



Removal of chromate by Amberlite A21: kinetics and equilibrium studies

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ABSTRACT

In the present study, batch experiments were performed to characterize the effectiveness of Amberlite A21 in the removal of Cr(VI) ions from aqueous solutions. The retention by the resin is studied as a function of pH, temperature, chromate concentration and the presence of foreign ions. The exchange kinetics and isotherms are evaluated in the absence and in the presence of foreign ions at different pH. The obtained results show that the highest removal efficiency occurs in the pH range 3–5. The chromate removal increases with the increase in temperature. The calculated thermodynamic data imply that the process is endothermic. Whatever the pH and the competitive ion, the chromate removal kinetics is well described by the first-order model. Both Langmuir and Freundlich isotherms can describe the experimental data. At pH 3.3, the exchange capacity calculated by the Langmuir equation is estimated to 106 mg (Cr(VI)/g (resin)) in single system, 118 mg/g in the presence of chloride and 105 mg/g in the presence of sulfate.

Keywords: Chromate; Ion exchange; A21; Competitive ions; Water treatment

1. Introduction

Industrial wastewaters from many factories contain heavy metals. Among these metals, hexavalent chromium is known as toxic and carcinogenic [1]. The most abundant form of DNA damage induced by Cr(VI) is Cr-DNA adducts, which cause mutations and chromosomal breaks [2]. Chromium (VI) pollution arises from industries like metal cleaning, plating and electroplating, leather and mining industries [3]. The most popular method to treat heavy metals in wastewaters is chemical precipitation using alkali to raise the solution pH to allow the formation of their hydroxides [4]. But the important production of sludge remains a problem and lets to the use of other methods. Ion exchange is a common technology used in water treatment. Its main advantage is the possible recuperation of the removed species. Several studies have been interested to the use of resins in chromium removal from water [5–10].

However, the most experiments have been undertaken in single system; whereas the real wastewater contains several ions. In the present work, the chromium removal is undertaken in the absence and in the presence of other ions by the commercial resin Amberlite A21, which has not been used in such treatment.

2. Material and methods

All chemicals used in this study were of analytical grade reagent, and no purification was used. Amberlite A21 (Merck, Germany) is a tertiary amine macroporous polystyrene resin. It was regenerated by NaOH (5%), rinsed with distilled water and dried at 40°C. The main properties of the resin are listed in Table 1. Chromate solutions were prepared by dissolving $\text{Na}_2\text{Cr}_2\text{O}_7$. The pH was adjusted by adding NaOH or HCl (1 N) solutions prior to each experiment.

Chromate removal was undertaken in batch system; the effects of pH, temperature, contact time and

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initial concentration were evaluated. In each experiment, one parameter was changed. The effects of competitive ions were evaluated as a function of contact time and initial concentration. Except, in the kinetics experiments, the formed suspensions were agitated for 60 min. After centrifugation, residual chromate concentrations were measured in the recovered solutions by a UV-visible spectrophotometer (Shimadzu 1650PC).

Table 1
Characteristics of Amberlite A21

Physical form	Spherical particles
Particle size	0.3–1.2 mm (15–50 mesh)
Whole beads	Macroporous
Resin skeleton	Polystyrene
Conditioned under form	Free base (FB)
Functional groups	Tertiary amine

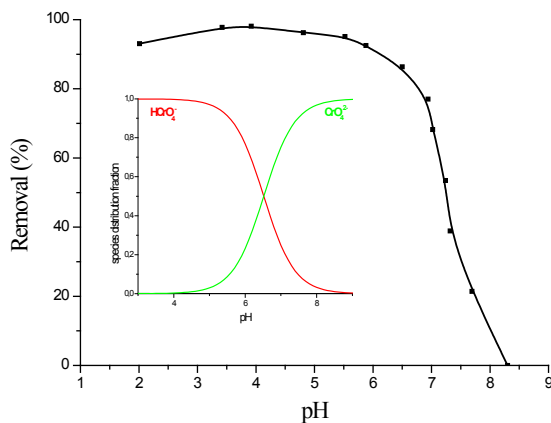


Fig. 1. Effect of pH on chromate removal by A21 (C_0 : 25 mg/L; t : 60 min; resin dose: 1 g/L).

