

Sorption Equilibrium of Cr(VI) Ions by Strong Base Anion Exchangers with Pyridine Structures

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ABSTRACT: Chromate sorption on pyridine strong base anion exchangers with different functional groups (methyl, ethyl, and butyl groups), at the quaternary nitrogen atoms, was studied as a function of various initial concentrations (100–1500 mg Cr/L) and counterion type. The studied resins in the Cl⁻ form have higher Cr(VI)-retention capacities than those in the SO₄²⁻ form. The pyridine strong base anion exchangers showed a selectivity reversal for the sulfate and chromate anions compared to that of the commercial resins. The alkyl substituent length of the quaternary nitrogen atoms exerted a substantial influence on the Cr(VI)-retention

capacity values for the resins in the Cl⁻ form; the chromate anions preferred resins with methyl functional groups, that is, resins with a greater hydrophilic structure. For the resins in the SO₄²⁻ form the length of the substituent at the quaternary nitrogen atom had only a negligible influence on their Cr(VI)-retention values. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1957–1963, 2004

Key words: functionalization of polymers; ion exchangers; selectivity; thermodynamics; resins

INTRODUCTION

The increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium compounds are extensively used in electroplating, anodizing operations in the surface finishing industry, corrosion control, oxidation, leather, glass, ceramic, photography, textile, dyeing, and tanning industries. The two common oxidation states for chromium in natural water are Cr(III) and Cr(VI). Cr(III) is not a significant groundwater contaminant, whereas Cr(VI) is approximately 100 times more toxic than Cr(III). Various technologies have been developed over recent years for the removal of the chromate ions from wastewater, thereby preventing the pollution of surface and groundwater. Precipitation is the traditional method of treating Cr(VI) containing wastewater.^{1,2} This requires that Cr(VI) should be reduced to Cr(III) before chemical precipitation to form poorly soluble Cr(III) hydroxide. This method leads to the higher residual levels of Cr(VI) than allowed by discharge limits. Solvent extraction is a convenient technique for the removal of chromate ions from aqueous solutions. Literature data report that the tertiary amine extractants Alamine 336 and

Aliquat 336 are effective reagents for the removal of Cr(VI).^{3–5}

The major drawback of solvent extraction is the loss of extractant/solvent in large-scale industrial applications. Solvent-impregnated resins have been used as a new alternative method in various applications for the treatment of metal effluent containing heavy metals.^{6–11} Anion-exchange processes can be used for the removal of Cr(VI) from wastewater at alkaline and acidic pH in the presence of a high concentration of chloride, sulfate, bicarbonate, and nitrate ions.^{12,13} The selectivity of chromate anions for commercial styrene strong base anion exchangers in the pH range 3–6 is very high, whereas at neutral to alkaline pH, the chromate removal capacity is drastically reduced.^{14–23} The synthesis of the new ligand anion exchanger with higher chromate affinity than that of commercially available anion exchangers was reported in the literature.²⁴ Recently, a modified poly(4-vinylpyridine)-coated silica gel with very fast kinetics for Cr(VI) removal was prepared.²⁵

The primary objective of the present article is the study of the removal of Cr(VI) from aqueous solution by pyridine strong base anion-exchange resins with different functional groups, obtained by the quaternization reactions of 4-vinylpyridine (4-VP) : 8%divinylbenzene (8%DVB) copolymer, gel type, with halogenated compounds such as methyl iodide, ethyl iodide, and butyl iodide. The influences of functionality of the matrix and counterion type were investigated.

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TABLE I
pH Values for the Different Concentrations of K_2CrO_4 Aqueous Solution

C, mg Cr/L	100	250	500	750	1000	1250	1500
pH	7.49	7.76	7.84	8.05	8.10	8.11	8.14

EXPERIMENTAL

Materials

4-Vinylpyridine (4-VP, supplied from Fluka Chemie, Buchs, Switzerland) was purified by vacuum distillation immediately before use. Divinylbenzene (DVB, Fluka), technically pure (80%), contained residual mainly of 3- and 4-ethyl vinylbenzene.

