Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.929037

55 (2015) 1840–1850
August

Taylor & Francis
Taylor & Francis Group

Comparison study on Cr(VI) removal by anion exchange resins of Amberlite IRA96, D301R, and DEX-Cr: isotherm, kinetics, thermodynamics, and regeneration studies

Xiaoqian Liu, Yan Li, Can Wang*, Min Ji

School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China, Tel./Fax: 86 22 2740 6057; emails: yuchi1126@163.com (X. Liu), libaolanse@163.com (Y. Li), wangcan@tju.edu.cn (C. Wang), jimin@tju.edu.cn (M. Ji)

Received 2 January 2014; Accepted 21 May 2014

ABSTRACT

The adsorption of Cr(VI) by three resins of Amberlite IRA96, D301R, and DEX-Cr was studied under varying experimental conditions including pH, resin amount, contact time, and temperature. The results showed that the maximum removal could be achieved at pH 3 for the three resins. The removal efficiencies of Cr(VI) by the resins all increased with increasing the resin amounts, whereas the adsorption capacity decreased. DEX-Cr presented the highest adsorption capacity (248 mg/g) and the longest equilibrium time (80 min). The resins all processed well at high temperature but presented different tolerance to temperature changes, which was dependent on moisture holding capacity. The thermodynamic results indicated that the uptake of Cr(VI) was endothermic and spontaneous. The adsorption equilibrium of DEX-Cr and D301R fit well with Freundlich and Langmuir isotherm, respectively, while Amberlite IRA96 showed better correlation to both two models. Kinetic analysis indicated that the adsorption followed both first-order and second-order equations. Intraparticle diffusion and chemical reaction were the rate-limiting steps. Desorption study revealed the addition of NaCl to NaOH helped improve desorption efficiency significantly, and the optimal dosage of the eluant was 6% NaOH (mass fraction) with 10% NaCl (mass fraction).

Keywords: Cr(VI) removal; Anion exchange resin; Adsorption isotherms; Adsorption kinetics; Desorption

1. Introduction

Industrial wastewater often contains considerable amount of heavy metals that would endanger the environment and public health if discharged without reasonable treatment. Major anthropogenic sources of heavy metals in the environment include metal extraction, metal fabrication and surface finishing, paints and pigments as well as manufacture of batteries [1]. Electroplating waste, which generates a large amount of liquid, is a major contributor to hexavalent chromium [Cr(VI)] pollution [2]. Cr(VI) is a strong oxidizing agent that irritates plant and animal tissues, carcinogenic and mutagenic, and has an adverse potential to modify DNA transcription. Therefore, it is important to reduce the amount of Cr(VI) to a permissible limit before discharging into natural water streams [3,4].

Several studies that considered Cr(VI) removal using phytoextraction, reverse osmosis, adsorption,

---

*Corresponding author.

precipitation, ion exchange, membrane, and biological technologies have been reported [5–9]. Among these technologies, ion exchange has been widely used during the past several decades owing to its advantages of metal value recovery, selectivity, less sludge produced, and the meeting of strict discharge specifications [10]. The synthetic anion resin employed in ion exchange technology in general can be classified into strongly basic anion and weakly basic anion resin, and the latter type is preferred due to its better regeneration efficiency [11]. Styrene polymers are one of the most popular precursor copolymers for synthetic anion exchange resin with different functionalities and morphologies [12]. The resins based on styrene–divinylbenzene copolymer bearing amine groups have attracted great attention. Gode and Pehlivan [13] studied the adsorption behavior of Cr(VI) by two Lewatit-anion exchange resins (Lewatit MP 62 and Lewatit 610) which contain tertiary amine group. It was observed that the maximum adsorption capacity of 0.40 mmol of Cr(VI)/g for Lewatit MP 62 and 0.41 mmol of Cr(VI)/g for Lewatit 610. Mustafa et al. [14] conducted Cr(VI) removal experiments with Amberlite IRA-400 and Dowex 1 × 8 [15], respectively, where the resins containing quaternary amine group were used. The results showed that the Cr(VI) adsorption capacity of 0.32 and 0.54 mmol/g were achieved, respectively.

These involved resins have the function group of tertiary amine or quaternary amine group. The superiority of the resins with both tertiary and quaternary amine groups in the removal of Cr(VI) has also been reported. Pehlivan and Cetin [16] found that the resin Lewatit MP 64 with tertiary and quaternary amine groups achieved maximum Cr(VI) adsorption much more quickly than Lewatit MP 500 with single quaternary amine group. The new acrylic anion resin with tertiary amine, quaternary amine, and ketone groups also showed the advantages in cyclic application in the research of Wójcik et al. [17]. DEX-Cr, which is used in this study, is a new type of anion exchange resin that has both tertiary and quaternary amine groups as its function groups. The appropriate mixed ratio of these two groups makes the adsorption capacity significantly higher than that of other resins which only have a single group.

This study aims to compare the adsorption behavior of DEX-Cr with the resin Amberlite IRA96 and D301R which contain single quaternary amine group. The single factor experiments were conducted to investigate their adsorption ability. Moreover, the adsorption isotherms, kinetics, and thermodynamics, as well as desorption properties of the resins, were studied.

2. Experiment

2.1. Experimental materials

The anion-exchange resin Amberlite IRA96, D301R, and DEX-Cr used in this study were purchased from Nankai Chem. Co. and Zhengzhou Qinshi Technology Co., Ltd, respectively. The main properties and specifications are shown in Table 1. Cr(VI) stock solution was prepared from dissolving potassium salts of dichromate using distillated water. The NaOH and HCl solution (0.01 mol/L) was used for pH adjustment. All the chemical reagents used in this study were of AR grade.

2.2. Experimental methods

Prior to use, the three resins were all conditioned with 10% NaCl (mass fraction), 4% HCl (mass fraction), and 4% NaOH (mass fraction) for several hours in order to remove inorganic and organic matter. After these steps, the three resins were transformed into hydroxylated resin.

