Column Adsorption of Chromium(VI) by Strong Alkaline Anion-Exchange Fiber

Wenqing Wang, Mingyu Li, Qingxuan Zeng

School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

ABSTRACT: The removal of chromium(VI) from saturated sodium chloride (NaCl) solution by strong alkaline anion-exchange fiber (SAAEF) was achieved with column experiments. Factors affecting the adsorption, such as the pH value, loading density, flow rate, and operational temperature, were investigated. The results show that Cr(VI) removal was remarkably pH dependent. The optimal operational conditions were as follows: pH value = 2.0, loading density = 0.12–0.19 g/cm^3, room temperature, and flow rate = 6–12 BV/h. The SAAEF column could be regenerated completely by 2% NaOH in saturated NaCl or 2% KOH in 15% KCl as an eluent. Cr(VI) was recycled as $Na_2Cr_2O_7$ and $K_2Cr_2O_7$, respectively. The desorption rate of Cr(VI) reached 98.09%. The adsorption ability of the SAAEFs was stable after repeated use. Overall, the results indicate that SAAEF proved to be an effective material for the adsorption of high concentrations of Cr(VI) from a saturated NaCl solution. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: adsorption; fibers; functionalization of polymers; ion exchangers

INTRODUCTION

Chromium is one of main environmental pollutants. The steel fabrication, cement preservation, electroplating, paint, leather tanning, and chromate preparation industries[1,2] produce large quantities of chromium-containing waste effluents. Cr(VI) is carcinogenic and mutagenic.[3,4] Cr(VI) must be strictly controlled before it is discharged. The World Health Organization has made a regulation stating that the maximum permissible limit for Cr(VI) discharge is 0.005 mg/L.[5] High concentrations of Cr(VI) in waste effluents should also be reclaimed; this would be both ecofriendly and economical.

During the past several decades, chemical precipitation following the reduction of Cr(VI) to Cr(III) has been the traditional technique used for Cr(VI) removal. It produces toxic solid residues, which easily cause secondary pollution.[6] Recently, adsorption, membrane-ion exchange, and biological processes based on physical, chemical, and biological mechanisms have been advised.[7] Ion-exchange technology has more advantages over other technologies, including the recovery of metal, selectivity, a lower sludge volume produced, and the meeting of strict discharge specifications.[8]

Strong alkaline anion-exchange fiber (SAAEF) is a new kind of fabric absorption and separation material. It has higher adsorption/desorption rates and better antipollution ability than ion-exchange resins.[9,10] The functional groups of SAAEF are on its surface, but the resins are in its inner pores. Film diffusion exists only during the adsorption on SAAEF, whereas both film diffusion and intraparticle diffusion occur during adsorption on the resin. Furthermore, resins can be easily poisoned by some inorganic and organic compounds, and their pores may become clogged by colloids in raw water. Also, there are many applications for fiber, including yarn, woven fabric, and nonwoven fabric. SAAEF has been applied in metal recovery, gas purification and separation, extraction and separation of radioactive and rare earth elements, and water purification.[11] Recently, it was also been proposed for use as an ion-exchange fiber in medical and pharmaceutical applications.[12]

In this study, SAAEF was applied to the adsorption of Cr(VI) from a saturated NaCl and potassium dichromate ($K_2Cr_2O_7$) mixed solution with a high Cr(VI) concentration to separate them through column experiments. This study was performed to evaluate SAAEF as an adsorbent for Cr(VI) uptake from a saturated NaCl solution by the systematic evaluation of the parameters involved, such as the initial pH value of the mixture solution, loading density, operational temperature, and flow rate. Also, several eluents were compared to find ideal regenerants.
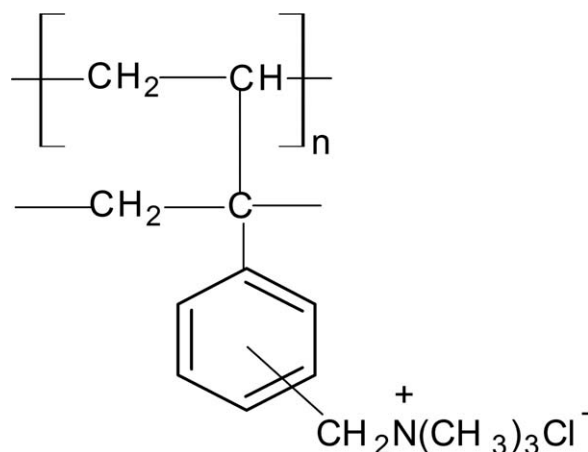
Figure 1 SAAEF chemical structure.