The starting 4-VP : 8%DVB copolymers were obtained by aqueous suspension copolymerization of 4-VP with DVB using 1.5 wt % of benzoyl peroxide as initiator. The aqueous phase consisted of 3 wt % NaCl, 0.12 wt % gelatin, and 0.5 wt % ammonium salt of poly(styrene-co-maleic anhydride). The organic/aqueous phase ratio was 1 : 3 v/v.

The copolymerization reaction was allowed to proceed for 10 h at 80°C and 2 h at 90°C. After copolymerization, the copolymer beads were separated with methanol, in a Soxhlet apparatus, to remove traces of residual monomers and linear oligomers of 4-VP, and finally dried at 50°C for 48 h.

The samples (0.4–0.8 mm diameter) were characterized by their nitrogen content as determined by elemental analysis. The experimental nitrogen content was 9% compared to the theoretical one (11%); thus, only part of the initial 4-VP amount reacted with DVB.

The pyridine strong base anion-exchange resins were obtained by the nucleophilic substitution reactions of 4-VP : 8%DVB copolymer, gel type, with methyl iodide (MeI), ethyl iodide (EtI), or butyl iodide (BuI), followed by the treatment of the quaternized product with 5% NaCl aqueous solution. The quaternization reactions were performed in a glass round-bottom flask, equipped with a stirrer, reflux condenser, and thermometer. The quantities of MeI, EtI, and BuI correspond to a nitrogen : halogenated compound molar ratio of 1 : 2. The reactions were carried out at 60°C for 48 h. After this, the beads were isolated by filtration and washed with methanol and finally with distilled water. The treatment with NaCl meant the passing of NaCl aqueous solution of 5% concentration through the beads packed into column until the absence of I^- ions in the effluent solution was detected. Samples of anion exchangers were regenerated with 5% NaCl solution, followed by washing with deionized water until complete removal of chlorine ions. The synthesized strong base anion exchangers were characterized by strong base exchange capacities, determined by the ion exchange of Cl^- for SO_4^{2-} . The volumetric strong base anion-exchange capacity

was determined by the elution of Cl^- anions with 5% Na_2SO_4 aqueous solution, and the chlorine ions were potentiometrically determined with 0.02N $AgNO_3$ aqueous solutions. To calculate the gravimetric strong base anion-exchange capacity, the resins were dried at 110°C to constant weight. All the resins were sieved at a particle size of 0.4–0.8 mm. After air drying, the resins were stored for the sorption studies. The chromate solutions were prepared in distilled water from a stock solution of K_2CrO_4 .

Methods

All sorption experiments were performed under static conditions at room temperature ($20 \pm 2^\circ C$).

The Cr(VI)-retention capacity was determined as follows: the resin samples, of 0.5–0.6 g in the dry state, originally completely loaded with Cl^- or SO_4^{2-} anions, were placed in 100 mL K_2CrO_4 aqueous solution of concentrations ranging from 100 to 1500 mg Cr/L in conical flasks. The pH values of these solutions were measured with a digital pH meter (GTE 4112 Model, Seibold, Vienna, Austria). The anion exchangers were equilibrated for 24 h on a shaker; from preliminary measurements the contact time of 24 h was determined to be sufficient for reaching equilibrium. Similar experiments, performed on the commercial strong base anion exchanger Amberlite IR-400 (Rohm and Haas, Philadelphia, PA), showed that the time to achieve equilibrium was only 6 h.²⁰ After contact, the beads were filtered and the filtrate was analyzed for chromate ions by a photocolometric method using diphenylcarbazide, a filter of 540 nm, and standard solutions of 0.1–0.8 mg Cr/L concentrations.²⁶

RESULTS AND DISCUSSION

The pH values of the K_2CrO_4 aqueous solution at different concentrations are presented in Table I.

