Adsorption of metal anions of vanadium(V) and chromium(VI) on Zr(IV)-impregnated collagen fiber

Xue-Pin Liao · Wei Tang · Rong-Qing Zhou · Bi Shi

Abstract The metal anions of vanadium (V) and chromium (VI) in aqueous solution can be effectively adsorbed by Zr(IV)-impregnated collagen fiber (ZrICF). The maximum adsorption capacity of V(V) takes place within the pH range of 5.0 to 8.0, while that of Cr(VI) is within the pH range of 6.0 to 9.0. When the initial concentration of metal ions was 2.00 mmol L^{-1} and the temperature was 303 K, the adsorption capacity of V(V) on Zr-ICF was 1.92 mmol g^{-1} at pH 5.0, and the adsorption capacity of Cr(VI) was 0.53 mmol g^{-1} at pH 7.0. As temperature increased, the adsorption capacity of V(V) increased, while that of Cr(VI) was almost unchanged. The adsorption isotherms of the anionic species of V(V) and Cr(VI) can be fit by the Langmuir equation. The adsorption rate of V(V) follows the pseudo-first-order rate model, while the adsorption rate of Cr(VI) follows the pseudo-second-order rate model. Furthermore, ZrICF shows high adsorption selectivity to V(V) in the mixture solution of V(V) and Cr(VI). Practical applications of ZrICF could be expected in consideration of its performance in adsorption of V(V) and Cr(VI).

Keywords Zr(IV) · Collagen fiber · Adsorbent · Vanadium(V) · Chromium(VI) · Metal anion · Adsorption

Abbreviations
q_e Adsorption capacity at equilibrium (mmol g^{-1})
C_e Concentration at equilibrium (mmol L^{-1})
q_{max} Maximum adsorption capacity of metal anion (mmol g^{-1})
b Coefficient related to the strength of adsorption, $b = k_a/k_d$ (k_a is the rate constant of adsorption, k_d is the rate constant of desorption)
q_t Adsorption capacity (mmol g^{-1}) at time t (min)
k_1 Rate constant of pseudo-first-order rate model (min^{-1})
k_2 Rate constant of pseudo-second-order rate (mmol g^{-1} min^{-1})
k_i Intraparticle diffusion rate constant (mmol g^{-1} min$^{-0.5}$)

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1 Introduction

The discharge of heavy metals into water causes serious environmental problems. Heavy metals are not biodegradable and tend to accumulate in living organisms, leading to various diseases and disorders (Bailey et al. 1999). It has been reported that Cr(VI) is one of the undesirable heavy metals because it affects human physiology, accumulates in food chain, and causes several ailments (Park and Jung 2001). V(V) is a widely used metal and it should be recovered, though its toxicity is less established than that of Cr(VI). Therefore, the removal or recovery of Cr(VI) and V(V) from wastewaters is one of the most essential issues in view of environmental protection and conservation.

Many approaches have been practiced in eliminating heavy metal ions, like chemical precipitation, biological treatment, membrane filtration, ion exchange, adsorption, etc. Among these techniques, adsorption is the most common and cost-effective method in recovering and eliminating heavy metal ions from dilute solutions. The particular advantages of adsorption are its high selectivity for recovering precious metals, producing less sludge volume, and

being able to meet strict discharge specifications. The adsorption of V(V) and Cr(VI) in aqueous solutions by activated carbon (Park and Jung 2001), goethite (Caroline et al. 2004; Samad and Watson 1997; Lehmann et al. 2001), tannin gel (Nakajima and Baba 2004; Nakano et al. 2001; Nakajima 2002), exchange resins (Gode and Pehlivan 2005; Chassary et al. 2004; JanssonCharrier et al. 2001), agriculture by-products (Guo et al. 2002; Li et al. 2004), microorganism (Sheng et al. 2004) and other materials (Bailey et al. 1999) have been reported.

In general, V(V) and Cr(VI) exist as anions in aqueous solutions, and their adsorption behaviors are different from those of metal cations. In recent years, it has been found that Zr(IV), Al(III), Fe(III) and rare earth elements have specific affinity to inorganic anions, such as fluoride, phosphate and arsenic (Liu et al. 2002). Thus, adsorbents loaded with various rare earth compounds, Al(III), Fe(III) and Zr(IV) have been developed, and they have shown promising results in the removal of hazardous inorganic anions from wastewater (Wasay et al. 1996; Ghosh et al. 2003). It was reported that the adsorption capacity of fluoride on aluminumimpregnated carbon is 3 to 5 times higher than that of plain activated carbon (Leyva Ramos et al. 1999). It was also found that Fe(III)- and Zr(IV)-bearing materials exhibited a specific affinity to arsenic species and presented remarkable selectivity of adsorption (Munoz et al. 2002). However, the adsorption kinetics of absorbents prepared by loading metal ions onto the porous materials is still unsatisfactory.

Collagen fiber, an abundant natural biomass, comes from the skins of domestic animals and has been traditionally used as a raw material in leather manufacturing. As a kind of structural protein, the collagen molecule is composed of three polypeptide chains with a triple-helical structure, and they are aggregated through hydrogen bonds to form collagen fiber (Friess 1998). Collagen fiber is water-insoluble but is a hydrophilic material. According to the principles of leather processing, collagen fiber that has abundant functional groups is capable of chemically reacting with many kinds of metal ions, such as Cr(III), Al(III), Zr(IV), Fe(III), etc. (Evans et al. 1987).

Recently, fibrous adsorbents have received more attention because of their excellent kinetic characteristics, associated with their physico-chemical structure. The major advantages include a large specific surface, high swelling capacity, good mechanical strength, and convenient use (Liu et al. 2002). In fact, some fibrous adsorbents have been successfully used for removing metal ions (Shubo Deng and Renbi Bai 2004), dyes (Yoshida and Takemori 1997) and other pollutants from wastewater (Martin-Gulion and Font 2001). Therefore, excellent performance of fibrous adsorbents can be expected on the basis of collagen fiber.

