Cr(VI)-Containing Wastewater Treatment by Means of Ion Exchange on Weak- and Strong-Base Anion Exchangers

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ABSTRACT: The aim of this research work was a thermodynamic and kinetic study of the retention of Cr(VI) ions from a K_2CrO_4 solution on macroporous weak- and strong-base anion exchangers, Lewatit M 64 A and Lewatit MP 500 A, respectively. Also, the correlations among the ion-exchange rate, the retention capacity of Cr(VI), and some process parameters were established. The parameters studied mainly were the concentration of Cr(VI) ions and the type of the counterions coupled with active groups from the anion exchangers. The results led to the conclusion that, for the Lewatit M 64 A resin, there is the following order of the Cr(VI) retention capacity: $RCl > R_2SO_4 > ROH$, while for the strong-base anion exchanger, the retention capacity for the Cr(VI) ions is different: $ROH > RCl > R_2SO_4$. In the Cl^- form, both anion exchangers have the same retention-capacity values. On the other side, the weak-base anion exchanger in SO_4^{2-} and OH^- forms presents the lowest retention-capacity values. The process kinetics also presents some differences: for the Lewatit M 64 A resin, the ion-exchange rate has lower values, especially in the OH^- form. This result is attributed to the increase of the OH^- ion concentration in the solution and its presence hinders the dissociation of the active groups of a weak-base anion exchanger. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2093–2098, 2002

Key words: ion exchangers; selectivity; kinetics; thermodynamics

INTRODUCTION

Chromium ions induce a strong toxicity of wastewaters, their removal being admitted only after advanced treatment processes. Due to the toxic and carcinogenic effects of the hexavalent ionic form, the allowed concentration value in drinking water is very low (0.005 mg/L).[1,2] Cr(III) ions are considered a polluting agent with a significant lower toxicity. The state of chromium ions in water is determined by the nature of the pollution source, its concentration, the pH value of the solution, and the reactions with other covalent or ionic species.[2–6] The efficiency of the Cr(VI)-containing wastewater treatment by means of ion exchange depends on the type and the characteristics of the anion exchanger, its ionic form, and the solution pH value.[7–14] For the strong-base anion exchangers, the presence of other anions influences their ion-exchange affinity in the following order: $Cr_2O_7^{2-} > CrO_4^{2-} > PO_4^{3-} > SO_4^{2-} > Cl^- > OH^-$.[10,11,15] The strong-base anion exchangers with a macroporous structure are most frequently used but they present drawbacks regarding to the regeneration and washing operations.[2,9] Ion exchange is a stoichiometric process and an equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a different counterion. At equilibrium, the ion exchanger and the solution contain both competing counterion species. The exchange is, as a rule, reversible and the final equilibrium distribution of the counterions is the same in either case, provided that the amounts of all the components in the system are the same. The electroneutrality condition induces the equality of the ion flows for the ions which take part in the process. The ion flows are coupled by the diffusion potentials as well as those which appear between the counterions from the free solutions; the electric forces are the most important parameters in the kinetics of ion exchange.

The rate of ion exchange is determined by the rate of ion diffusion across the diffusion layer (in the case of slow mixture and very dilute solutions) and the rate of diffusion of ions inside the resin phase (in the case of high mixture and concentrated solutions).[16] The rate of ion exchange strongly depends on the ion mobility, charge, and weight of the ion and on the pH value of the solution. The order of magnitude for the diffusion coefficients is about 10^{-8} cm^2/s.[16,17] The aim of this work was a thermodynamic and kinetic study of the comparative retention of Cr(VI) ions from a K_2CrO_4 solution on the macroporous weak- and strong-base anion exchangers, Lewatit M 64 A and Lewatit MP 500 A, respectively.