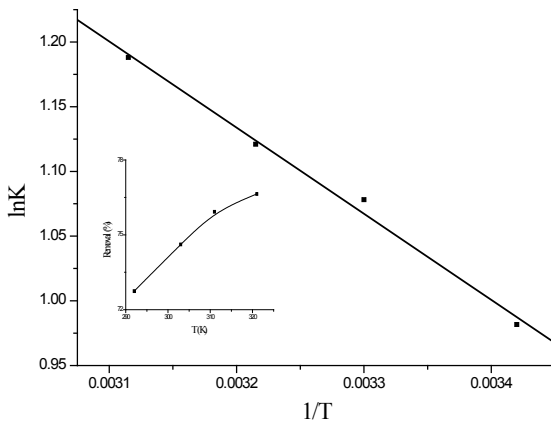


Fig. 2. Effect of temperature on chromate removal by A21 (C_0 : 25 mg/L; t : 60 min; resin dose: 1 g/L; pH 5).

3. Results and discussion

3.1. Effect of pH

As it can be seen from Fig. 1, the chromate removal is about 93% at pH 2. It increases gradually to reach a maximum at around pH 4; then decreases slightly to attain 86% at pH 6.5. A sharp decrease is observed at pH > 7 and only 11.82% is removed at pH 7.7. This decrease is attributed to the competition of hydroxyl ions for the effective adsorption sites. Identical evolution has been observed for sulfate removal by the same resin [11]. The speciation diagram included in Fig. 1 implies that the main species involved in the exchange process is $HCrO_4^-$. Consequently, the chromium exchange reaction can be written as follows:

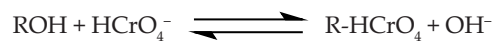


Table 2
Thermodynamic parameters for chromate removal by A21

ΔH (KJ.mol ⁻¹)	ΔS (J.mol ⁻¹)	ΔG (KJ.mol ⁻¹)			
		T = 292 K	T = 303 K	T = 311 K	T = 321 K
5.534	27.14	-2.383	-2.716	-2.898	-3.170

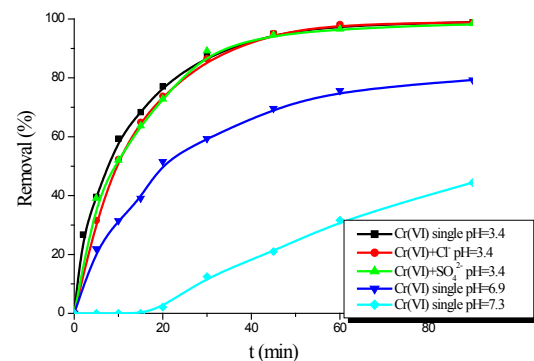


Fig. 3. Adsorption kinetics of chromate removal by A21 (C_0 : 25 mg/L, resin dose: 1 g/L).

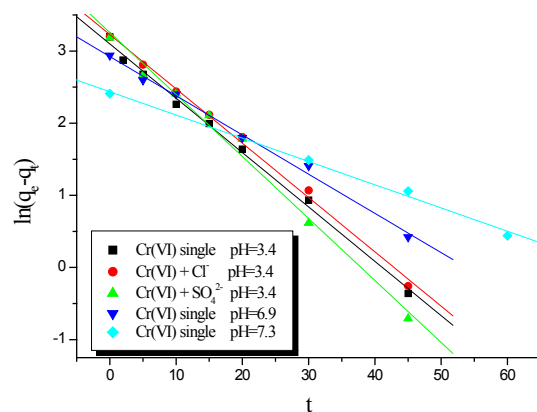


Fig. 4. First-order plots for chromate removal by A21.