It was indicated in our previous study that the Zr(IV)-impregnated collagen fiber (ZrICF) exhibits high adsorption capacity and excellent dynamic behavior in adsorption

of fluoride (Liao and Shi 2005). It could be inferred that V(V) and Cr(VI) anions would be well adsorbed by ZrICF. In this study, the fundamental adsorption aspects of V(V) and Cr(VI) on ZrICF, including the effect of pH and ionic strength on adsorption, adsorption isotherm, adsorption kinetics and adsorption selectivity, were investigated.

2 Materials and methods

2.1 Materials

$Zr(SO_4)_2$ was a commercial product and its content, expressed as ZrO_2, was 31.6% (wt%). NH_4VO_3, K_2CrO_4 and other chemicals were all analytical reagents.

Zr(IV)-impregnated collagen fiber (ZrICF) was prepared according to the procedures in our previous work (Liao and Shi 2005). The optimum reaction conditions of preparation ZrICF is as follows: 15.0 g collagen fiber was soaked in 400 ml distilled water for 24 h at room temperature. The pH of the distilled water was pre-adjusted to 1.8 to 2.0 by HCOOH and H_2SO_4 solutions. Then, 40.0 g of $Zr(SO_4)_2$ was added and reacted with constant stirring for 4 h at 30°. A proper amount of $NaHCO_3$ solution (15%, w/w) was gradually added within 2 h, in order to increase the pH of the solution to between 4.2 and 4.5, and then continued the reaction at 40° for another 4 h. When the reaction was completed, the product was collected by filtration, washed with distilled water and vacuum-dried at 50° for 12 h, and then the adsorbent in the form of Zr(IV) impregnated collagen fiber (ZrICF) was obtained.

DSC (Differential Scanning Calorimetry, DSC 200PC, NETZSCH, Germany) was used to determine the denaturation temperature of the raw collagen fiber and ZrICF adsorbent. The pH of point of zero charge (denoted as pH_{PZC}) of the adsorbent was determined by the solid addition method (Tripathy and Kanungo 2005). The other physical properties were determined by common methods. The physical properties of ZrICF were summarized in Table 1.

Table 1 Physical properties of ZrICF adsorbent

Item	Value
Particle size (mm)	0.1 to 0.25
Water content (wt%)	10 to 12
Specific area ($m^2\,g^{-1}$, BET)	2.07 to 3.87
Density (in dry state, $g\,cm^{-3}$)	0.89 to 0.95
Zr(IV) content ($mmol\,g^{-1}$)	6.667
pH_{PZC} (Solid added method)	10.3 to 10.7
Water absorptivity ($g\,H_2O\,g^{-1}$)	0.86 to 1.15
Denaturation temperature (K)	359 to 362

2.2 Effect of pH on adsorption capacity

Stock solutions of V(V) and Cr(VI) were prepared, respectively, with deionized water and were further diluted to desired concentrations for experiments. 0.100 g ZrICF adsorbent was suspended in 100 ml V(V) and Cr(VI) solutions, respectively, in which the concentration of V(V) or Cr(VI) was 2.00 mmol L^{-1}. The initial pH values of the V(V) and Cr(VI) solutions were adjusted to 3.0 to 11.5 with 0.1 M NaOH or 0.1 M HNO_3. A series of preliminary experiments was undertaken to determine the time required to reach adsorption equilibrium, and it was found that 8 h and 11 h were enough for the adsorption of Cr(VI) and V(V), respectively. Therefore, the adsorption experiments were conducted by constant shaking at 303 K for 24 h. At the end of adsorption, the concentrations of V(V) and Cr(VI) in the residual solutions were analyzed by ICP-AES (ICP, Perkin-Elmer Optima 2100DV, Germany). The adsorption capacities at different initial pH values were obtained by mass balance calculation. The content of Zr(IV) in residual solutions after adsorption was also determined by means of ICP.

2.3 Adsorption isotherms

0.100 g ZrICF adsorbent was suspended in 100 ml V(V) and Cr(VI) solutions, respectively. The concentrations of V(V) were 2.000, 3.000, 4.000, 5.000 and 6.000 mmol L^{-1}, respectively and the initial pH was 5.0. The concentrations of Cr(VI) were 0.40, 0.80, 1.20, 1.60 and 2.00 mmol L^{-1} respectively and the initial pH was 7.0. The adsorption temperature was 303 K, 313 K and 323 K, respectively. The adsorption time was 24 h. Determination procedures were the same as those in Sect. 2.2.

2.4 Effect of electrolyte on adsorption capacity

The adsorption procedures were similar to those in Sect. 2.3. But the concentrations of $NaNO_3$ in the solutions were 0.1, 0.5 and 1.0 mol L^{-1} respectively, and the adsorption trials were undertaken only at 303 K.

2.5 Adsorption capacity in buffer solutions

The adsorption procedures were similar to those in Sect. 2.3, but the adsorption tests of V(V) and Cr(VI) were undertaken in HAc-NaAc buffer solution (pH = 5.0) and triethanolamine-HCl buffer solution (pH = 7.0), respectively, at 303 K.

2.6 Adsorption kinetics

0.100 g ZrICF adsorbent was suspended in 100 ml V(V) and Cr(VI) solutions respectively. The procedures of adsorption kinetics investigations were similar to those in the

Sect. 2.3, but the concentrations of V(V) or Cr(VI) during these tests were analyzed at regular intervals. Each sample was analyzed three times and the resulting average value was adopted.

2.7 Adsorption selectivity

The mixture solutions of V(V) and Cr(VI) were prepared, in which the concentration of V(V) was 2.00 mmol L^{-1}, while the concentrations of Cr(VI) were 0, 0.40, 0.80, 1.20, 1.60 and 2.00 mmol L^{-1}, respectively. The pH of all the solutions was adjusted to 5.0 and the adsorption tests were undertaken at 303 K. The adsorption procedures were as the same as those in Sect. 2.3.