TABLE I
Characteristics of the Anion Exchangers with Macroporous Structures

Characteristics	Code sample	
	Lewatit MP 500 A	Lewatit M 64 A
Morphology	Macroporous	Macroporous
Base strength	Strong base	Weak base
Functional groups	$—N(CH_3)_3]^+$	$—NH(CH_3)_2]^+$
C_s (meq/g)	5.40	7.98
Moisture (%)		
ROH	60.43	58.37
RCl	57.70	61.65
R_2SO_4	53.30	38.85

EXPERIMENTAL

The research project was conceived for the thermodynamics and kinetics characterization of the following systems: strong-base anion exchanger with a macroporous structure (Lewatit MP 500 A)—synthetic solution of K_2CrO_4, and the second one, the weak-base anion exchanger with a macroporous structure (Lewatit M 64 A)—synthetic solution of K_2CrO_4. The influence of the Cr(VI) ion concentration in the solution and the counterion types of the active groups from the anion exchangers on the Cr(VI) retention capacity was studied.

Prior to any experiments, the resins were carefully treated for the obtention of the ion-exchanger forms, ROH, RCl, and R_2SO_4. Also, the moisture content and the ion-exchange capacities for dynamic conditions were determined for all the resins (Table I).

The equlibrium experiments were performed in static conditions at room temperature. For measurements of the exchange equilibria, a series of samples of swollen resin (~0.5 g in the dry state) originally completely loaded with one kind of species, OH^-, Cl^-, or SO_4^{2-}, was always equilibrated with a 0.1 L K_2CrO_4 solution of different concentrations (100–2000 mg Cr/L) for 24 h, with an irregular slow mixture.

Kinetics measurements were performed in a glass vessel equipped with a mechanical stirrer in static conditions. Samples of the resins in the swelling form (0.25 g in the dry state) were contacted with a 0.2 L K_2CrO_4 solution of a known concentration (0.1 g Cr/L). The concentration of Cr(VI) ions from the aqueous solution was determined at known time intervals. The analysis of Cr(VI) ions was performed photocolorimetrically by use of diphenylcarbazide, a 540-nm filter, and standard solutions of 0.1–0.8 mg Cr/L concentrations.

RESULTS AND DISCUSSION

Ion-exchange isotherms

Figures 1 and 2 present the dependence of the Cr(VI) ion concentrations at equilibrium in the liquid and
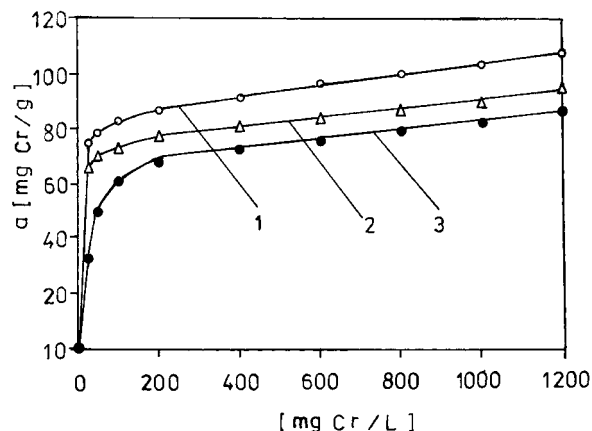

Figure 1 Influence of the Cr(VI) ion concentration on the retention capacity for the Lewatit MP 500 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.

solid phases. Figures 3 and 4 present the dependence of the solution and the ion exchangers' ionic fraction at equilibrium. In the case of the strong-base anion exchanger, Lewatit MP 500 A, the ion-exchange isotherms have similar forms (Fig. 1). The retention capacities values for the Cr(VI) ions are almost identical and the ionic forms of the resin have the following selectivity order: ROH > RCl > R_2SO_4. At low concentrations of the Cr(VI) ions in the solution, the strong-base anion exchanger has a high retention capacity and this means that the Lewatit MP 500 A resin can be used for the purification of the wastewaters which contain Cr(VI) ions.