The batch adsorption experiments were conducted with 50 mL Cr(VI) solution of 2,000 mg/L in a conical

Table 1
Physicochemical properties of Amberlite IRA96, D301R and DEX-Cr

Resin	Amberlite IRA96	D301R	DEX-Cr
Matrix	Macroporous styrene divinylbenzene copolymer	Macroporous styrene divinylbenzene copolymer	Macroporous styrene divinylbenzene copolymer
Functional groups	Tertiary amine group	Tertiary amine group	Tertiary and quaternary amine groups
Moisture holding capacity (%)	60 (57–63)	53 (48–58)	55 (50–60)
Shipping weight (g/mL)	0.61–0.68	0.65–0.72	0.65–0.72
Specific gravity (g/mL)	1.04–1.06	1.03–1.06	1.03–1.06
Uniformity coefficient	≤1.5	≤1.6	≤1.6
Particle size (mm)	0.7 (0.6–0.8)	0.78 (0.315–1.25)	0.55 (0.4–0.7)

flask placed in a thermostatic oscillator at the rotational speed of 140 r/min. The effects of pH, resin amount, contact time, and temperature on Cr(VI) adsorption were investigated by ranging their values within an appropriate range.

Desorption experiments were conducted using eluant containing NaOH and NaCl. Various mass fractions of NaOH mixed with NaCl were used to release the adsorbed Cr(VI) from resin. Eluant of certain volume was added to 0.2 g exhausted resin for 2 h with thermostatic shaking at temperature 35℃.

2.3. Analytical methods

Filtration was necessary for separating resin from solution. An atomic adsorption spectrometry named WFX-130 A A Spectrophotometer (China) was used for metal analysis with a chromium hollow cathode lamp at the wavelength of 359.3 nm. The total adsorbed Cr(VI) amount (Q_t, mg/g) was calculated according to concentration of Cr(VI) in the initial solution and filtrate [18]. Desorption efficiency was calculated according to the concentration of Cr(VI) in desorption solution and the saturated adsorption capacity of resins [19,20].

3. Results and discussion

3.1. Effects of initial pH on Cr(VI) removal

The existing forms of Cr(VI) in the aqueous solution involve H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^-$, and $Cr_2O_7^{2-}$. The exactly existed species depend on both solution pH and Cr(VI) concentration. It has been reported that only CrO_4^{2-} ions exist in the solution throughout the experimental concentration range when pH > 6.5. In the pH range from 0 to 6.5, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are predominant [21]. This phenomenon makes that the acidic condition is more beneficial for Cr(VI) uptake than the alkali condition [16]. Moreover, higher pH value is not preferable due to the Cr(VI) precipitation. According to these findings, the pH value was ranged from 1 to 6 to investigate the effects of initial pH on Cr(VI) removal by the three resins.

Fig. 1 shows the uptake of Cr(VI) by the resins of Amberlite IRA96, D301R, and DEX-Cr as a function of initial pH. The pH value of the solution was an important factor that controlled the sorption of Cr(VI). The sorption of Cr(VI) by the three resins was clearly very favorable at pH 3. At this pH value, the surface of the resin was surrounded by hydrogen ions which could enhance the attractive force between Cr(VI) and the binding sites of the adsorbents [22]. At lower pH values (less than 3), the hydrogen ions would be excessive and competed with Cr(VI) for binding sites, which resulted in a decrease in Cr(VI) uptake [12].

Compared with the other two resins, DEX-Cr presented much better adsorption performance. When pH value was 3, the adsorption capacity was nearly 218 mg/g, which was higher than those of Amberlite IRA96 (182 mg/g) and D301 (201 mg/g). This result might be caused by the different structure of the three resins. DEX-Cr has both tertiary and quaternary amine group as its function groups, while the resin

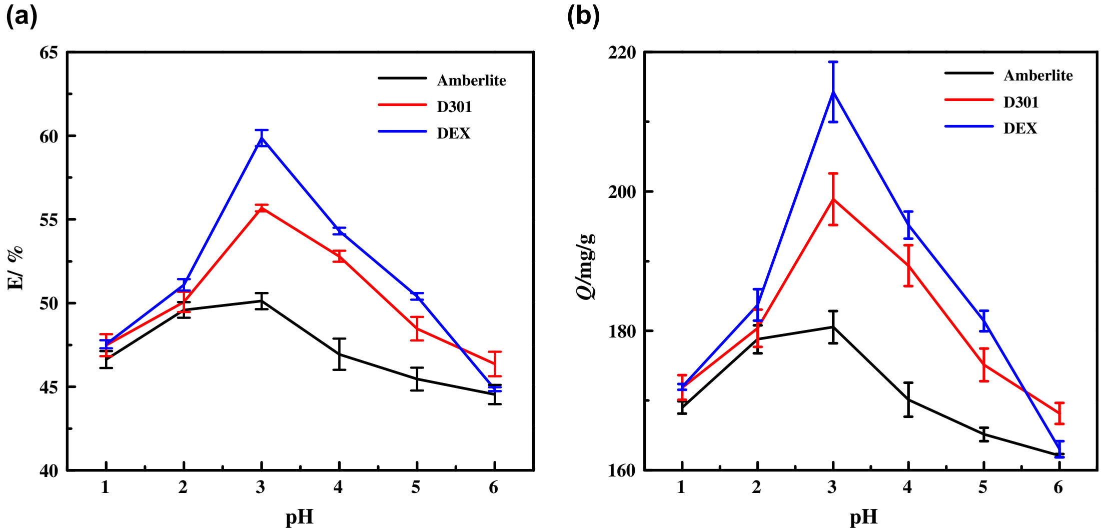

Fig. 1. The effects of initial pH on (a) adsorption capacity and (b) removal efficiency of Cr(VI) by Amberlite IRA96, D301R and DEX-Cr (conditions: initial concentration of Cr(VI), 2,000 mg/L; resin amount, 0.3 g; volume of adsorption medium, 50 mL; temperature, 35℃; contact time, 120 min; stirring rate, 140 rpm).

Amberlite IRA96 and D301R only have tertiary amine group. Moreover, higher moisture holding capacity of Amberlite IRA96 may tend to perturb the ions diffusion through the polymeric matrix of the resin (Intraparticle diffusion), which leads to an unsatisfactory performance.