The characteristics of the pyridine strong base anion exchangers used in Cr(VI) sorption study are shown in Table II. From this table, it can be seen that all the synthesized pyridine anion exchangers have good values of strong base exchange capacities.

The Cr(VI)-retention capacities [a (mg Cr/g)] for the pyridine resins in the Cl^- and SO_4^{2-} forms are presented as a function of Cr(VI) concentration in Figures 1 and 2, respectively.

All the isotherms show a preference of the resins for the incoming chromate anions over that of the outgo-

TABLE II
Characteristics of the Pyridine Strong Base Anion Exchangers

Code sample	Ionic form of the resin (X^-)	Functional group	Strong base exchange capacity	
			mequiv/g	mequiv/mL
4-VP:8%DVB + MeCl	Cl^-	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N}^+ \text{X}^- \\ \\ \text{CH}_3 \end{array}$	4.30	1.75
4-VP:8%DVB + MeSO ₄	SO_4^{2-}	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N}^+ \text{X}^- \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	4.80	2.10
4-VP:8%DVB + EtCl	Cl^-			
4-VP:8%DVB + EtSO ₄	SO_4^{2-}	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N}^+ \text{X}^- \\ \\ (\text{CH}_2)_3 \\ \\ \text{CH}_3 \end{array}$	4.50	2.05
4-VP:8%DVB + BuCl	Cl^-			
4-VP:8%DVB + BuSO ₄	SO_4^{2-}			

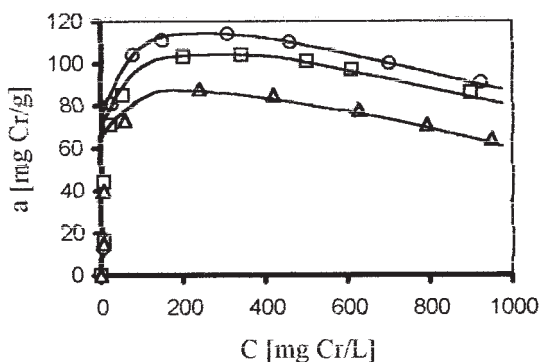


Figure 1 Uptake of Cr(VI) on the pyridine resins in Cl^- form as a function of Cr(VI) concentration solution at equilibrium: (O) 4-VP:8%DVB + MeCl; (□) 4-VP:8%DVB + EtCl; (Δ) 4-VP:8%DVB + BuCl.

ing chloride or sulfate anions. Several conclusions may be drawn from these figures:

- The pyridine resins in the Cl^- form have the same behavior with respect to the retention of Cr(VI) ions. All the resins have the highest retention capacity values in the low concentration range (200–400 mg Cr/L) of the chromate solution at equilibrium. At concentrations higher than 400 mg Cr/L, gradual decreases of the Cr(VI) uptake are observed. It is very interesting to note that at equilibrium, the retention capacity value of Cr(VI) for the concentration of 1000 mg Cr/L is identical to that for a very low concentration (~ 40 mg Cr/L). The explanation of this result consists of the presence of the $HCrO_4^-$ and CrO_4^{2-} monovalent and divalent ionic species of Cr(VI) ions. At low values of Cr(VI) concentration, even in the neutral pH range, there are both $HCrO_4^-$ and

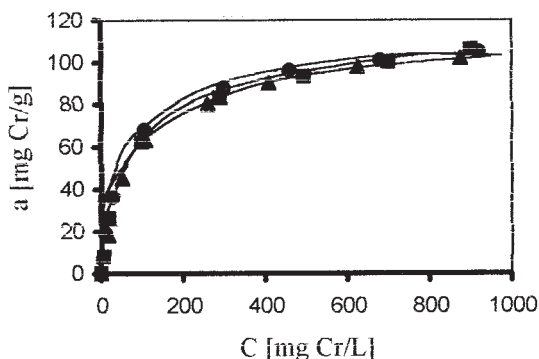


Figure 2 Uptake of Cr(VI) on the pyridine resins in SO_4^{2-} form as a function of initial concentration of Cr(VI) solution at equilibrium: (●) 4-VP:8%DVB + MeSO_4 ; (■) 4-VP:8%DVB + EtSO_4 ; (▲) 4-VP:8%DVB + BuSO_4 .