Furthermore, a fatigue experiment was carried out to determine the reusability of the SAAEF column.

EXPERIMENTAL

Materials and methods

SAAEF was synthesized by the grafting copolymerization of styrene onto polypropylene fibers, which was induced by ^{60}Co γ-ray irradiation cholormethylation and amination reactions.[13] Before use, SAAEF was converted to the Cl^- type from the OH^- type by dipping in 1 : 1 HCl. Figure 1 shows the structure of the SAAEF used in Cr(VI) removal. The saturated NaCl and $K_2Cr_2O_7$ mixture solution, with an initial concentration of Cr(VI) of up to 4.34–6.89 g/L, was provided by Anxian Town (Sichuan Province, People's Republic of China). All of the chemicals and reagents used were analytical grade and were used without further purification.

A PHS-25 precision acidity meter was provided by Shanghai Precision & Scientific Instrument Co., Ltd. An AR2140 electronic balance was provided by Ohaus Co. (Shanghai, People's Republic of China). A 725P ultraviolet–visible spectrophotometer was provided by Aplsh Instrument Co., Ltd. (Shanghai, People's Republic of China). A DHG-9055A electric blast oven was provided by Shanghai Yi Heng Scientific Instrument Co., Ltd. A YZ1515x peristaltic pump was provided by Longer Precision Pump Co., Ltd. (Baoding, Hebei Province, People's Republic of China) A BSZ-160F computerized automatic collector was provided by Shanghai Jing Ke Industrial Co., Ltd. A 501A superdigital display constant-temperature water bath was provided by Shanghai Sheng Xin Scientific Instrument Co., Ltd.

Analysis method

The concentration (c) of Cr(VI) was determined by the ultraviolet–visible spectrophotometer with 0.2 wt % 1,5-diphenyl carbazide as the complexing agent at a wavelength of 540 nm. There was a strong correlation between the absorbance (A) of the purple-colored solution and the concentration of hexavalent chromium. The linear equation was $A = 0.7749c + 0.0024$, $R^2 = 0.9999$.

The adsorption capacity of SAAEF was calculated by the following equation:

$$q_e = \frac{c_0 V_0 - c_1 V_1}{m} \tag{1}$$

Desorption rate was defined as

$$\text{Desorption rate} = \frac{c_2 V_2}{c_0 V_0} \tag{2}$$

where c_0, c_1, and c_2 are the Cr(VI) concentrations of the original aqueous solution, effluent liquid, and desorption liquid, respectively (g/L); V_0, V_1, and V_2 are the volumes of the inlet original aqueous solution, effluent liquid, and desorption liquid, respectively (mL); and m is the weight of SAAEF (g).

Column experiments

The experimental system was composed of an ion-exchange column (Column Height $h = 12$ cm, Column Diameter $d = 1.0$ cm) with a heating jacket, a peristaltic pump, and a computerized automatic collector.

SAAEF (1.00 g) was filled to a certain height in the column by wet loading. The saturated NaCl/$K_2Cr_2O_7$ mixture solution was pumped to the SAAEF column at a fixed flow rate. The temperature of the stream feeding solution and the column were controlled at a constant value through a thermostatic bath. The effluent liquid was withdrawn at definite time intervals and analyzed.

SAAEF regeneration experiment was carried out when the SAAEF adsorption achieved saturation. A certain eluent was pumped to the exhausted SAAEF column at a fixed flow rate. The desorption liquid was withdrawn at definite intervals and analyzed. The column experiment system is shown in Figure 2.