3.2. Effects of resin amount on Cr(VI) removal

In order to investigate the effects of resin amount on Cr(VI) removal by Amberlite IRA96, D301R, and DEX-Cr the adsorption experiments were conducted with ranging the resin amounts from 2 to 14 g/L. It was apparently known from Fig. 2 that removal efficiency of Cr(VI) by Amberlite IRA96, D301R, and DEX-Cr all increased with increasing the resin amounts, whereas the adsorption capacity showed the opposite tread. The reason was that high amount of the resins could provide more available adsorption sites, which decreased the equilibrium concentrations and enhances the removal efficiencies [23,24]. On the other hand, high amount of the resins resulted in lower capacity since the number of the unsaturated adsorption sites increased [25].

The dosage of DEX-Cr played more important role than those of Amberlite IRA96 and D301R on the removal of Cr(VI). When the resin amount increased from 2 to 14 g/L, the removal efficiency of DEX-Cr went up from 53 to 96% (by 43%), while the removal efficiencies increased from 35 to 66% (by 21%) for Amberlite IRA96 and from 50 to 81% (by 31%) for D301R. It was easily understood that resin amount presented greater influence on Cr(VI) removal by the resin with higher adsorption capacity.

3.3. Effects of contact time on Cr(VI) removal

Fig. 3 illustrates the removal of Cr(VI) by the three resins as contact time function. The greatest adsorption rates could be readily observed within the first 20 min. After 20 min reaction, the removal efficiency of DEX-Cr had achieved more than 40% with the adsorption capacity of 146 mg/g. Meanwhile, the Cr(VI) removal values of Amberlite IRA96 and D301R were only 30%, and the adsorption capacities were lower than 115 mg/g. Although, both the Cr(VI) removal efficiency and adsorption capacity of all the resins kept increasing with adsorption progressing, the adsorption rates slowed down gradually. The reaction of Amberlite IRA96 and D301R attained equilibrium when the contact time reached 60 min. On that occasion, the adsorption capacities of Amberlite IRA96 and D301R were 158 and 176 mg/g, respectively, and their removal efficiencies were both below 50%. However, the Cr(VI) removal by DEX-Cr still kept running. After 80 min, DEX-Cr presented an adsorption capacity of 200 mg/g and 68.4% removal efficiency. From then on, the Cr(VI) removal by DEX-Cr also attained equilibrium, and its value did not change conspicuously.

3.4. Effects of temperature and thermodynamics analysis

Fig. 4 shows the effects of temperature on Cr(VI) adsorption by Amberlite IRA96, D301R, and DEX-Cr.

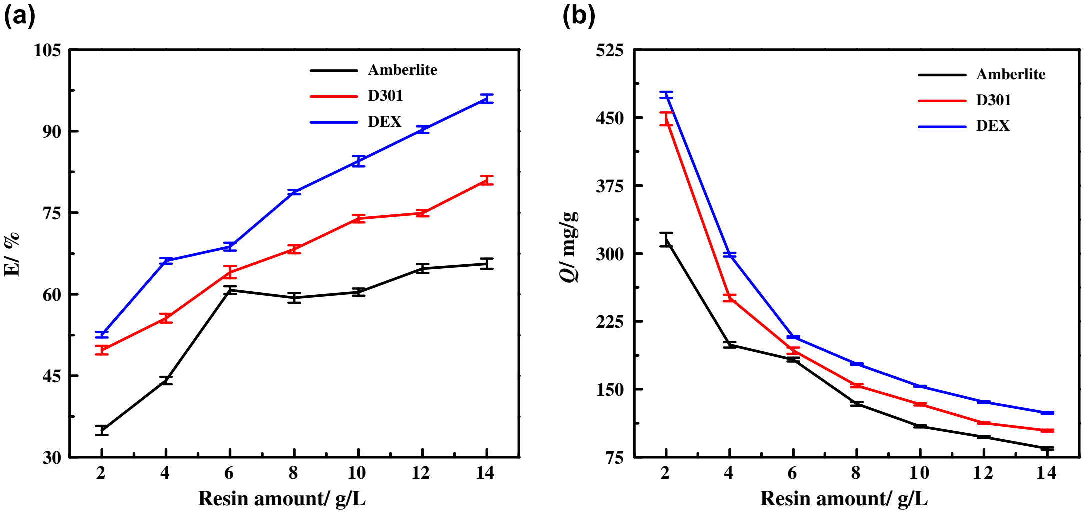

Fig. 2. The effects of resin amount on (a) adsorption capacity and (b) removal efficiency of Cr(VI) by Amberlite IRA96, D301R and DEX-Cr (conditions: initial concentration of Cr(VI), 2,000 mg/L; initial pH, 3; volume of adsorption medium, 50 mL; temperature, 35℃; contact time, 120 min; stirring rate, 140 rpm).

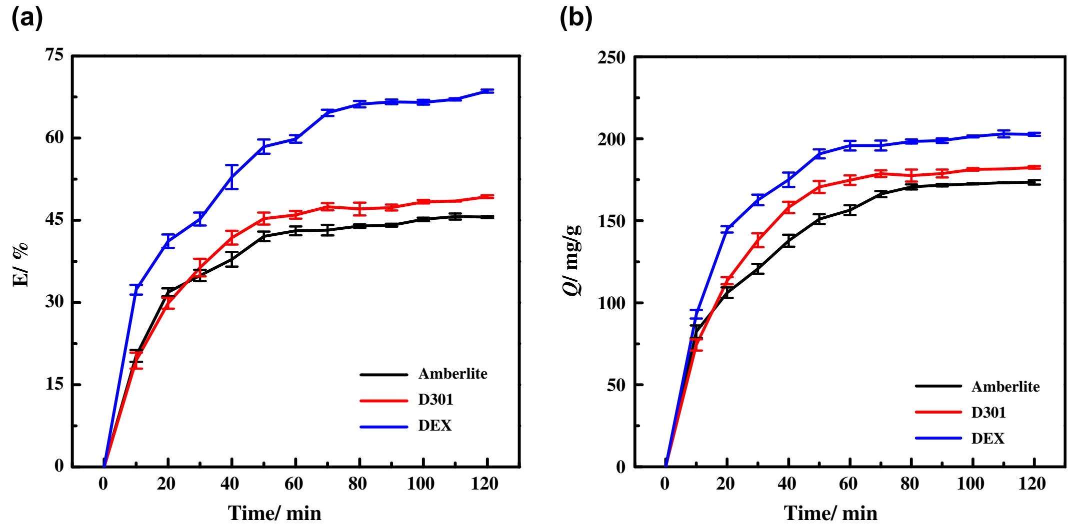

Fig. 3. The effects of contact time on adsorption of Cr(VI) by Amberlite IRA96, D301R and DEX-Cr (conditions: initial concentration of Cr(VI), 2,000 mg/L; initial pH, 3; resin amount, 0.3 g; volume of adsorption medium, 50 mL; temperature, 35℃; stirring rate, 140 rpm).