3.2. Effect of temperature

The exchange capacity and the equilibrium constant increase when the temperature increases (Fig. 2), showing the endothermic nature of the process. The calculated thermodynamic parameters are summarized in Table 2. The negative values of ΔG indicate that the chromate exchange is spontaneous. The calculated ΔH value confirms that the exchange reaction is endothermic and indicates that chromate uptake by A21 is a physical process with no chemical bound [12]. Controversy results are found in the literature about the effect of temperature enhancement on chromium removal by resins. It has been observed an increase in the case of D314, and a decrease in the case of D301, D354 [13] and Dowex 1 × 8 [14].

3.3. Effect of contact time – kinetic study

As a function of time, the chromate removal increases rapidly during the first 20 min, then slows to stabilize and reach equilibrium at 60 min at pH 3.4 and 6.9 (Fig. 3). At pH 5, high chromium removal by Lewatit MP 64 and Lewatit MP 500 was also observed within 60 and 75 min, respectively [15].

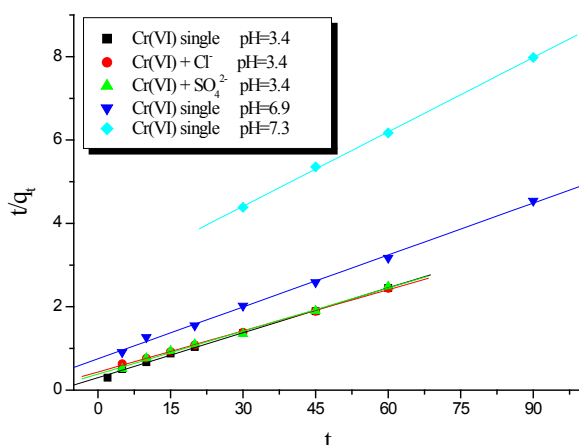


Fig. 5. Second-order plots for chromate removal by A21.

At pH 7.3, the chromate removal by A21 begins after 15 min. This can be related to the slow diffusion to the exchange sites induced by the increase in OH^- concentration. At this pH, the removal increases gradually, and the equilibrium is not reached. For the same contact time, the chromate removal rate at pH 3.4 is about three times higher than that at pH 7.3. In the presence of sulfate or chloride, slight effect is observed only in the first 30 min.

The experimental data are fitted by the first-order and the second-order models according to the following equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

The obtained results are illustrated in Figs. 4 and 5, and the calculated parameters are summarized in Table 3; where q_e is the exchange capacity at equilibrium and k is the rate constant. Regarding the correlation coefficients values, the chromate exchange reaction can be described by both the two models at the three tested pH. However, the equilibrium adsorption capacities (q_e) estimated by the first-order model are more reasonable implying that this model is more appropriate. This is in agreement with the results of chromium exchange by two lewattit resins [15] but in contrast with those obtained in other studies on chromium removal by ion exchange [16–18]. The calculated kinetic constants reveal that effectively the exchange speed decreases when the pH increases implying the slowdown of the chromate removal. In the presence of chloride or sulfate, the second-order constants decrease indicating the competition for the exchange sites.

To evaluate the suitable mechanism of chromate diffusion to the resin exchange sites, three diffusion models are used (Eqs. (3)–(5)):

$$q_t = K_{d1} t^{1/2} + C \quad (3)$$

Table 3
Kinetic parameters for chromate removal by A21

Model	Parameter	pH: 3.4			pH: 6.9	pH: 7.3
		Cr(VI) single	Cr(VI) + Cl^-	Cr(VI) + SO_4^{2-}	Cr(VI) single	Cr(VI) single
Pseudo-first-order	k_1 (min^{-1})	0.075	0.075	0.085	0.054	0.032
	q_e (mg/g)	22.2	25.24	25.97	18.6	11.4
	R^2	0.997	0.998	0.994	0.997	0.997
Pseudo-second-order	k_2 (g/mg.min)	0.004	0.002	0.003	0.002	0.001
	q_e (mg/g)	27.85	30.38	29.04	24.1	16.8
	R^2	0.998	0.999	0.997	0.998	0.999
Intraparticulaire diffusion	k_{d1} ($\text{mg/g.min}^{1/2}$)	2.862	2.965	2.735	2.068	1.108
	R^2	0.965	0.961	0.964	0.964	0.995
Interparticulaire diffusion	K_{d2} (min^{-1})	0.074	0.075	0.087	0.049	0.035
	R^2	0.998	0.997	0.993	0.995	0.994
Film diffusion	K_{d3} (min^{-1})	0.064	0.066	0.078	0.041	0.030
	R^2	0.992	0.991	0.987	0.987	0.991