3 Results and discussion

3.1 Effect of pH on adsorption capacity

The effect of pH on the adsorption of anionic species of V(V) and Cr(VI) on ZrICF is shown in Fig. 1. The pH of aqueous solution is an important factor that influences the adsorption of metal anions at solid-liquid interfaces. The adsorption capacity of V(V) increased with pH at the beginning, and then attained a plateau in the pH range from 4.0 to 8.0. Afterwards, the adsorption capacity dramatically decreased. In the case of Cr(VI), the adsorption capacity gradually increased in the pH range from 3.0 to 7.0, and then slightly decreased in the pH range from 7.0 to 10.0. Afterwards, the adsorption capacity greatly decreased. The difference of the effect of pH on the adsorption of V(V) and Cr(VI) suggests that ZrICF has adsorption selectivity to different metal anions under proper conditions, and this property could be used for separation of V(V) from the mixture solution of V(V) and Cr(VI).

The pH-dependent adsorption behavior of V(V) and Cr(VI) on ZrICF is greatly related to the state of V(V) and Cr(VI) in aqueous solution. Thermodynamic calculations revealed that V(V) in aqueous solution exists predominately as $H_3V_2O_7^-$ in the pH range of 2.5 to 7.0 when the concentration of V(V) is 2.0 mmol L^{-1}, as shown in Fig. 2a. Therefore, it could be concluded that the single charged species ($H_3V_2O_7^-$) favors the adsorption of V(V) on ZrICF. However, the speciation of V(V) in aqueous solution is also related to the concentration of V(V). For example, when the concentration of V(V) is changed, the kind and their relative ratio of chemical species are also somewhat changed, as indicated by Caroline and Nakajima (Nakajima 2002; Caroline et al. 2004). Similar phenomena were also found for the speciation of Cr(VI) in aqueous solutions (Nakajima and Baba 2004; Hamadi et al. 2001).

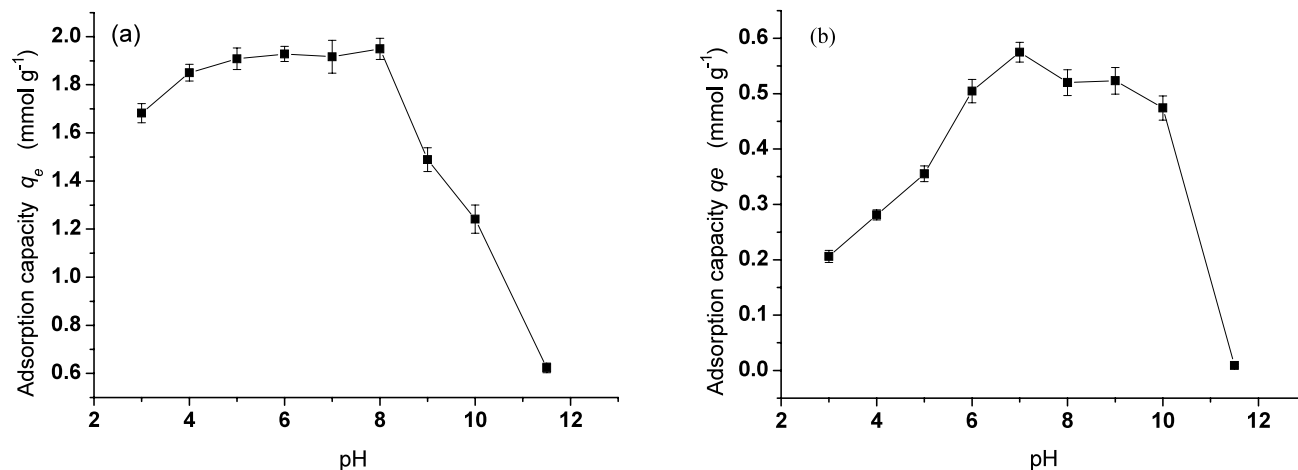In aqueous solutions, Cr(VI) exists mainly as $HCrO_4^-$ at pH < 6.0, while the predominant species of Cr(VI) is

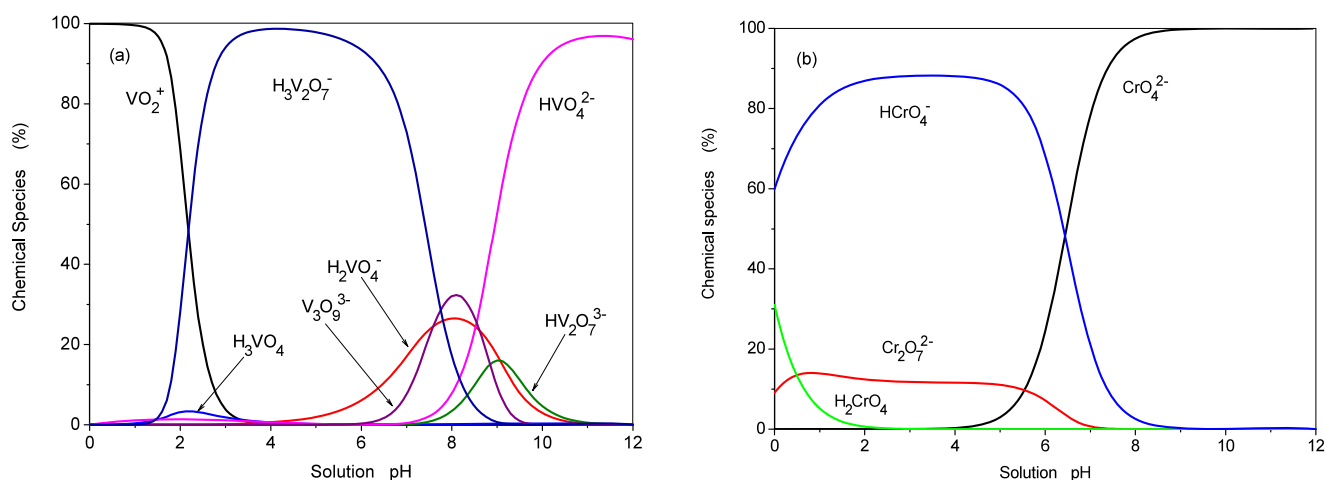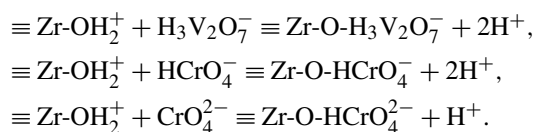**Fig. 1** Effect of pH on adsorption capacity. **a** V(V), **b** Cr(VI)