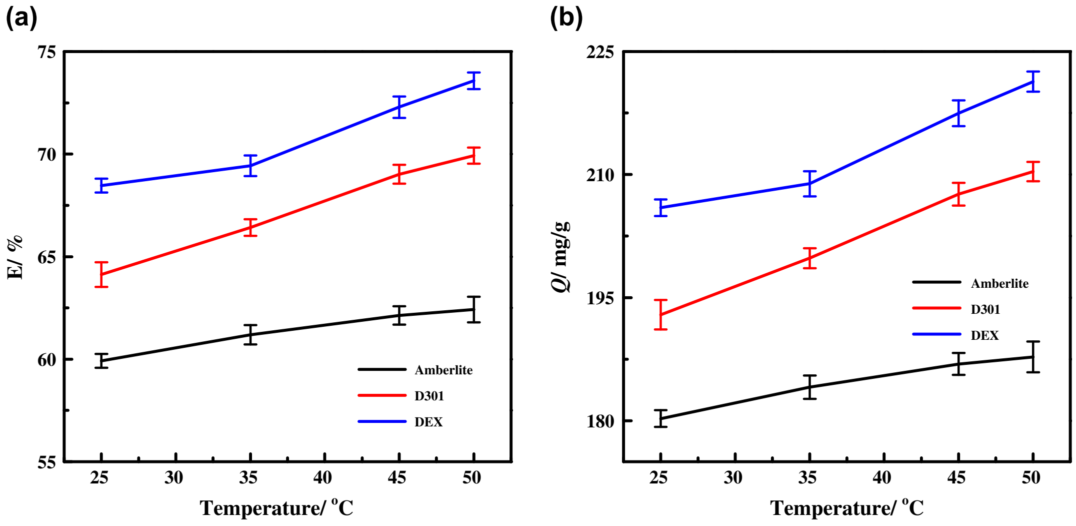

Fig. 4. The effects of temperature on adsorption of Cr(VI) by Amberlite IRA96, D301R and DEX-Cr (conditions: initial concentration of Cr(VI), 2,000 mg/L; initial pH, 3; resin amount, 0.3 g; volume of adsorption medium, 50 mL; contact time, 120 min; stirring rate, 140 rpm).

The experiments were conducted with varying temperature from 25 to 50℃. Apparently, the equilibrium level of D301R and DEX-Cr increased with increasing temperature, suggesting that the Cr(VI) adsorption process was endothermic. However, this trend did not reflect obviously in the resin of Amberlite IRA96, which might be due to the high-moisture holding capacity (Table 1). The resins with high-moisture holding capacity were more inclined to maintain high-water content and presented high tolerance to temperature changes [26]. Therefore, Amberlite IRA96 demonstrated relatively stable performance under various temperatures.

The adsorption thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) can be calculated by following equations [13]:

$$K_{\mathrm{C}} = \frac{C_{\mathrm{Ae}}}{C_{\mathrm{e}}} \tag{1}$$

$$\Delta G = -RT \ln K_C \tag{2}$$

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{3}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L), and C_{Ae} is the solid-phase concentration at equilibrium (mg/L).

The linear plot of log K_c against $1/T$ can be used to calculate the value of thermodynamic parameters ΔG, ΔH, and ΔS (Table 2). The calculated ΔH values of Cr(VI) adsorption by Amberlite IRA96, D301R, and DEX-Cr were all positive, which indicated that the adsorption is endothermic. This result explained the positive effects of temperature on Cr(VI) removal: the higher the temperature was, the more easily the adsorption developed. ΔS was positive, which implied that the degree of freedom increased at the solid–liquid interface during the adsorption process. The negative values of ΔG under various temperatures reflected the adsorption of Cr(VI) could take place spontaneously.

3.5. Adsorption isotherms

Adsorption isotherms can be used to describe how solutes interact with the resin in the equilibrium. Langmuir and Freundlich isotherms are two kinds of frequently used models. Such isotherms depict the relationship between the amount exchange (Q_e) and the remaining concentration (C_e) in solution. In this study, the Cr(VI) uptake per unit weight of resin was related to the equilibrium Cr(VI) concentration.

The general forms of Langmuir and Freundlich models are described as follows [27]:

Langmuir equation:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_mC_e} \tag{4}$$

where Q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium Cr(VI) concentration in solution (mg/L), and the Langmuir constants Q_m and b represent the maximum adsorption capacity (mg/g) and the adsorption energy (L/mg), respectively.

Freundlich equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where K_F (mg/g) and $1/n$ provide an indication of the adsorption capacity and the adsorbent intensity, respectively.

The results of experimental data fitting for the two models are shown in Fig. 5(a) and (b). The parameters correlated with the isotherms are shown in Table 3. For DEX-Cr, Freundlich model was more appropriate to describe Cr(VI) uptake process than Langmuir model, since the correlation coefficient (R^2) value of Freundlich model was closer to 1. For D301R, the experimental data showed more satisfactory correlation with Langmuir model for the whole concentration range. But for Amberlite IRA96, the R^2 values of Langmuir equation and Freundlich equation were both greater than 0.9, indicating that the two models were both appropriate to describe the data.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites [28], while the Freundlich model depicts multilayer adsorption well on an energetically heterogeneous surface [23]. Better correlation with Freundlich model indicated that a multilayer adsorption process occurred for the resin DEX-Cr, while the Cr (VI) was adsorbed in a monolayer on the interface of D301R.