RESULTS AND DISCUSSION

Adsorption column experiment

The effects of the pH value, loading density, temperature, and flow rate on the absorption capacity of SAAEF were investigated. Breakthrough curves show the loading behavior of metal to be removed from a solution in a fixed bed and are usually expressed in terms of the adsorbed metal concentration ($c_0 - c_t$) or the ratio of the effluent metal concentration (c_t) to c_0 as a function of time (t) or the volume of the effluent (V) for a given bed height.[14]
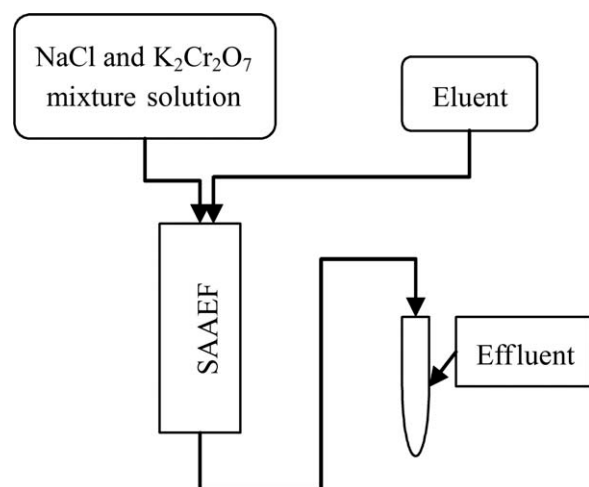
Figure 2 Column experimental system. Injection System, Adsorption Column and Collection System. During the adsorption process, NaCl and $K_2Cr_2O_7$ mixture solution was pumped into the column while in the eluent process, eluent was pumped into the saturated column to regenerate SAAEF.

From the breakthrough curve, we obtained the volume when breakthrough appeared and the dynamic response of the adsorption column.

Effect of the SAAEF pretreatment

Pretreatment is a common practice before materialuse. In Cr(VI) removal, the type of active site greatly influences the ion-exchange process. Pretreatment led to the total conversion of OH^- to Cl^- as the active site in SAAEF by dipping in 1.00 mol/L HCl for 24 h and then washing with distilled water to neutral to remove excess H^+ ions.

Amounts of 1.00 g of pretreated and untreated SAAEF were, respectively, packed in a column 7.20 cm in height. A saturated NaCl/$K_2Cr_2O_7$ mixture solution with an original Cr(VI) concentration of 6.89
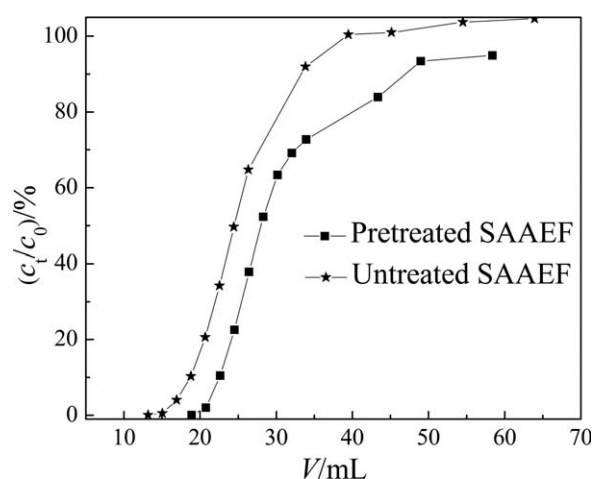

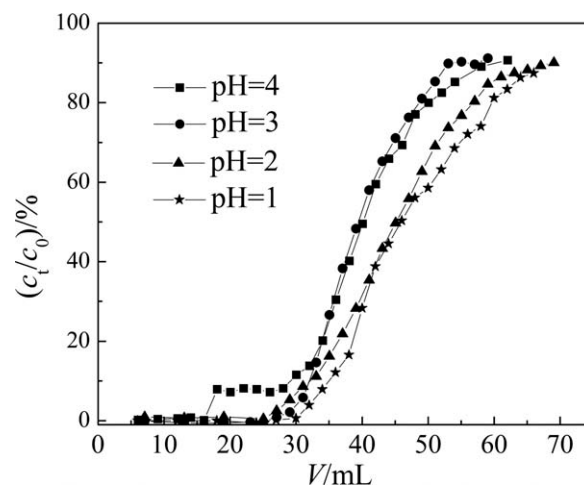**Figure 3** Effect of SAAEF pretreatment on Cr(VI) adsorption.