Fig. 2 Metal ion species in aqueous solution for (**a**) V(V) and (**b**) Cr(VI) (calculated by using Visual MINEQL ver. 2.40b, $C_{total} = 2.0$ mmol L^{-1})

CrO_4^{2-} at pH > 6.0 when the concentration of Cr(VI) is 2.0 mmol L^{-1}, as illustrated in Fig. 2b. Combined with Fig. 1b, it can be inferred that the adsorption of Cr(VI) on ZrICF is favored as CrO_4^{2-} even though significant adsorption is observed for $HCrO_4^-$. However, apparently due to the competitive adsorption of hydroxyl ions, the adsorption capacity was greatly decreased with further increase of pH, as shown in Fig. 1b.

The pH$_{PZC}$ (point of zero charge) of ZrICF is around 10.5, which implies that the outer surface of ZrICF is positively charged at lower pH. In addition, the pH values of the solutions all decreased after adsorption, as shown in Fig. 3. The pH decrease during adsorption indicates that protons are exchanged. Therefore, an ion exchange mechanism can be suggested for the adsorption of V(V) and Cr(VI) on ZrICF. The ion exchange mechanism might be suggested as the following scheme, but it needs further study:

$$\equiv Zr\text{-}OH_2^+ + H_3V_2O_7^- \equiv Zr\text{-}O\text{-}H_3V_2O_7^- + 2H^+,$$
$$\equiv Zr\text{-}OH_2^+ + HCrO_4^- \equiv Zr\text{-}O\text{-}HCrO_4^- + 2H^+,$$
$$\equiv Zr\text{-}OH_2^+ + CrO_4^{2-} \equiv Zr\text{-}O\text{-}HCrO_4^{2-} + H^+.$$

Investigation of V(V) adsorption onto goethite by EXAFS spectroscopy, by Caroline et al. (2004), confirmed the following adsorption mechanism.

$$2FeOH_2^+ + VO_2^+ = Fe_2O_2V(OH)_2^+ + 2H^+ \quad \text{and}$$
$$2FeOH + HVO_4^{2-} = Fe_2O_2V(OH)^0 + 2OH^-.$$
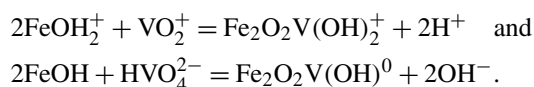
It has been reported that the adsorption of phosphate on an ion exchanger containing Zr(IV) is not only the result of ion exchange, but also the result of the nucleophilic SN2-i-replacement of OH-groups combined with Zr atoms by phosphates with the formation of an intermediate six-member complex (Chubar et al. 2005). This is very different from our present studies. Therefore, the adsorption mecha-
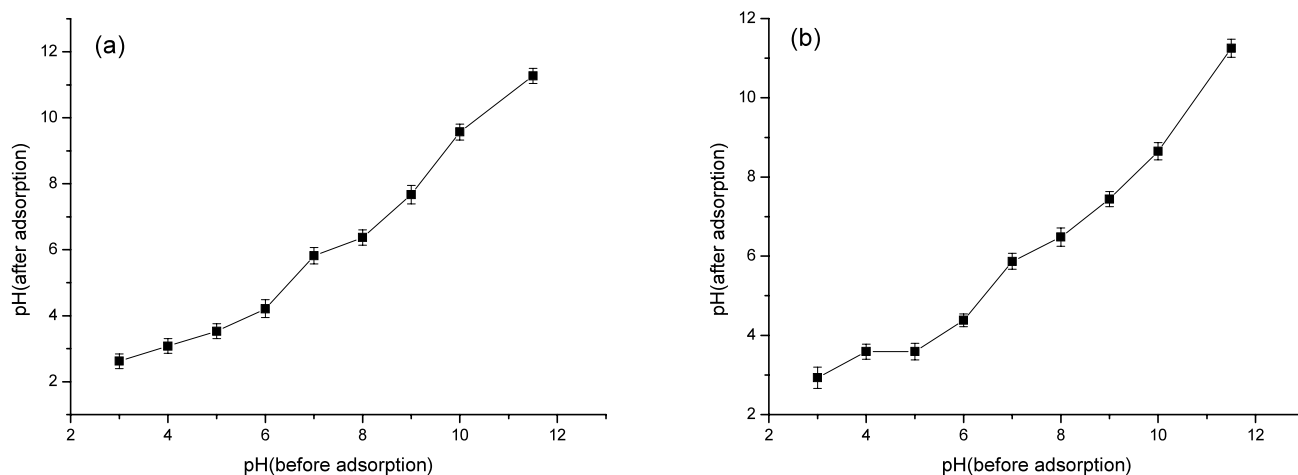
Fig. 3 The pH of solutions before and after adsorption. **a** V(V), **b** Cr(VI), (303 K, initial conc. $= 2.00\ \text{mmol L}^{-1}$)
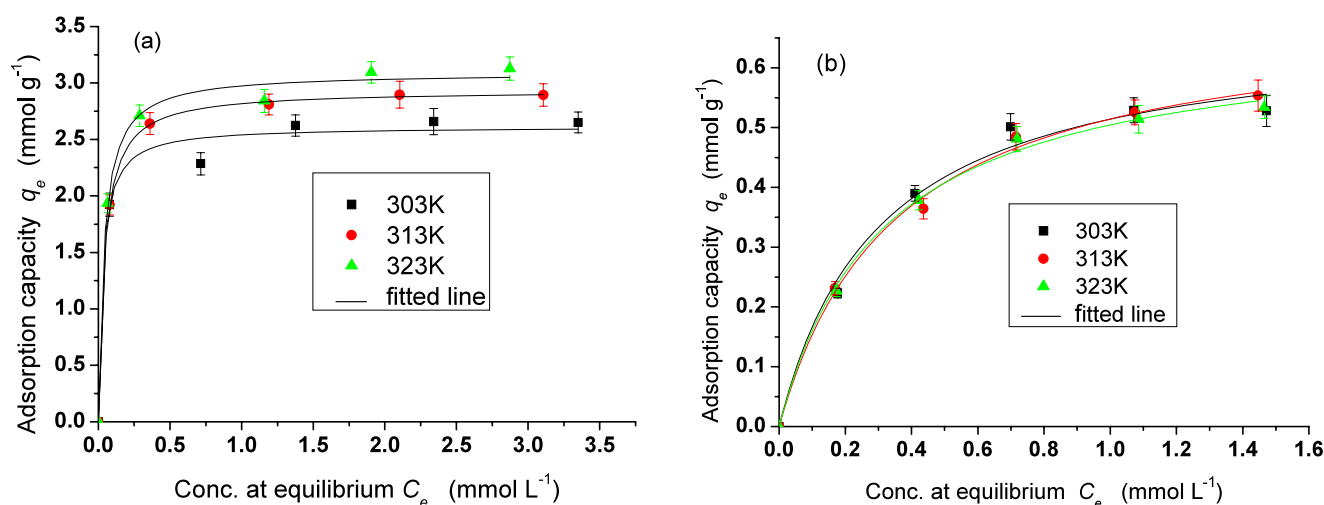