According to the equilibrium experimental results, the adsorption capacities of the three resins increased with increasing the Cr(VI) concentration, and then became equilibrium gradually. The maximum hexavalent Cr(VI) adsorption capacity of resin Amberlite IRA96, D301R, and DEX-Cr at pH 3 was 194, 206, and 248 mg/g, respectively. At the initial Cr(VI)

Table 2
Thermodynamic parameters for the adsorption of hexavalent Cr by Amberlite IRA96, D301R and DEX-Cr

			ΔG/J mol			
Resin	ΔH/J mol	ΔS/J mol K	T = 298 K	T = 308 K	T = 318 K	T = 323 K
Amberlite IRA96	2,237.4	25.163	−5,259.7	−5,525.3	−5,769.1	−5,889.3
D301R	5,700.7	37.700	−5,549.1	−5,896.0	−6,305.3	−6,481.5
DEX-Cr	5,918.4	39.371	−5,858.1	−6,145.4	−6,608.4	−6,833.3

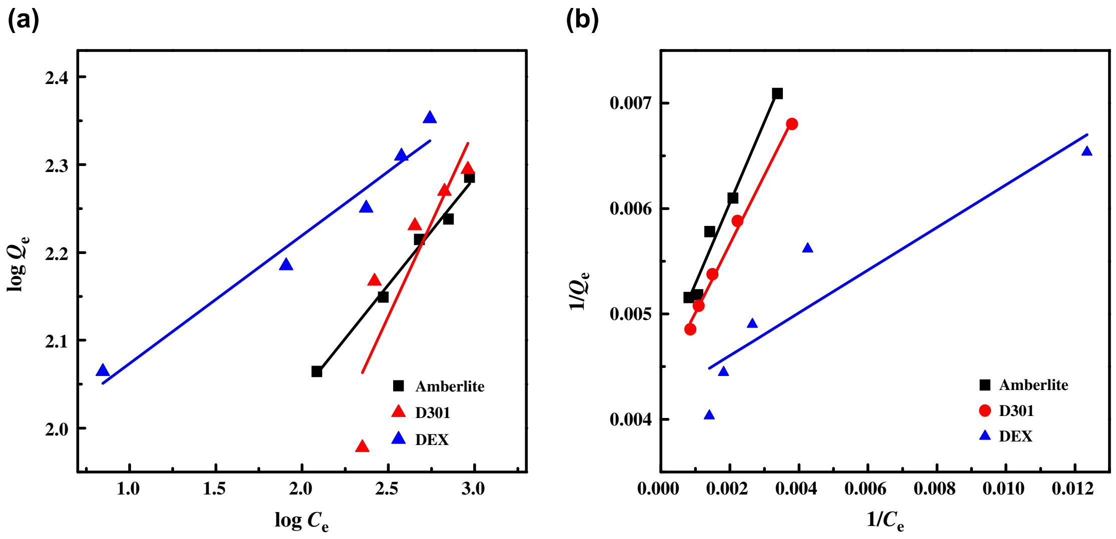

Fig. 5. (a) Freundlich and (b) Langmuir plot for adsorption of Cr(VI) on Amberlite IRA96, D301R and DEX-Cr.

Table 3
Parameters of isotherms for adsorption of Cr by Amberlite IRA96, D301R and DEX-Cr

	Freundlich model			Langmuir model		
Resin	K_F	n	R^2	b	Q_m	R^2
Amberlite IRA96	35.48	4.077	0.9877	0.00589	221.2	0.9703
D301R	11.49	2.343	0.6862	0.00669	229.4	0.9931
DEX-Cr	84.71	6.862	0.9524	0.02074	238.1	0.8026

concentration range of 700–2,200 mg/L, DEX-Cr definitely showed the best adsorption property.

3.6. Kinetic analysis

Kinetic analysis helps to reveal the transport mechanisms and potential rate-controlling steps in adsorption process. The pseudo-first-order and second-order equations were used to test the experimental data for understanding Cr(VI) uptake rate.

The pseudo-first-order equation of Lagergren is generally expressed as follows [29]:

$$\frac{dQ}{dt} = k_1(Q_e - Q) \tag{6}$$

This equation can be integrated using the initial condition $q = 0$ when $t = 0$, obtaining:

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{7}$$

where Q_e and Q_t are the adsorption capacities at equilibrium and at time t, respectively, (mg/g) and k_1 is the rate constant of the pseudo-first-order adsorption (L/min).

If the adsorption rate is a second-order mechanism, the pseudo-second-order kinetic rate equation is expressed as [29]:

$$\frac{dQ}{dt} = k_2(Q_e - Q)^2 \tag{8}$$

Integrating this equation by boundary conditions for $t = 0$, $q = 0$ gives:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + Q_e k_2 t} \tag{9}$$

The plot of Q_t against t for the first- and second-order equations in terms of Cr(VI) adsorption on resin Amberlite IRA96, D301R, and DEX-Cr was analyzed, and the results were shown in Fig. 6. The parameters calculated by both pseudo-first-order and second-order adsorption kinetics are shown in Table 4.

The correlation coefficients (R^2) of the pseudo-first-order and second-order non-linear plots for the resin

