cause errors in the determination of the values of the constants. Thus, it is more appropriate to iterate the experimental data in order to get the least error [28], the known statistical value χ^2 , which can be expressed as follows:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (5)$$

In this expression, q_e is the experimental adsorbed amount, and $q_{e,m}$ denotes the adsorbed amount given by the sorption model. Using the experimental data, a Lavenberg–Marquadt iteration routine was used to obtain the least error values.

Langmuir's model represents a monolayer-type adsorption over a homogeneous surface, meaning that all available sites have the same shape and heat of adsorption. The model also makes the assumption that there are no lateral interactions between adsorbed molecules and between adsorbed and non-adsorbed ones. Langmuir's isotherm is expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_e denotes the amount in mmol g⁻¹ adsorbed at equilibrium, q_m is the maximum charge capacity in mmol g⁻¹, K_L is Langmuir's constant in L mmol⁻¹, which relates the affinity of the adsorbent for the adsorbate, and C_e is the metal concentration in mmol L⁻¹ that remains in solution after the extraction.

On the other hand, Freundlich's isotherm is an empirical model that explains multilayer adsorption on heterogeneous surfaces, meaning that after all available sites are occupied, additional layers are formed. It takes into consideration that lateral interactions may be present between adsorbed molecules as well with non-adsorbed ones. Freundlich's isotherm is depicted by the following equation:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where q_e corresponds to the amount adsorbed at equilibrium in mmol g⁻¹, n is a constant related to the intensity of the adsorption, K_F is Freundlich's constant in L⁻ⁿ mmol⁻ⁿ, and C_e is the adsorbate concentration in the solution in mmol L⁻¹.

Table 3 presents the results of applying both adsorption models to the observed experimental values between 303 and 333 K. It is clear that Langmuir's model fits the experimental data better. Freundlich's model gave a low correlation of data, meaning that the chemisorption process would occur in a monolayer over a homogeneous surface. Fig. 5 represents how consistent the experimental data are with Langmuir's adsorption model. In general, all isotherms

Table 3
Adsorption equilibrium isotherm parameters.

T [K]	Model	q_m [mmol g ⁻¹]	K_L [L mmol ⁻¹], K_F [L ⁻ⁿ mmol ⁻ⁿ]	n	χ^2 [mmol g ⁻¹]	r^2
303	Langmuir	0.857	28.57	3.741	0.0073	0.9274
	Freundlich		0.86		0.0257	
313	Langmuir	0.863	21.12	3.347	0.0068	0.9317
	Freundlich		0.847		0.0254	
323	Langmuir	0.890	11.86	2.862	0.0062	0.9379
	Freundlich		0.86		0.0187	
333	Langmuir	0.966	3.12	2.340	0.0021	0.9765
	Freundlich		0.67		0.0092	

show a high initial slope that may be associated with a high affinity between the adsorbent and the adsorbate. In fact, in most of the experiments, a metal removal extent close to 99% was measured. The homogeneity of the surface may be understood by the fact that Cr(VI) extraction occurs only by its chemical reaction with Aliquat 336, since the polymer matrix by itself does not have adsorptive properties. In fact, some similar experiments were carried out with microcapsules synthesized without the extractant compounds, and they displayed no adsorption at all. The monolayer adsorption and the high initial slope may also be explained by taking into account that when an acid chromate molecule is extracted from the aqueous solution, this molecule diffuses into the polymer matrix, but a fresh Aliquat 336 molecule immediately appears at the entrance of the pore ready for extraction, repeating the process until all extractant molecules are consumed.

Table 3 shows important values for Langmuir's monolayer capacity compared to other current adsorbents. It is also seen in Fig. 5 that the maximum monolayer charge capacities tend to converge to a practically constant value for the entire studied temperature range, while a temperature increase causes a decrease of K_L values. Fig. 5 also shows that the initial slopes of the curves decrease as the temperature increases.

Comparing these microcapsules with commercial sorbent resins, the microspheres used in this study showed a maximum sorption capacity between 0.857 and 0.966 mmol g⁻¹ and a Langmuir constant between 3.12 and 28.57 L mmol⁻¹, all values reported in Table 3. Baran et al. in a study of different materials used for chromium VI extraction under relatively similar conditions to those of the present study, reported a maximum adsorption capacity value in a range of 1.717–2.434 mmol g⁻¹ and a Langmuir constant that varies between 0.129 and 0.223 L mmol⁻¹ for Purolite CT-275 and Purolite MN-500 ion-exchange resins, respectively [29]. Even though the microcapsules present a lower sorption capacity with respect to these commercial resins, the Langmuir constant shows that the equilibrium is much more displaced to the formation of product in the case of the microcapsules with respect to IX resins, resulting in a more stable product compared to the one formed between the adsorbate and the ion-exchange resin under these experimental conditions.

3.4. Thermodynamics analysis

In order to obtain thermodynamics parameters of the chromium adsorption process onto the microcapsules, the linear form of the Van't Hoff equation was used:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where K_L is Langmuir's constant in L mol⁻¹, R is the gas constant, 8.314 J mol⁻¹ K⁻¹, T is the temperature in K, ΔS^0 denotes the standard entropy change in J mol⁻¹ K⁻¹, and ΔH^0 is the standard enthalpy in J mol⁻¹. As is known, Eq. (8) is valid if the enthalpy

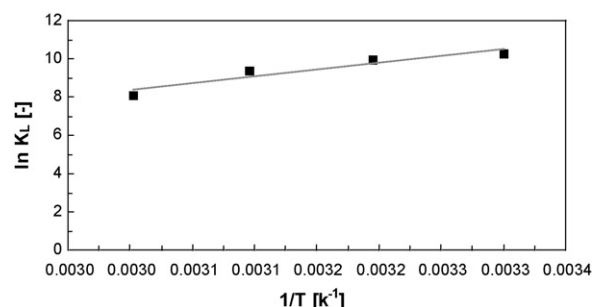


Fig. 6. Van't Hoff plot for the adsorption of Cr(VI) onto microcapsules loaded with Aliquat 336.

change (ΔH) is constant along the studied temperature range. In Fig. 6, plotting $\ln K_L$ as a function of $1/T$, the standard enthalpy can be obtained from the slope and the standard entropy from the intercept.