Figure 4 Effect of the pH on Cr(VI) adsorption.

g/L flowed through the column at 10 BV/h. Figure 3 shows the breakthrough curves of SAAEFs with different treatments. The breakthrough was delayed from 13.16 to 18.80 mL, and the exhaustion solution volume increased from 37.61 to 58.19 mL. After pretreatment, the adsorption capacity of SAAEF became larger.

Pretreated SAAEF was changed to the Cl^- type. All active sites on SAAEF were changed to Cl^- instead of a mixture of Cl^- and OH^-. The competitive order among Cl^-, OH^-, and $Cr_2O_7^{2-}$ was $OH^- > Cr_2O_7^{2-} > Cl^-$.[15] Cl^- was more easily exchanged with $Cr_2O_7^{2-}$ than OH^-; therefore, the adsorption effect of SAAEF became better after pretreatment.

Effect of pH

The breakthrough curves of Cr(VI) absorption by 1.00 g of pretreated SAAEF at different pH values of the NaCl/$K_2Cr_2O_7$ mixture solution and at fixed bed height of 9.0 cm are shown in Figure 4. The initial concentration of Cr(VI) was 4.91 g/L, and the flow rate was 0.76 m/h. A slightly moving-forward breakthrough point and exhaustion time were observed as the pH value was changed from 1.0 to 3.0. When the pH was greater than 3.0, the SAAEF column broke through sharply at a low V of 16.0 mL. This indicated that the SAAEF column adsorption of Cr(VI) became worse when the pH was higher than 3.0.

The effect of acidity played a significant role in the adsorption process. The species of Cr(VI) are various and convertible in aqueous solutions. When the pH is greater than 6.5, CrO_4^{2-} is stable. In the pH value range 3.0–6.0, Cr(VI) mainly exists as $HCrO_4^-$ and $Cr_2O_7^{2-}$ species. At still lower pH values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed.[16] Thus, decreasing the pH value results in the formation of more polymerized chromium oxide species. Fewer active sites
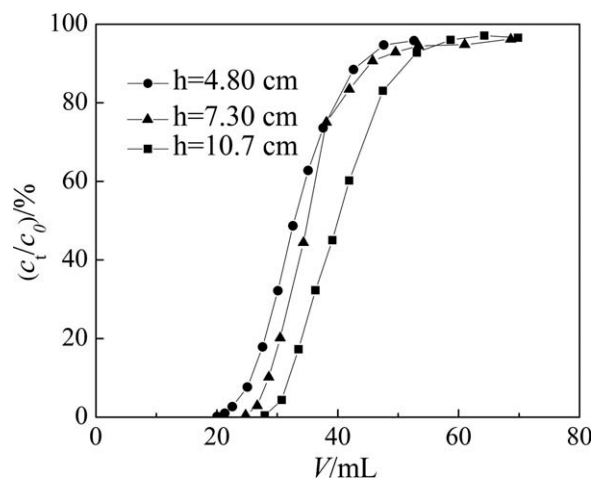
Figure 5 Effect of the loading density on Cr(VI) adsorption.

on SAAEF were needed to finish the ion exchange with more polymerized chromium oxide species with the same electric charge; this led to a higher level of Cr(VI) ion uptake. Also, an excess of OH^- could compete effectively with Cr(VI) ions for the bonding sites when the pH value was increased. In the pH value range of 2.0–7.0 for SAAEF, the optimum pH value was chosen as 2.0.

Effect of the loading density

Figure 5 shows the effect of the loading density on the absorption breakthrough curves. This was obtained by changes in the SAAEF column loading density at different heights (4.8, 7.3, and 10.7 cm). The loading densities were 0.12, 0.18, and 0.27 g/cm^3, respectively. The original Cr(VI) concentration of the mixture solution at pH 2.00 was 6.89 g/L, and the flow rate was 10 BV/h.

With increasing loading density, the breakthrough point was delayed, and the breakthrough curve became gentler. This indicated that high loading density was advantageous for Cr(VI) adsorption with a later breakthrough point and a longer exhaustion time. At relatively low loading densities, the exchange between $Cr_2O_7^{2-}$ and Cl^- was more effective. However, SAAEF in the column with too small a loading density was loose; this was not conducive to the steady flow of the solution. A loading density of the SAAEF column in the range 0.12–0.18 g/cm^3 was acceptable.