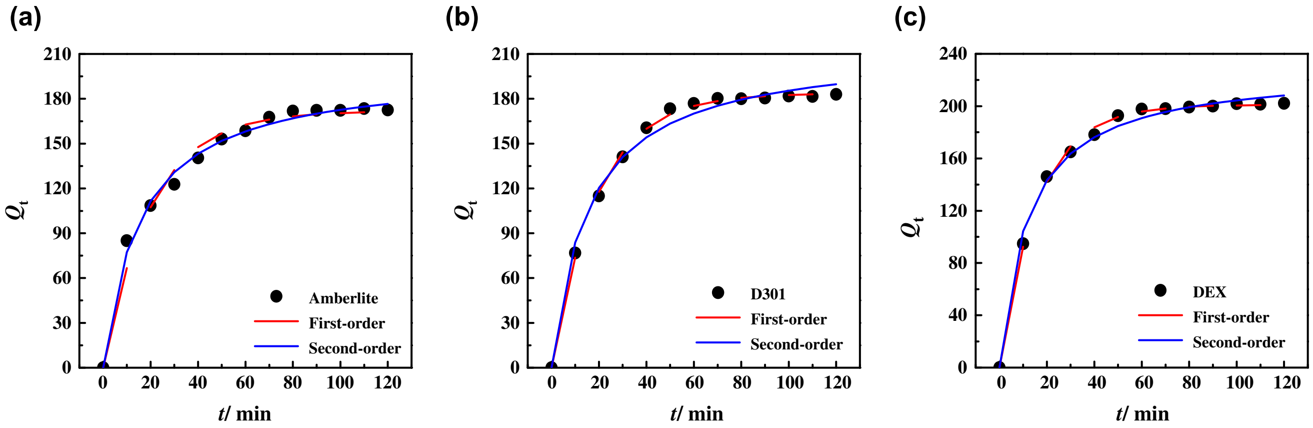

Fig. 6. Pseudo first-order and pseudo second-order sorption kinetics of Cr(VI) on (a) Amberlite IRA96, (b) D301R and (c) DEX-Cr.

Table 4
Kinetic model parameters for Cr adsorption by Amberlite IRA96, D301R and DEX-Cr

	Pseudo first-order equation			Pseudo second-order equation		
Resin	Q_e (mg/g)	R^2	k_1	Q_e (mg/g)	R^2	k_2
Amberlite IRA96	171.7	0.9803	0.0491	199.9	0.9924	0.0003162
D301R	183.6	0.9386	0.0513	214.4	0.9884	0.0002984
DEX-Cr	201.0	0.9979	0.0616	228.8	0.9923	0.0003661

Amberlite IRA96, D301R, and DEX-Cr were all greater than 0.9, which indicated that both first-order and second-order equations were fit to describe Cr(VI) uptake onto the three resins. However, the facts of R^2 values of pseudo-second-order being closer to 1 and the adsorption capacities calculated by pseudo-second-order equation being more consistent with the experimental results (Section 3.5) could also be observed from Table 4.

3.7. Analysis of rate-limiting step

Adsorption in heterogeneous process between solids and liquids, such as the uptake of Cr(VI) onto the

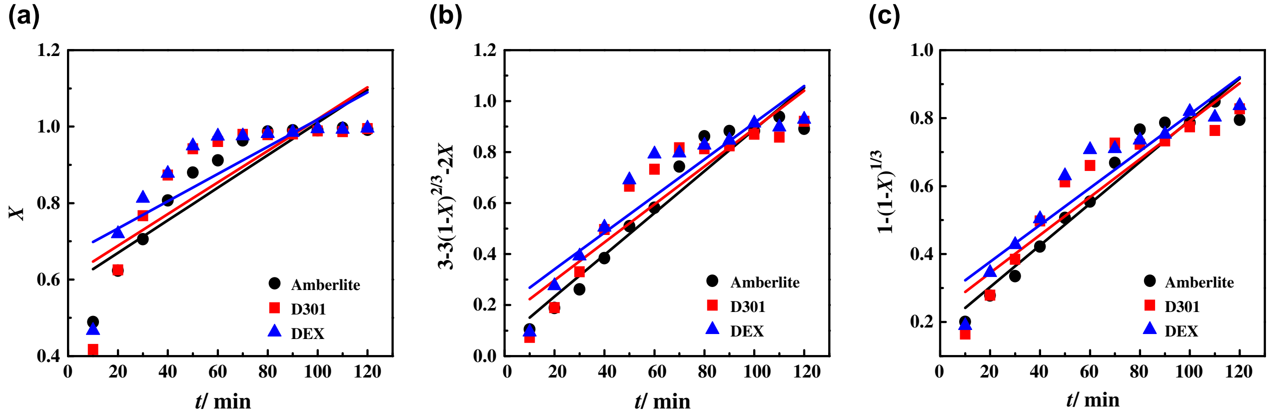

Fig. 7. Reaction process analysis of (a) Amberlite IRA96, (b) D301R and (c) DEX-Cr.

resin Amberlite IRA96, D301R, and DEX-Cr can be explained through three sequential processes that determine the rate of the reaction: (a) diffusion of Cr (VI) through the liquid film surrounding the particle, (b) diffusion of Cr(VI) through the polymeric matrix of the resin and (c) chemical reaction (CR) with the function groups attached to the matrix. If one of the steps offers much greater resistance than the others, it can be considered as the rate-limiting step of the reaction [28]. Therefore, the three processes can be defined as: (a) liquid film diffusion control step (LFDC), (b) particle diffusion control step (PDC) and (c) CR step.

Shell progressive model that describes the relationship between contact time (t) and adsorption degree ($X = Q_t/Q_e$) has been widely used to analyze the rate-limiting step by fitting ion exchange data, and the results can be expressed as follows [30]:

(a) LFDC: X and t presents good linear relationship.
(b) PDC: $[3-3(1-X)^{2/3}-2X]$ and t presents good linear relationship.
(c) CR: $[1-(1-X)^{1/3}]-t$ and t presents good linear relationship.

Table 5
The fitting results of LFDC, PDC and CR equation for Amberlite IRA96, D301R and DEX-Cr

	Values of correlation coefficients (R^2)		
Resin	LFDC	PDC	CR
Amberlite IRA96	0.7896	0.9252	0.9349
D301R	0.6310	0.8434	0.8583
DEX-Cr	0.6061	0.8483	0.8714

Experiments under the rotation speed of 140 rpm were conducted to evaluate the Cr(VI) adsorption, shown in Fig. 7 and Table 5. The relatively low-correlation coefficients of LFDC equation for the three resins suggested that the liquid film diffusion was not the rate-limiting step of Cr(VI) adsorption. However, the good fit to PDC equation and CR equation for the resin Amberlite IRA96, D301R, and DEX-Cr indicated