The weak-base anion exchanger, Lewatit M 64 A, has a different behavior (Fig. 2). Its ion-exchange isotherms are of all sizes and this means that, for this type of resin, there is a greater influence of the counterion kind on the Cr(VI) retention capacity than in the case of the strong-base anion exchanger. Therefore, the
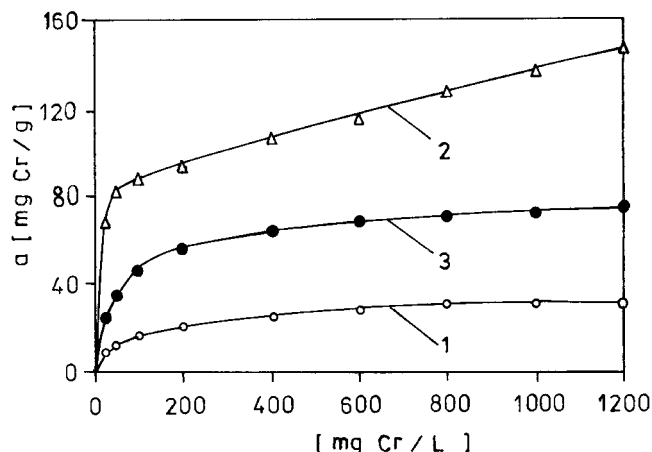

Figure 2 Influence of the Cr(VI) ion concentration on the retention capacity for the Lewatit M 64 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.
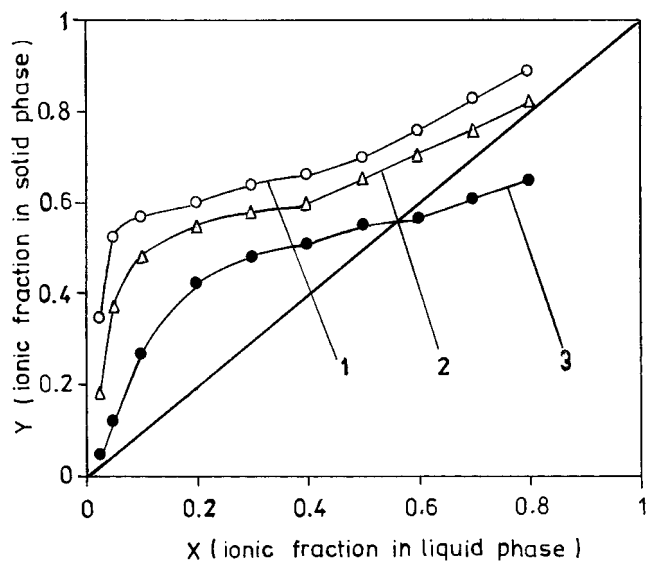
Figure 3 Ion-exchange isotherms for Lewatit MP 500 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.

Cr(VI) retention capacity follows the succession RCl $\gg$ $R_2SO_4 \gg$ ROH.

The ion-exchange isotherms give additional information about the selectivity of the two types of the anion exchangers for the CrO_4^{2-} anions comparatively with the other ones: OH^-, Cl^-, and SO_4^{2-} anions. For strong-base anion exchangers, the ion-exchange isotherms are located above the diagonal in the wide range of the ionic fraction of CrO_4^{2-} ions in the solution (Fig. 3). These results lead to the conclusion that Lewatit MP 500 A presents a good selectivity for CrO_4^{2-} anions independent by of the counterion type. The influence of the resin ionic form is illustrated by the following order: ROH > RCl > R_2SO_4, and the
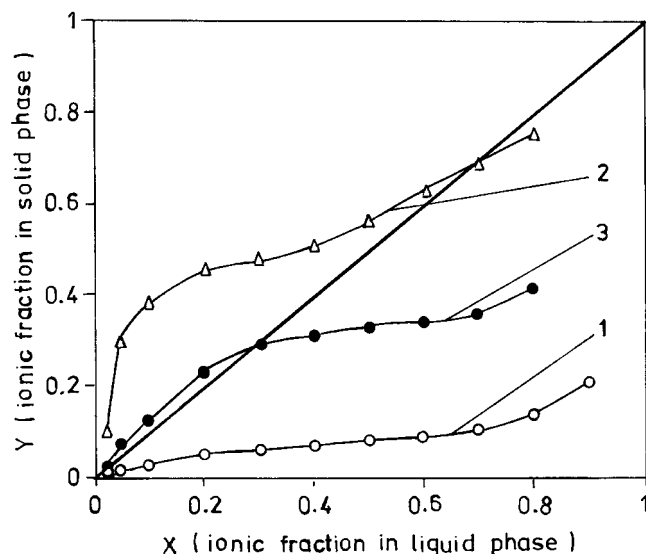