The figure shows the Van't Hoff plot, showing a good correlation of the plotted data ($r^2 = 0.88$). The entropy, enthalpy, and Gibbs free energy values are obtained from Eq. (8) and by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

Table 4 presents the results of these thermodynamic parameters in the studied temperature range. The obtained results show that the adsorption process of Cr(VI) onto P(S-co-EGDMA) microcapsules containing the quaternary ammonium salt extractant is exothermic ($\Delta H^0 = -60$ kJ mol⁻¹), which is consistent with the consideration that in these experiments, the chemical reaction between the extractant and the metal ion is the main adsorption process.

This high enthalpy change value also indicates that the adsorption of Cr(VI) occurs primarily on the surface of the porous microcapsules, with a lower importance of sorption inside the pores [30].

Table 4 also shows a negative value for the entropy change, indicating that the adsorbent does not undergo important changes in its structure during the chemisorption process, enabling the reuse of the same microcapsules in repetitive adsorption–desorption cycles, as has been tested. Although, in the table, a decrease in the spontaneity of the process is seen as the temperature increases from 303

Table 4
Thermodynamics parameters for Cr(VI) adsorption onto P(S-co-EGDMA) microcapsules loaded with Aliquat 336.

T [K]	ΔH^0 [kJ mol ⁻¹]	ΔS^0 [J mol ⁻¹ K ⁻¹]	ΔG^0 [kJ mol ⁻¹]
303	-60.0	-110	-26.7
313			-25.6
323			-24.5
333			-23.4

to 333 K, the chemisorption process is spontaneous at all studied temperatures. The high spontaneity of the reaction is in agreement with what was seen during the experiments, where an extremely fast extraction of chromium was observed. All thermodynamics values are comparable with those reported in the literature for the liquid–liquid extraction of chromium(VI) from aqueous solution with the same compound as extractant, for which the authors report a standard enthalpy of -40 kJ mol^{-1} , a standard entropy of -90 J mol^{-1} , and a Gibbs free energy value of $-12.35 \text{ kJ mol}^{-1}$ [31].

However, the lower entropy value observed in our study may be explained by the removal of an acid chromate ion from the solution, which is replaced by a chloride ion. The former is a much heavier and larger ion that has more degrees of freedom than the halide ion. Furthermore, the difference in the entropy values between those obtained in the liquid–liquid extraction of metal using Aliquat 336 in the organic phase and those observed in this work with the same extractant but immobilized onto the microcapsules can be attributed to the fact that the Cr(VI) ions bonded to the extractant on the microspheres present a more orderly system than in two dispersed liquid solutions, where the trend to disorder is obviously higher.

It is clear that the results presented here show the ability of these microcapsules to uptake heavy metals from dilute aqueous solutions. Exploratory experiments have also shown the stability of the extractant in the microcapsules, which kept their extractive properties even after several months of being synthesized and used in numerous sorption–desorption cycles.

4. Conclusions

The sorption behavior of Cr(VI) ions from acidic aqueous solutions onto microcapsules with Aliquat 336, a quaternary ammonium salt-type extractant immobilized in their porous structure, was studied. The following information was obtained:

It was found that most of the organic extractant added during the synthesis was incorporated into the structure of the microcapsules, which retained it due to their suitable hydrophobic character. The microcapsules prepared in this work were found to be efficient adsorbents for Cr(VI) ions from aqueous solutions, measuring a high initial adsorption rate of around $1.67 \text{ g metal g}^{-1} \text{ min}^{-1}$ and an average removal extent of about 99%.

Assuming a pseudo-second-order kinetics model, which usually fits well with the experimental results obtained in this sort of experiments, an activation energy of 82.7 kJ mol^{-1} was measured, a value that indicates the predominant role of the chemical reaction between the metal and the extractant on the surface of the microcapsules in the adsorption process.

The adsorption equilibrium results were fairly well explained at all temperatures by Langmuir's isotherm model, which means that the chemisorption process would occur in a monolayer over a homogeneous surface. The adsorption of Cr(VI) ions from aqueous solution on synthesized polymeric microcapsules is an exothermic process, confirming that the chemical bonding of Cr(VI) ions to the extractant molecule at the adsorption sites is thermodynamically the prevalent adsorption process.

The chemisorption process was spontaneous at all studied temperature, which is consistent with the extremely fast reaction of chromium with the extractant that took place in the experiments. An entropy value lower than that measured in analogous liquid–liquid extraction experiments was determined, indicating that the Cr(VI) ions bonded to Aliquat 336 on the microcapsules leads to a less chaotic system.

As a global conclusion, the results presented here show the feasibility of the recovery or removal of valuable and non-valuable metals from dilute aqueous solutions using this method. Microcap-

sules, prepared from cheap monomers and commercial extractants, behave as efficient and recyclable adsorbents. From an economical point of view, this fact attests to the potential usefulness of this separation process in industrial applications by means of continuous columns packed with microcapsules loaded with appropriate extractants.

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