$$-\ln\left(1 - \frac{q_t}{q_e}\right) = K_{a2}t \quad (4)$$

$$-\ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) = K_{a3}t \quad (5)$$

The obtained results (Figs. 6–8 and Table 3) show that the external diffusion models are more appropriate. As the pH increases in single system, the diffusion constants calculated for the three models decrease. Consequently, the main obstacle of chromate species diffusion to the exchange sites is the increase of OH⁻ concentration. In the presence of foreign ions, the calculated diffusion constants imply that the enhancement of the ionic strength does not prevent the chromate species to diffuse to the resin sites.

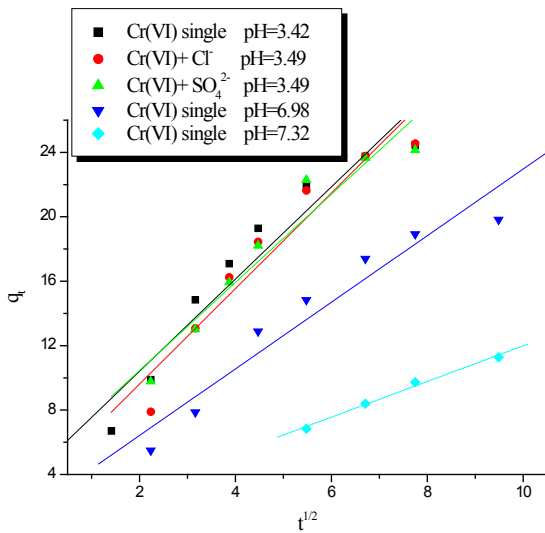


Fig. 6. Intraparticles diffusion plots for chromate removal by A21.

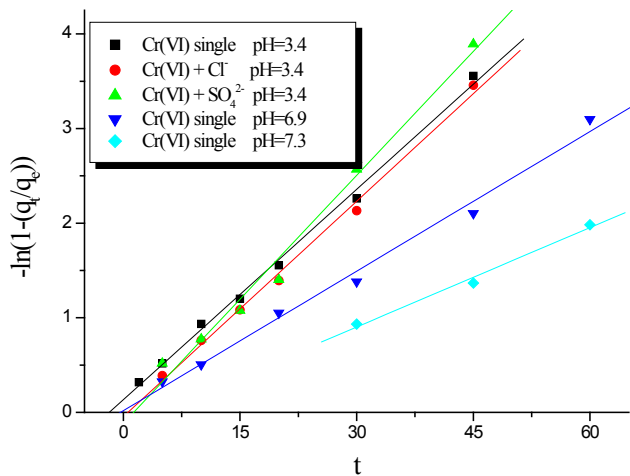


Fig. 7. Interparticles diffusion plots for chromate removal by A21.

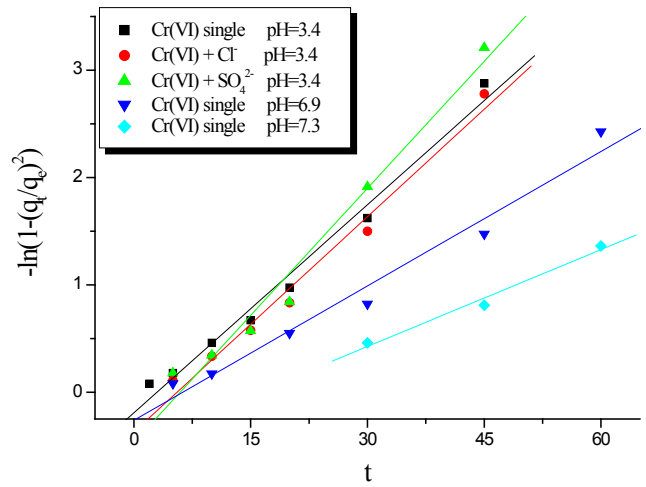


Fig. 8. Film diffusion plots for chromate removal by A21.