Figure 4 Ion-exchange isotherms for Lewatit M 64 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.
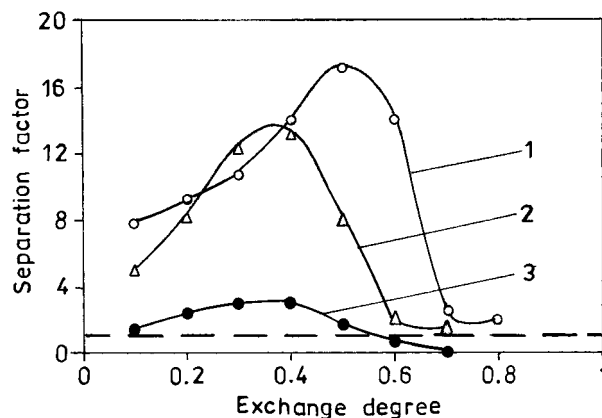

Figure 5 Influence of the exchange degree on the separation factor for Lewatit MP 500 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.

selectivity sequence of these anions is $CrO_4^{2-} > SO_4^{2-} > Cl^- > OH^-$.

The weak-base anion exchanger, Lewatit M 64 A, has a similar behavior with the strong-base one, only for the Cl^- ionic form (Fig. 4). For other anions, SO_4^{2-}, and especially for the OH^- ions, the ion-exchange isotherms are located below the diagonal; therefore, there is a different selectivity order: RCl > R_2SO_4 > ROH and another selectivity sequence of the anions, $OH^- > CrO_4^{2-} \approx SO_4^{2-} > Cl^-$.

The presence of the ion exchanger for one of two counterions is often expressed by the separation factor:

$$\alpha_{A^{-n}}^{CrO_4^{2-}} = \frac{\left[\dfrac{CrO_4^{2-}}{A^{-n}}\right]_s}{\left[\dfrac{CrO_4^{2-}}{A^{-n}}\right]_l}$$
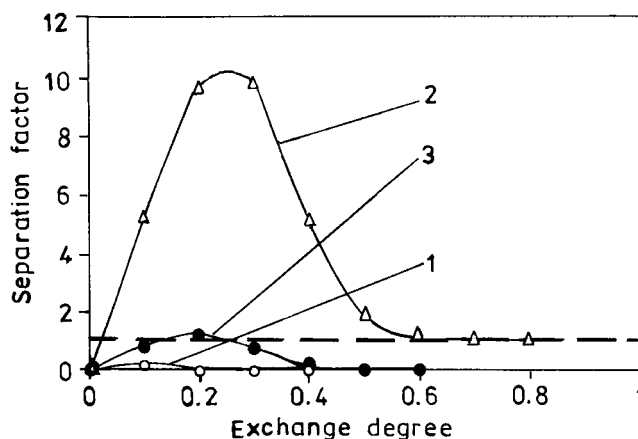