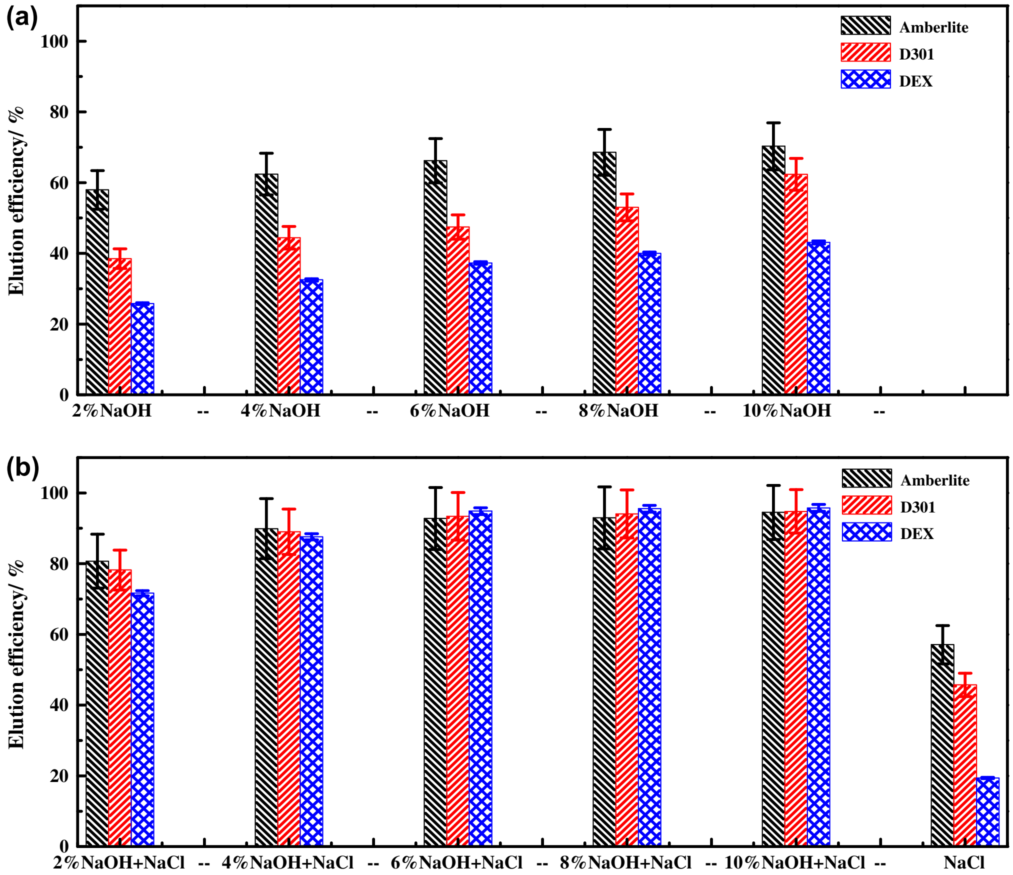

Fig. 8. Desorption efficiency of Cr(VI) by using eluant of (a) NaOH and (b) NaOH combined with NaCl (conditions: eluant volume, 2 mL; resin amount, 0.2 g; temperature, 35℃; contact time, 120 min).

that the particle diffusion through the polymeric matrix of the resin (Intraparticle diffusion) and CR between the Cr(VI) anion and the resin controlled the adsorption collectively. It is easily understood that Cr (VI) anion diffuses fast through the solution under high-rotation speed, thus the intraparticle diffusion and CR become the rate-limiting steps.

3.8. Desorption experiment

The desorption of Cr(VI) from Amberlite IRA96, D301R, and DEX-Cr was studied using NaOH alone or mixed with NaCl (10%, mass fraction), as shown in Fig. 8.

Although increasing the NaOH concentration could improve desorption efficiency (Fig. 8(a)), the overall values of all the resins using NaOH as the standalone eluant were below 65%. Adding NaCl (10%) to the NaOH solution, the desorption efficiencies of the three resins all improved dramatically. This phenomenon was particularly obvious on the Cr(VI) extraction from DEX-Cr. Desorption efficiencies of DEX-Cr by the combination of NaOH and NaCl were higher than 70%, and the maximum value even reached as high as 95%. The desorption efficiencies grown up with the increase of the mass fraction of NaOH (from 2 to 6%) when mixed with NaCl. However, further increase in the mass fraction of NaOH (higher than 6%) did not result in a continuous increase of desorption efficiencies. Therefore, the optimal combination of eluant was determined as 6% NaOH with 10% NaCl.

Furthermore, the test of Cr(VI) desorbed by standalone 10% NaCl solution presented quite low-desorption efficiencies. These results indicated that the high-desorption efficiency could not be attributed to NaCl but to the combination of NaOH and NaCl. Such synergistic effect was mainly due to that the NaCl solution was utilized to remove the inorganic contaminants inside the resins, while the NaOH solution was used to dissolve the organic contaminants from resins [23].

4. Conclusions

The Cr(VI) removal by the resins of Amberlite IRA96, D301R, and DEX-Cr was evaluated. The results showed that the resins all performed high-adsorption behavior at the pH of 3. DEX-Cr, having both tertiary and quaternary amine groups as function groups, showed the fastest adsorption rate and longest equilibrium time among the three resins. D301R performed better than Amberlite IRA96 in the single factor experiments could ascribe to its low-moisture content that provides less resistance in intraparticle diffusion. High temperature resulted in enhancement of removal performance for the resins. However, Amberlite IRA96 presented high tolerance to temperature changes due to its high-moisture holding capacity. The thermodynamic results indicated that the adsorption process was endothermic and the degree of freedom increased at the solid–liquid interface. The negative values of ΔG reflect the adsorption of Cr(VI) could take place spontaneously.

The Freundlich isotherm is more efficient in describing the Cr(VI) removal by DEX-Cr, while the Langmuir model is more applicable for Cr(VI) adsorption process by D301R. Both Freundlich and Langmuir model fitted the data of Amberlite IRA96 well. Kinetic analysis showed both first-order and second-order equations could describe the Cr(VI) adsorption by the three resins. Intraparticle diffusion and CR might be the rate-limiting steps. Research on desorption of Cr (VI) from loaded resins suggested that the synergistic effect of NaOH and NaCl help to improve the desorption efficiencies dramatically. The optimal dosage of the eluant was 6% NaOH (mass fraction) with 10% NaCl (mass fraction).