CrO_4^{2-} anions. In this condition, the resins in the Cl^- and SO_4^{2-} forms show a higher selectivity for HCrO_4^- anion than for CrO_4^{2-} anion. The order of selectivity is as follows: $\text{HCrO}_4^- > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$. Therefore, in the low concentration range, Cr(VI) is retained in major ratio by the resins in the Cl^- form according to the well-known sequence of selectivity of the commercial strong base anion exchangers for the common anions.²⁷ As the concentration of Cr(VI) increases, the pH value of the aqueous phase also increases, and divalent CrO_4^{2-} anions are the dominant ionic species. These anions have a high diameter of the hydrated form that do not allow easy access into the resins at the ion-exchange groups. Also, as the concentration of aqueous phase electrolyte is increased, the counterions of lower valence become more selective compared to the counterions of higher valence.²⁰ In the case of the RCl resin form, the monovalent counterions Cl^- become more selective compared to divalent CrO_4^{2-} anions and the Cr(VI)-retention capacity of anionites decreased. In the case of the R_2SO_4 resin form, both SO_4^{2-} and CrO_4^{2-} ions are divalent and CrO_4^{2-} ions are selectively retained and Cr(VI)-retention capacity of the anionite increases.

- The chemical structure of the pyridine resins in the Cl^- form has a substantial effect on their Cr(VI)-retention capacities. The increase of the substituent length at the quaternary nitrogen atom leads to the decrease of the Cr(VI)-retention value in the following order: 4-VP:8%DVB + MeCl > 4-VP:8%DVB + EtCl > 4-VP:8%DVB + BuCl . This behavior can be explained by the affinity of the hydrated chromate anions for the high hydrophilic resin.
- Resins in the SO_4^{2-} form present similar ion-exchange isotherms and their shapes are typical for the ion-exchange isotherms of the strong base

anion exchangers. Cr(VI)-retention capacity increases with the increasing K_2CrO_4 concentration. At equilibrium for concentrations higher than 400 mg Cr/L, in the liquid phase there are only divalent species (SO_4^{2-} and CrO_4^{2-} ions) and thus the resins selectively retained CrO_4^{2-} anions in contrast to the $\text{RCl}/\text{K}_2\text{CrO}_4$ system.

- For resins in the SO_4^{2-} form the Cr(VI)-retention capacity values increase with the increasing chromate concentration and depend significantly on the alkyl substituent length at the quaternary nitrogen atom. This unusual behavior is attributed to the lower selectivity of the CrO_4^{2-} anions for the resins in the SO_4^{2-} form (divalent/divalent ion exchange) than for the resins in the Cl^- form (monovalent/divalent ion exchange). These values were obtained from the separation factor values that are presented in Tables III–VI. Therefore, in the case of the resins in the SO_4^{2-} form, the substituent type at the quaternary nitrogen atom has a negligible influence on the Cr(VI)-retention capacity.

The degrees of usage of the strong base anion-exchange capacities for the studied pyridine resins are presented in Figures 3 and 4.

In the case of resins in the chloride form, the degree of usage of the strong base anion-exchange capacity is 100% only for the anion exchanger with methyl groups at the quaternary nitrogen atoms, whereas the resins with ethyl or butyl functional groups have degrees of usage of their capacities close to 80%.