Fig. 4 Adsorption isotherms of V(V) and Cr(VI) on ZrICF. **a** V(V), pH $= 5.0$, **b** Cr(VI), pH $= 7.0$

nism of V(V) and Cr(VI) on ZrICF might be more complex and needs to be further investigated.

In addition, leaching of Zr(IV) was determined during the adsorption processes by ICP and it was found that there is no leaching if pH > 2.0.

3.2 Adsorption isotherms

The adsorption isotherms of V(V) and Cr(VI) were summarized in Fig. 4. In general, the adsorption capacity of V(V) on ZrICF is significantly higher than that of Cr(VI). The adsorption capacity of V(V) increased with temperature, while it was almost unchanged for the adsorption of Cr(VI). The isotherms should be the type of L1 according to the classification of Giles et al. (1960), and these isotherms of Langmuir type are generally associated with monolayer adsorption.

The adsorption capacities of ZrICF to V(V) and Cr(VI) at 303 K were about 2.50 mmol g^{-1} and 0.50 mmol g^{-1}, respectively. It has been reported that the adsorption capacities of V(V) on goethite and persimmon were about 0.50 mmol g^{-1} and 1.0 mmol g^{-1}, respectively, smaller than that on ZrICF (Nakajima 2002; Caroline et al. 2004). The maximum adsorption capacity of Cr(VI) reported in the literature is 1.10 mmol g^{-1} (Bailey et al. 1999), which is higher than that on ZrICF. Anyway, considering the significant adsorption capacity and good mass transfer property due to the fibrous structure of ZrICF, this new adsorbent might be practically applicable.

The adsorption isotherm data of V(V) and Cr(VI) on ZrICF follow the rearranged Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \tag{1}$$

where q_e and C_e are the amount adsorbed (mmol g^{-1}) and the bulk concentration (mmol L^{-1}), respectively, at equilibrium; q_{max} is the maximum adsorption capacity of metal ion (mmol g^{-1}); b is the coefficient related to the strength of adsorption, $b = k_a/k_d$ (k_a is the rate constant of adsorption, k_d is the rate constant of desorption). The Langmuir parameters q_{max} and b were determined from the slope and intercept of the linear plot of C_e/q_e versus C_e, and they were summarized in Table 2.

For the adsorption of V(V), the q_{max} values in Table 2 are close to those actually determined as shown in Fig. 4a. Meanwhile, the q_{max} values of Cr(VI) are slightly higher than those actually determined.

3.3 Effect of electrolyte on adsorption capacity

The effects of electrolyte on adsorption capacities of V(V) and Cr(VI) are presented in Fig. 5. For comparison and mechanism elucidation, the results without electrolyte are also shown. It can be found that the adsorption capacities of V(V) and Cr(VI) increased to some extent in the presence of electrolyte. Chubar et al. (2005) have reported the effect

of electrolyte on the adsorption of phosphate by Zr ion exchangers, and it was found that the adsorption capacity was considerably increased in the presence of 0.1 M NaCl. It has been suggested that the Cl$^-$ anion might participate in the adsorption process. At the first stage, Cl$^-$ chelates with Zr(IV) to form an intermediate. Then, H$_2$PO$_4^-$ replaces the surface Cl$^-$ (Chubar et al. 2005). The formation of intermediate complex of Cl$^-$ and Zr(IV) may reduce the activation energy of the chelating reaction between H$_2$PO$_4^-$ and Zr(IV). Therefore, it could be inferred that a similar mechanism might be involved in the adsorption process of V(V) and Cr(VI) on ZrICF in the presence of NaNO$_3$.

3.4 Adsorption capacity in buffer solutions

Figure 6 shows that the adsorption capacity of V(V) on ZrICF is almost unchanged in HAc-NaAc buffer solution. Meanwhile, the adsorption capacity of Cr(VI) obviously decreased in triethanolamine-HCl buffer solution. These phenomena might be caused by the different competitive adsorption behavior of Ac$^-$ and triethanolamine with metal anions on ZrICF, and that the complexing ability of Ac$^-$ and triethanolamine with metal ions in aqueous solution are also different, which will affect the chemical species of metal anions.