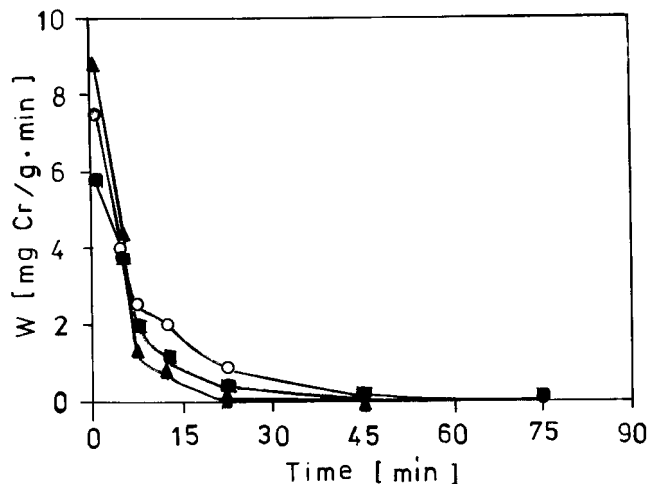**Figure 6** Influence of the exchange degree on the separation factor for Lewatit M 64 A resin: (1) ROH; (2) RCl; (3) R_2SO_4.

Figure 7 Ion-exchange rates for the retention of CrO_4^{2-} anions on different ionic forms of Lewatit MP 500 A resin: (▲) ROH; (○) RCl; (■) R_2SO_4.

where $(CrO_4^{2-})_s$ and $(CrO_4^{2-})_l$ are ionic fractions of CrO_4^{2-} anions in the solid and liquid phases, and $(A^{-n})_s$ and $(A^{-n})_l$, the ionic fractions of OH^-, Cl^-, or SO_4^{2-} anions in the solid and liquid phases. The values of the separation factor versus the exchange degree for the weak- and strong-base anion exchangers are plotted in Figures 5 and 6.

In the case of the strong-base anion exchanger, the values of the separation factor are $\gg 1$ and depend on the exchange degree. For the OH^-, Cl^-, and SO_4^{2-} forms of the resin, the maximum values of the separation factor are 0.50; 0.40, and 0.35. The order of the magnitude for this parameter is

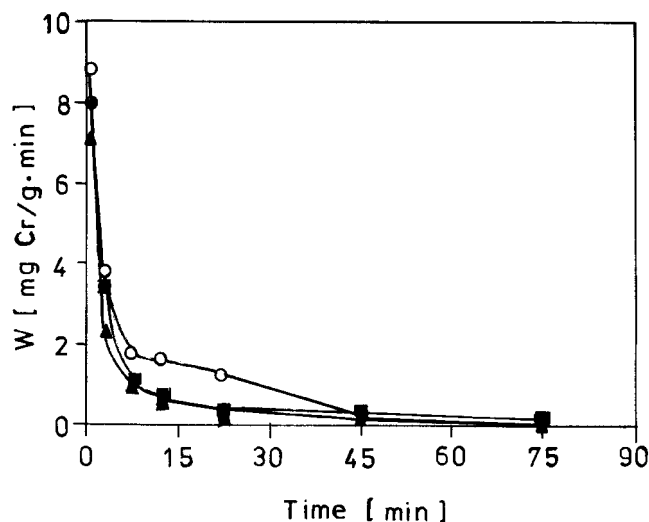$$\alpha_{OH^-}^{CrO_4^{2-}} > \alpha_{Cl^-}^{CrO_4^{2-}} \gg \alpha_{SO_4^{2-}}^{CrO_4^{2-}}$$

Figure 8 Ion-exchange rates for the retention of CrO_4^{2-} anions on different ionic forms of Lewatit M 64 A resin: (▲) ROH; (○) RCl; (■) R_2SO_4.

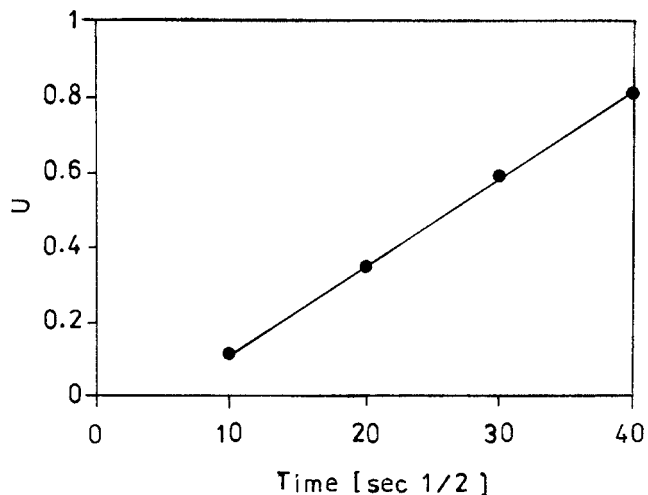**Figure 9** $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit MP 500 A resin in the RCl—K_2CrO_4—H_2O system.