The 4-VP:8%DVB + MeSO_4 resin has a degree of usage capacity lower than that of 4-VP:8%DVB + MeCl resin. Both anion exchangers in the chloride and sulfate forms, with ethyl and butyl functional groups, present the same values of the degree of usage of their exchange capacities.

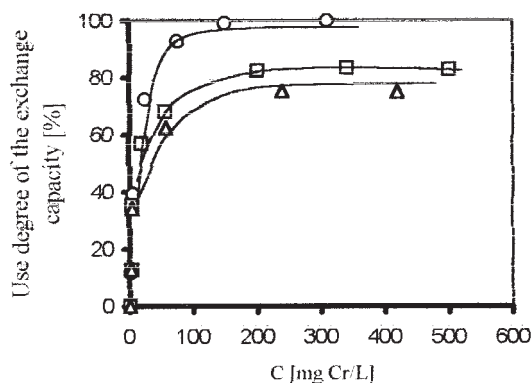


Figure 3 Degree of usage of the strong base anion-exchange capacity for the pyridine anion exchangers in the Cl^- form: (○) 4-VP:8%DVB + MeCl ; (□) 4-VP:8%DVB + EtCl ; (△) 4-VP:8%DVB + BuCl .

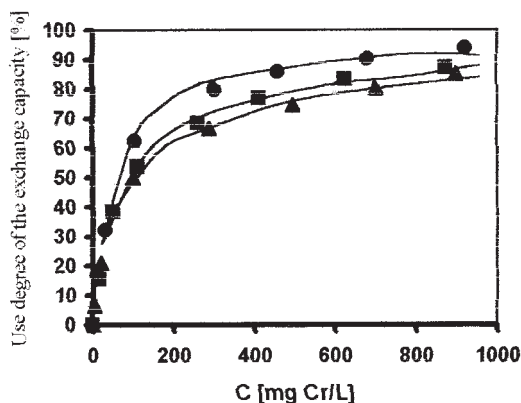


Figure 4 Degree of usage of the strong base anion-exchange capacity for the pyridine anion exchangers in the SO_4^{2-} form: (●) 4-VP : 8%DVB + MeSO_4 ; (■) 4-VP : 8%DVB + EtSO_4 ; (▲) 4-VP : 8%DVB + BuSO_4 .

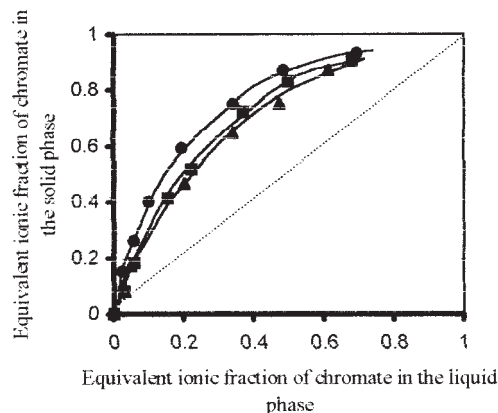


Figure 6 Sulfate/chromate ion-exchange isotherms for the pyridine anion exchangers in the SO_4^{2-} form: (●) 4-VP : 8%DVB + MeSO_4 ; (■) 4-VP : 8%DVB + EtSO_4 ; (▲) 4-VP : 8%DVB + BuSO_4 .

The individual chloride/chromate and sulfate/chromate ion-exchange isotherms for the pyridine anion exchangers are plotted in Figures 5 and 6.

Figures 5 and 6 show the ion-exchange isotherms at the dependency of chromate ion fraction in the solid and liquid phases at equilibrium for the presented experimental data. These isotherms allowed us to evaluate the selectivity of the pyridine strong base anion exchangers for the Cr(VI) by calculation of the separation factor.

These plots also suggested that the resins in the Cl^- form, with different functional groups, have similar isotherms. It is obvious that, regardless of the alkyl substituent type, at equilibrium the selectivity of the pyridine anion exchangers for the chromate anion is dependent on the ionic fraction of the Cr(VI) ions in the liquid and solid phases.