3.5 Adsorption kinetics

The adsorption kinetics of V(V) and Cr(VI) on ZrICF are remarkably different, as shown in Fig. 7. Figure 7a shows that the adsorption quantity of V(V) gradually increased with time, and that adsorption equilibrium is not attained in 360 min. However, the adsorption rate of Cr(VI) on ZrICF is very fast, and the adsorption equilibrium is attained in about 160 min, as shown in Fig. 7b. In addition, the adsorption

Table 2 Parameters of Langmuir isotherms for adsorption of V(V) and Cr(VI) on ZrICF

Metal ions	Temp. (K)	q_{max} (mmol g^{-1})	b (L mmol^{-1})	R^2
V(V)	303	2.71	15.1	1.00
	313	2.94	23.3	1.00
	323	3.18	15.1	0.999
Cr(VI)	303	0.645	3.61	0.994
	313	0.691	2.90	0.998
	323	0.653	3.33	0.999

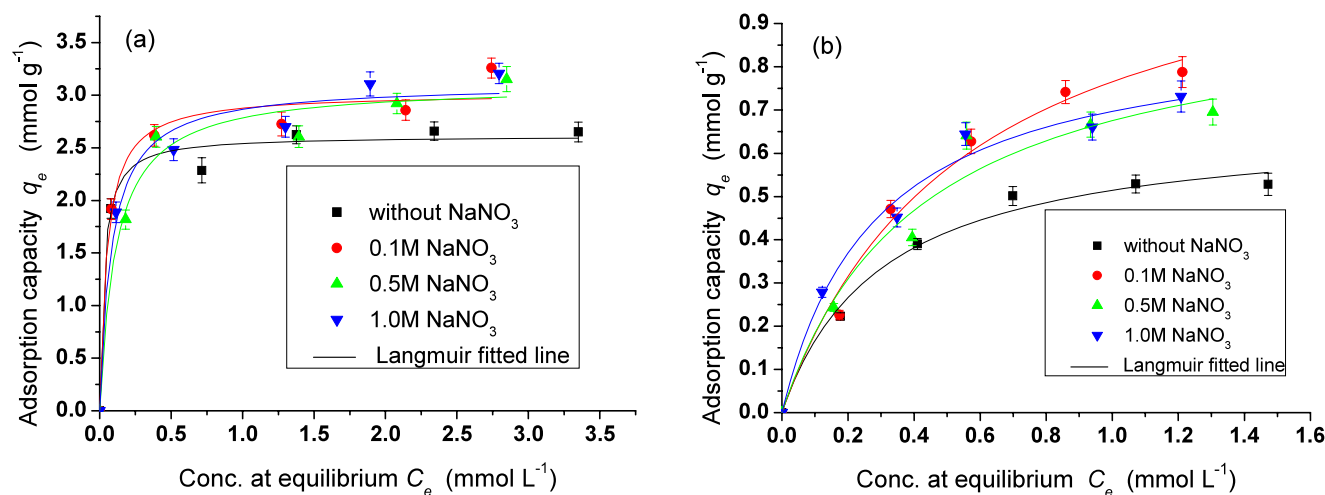**Fig. 5** Effect of electrolyte on adsorption capacity of V(V) and Cr(VI) by ZrICF. **a** V(V), pH = 5.0, **b** Cr(VI), pH = 7.0, T = 303 K
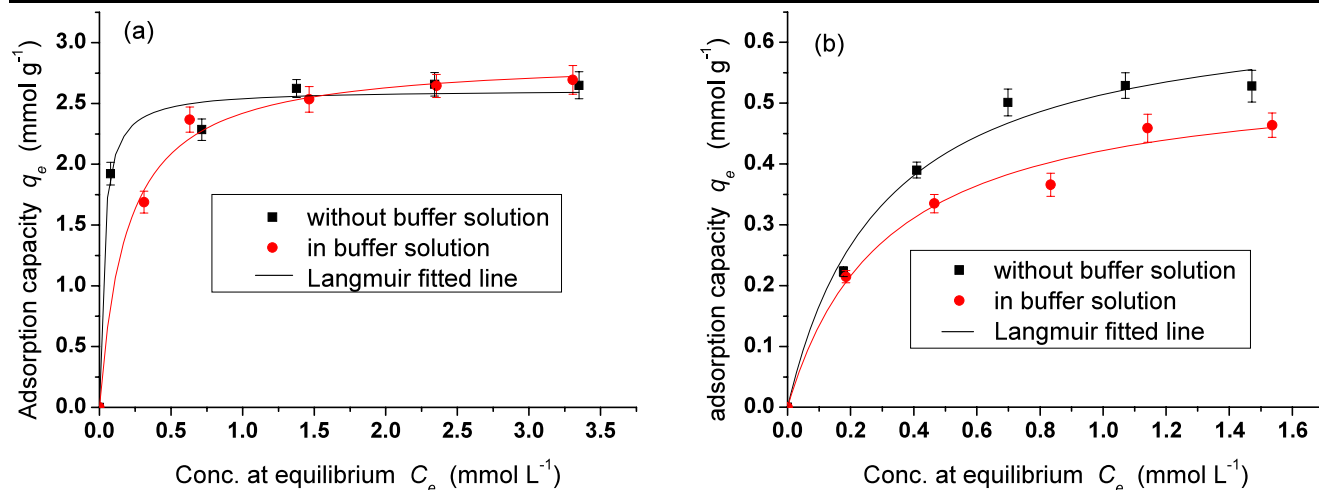
Fig. 6 Adsorption capacity of V(V) and Cr(VI) on ZrICF in buffer solutions. **a** V(V), pH = 5.0, **b** Cr(VI), pH = 7.0
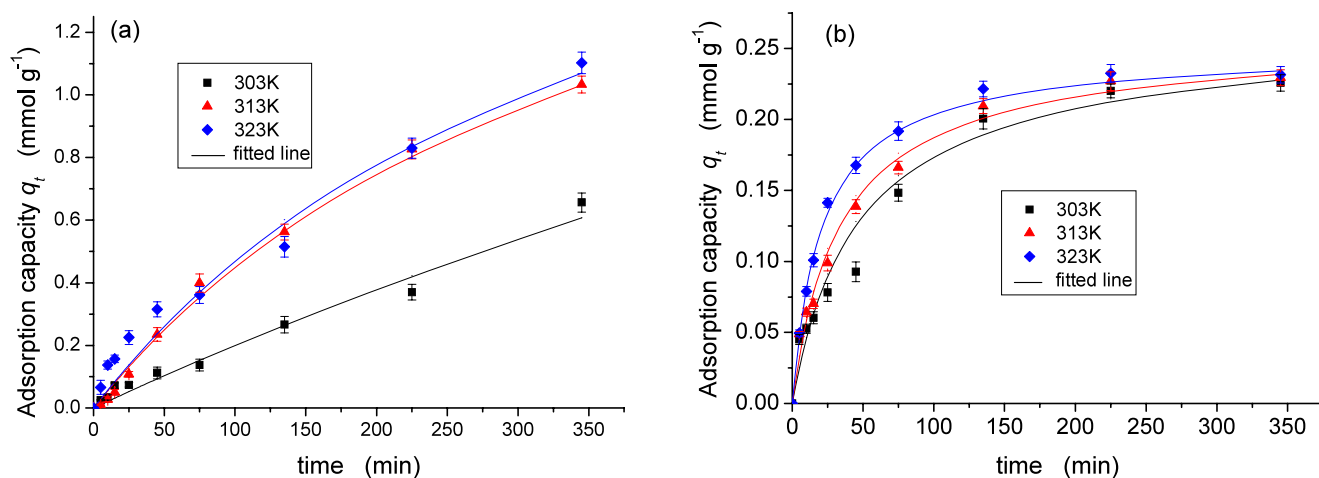