The weak-base anion exchanger has $\alpha > 1$ only for the Cl^- form, whereas for the OH^- and SO_4^{2-} forms, $\alpha < 1$. In this case, the order of the magnitude for the separation factors is

$$\alpha_{Cl^-}^{CrO_4^{2-}} \gg \alpha_{SO_4^{2-}}^{CrO_4^{2-}} \gg \alpha_{OH^-}^{CrO_4^{2-}}$$

Ion-exchange kinetics

Ion-exchange kinetics can be established from the analyses of the Cr(VI) concentration in the solution at known time intervals. The ion-exchange rates were obtained by derivation of the integral kinetics curves. Figures 7 and 8 show the influence of the time on the ion-exchange rate expressed as mg Cr/g min. The kinetics results lead to the conclusion that, for both resins, the counterion type has a relative influence on
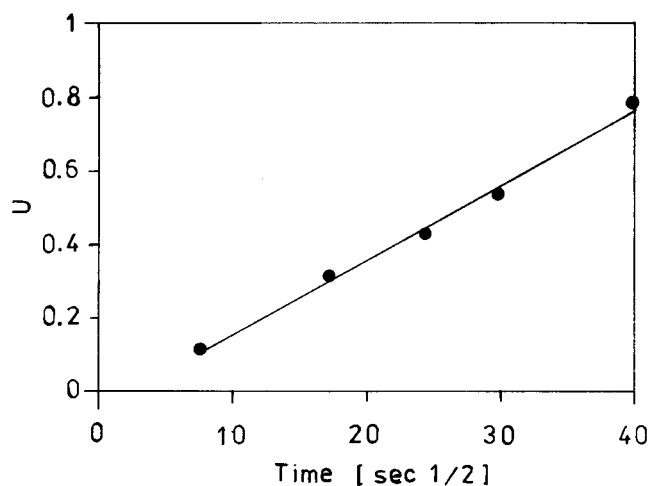

Figure 10 $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit M 64 A resin in the RCl—K_2CrO_4—H_2O system.
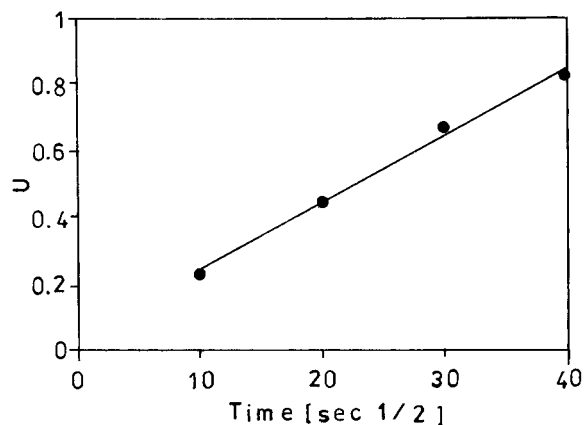
Figure 11 $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit MP 500 A resin in the R_2SO_4—K_2CrO_4—H_2O system.

the ion-exchange rates. For the Lewatit MP 500 A resin, the values of the ion-exchange rates are in the following order: ROH > RCl > R_2SO_4, which is correlated with the decrease of the ion weights: OH^- < Cl^- < SO_4^{2-}.