Up to 0.6–0.7 ionic fraction of Cr(VI) ions in the aqueous phase, the ion-exchange isotherms for the

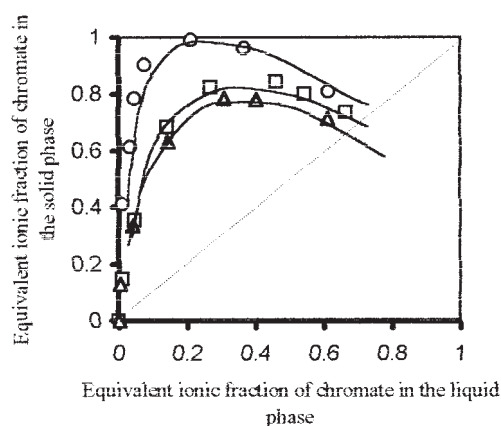


Figure 5 Chloride/chromate ion-exchange isotherms for the pyridine anion exchangers in the Cl^- form: (○) 4-VP : 8%DVB + MeCl ; (□) 4-VP : 8%DVB + EtCl ; (△) 4-VP : 8%DVB + BuCl .

studied resins are above the diagonal of the equilibrium diagram; therefore, all the resins show a high affinity for the chromate anions. The highest affinity is registered for the resin with methyl groups as functional sites. The functionality of the matrix has an influence on the Cr(VI) selectivity of the resins; the order of the Cr(VI) selectivity for the pyridine resins in the chloride form is $4\text{-VP} : 8\% \text{DVB} + \text{MeCl} \gg 4\text{-VP} : 8\% \text{DVB} + \text{EtCl} > 4\text{-VP} : 8\% \text{DVB} + \text{BuCl}$. The pyridine anion exchangers, in the sulfate form, have a nonconventional behavior toward the chromate ions, unlike that of the commercial strong base anion exchangers. The selectivity order for the common anions of the commercial anion exchangers is as follows: $\text{SO}_4^{2-} > \text{I}^- > \text{CrO}_4^{2-} > \text{Br}^- > \text{Cl}^-$.²⁷ In our case, the studied resins have a selectivity reversal: $\text{CrO}_4^{2-} > \text{SO}_4^{2-}$; this selectivity is valid over the entire concentration range of 100–1500 mg Cr(VI)/L and depends only to a negligible degree on the substituent type at the quaternary nitrogen atom.

The preference of the ion exchanger for one of the two counterions is often expressed by the separation factor α_B^A . It is the quotient of concentration ratios of the two counterions in the ion exchanger and the solution. If ion A is preferred, the separation factor α_B^A is larger than unity and, if B is preferred, the α_B^A is smaller than unity. The numerical value of the separation factor is not affected by the choice of the concentration units. The separation factor value depends on the total concentration of the solutions, temperature, and equivalent fraction of the ion.

The separation factor $\alpha_{\text{Cl}^-(\text{SO}_4^{2-})}^{\text{CrO}_4^{2-}}$ is a measure of the selectivity because the magnitude of α is independent of the concentration units used and it is the most straightforward measure of relative affinity.

The separation factors for the studied monovalent/divalent and divalent/divalent ion exchanges are defined, respectively, by eqs. (1) and (2):

TABLE III
Separation Factor as a Function of Equivalent Ion Fraction for the Chromate Anions at Equilibrium in the RCl Resins