Fig. 7 Adsorption kinetics of ZrICF to V(V) and Cr(VI). **a** V(V), initial conc. = 2.00 mmol L^{-1}, pH = 5.0, **b** Cr(VI), initial conc. = 0.400 mmol L^{-1}, pH = 7.0

rate of Cr(VI) increased with temperature. But the adsorption rate of V(V) was almost unchanged when temperature increased to 313 K. In the case of Cr(VI), the equilibrium adsorption capacities obtained at different temperatures are nearly the same. In adsorption isotherms studies, the adsorption capacity of V(V) increased with temperature, while it was almost unchanged for the adsorption of Cr(VI). From all the results, it can be concluded that the temperature dependence of the adsorption isotherms and adsorption kinetics are coincident.

In order to investigate the mechanism of adsorption, the following three models were used to test adsorption kinetics data: pseudo-first-order adsorption, pseudo-second-order adsorption, and intraparticle diffusion. The pseudo-first-order-rate expression of Lagergren is given as (Chiou and Li 2003):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

where q_e and q_t are the amount of metal ions adsorbed on adsorbent (mmol g^{-1}) at equilibrium and at time t (min), respectively, and k_1 is the rate constant (min^{-1}).

The pseudo-second-order rate model is expressed as (McKay and Ho 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (3)$$

where k_2 is the constant of pseudo-second-order rate (mmol g^{-1} min^{-1}). Based on (3) and experimental data of q_t versus *time*, q_e and k_2 can be determined by the slope and intercept of the plot of t/q_t against t.

Table 3 Adsorption rate constant of V(V) and Cr(VI) on ZrICF

Temp. K	Adsorption of V(V) pseudo-first-order-kinetic model				Adsorption of Cr(VI) pseudo-second-order-kinetic model			
	$q_{e.exp.}$ mmol g^{-1}	$k_1 \times 10^3$ min^{-1}	$q_{e.cal.}$ mmol g^{-1}	R^2	$q_{e.exp.}$ mmol g^{-1}	k_2 g mmol^{-1} min^{-1}	$q_{e.cal.}$ mmol g^{-1}	R^2
303	1.92	1.11	1.91	0.989	0.223	0.0850	0.258	0.995
313	1.92	2.32	1.90	0.995	0.231	0.119	0.254	0.998
323	1.94	2.31	1.86	0.996	0.227	0.200	0.248	1.00

The intraparticle diffusion equation can be described as (McKay and Ho 1999):

$$q_t = k_i t^{0.5} \tag{4}$$

where k_i is intraparticle diffusion rate constant (mmol g^{-1} min$^{-0.5}$), which can be determined by the slope of straight-line portion of plot q_t vs $t^{0.5}$.

The kinetics parameters were obtained by non-linear regression. It is found that the adsorption rate of V(V) on ZrICF can be well described by the pseudo-first-order model, while the pseudo-second-order model gives a satisfactory fit of the adsorption rate of Cr(VI) on ZrICF, as shown in Table 3. It was indicated in Table 3 that the adsorption capacities of V(V) and Cr(VI) calculated by the pseudo-first-order and pseudo-second-order rate models, respectively, were close to the experimental results. It has been reported that the adsorption kinetics of anionic species of Cr(VI) on Lewatit exchange resins (Gode and Pehlivan 2005) and on chemically modified activated carbon (Park and Jung 2001) followed first-order kinetics, but it followed pseudo-second-order model when adsorbed by Moroccan stevensite (Sheng et al. 2004). Lazaridis and Asouhidou (2003) found that the adsorption rate of anionic species of Cr(VI) by Mg-Al-CO$_3$ hydrotalcite can be described by pseudo-first-order, pseudo-second-order, and Elovich models, but the pseudo-first-order seems to be more appropriate than the others due to its better prediction of the equilibrium adsorption capacity. In general, the degree of fit exhibited by different rate models indicates the degree of consistency with the assumed rate-determining step for a given adsorption rate test. The intraparticle diffusion model means that the intraparticle diffusion is the rate-determining step, while both the pseudo-first order model and the pseudo-second order model mean that the adsorption reaction should be the rate-determining step. The difference between the pseudo-first order model and the pseudo-second order model is only the difference of the apparent adsorption reaction order. In addition, the adsorption kinetics of metal anions depends on both the state of anions and the structure of adsorbents. It was found that the adsorption kinetics models of different metal anions on different adsorbents varied even through

they share same ion exchange mechanism. For the adsorption of V(V), the single charged species (H$_3$V$_2$O$_7^-$) applies to the adsorption of V(V) on ZrICF. In the case of Cr(VI), either CrO$_4^{2-}$ or HCrO$_4^-$ species may represent the adsorption of Cr(VI) on ZrICF. As shown in Fig. 7, the adsorption capacity of V(V) increased with temperature, while temperature had little impact for the adsorption of Cr(VI). Therefore, it could be concluded that the adsorption reaction is the rate-determining step for the adsorption of V(V) and Cr(VI) on ZrICF, but their adsorption reaction orders are different.