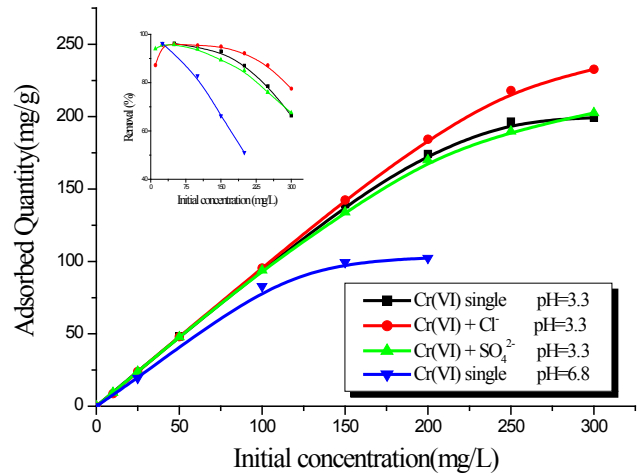


Fig. 9. Effect of initial concentration on chromate removal by A21 (resin dose: 1 g/L; t: 60 min).

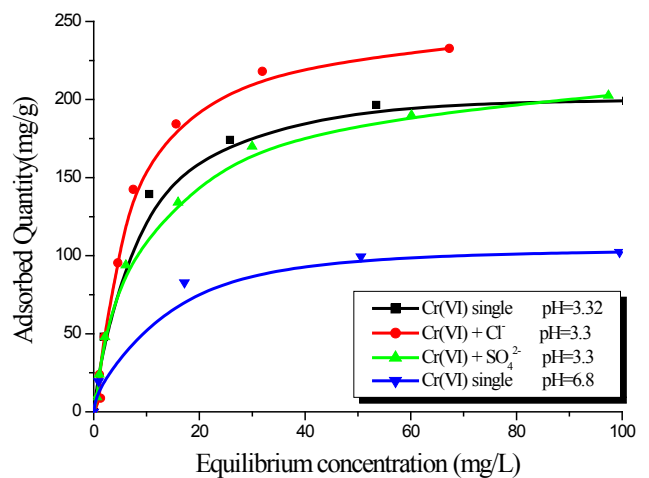


Fig. 10. Exchange isotherms of chromate removal by A21 (resin dose: 1 g/L; t: 60 min).

3.4. Effect of initial concentration – isotherms

The evolution of chromate removal in a function of the initial concentration (Fig. 9) shows that at pH 3.3, saturation is reached at about 250 mg/L. As the pH increases, the saturation is observed at lower initial concentration. At higher

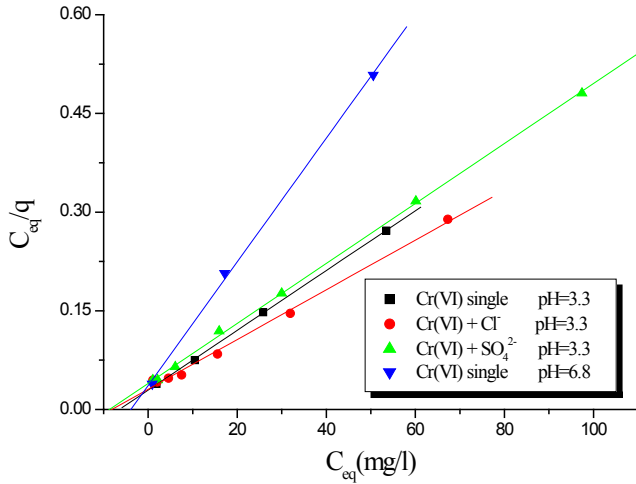


Fig. 11. Langmuir model plots for chromate removal by A21.