System	$Y_{CrO_4^{2-}}$							
	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
4-VP:8%DVB + MeCl	—	28.2	30.6	32.3	36.0	44.3	53.1	81.0
4-VP:8%DVB + EtCl	27.1	25.8	21.6	19.0	16.2	15.6	14.2	—
4-VP:8%DVB + BuCl	15.4	13.8	12.7	11.5	9.6	7.8	—	—

$$\alpha_{Cl^-}^{CrO_4^{2-}} = \left(\frac{Y_{CrO_4^{2-}}}{Y_{Cl^-}} \right) / \left(\frac{X_{CrO_4^{2-}}}{X_{Cl^-}} \right) = \frac{Y_{CrO_4^{2-}} X_{Cl^-}}{Y_{Cl^-} X_{CrO_4^{2-}}} = \frac{Y_{CrO_4^{2-}} (1 - X_{CrO_4^{2-}})}{(1 - Y_{CrO_4^{2-}}) X_{CrO_4^{2-}}} \quad (1)$$

$$\alpha_{SO_4^{2-}}^{CrO_4^{2-}} = \left[\frac{Y_{CrO_4^{2-}}}{Y_{SO_4^{2-}}} \right] / \left[\frac{X_{CrO_4^{2-}}}{X_{SO_4^{2-}}} \right] = \frac{Y_{CrO_4^{2-}} X_{SO_4^{2-}}}{Y_{SO_4^{2-}} X_{CrO_4^{2-}}} = \frac{Y_{CrO_4^{2-}} (1 - X_{CrO_4^{2-}})}{(1 - Y_{CrO_4^{2-}}) X_{CrO_4^{2-}}} \quad (2)$$

where X_x^- is the equivalent ion fraction of counterions (CrO_4^{2-} ; Cl^- ; SO_4^{2-}) in the liquid phase and Y_x^- is the equivalent ion fraction of counterions (CrO_4^{2-} ; Cl^- ; SO_4^{2-}) in the ion exchanger.

Tables III–VI present the separation factor values calculated from the ion exchange isotherms (Figs. 5 and 6).

In the case of the strong base anion exchangers in the chloride and sulfate form, the values of the separation factor are greater than 1.0 over the entire concentration range under investigation, which means a preference for chromate anions, and the magnitude of $\alpha_{Cl^-}^{CrO_4^{2-}}$ indicates the magnitude of the preference. The 4-VP : 8%DVB + MeCl anion exchanger shows the greatest degree of affinity for the chromate anions. The separation factor values decrease with the increasing equivalent ion fraction for chromate anions in the ion exchangers (Table III) and solution for the resins with ethyl and butyl groups (Table IV). The order of the selectivity of the pyridine strong base anion exchang-

TABLE IV
Separation Factor as a Function of Equivalent Ion Fraction for the Chromate Anions at Equilibrium in the Solution for the RCl Resins

System	$X_{CrO_4^{2-}}$							
	0.025	0.05	0.1	0.2	0.3	0.4	0.5	0.6
4-VP:8%DVB + MeCl	31.9	44.3	81.0	196.0	231.0	48.5	11.5	3.5
4-VP:8%DVB + EtCl	22.9	19.0	16.7	14.2	12.2	7.3	4.0	2.0
4-VP:8%DVB + BuCl	17.5	12.7	11.0	8.5	6.3	6.3	2.3	1.1

TABLE V
Separation Factor as a Function of Equivalent Ion Fraction for the Chromate Anions at Equilibrium in the R_2SO_4 Resins

System	$Y_{CrO_4^{2-}}$								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
4-VP:8%DVB + MeSO ₄	5.4	6.0	5.7	6.0	5.7	5.6	5.4	6.0	7.9
4-VP:8%DVB + EtSO ₄	3.1	3.3	3.1	3.7	4.1	4.1	4.1	4.7	—
4-VP:8%DVB + BuSO ₄	2.7	2.7	2.7	3.2	3.3	3.5	3.5	3.8	—

ers in the Cl^- form for the chromate anions is the following: 4-VP : 8%DVB + MeCl \gg 4-VP : 8%DVB + EtCl > 4-VP : 8%DVB + BuCl, and it is in good agreement with the order of retention capacities.