Acknowledgments

The authors would like to thank the research funding program of the Key Technology Development and Demonstration of the Green Campus Construction and Management, China [grant number 2012BAC13B05].

References

[1] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87 (2001) 273–287.

[2] M. Ajmal, R.A. Khan Rao, B.A. Siddiqui, Studies on removal and recovery of Cr(VI) from electroplating wastes, Water Res. 30 (1996) 1478–1482.

[3] E. Korngold, N. Belayev, L. Aronov, Removal of chromates from drinking water by anion exchangers, Sep. Purif. Technol. 33 (2003) 179–187.

[4] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, Ind. Eng. Chem. Res. 34 (1996) 2612–2617.

[5] Y. Çengeloğlu, A. Tor, E. Kir, M. Ersöz, Transport of hexavalent chromium through anion-exchange membranes, Desalination 154 (2003) 239–246.

[6] E. Pehlivan, G. Arslan, Comparison of adsorption capacity of young brown coals and humic acids prepared from different coal mines in Anatolia, J. Hazard. Mater. 138 (2006) 401–408.

[7] K. Yamagiwa, T. Yamashita, T. Kamimura, T. Shimizu, A. Ohkawa, Recovery of hexavalent chromium ion from methanol with ion exchange resin, J. Chem. Eng. Jpn. 40 (2007) 447–453.

[8] B.J. Stoecker, Chromium absorption, safety, and toxicity, J. Trace Elem. Exp. Med. 12 (1999) 163–169.

[9] S. Chiarle, M. Ratto, M. Rovatti, Mercury removal from water by ion exchange resins adsorption, Water Res. 34 (2000) 2971–2978.

[10] S.A. Abo-Farha, A.Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, Removal of some heavy metal cations by synthetic resin purolite C100, J. Hazard. Mater. 169 (2009) 190–194.

[11] C. Balan, I. Volf, D. Bilba, Chromium(VI) removal from aqueous solutions by purolite base anion-exchange resins with gel structure, Chem. Ind. Chem. Eng. Q. 19 (2013) 619–628.

[12] B. Galán, M. Calzada, I. Ortiz, Separation and concentration of Cr(VI) from ground waters by anion exchange using Lewatit MP-64: Mathematical modelling at acidic pH, Solvent Extr. Ion Exch. 24 (2006) 621–637.

[13] F. Gode, E. Pehlivan, Removal of Cr(VI) from aqueous solution by two Lewatit-anion exchange resins, J. Hazard. Mater. 119 (2005) 175–182.

[14] S. Mustafa, T. Ahmad, A. Naeem, K.H. Shah, M. Waseem, Kinetics of chromium ion removal from tannery wastes using Amberlite IRA-400 Cl^- and its hybrids, Water Air Soil Pollut. 210 (2010) 43–50.

[15] S. Edebali, E. Pehlivan, Evaluation of Amberlite IRA96 and Dowex 1×8 ion-exchange resins for the removal of Cr(VI) from aqueous solution, Chem. Eng. J. 161 (2010) 161–166.

[16] E. Pehlivan, S. Cetin, Sorption of Cr(VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV–visible spectrophotometer, J. Hazard. Mater. 163 (2009) 448–453.

[17] G. Wójcik, V. Neagu, I. Bunia, Sorption studies of chromium(VI) onto new ion exchanger with tertiary amine, quaternary ammonium and ketone groups, J. Hazard. Mater. 190 (2011) 544–552.

[18] F. Chen, C. Zhou, G. Li, F. Peng, Thermodynamics and kinetics of glyphosate adsorption on resin D301, Arab. J. Chem. (2012).

[19] M. Srimurali, A. Pragathi, J. Karthikeyan, A study on removal of fluorides from drinking water by adsorption onto low-cost materials, Environ. Pollut. 99 (1998) 285–289.

[20] M.A. Khan, T.S.Y. Choong, T.G. Chuah, R. Yunus, Y.H.T. Yap, Desorption of β-carotene from mesoporous carbon coated monolith: Isotherm, kinetics and regeneration studies, Chem. Eng. J. 173 (2011) 474–479.

[21] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.

[22] C. Jung, J. Heo, J. Han, N. Her, S. Lee, J. Oh, J. Ryu, Y. Yoon, Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, Sep. Purif. Technol. 106 (2013) 63–71.

[23] Y.S. Ho, D.A. John Wase, C.F. Forster, Batch nickel removal from aqueous solution by sphagnum moss peat, Water Res. 29 (1995) 1327–1332.

[24] S. Kocaoba, G. Akcin, A kinetic investigation of chromium, Adsorption 9 (2003) 143–151.

[25] F. Gode, E. Pehlivan, Removal of chromium(III) from aqueous solutions using Lewatit S 100: The effect of pH, time, metal concentration and temperature, J. Hazard. Mater. 136 (2006) 330–337.

[26] H. Li, Z. Xia, G. Ma, Effects of water content variation on soil temperature process and water exchange, J. Hohai Univ. (Nat. Sci.) 35 (2007) 172–175 (in Chinese).

[27] D. Duranoğlu, İ.G. Buyruklardan Kaya, U. Beker, B.F. Şenkal, Synthesis and adsorption properties of polymeric and polymer-based hybrid adsorbent for hexavalent chromium removal, Chem. Eng. J. 181–182 (2012) 103–112.

[28] T. Shi, Z. Wang, Y. Liu, S. Jia, D. Changming, Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins, J. Hazard. Mater. 161 (2009) 900–906.

[29] R. Ocampo-Pérez, J. Rivera-Utrilla, C. Gómez-Pacheco, M. Sánchez-Polo, J.J. López-Peñalver, Kinetic study of tetracycline adsorption on sludge-derived adsorbents in aqueous phase, Chem. Eng. J. 213 (2012) 88–96.

[30] C. Valderrama, J.I. Barios, M. Caetano, A. Farran, J.L. Cortina, Kinetic evaluation of phenol/aniline mixtures adsorption from aqueous solutions onto activated carbon and hypercrosslinked polymeric resin (MN200), React. Funct. Polym. 70 (2010) 142–150.