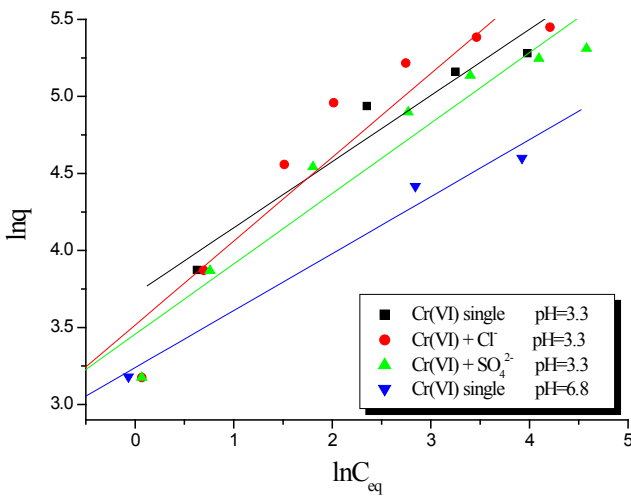


Fig. 12. Freundlich model plots for chromate removal by A21.

Table 4 Isotherms parameters for chromate removal by A21

Model	Parameter	pH: 3.3			pH: 6.8
		Cr(VI) single	Cr(VI) + Cl ⁻	Cr(VI) + SO ₄ ²⁻	Cr(VI) single
Langmuir	q_{max} (mg Cr(VI)/g)	106.05	118.71	105.59	51.04
	k_L (L/mg)	0.19	0.13	0.11	0.25
	R^2	0.999	0.997	0.999	0.999
Freundlich	n	41.17	33.65	3.68	25.52
	K_f	2.3	1.83	2.18	2.7
	R^2	0.966	0.943	0.963	0.989

concentrations, the available exchange sites became fewer, and subsequently, a decrease in removal rate is observed.

The presence of chloride or sulfate ions has no effect on chromate removal for initial concentration less than 100 mg/L. However, at higher concentration, an enhancement is observed in the presence of chloride.

The plot of the relation between the amount adsorbed and the residual concentration named equilibrium isotherm describes how solutes interact with the solid surface. Whatever the pH and the foreign ion, the obtained experimental curves illustrated in Fig. 10 show the same tendency of chromate removal.

The application of Langmuir and Freundlich equations (Eqs. (6) and (7)) to the obtained results (Figs. 11 and 12) gives the parameters summarized in Table 4.

$$\frac{C_{eq}}{q} = \frac{1}{q_{max} \cdot K_L} + \frac{C_{eq}}{q_{max}} \tag{6}$$

$$\ln q = \ln K_F + n \ln C_{eq} \tag{7}$$

The correlation coefficients values indicate that the two models can be used for describing the experimental data. These results are in agreement with that found about chromium retention by several resins [19–21]. The calculated exchange capacities indicate that the effect of pH is more important than that of the competing ions.

The results of the present study reveal that the chromate exchange capacity of A21 is higher than that obtained using several other weak resins (Table 5).

Table 5 Comparison of Amberlite A21 chromate exchange capacity with other resins

Resin	pH	q_{max} (mg Cr(VI)/g)	Reference
Amberlite IRA96	5	23.9	[14]
Lewatit MP 64	5	20.8	[15]
Lewatit MP 62	5	20.8	[7]
Amberlite A21	3.3	106.1	This work
	6.8	51.1	

4. Conclusion

The adsorption efficiency of A21 toward chromate ions exceeds 95% within a pH range 3–4. The kinetics exchange is well described by the first-order model. The chromate diffusion mechanism is mainly external. The adsorption capacity obtained from the Langmuir isotherm model is about 220 mg/g at pH 3.3. The effect of pH is more important than the effect of the presence of competing ions. At acidic pH, Amberlite A21 is suitable for chromium removal from wastewater containing chloride and sulfate ions.

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