At the same time, increase of the exchange degree determines the following relationship for the exchange rates: RCl > R_2SO_4 > ROH. The Lewatit M 64 A resin has the same kinetics order: RCl > R_2SO_4 > ROH, and this behavior is attributed to the pH-value modification due to increase of the OH^- ion concentration inside the solution. The ion exchange, especially for the weak-base anion exchanger, is difficult in alkaline medium as a result of the OH^- ion elimination and, consequently, the exchange equilibrium is shifted to the left. Both resins have the same order of magnitude for the ion-exchange rates even if they are characterized by different values of the exchange capacities and base strength. In consequence, the ion exchange is mostly controlled by diffusion
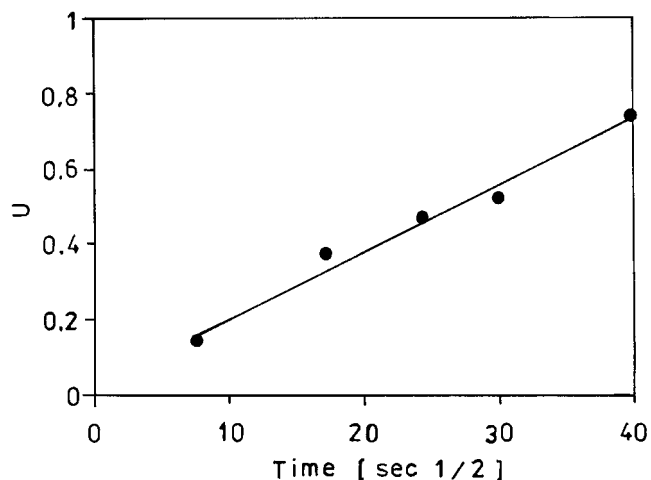
and, therefore, the kinetics can be defined by the Boyd–Adamson diffusion equation:

$$U(\tau) = 1 - \frac{6}{\pi^2} \sum_1^\infty \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2\tau}{r^2}\right)$$

where $U(\tau)$ is the exchange degree; n, the number of the anion-exchanger beads; r, the medium radius of the beads; and D, the ion-diffusion apparent coefficient.

For $U(\tau) \approx 0.30$ and spherical beads with radius r, the kinetics equation is a straight line $U(\tau) = (6/r)\sqrt{(D\tau/\pi)}$ and from its slope, $U(\tau) = (6/r)\sqrt{(D/\pi)}\sqrt{\tau}$, the ion-diffusion apparent coefficient value can be determined. The $U(\tau) = f(\sqrt{\tau})$ dependence for the studied ion exchangers is plotted in Figures 9–14. It can seen that straight lines are obtained for a wide range of the exchange degree. In consequence, for both

Figure 13 $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit MP 500 A resin in the ROH —K_2CrO_4—H_2O system.

Figure 12 $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit M 64 A resin in the R_2SO_4—K_2CrO_4—H_2O system.
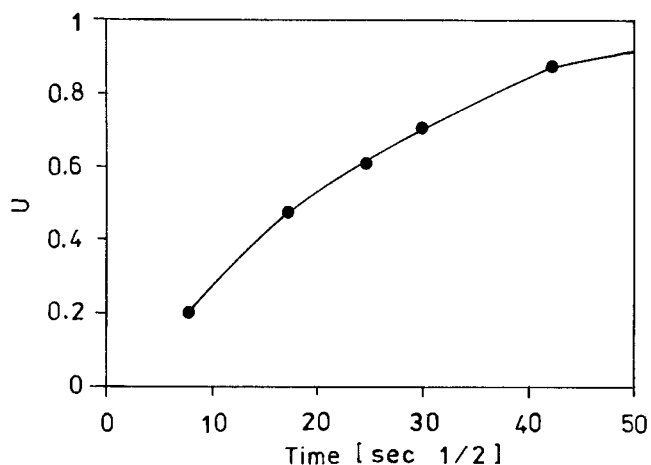

Figure 14 $U(\tau) = f(\sqrt{\tau})$ dependence for the Lewatit M 64 A resin in the ROH—K_2CrO_4—H_2O system.