Effect of the temperature

The breakthrough curves of Cr(VI) adsorption at different temperatures and at a constant flow rate of 0.76 m/h are given in Figure 6. The initial Cr(VI) concentration was 3.67 g/L. The breakthrough

points under 293 and 303 K were close to each other at nearly 30.0 mL, whereas the breakthrough took place at 18.0 mL under 333 K. The breakthrough curves became steeper with increasing temperature; this indicated that the exhaustion time was shortened. There was a decrease in Cr(VI) uptake with increasing temperature.

At higher temperature, the kinetic energy of the $Cr_2O_7^{2-}$ anion was higher than the attraction potential between the $Cr_2O_7^{2-}$ and active sites in SAAEF. This caused a decrease in the adsorption efficiency and showed that the adsorption was more of a physical than a chemical property.[17] Also, a lot of bubbles from the inner SAAEF were expelled under higher temperature, which broke the even distribution of SAAEF and obstructed mass transfer. The treated solution partly passed through bubble gaps without ion exchange. Operation under room temperature could be suitable for chromium(VI) removal.

Effect of the flow rate

SAAEF (1.00 g) was packed in the column with a height of 6.80 cm. A NaCl and $K_2Cr_2O_7$ mixture solution with a Cr(VI) concentration of 4.34 g/L was pumped through the column at different flow rates of 0.38, 0.76, and 1.50 m/h, which were 5.7, 11.3, and 22.6 BV/h, accordingly. Figure 7 displays the breakthrough curves at different flow rates. The breakthroughs at 0.38 and 0.76 m/h flow rates appeared at 27.0 mL, whereas the breakthrough point advanced to 18.0 mL with a 1.50 m/h flow rate. It was clear that breakthrough time and adsorption Cr(VI) concentration decreased when the flow rate increased.

This could be explained by the fact that Cr(VI) in the mixture solution could come into contact with SAAEF in a manner sufficient to finish the exchange
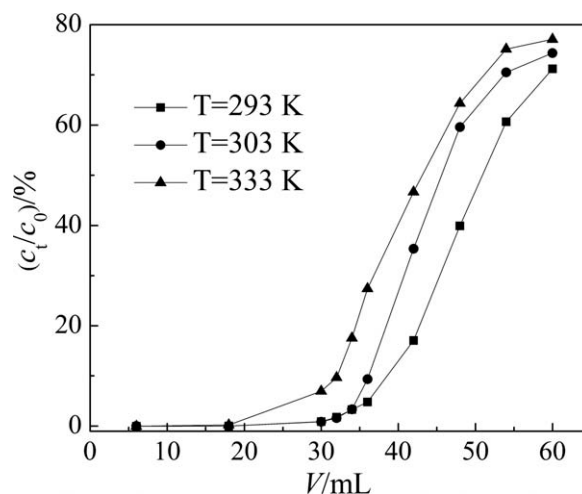

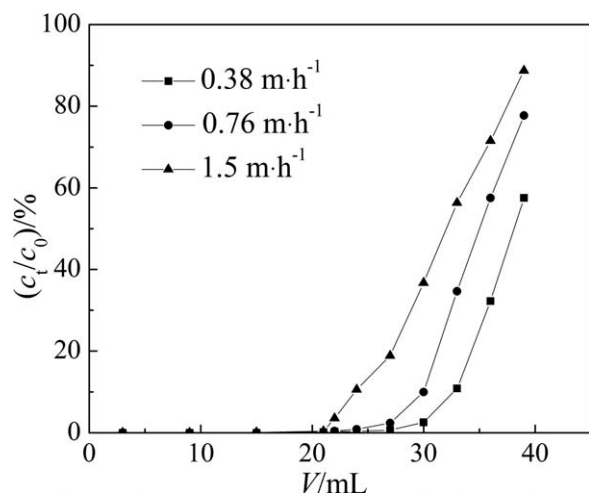**Figure 6** Effect of the temperature (T) on Cr(VI) adsorption.

Figure 7 Effect of the flow rate on Cr(VI) adsorption.