The resins in the SO_4^{2-} form have separation factor values > 1, which means that the ion exchangers selectively retain CrO_4^{2-} anions. Also, the values of the separation factor are lower than those for the resins in the chloride form, and thus selectivity of the resins in the sulfate form for the CrO_4^{2-} anions is reduced. In this case, the selectivity order of the resins for the chromate anions is 4-VP : 8%DVB + MeSO₄ > 4-VP : 8%DVB + EtSO₄ \gg 4-VP : 8%DVB + BuSO₄.

CONCLUSIONS

The pyridine strong base anion exchangers, with different lengths of substituent at the quaternary nitrogen atoms, have good Cr(VI)-retention capacity values over a concentration range of 100–1500 mg Cr/L.

Cr(VI)-retention capacity depends on the ionic form of the strong base anion exchangers and the substituent type at the quaternary nitrogen atom.

The chemical structure of the resins in the Cl^- form has a substantial effect on their chromate-retention capacities. The increase of the alkyl substituent length at the quaternary nitrogen atoms leads to the decrease of the chromate-retention value (4-VP : 8%DVB + MeSO₄ > 4-VP : 8%DVB + EtSO₄ > 4-VP : 8%DVB + BuSO₄); it is well known that chromate anions have a great affinity for the more hydrophilic resins.

The pyridine resins in the sulfate form present a nonconventional behavior in the sulfate/chromate ion exchange compared to the well-established selectivity

TABLE VI
Separation Factor as a Function of Equivalent Ion Fraction for the Chromate Anions at Equilibrium in the Solution for the R_2SO_4 Resins

System	$X_{CrO_4^{2-}}$					
	0.1	0.2	0.3	0.4	0.5	0.6
4-VP:8%DVB + MeSO ₄	6.0	5.7	5.4	6.0	7.3	12.6
4-VP:8%DVB + EtSO ₄	3.3	4.0	4.0	4.5	5.2	6.0
4-VP:8%DVB + BuSO ₄	2.8	3.4	3.5	3.5	3.7	4.5

order for the common anions in the case of the styrene commercial strong base anion exchanger. In this case, the substituent type at the quaternary nitrogen atom has a lesser influence on the Cr(VI)-retention capacity. This behavior is attributed to the lower selectivity for chromate anions in the $\text{CrO}_4^{2-}/\text{SO}_4^{2-}$ system than in the $\text{CrO}_4^{2-}/\text{Cl}^-$ system. As the concentration of Cr(VI) initial solution increases (>1000 mg Cr/L) the pH of aqueous solution also increases, and CrO_4^{2-} anions are the dominant ionic species. In this case, the counterions of lower valence become more selective compared to the counterions of higher valence. When the resins are in the Cl^- form, the monovalent counterions (Cl^-) become more selective compared to divalent CrO_4^{2-} anions and the Cr(VI)-retention capacity of the ion exchangers decreases. When the resins are in the SO_4^{2-} form, both sulfate and chromate anions are divalent species and CrO_4^{2-} anions are selectively retained and Cr(VI)-retention capacity increases.

Selectivity of the studied pyridine strong base anion exchangers, which was determined by separation factor, is influenced by the Cr(VI) concentration of K_2CrO_4 solution, the ionic form of the resins, and the substituent type at the quaternary nitrogen atom. For all studied anion exchangers, in the established conditions separation factor values are >1 , which indicates a preference of the resins for the chromate anions.

Selectivity for the chromate anions is higher for the resins in the Cl^- form than in the SO_4^{2-} form and strongly depend on the alkyl substituent length at the N^+ ($4\text{-VP} : 8\%\text{DVB} + \text{MeSO}_4 \gg 4\text{-VP} : 8\%\text{DVB} + \text{EtSO}_4 > 4\text{-VP} : 8\%\text{DVB} + \text{BuSO}_4$).

The resins in the SO_4^{2-} form have a lower selectivity for the chromate anions than that of the resins in the Cl^- form; in this case, the alkyl substituent length at the N^+ has a negligible influence on the selectivity.

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