TABLE II
Values of the Diffusion Apparent Coefficients

Ionic form of the resins	Diffusion coefficient, D (cm^2/s)	
	Lewatit MP 500 A	Lewatit M 64 A
ROH	2.12×10^{-7}	4.63×10^{-8}
RCl	2.40×10^{-8}	1.87×10^{-8}
R$_2$SO$_4$	1.90×10^{-8}	1.63×10^{-8}

resins (in Cl$^-$ and SO$_4^{2-}$ ionic forms), ion-exchange processes are controlled by diffusion.

Figures 13 and 14 show that straight lines are obtained only for low-exchange degrees. At high-exchange degrees, the process is carried out in the kinetics field. Table II presents the comparative values of the diffusion apparent coefficients.

CONCLUSIONS

Both strong- and weak-base anion exchangers (Lewatit MP 500 A and Lewatit M 64 A) with macroporous structures present good Cr(VI) retention capacities and can be used for the purification of wastewaters with high contents of this polluter. The thermodynamics and kinetics studies led to the conclusion that ion exchange is influenced by the functional groups and the counterion types of the anion exchangers.

In the case of a strong-base anion exchanger, the Cr(VI) retention capacity is in agreement with the following relationship: ROH > RCl > R$_2$SO$_4$, and does not depend on the counterion type. For a weak-base anion exchanger, the Cr(VI) retention capacity is in agreement with the RCl $\gg$ R$_2$SO$_4$ $\gg$ ROH relationship.

At low values of the ion-exchange degree for both resins, the process is controlled by the diffusion and the exchange rates and follows the order ROH $\gg$ RCl $\gg$ R$_2$SO$_4$. At high values of the ion-exchange degree, the process is controlled by diffusion for the Cl$^-$ and SO$_4^{2-}$ ionic forms and by kinetics for the OH$^-$ ionic form. The exchange rates are in agreement with the following relationship: RCl > R$_2$SO$_4$ > ROH.

References

1. Elovitz, M. S.; Fish, W. Environ Sci Technol 1995, 29, 1933–1943.
2. Zhao, D.; SenGupta, A. K.; Stewart, L. Ind Eng Chem Res 1998, 37, 4383–4387.
3. Seigneur, C.; Constantinou, E. Environ Sci Technol 1995, 29, 222–231.
4. Makos, J. D.; Hrncir, D. C. Environ Sci Technol 1995, 29, 2414–2419.
5. Tong, J. Y.; King, E. L. A. J Am Chem Soc 1953, 75, 6180.
6. Beattie, J. K.; Haight, G. P., Jr. Progr Inorg Chem 1972, 17, 93–145.
7. Lin, Q.; Yhao, G.; Yuan, W. Water Treat 1989, 4, 79–90.
8. Akimitsu, M.; Takaaki, O.; Midori, A.; Reiko, H. Jpn. Kokai 73, 14.575. [Cl13(7)A21,91C9,13(7)B7, 1973.
9. Golovnych, N. V.; Rzhechitskii, E. P.; Zavyalova, L. L.; Lipskaya, V. I. Zh Prikl Khim 1989, 62, 2212–2216.
10. Stary, P.; Peska, J.; Stamberg, J. Environ Prot Eng 1983, 9, 101–103.
11. SenGupta, A. K.; Clifford, D.; Subramonian, S. Water Res 1986, 20, 1177.
12. Sarre, M. J.; Mazet, M. Rev Sci Eau 1988, 1, 55–71.
13. Sengupta, A. K. Ion Exchange Technology; Technomic: Lancaster, PA, 1995; pp 115–147.
14. Kargman, V. B.; Balavadze, E. M.; Sokolova, L. P.; Fedtsova, M. A. Gal'vanotekh Abrab Poverkh 1993, 2(5), 65–73.
15. Untea, I.; Tudorache, E.; Florea, C. Rev Chim 2000, 51, 123–126.
16. Calmon, C.; Kressman, T. R. E. Ion Exchangers in Organic and Biochemistry; Academic Press: New York, 1957.
17. Untea, I.; Tudorache, E.; Florea, C. Rev Chim 2000, 51, 198–202.