TABLE I
Experimental Fatigue Results

Times used	1	5	10	20
Adsorption rate (%)	26.46	27.53	25.18	23.28
q_e (mg/g)	128.1	129.9	127.3	127.2

q_e is the adsorption capacity of SAAEF

process when the flow rates decreased. A relatively fast flow rate made the residence time of the solution in the column not long enough for adsorption equilibrium to be reached; thus, the breakthrough points and the exhaustion time appeared earlier. However, a flow rate that was too low easily caused mass-transfer problems. A flow rate of 6–12 BV/h was optimal for SAAEF column operation for Cr(VI) adsorption.

Regeneration experiment

The regeneration of the column and recovery of the metal are very important aspects in metal-containing aqueous solution treatment processes. Therefore, it was necessary to study the desorption of the SAAEF column. Elution curves, expressed in terms of the desorbed metal concentration (c_t) as a function of time (t) or V for a given bed height, were adopted to determine the regeneration effect. The peak value of the elution curve was the maximum recovery con-
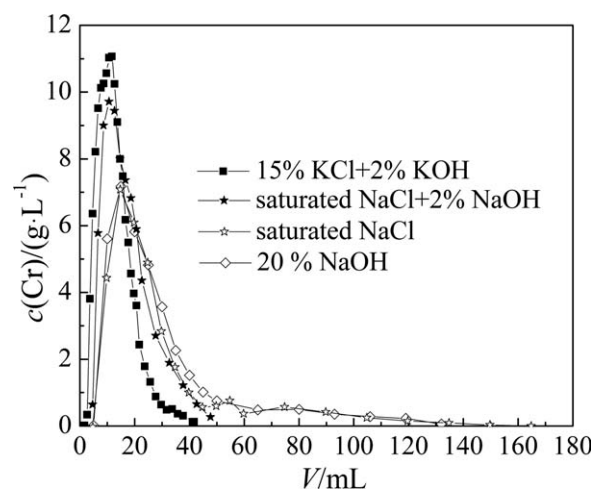

Figure 8 Elution curves of the different eluents.

centration of Cr(VI), and the elution time and eluent dosage were also obtained by the curve.

From the competitive order in ion exchange, alkali was necessary for SAAEF regeneration because OH^- could easily replace the adsorbed $Cr_2O_7^{2-}$ on SAAEF. A high-concentration salt is also a common eluent. So, saturated NaCl, 20% NaOH, and 2% NaOH in saturated NaCl and 2% KOH in 15% KCl were chosen as eluents to regenerate the saturated SAAEF column. The elution curves of different eluents at a height of 8.0 cm and a 12 BV/h elution rate are given in Figure 8.

The ideal eluents were 2% KOH in 15% KCl and 2% NaOH in saturated NaCl, and their elution curves were steeper than those of saturated NaCl and 20% NaOH, which indicated less eluent volume and a higher recovery concentration. When the concentration of Cr(VI) was lower than 0.5 g/L, at which we considered that the total regeneration of the SAAEF column had occurred, the responding eluent volumes of the four previous eluents were 80.0, 90.0, 43.0, and 32.2 mL, respectively. The maximum recovery concentrations of Cr(VI) by 2% KOH in 15% KCl and 2% NaOH in saturated NaCl were 11 and 9.7 g/L, respectively, whereas they were only 7.4 and 7.2 g/L with the saturated NaCl and 20% NaOH as regenerants compared to the original concentration of treated raw water at 4.34–6.89 g/L. This indicated that when the effluent liquid was collected when c_t was greater than or equal to c_0, a higher concentration Cr(VI) solution was obtained.

Cr(VI) was recycled as $K_2Cr_2O_7$ and $Na_2Cr_2O_7$ with 2% KOH in 15% KCl and 2% NaOH in saturated NaCl as eluents. The column regeneration was fast, and the desorption rate of Cr(VI) reached 98.09%. The recovery concentration was two times higher than initial.

Fatigue experiment

The reusability of the SAAEF column was a factor had be taken into consideration for industrial application. The adsorption capacity would theoretically get lower after repeated adsorption and desorption. The SAAEF column (1.00 g), with a height of 6.8 cm, was repeatedly used to treat Cr(VI) solutions with c_0 = 4.34 g/L at pH 2.0. The operational conditions were as follows: flow rate = 10 BV/h and room

temperature. The regeneration agent was 2% KOH in 15% KCl. Table I shows the Cr(VI) adsorption capacities after different usage times.