A specific area measurement indicated that the specific area of ZrICF is around 3.0 m^2 g^{-1}, which is much smaller than that of porous adsorbents. However, the adsorption capacities of ZrICF for V(V) and Cr(VI) are significant—on a unit mass basis—and the adsorption rate is also satisfactory. In addition, ZrICF exhibits a fibrous structure. Therefore, it can be suggested that adsorption takes place on the outer surface of ZrICF and thus the intraparticle diffusion resistance could be neglected.

3.6 Adsorption selectivity

Vanadium is a very valuable element due to its wide industrial application, such as in stainless steel production, ferrovanadium, and a variety of catalysts (Agrawal 2005). But vanadium often co-exists with other metals such as molybdenum, copper, chromium, etc. The Pan-zhi-hua Iron & Steel Corporation, located at the southwest of China, has found that it is difficult to separate vanadium from a solution of vanadium(V) and chromium(VI) in the processing of vanadium mineral. The concentration of V(V) and Cr(VI) are 12 to 20 mmol L^{-1} and 2 to 4 mmol L^{-1}, respectively, in the effluent discharged from the processing of vanadium mineral. Therefore, the adsorption selectivity of ZrICF to V(V) in a solution of V(V) and Cr(VI) was investigated.

Figure 8 shows that the adsorption selectivity of ZrICF to V(V) is remarkable. The adsorption quantity of V(V) was 1.92 mmol g^{-1} in the absence of Cr(VI), and it was almost unchanged as the Cr(VI) content in the solution increased. The adsorption quantity of V(V) was kept to 1.91 mmol g^{-1} even when the mole ratio of Cr(VI)/V(V) was 2:2. In contrast, the adsorption quantity of Cr(VI) was 0.36 mmol g^{-1}

Fig. 8 Adsorption selectivity of ZrICF to V(V) in the mixture solutions of V(V) and Cr(VI). pH = 5.0, T = 303 K
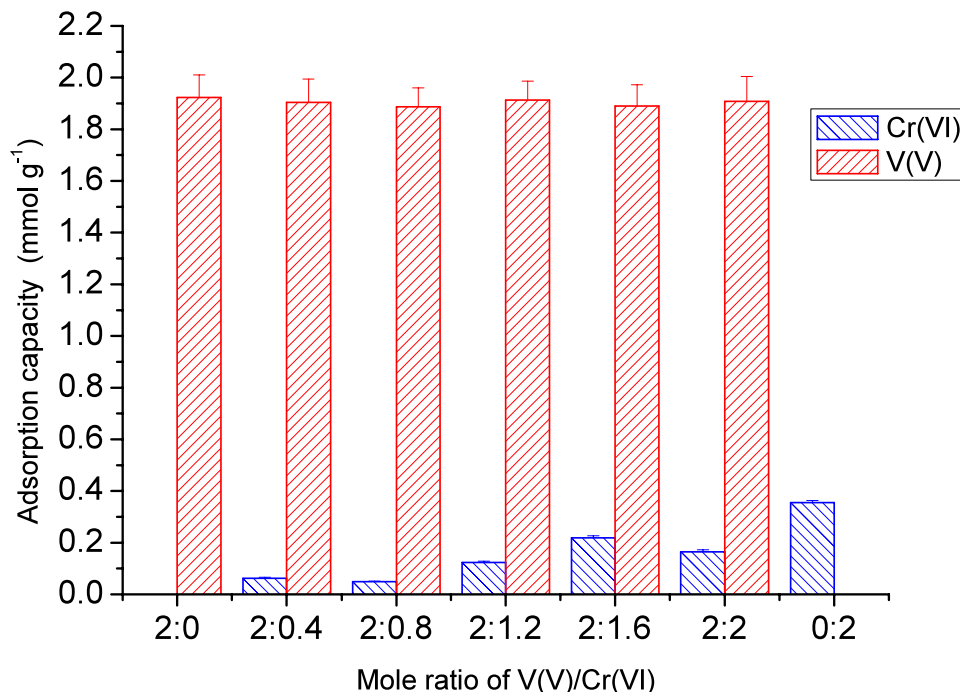
in absence of V(V), when initial concentration of Cr(VI) was 2.00 mmol L^{-1} and the pH was 5.0. However, it decreased to 0.17 mmol L^{-1} in the presence of V(V). These facts strongly suggest that the ZrICF is able to selectively adsorb V(V) from solutions containing both V(V) and Cr(VI).

A preliminary desorption investigation indicated that V(V) that has been adsorbed on ZrICF can be easily desorbed by using 0.1 M NH$_3$·H$_2$O solution, possibly due to the strong chelating ability of NH$_3$·H$_2$O with V(V) and Cr(VI). In fact, dilute acid solution is also effective for the desorption of ZrICF, but it will reduce the adsorption capacity because of the leakage of Zr(IV). V(V) in concentrated solution can be further purified by precipitation or crystallization (Luo et al. 2003). Therefore, the potential applications of ZrICF for the separation or purification of vanadium from mixture solutions can be expected.

4 Conclusion

As a novel adsorbent, Zr(IV)-impregnated collagen fiber is a promising material for removing metal anions of V(V) and Cr(VI) from aqueous solutions. The adsorption mechanism of metal anions on ZrICF seems to be ion exchange. The single charged species (H$_3$V$_2$O$_7^-$) favors the adsorption of V(V) on ZrICF, while the double charged species (CrO$_4^{2-}$) favors the adsorption of Cr(VI) on ZrICF, even though significant adsorption is observed when Cr(VI) exists as HCrO$_4^-$. There is no leaching of Zr(IV) during adsorption/desorption processes if pH > 2.0, indicating good stability of ZrICF.

Further investigation indicated that ZrICF is able to selectively adsorb V(V) from the mixture solutions of V(V) and Cr(VI), and the potential applications of ZrICF for the separation or purification of vanadium from mixture solutions can be expected.

In practice, some further investigations should be carried out, such as the relationship between adsorption capacity of metal anions and amount of Zr(IV) loaded, as well as the characteristics of column adsorption and regeneration.

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