After the column was used five times, the adsorption capacity became larger, going from 128.07 to 129.85 mg/g. This could be explained by the fact that the residual organic compounds on the SAAEF surface were washed away after several regeneration times. These organic compounds were against the contact between Cr(VI) in the solution and the active sites on SAAEF, which led to low Cr(VI) adsorption. With more uses, some active sites were destroyed and could not be regenerated; this led to a lower adsorption capacity of SAAEF. However, the change in the adsorption capacity was slight, and the adsorption capacity was stable at about 127 mg/g. This indicated that the SAAEF column showed good performance for Cr(VI) adsorption after repeated use.

CONCLUSIONS

1. SAAEF proved to be an effective adsorbent for the removal of Cr(VI) from a saturated NaCl and $K_2Cr_2O_7$ mixture solution with a high Cr(VI) concentration up to 4.34–6.89 g/L. Before the SAAEF column broke through, Cr(VI) could be completely removed from the saturated NaCl solution.
2. The adsorption was found to be strongly dependent on the acidity of the solution. SAAEF was not available at the initial pH value of 6.09, and the adsorption increased with decreasing pH value of the solution.
3. The optimal column operational conditions were as follows: pretreated SAAEF to convert to Cl^- type, pH value of aqueous solution =

2.0, loading density of the column = 0.12–0.18 g/cm^3, flow rate = 6–12 BV/h, and room temperature.
4. The SAAEF column could be regenerated by 2% NaOH in saturated NaCl and 2% KOH in 15% KCl at 12 BV/h. Cr(VI) could be recovered as $Na_2Cr_2O_7$ or $K_2Cr_2O_7$, respectively. The desorption rate of Cr(VI) was 98.09%.
5. The adsorption capacity of SAAEF basically remained constant after 20 uses. The SAAEF column had good repeat performance for application.

References

1. Dubey, S. P.; Gopal, K. J Hazard Mater 2007, 145, 465.
2. Andin, Y. A.; Aksoy, N. D. Chem Eng J 2009, 151, 188.
3. Zhang, R. H.; Wang, B.; Ma, H. Z. Desalination 2010, 255, 61.
4. Sarin, V.; Pant, K. K. Biores Technol 2006, 97, 15.
5. Kozlowski, C. A.; Walkowiak, W. Water Res 2002, 36, 4870.
6. Kimbrough, D. E.; Cohen, Y.; Winer, A. M.; Creelman, L.; Mabuni, C. Crit Rev Environ Sci Technol 1999, 29, 1.
7. Edebali, S.; Pehlivan, E. Chem Eng J 2010, 161, 161.
8. Rengaraj, S.; Yeon, K. H.; Moon, S. H. J Hazard Mater 2001, 87, 273.
9. Wang, F. The Current Ion-Exchange Technology (in Chinese); Chemical Industry Publishing House: Beijing, 1993.
10. Li, Y.; Wang, L. Q.; Zeng, Q. X. Trans Beijing Inst Technol 2003, 23, 255.
11. Zhou, S. J. Ion Exchange Adsorption (in Chinese) 2004, 20, 278.
12. Vuorio, M.; Manzanares, J. A.; Murtomaki, L.; Hirvonen, J.; Kankkunena, T.; Kontturi. K. J Controlled Release 2003, 91, 439.
13. Li, M. Y.; Zeng, Q. X.; Feng, C. G.; Sun, W. N.; Li, K. Mater Sci Technol (in Chinese) 2006, 14, 32.
14. Malkoc, E.; Nuhoglu, Y.; Dundar, M. J Hazard Mater B 2006, 138, 142.
15. He, B. L.; Huang, W. Q. Ion Exchange and Adsorption Resin; Shanghai Science and Technology and Education Press: Shanghai, 1995.
16. Mallick, S.; Dash, S. S.; Parida, K. M. A. J Colloid Interface Sci 2006, 297, 419.
17. Daneshvar, N.; Salari, D.; Aber, S. J Hazard Mater 2002, 94, 49.