Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.837006

53 (2015) 206–213
January

Taylor & Francis
Taylor & Francis Group

Application of ion exchange and chemical precipitation process for the treatment of acid-dissolution water of chromium sludge

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Received 7 May 2013; Accepted 11 August 2013

ABSTRACT

The purpose of this study was to selectively remove chromium from acid-dissolution water of chromium sludge using the continuous column and precipitation techniques. Column experimental results indicated that the Thomas model was found to predict reasonably well the ion exchange breakthrough performance. The best adsorption and desorption capacities occurred at 7.5 mL/min flow rate and low 150 mg/L Cr (III) solutions for all adsorbents. The cyclic experiments' results showed that chromium had the same sorption and elution pattern in the four sequences in synthetic solutions, while removal and elution efficiencies were decreased over the four cycles in acid-dissolution water. After passing 2.5% NaCLO-treated acid-dissolution water through IRN77 columns, IRN77 resin did not show any signs of performances diminution over the four consecutive sorption and elution cycles. The adsorption efficiency could reach 37% which was 62% of that in synthetic solution, and the elution efficiency remained above 95%. Residual chromium after successive treatments of acid-dissolution water with IRN77 could be extracted by coagulation–precipitation treatment with NaOH/MgO mixtures. This process led to the final effluent which contained less than 0.5 mg/L of chromium. The results suggested that the combination of oxidation/resin and coagulation–precipitation could make the advanced reuse of acid-dissolution water become a reality.

Keywords: IRN77 resin; Column experiments; Acid-dissolution water; Chromium sludge; NaOH/MgO mixtures

1. Introduction

Cr(III) salts are most widely used as tanning agent in the leather industry, and is an important source of contamination due to the large volume of exhausted liquid discharges and solid sludge produced [1]. About 300,000 dry *t* of Cr(III)-containing (1–4%) tannery sludge are annually produced by tanneries in China [2]. Land application provides an economical and attractive alternative for the final disposal of tannery sludge because it consists largely of organic

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substances and also contains nitrogen and phosphorus [3,4]. However, high Cr content in the sludge is always an issue restricting its general use [5].

Recovery of chromium from tannery sludge would not only minimize the prospective health risks during land application of sludge, but it would also reduce the volume of waste and prevent the loss of valuable raw material from an economic point of view. Shen et al. [6] have employed mineral acids to tannery sludge samples for extraction of Cr. Macchi et al. have investigated separation of Cr(III) with sulfuric acid and recovery by oxidation to Cr(VI) [7]. Zhou et al. [8] have employed a more environmentally acceptable bioleaching method of recovery chromium from tannery sludge using the mixture of ingenuous iron and sulfur-oxidizing bacteria. Kilic et al. [9] have employed saponin and oxidative remediation to recovery chromium from tannery sludge.

But, the effect of acid-dissolution water reuse as tanning agent is not always ideal due to complex compositions of acid-dissolution water of chromium sludge. Therefore, further purification of the chromium solution is imperative. Many separation techniques have been proposed for the removal of Cr(III) from aqueous solutions, including solvent extraction, ion exchange, co-precipitation, membrane processes, and sorption. Among these methods, ion exchange is highly popular and has been widely practiced for metal ions removal [10,11]. Inorganic contaminants are selectively recovered according to their chemical properties. The main advantages of the exchange technique are its high selectivity, the lack of sludge production, and the recovery of valuable metals. Ion exchange resins (IER) are made of a polymeric structure and tailored for selectivity of various metals with various acidic or chelating functional groups. Acidic IER have a high affinity for positively charged metals. Various studies report that there is good potential for Cr(III) removal from plating process effluents [12,13], tannery wastewater [14], nuclear plant cooling water [15], and electronic process wastewater [16].

The purpose of the present study is to demonstrate the feasibility of using IRN77 resin as adsorbents for removal of Cr(III) from acid-dissolution water of chromium sludge using a column technique under various conditions, and to subsequently allow for recycling.

2. Materials and methods

2.1. Materials

The cation-exchange resin IRN77 (M/s Rohm and Haas, SA, France) was used in this study. The physical and chemical properties of the resin are shown in Table 1. Before experiments, IRN77 resin was pretreated with 6 M HCl. A synthetic stock solution containing 1,000 mg/L Cr(III) was prepared by dissolving 5.12 g of $CrCl_3·6H_2O$ in 1,000 mL distilled water. Cr(III) solutions of desired concentrations were prepared by diluting the stock solution with distilled water. All the chemicals, including NaOH, MgO, and strong H_2SO_4, were analytical grades, supported by Fujian Fuyou Chemicals Company and used as received.

2.2. IER capacity study

The fixed-bed experiments were carried out in a water-jacketed glass column with an inner diameter of 4.0 mm and a full length of 90 mm. An aliquot of the fresh IRN77 resin (400 mg) was packed into the column. To avoid air bubbles, the column was carefully packed under water. Aqueous phases containing Cr (III) were fed to the top of the bed using a peristaltic pump at fixed inlet flow rates until the breakthrough curve was completed. The flow rate at the outlet of the columns was monitored by measuring the liquid volume during a known period of time. The samples in the outlet were taken at the preset time intervals and the concentrations of Cr(III) ions were determined by inductively coupled plasma atomic emission spectrophotometry (IRIS/AP, Thermo Jarrel Ash, USA). Elution of IRN77 resin was conducted with H_2SO_4 (10%) in columns. As for sorption, elution reagents were fed from the top of the bed at fixed inlet flow rates and samples were collected from the outlet of column at the preset time intervals. The sorption phase effluent and the elution phase effluent were kept for calculation of the total metal uptake and release by the sorbent media.

The continuous column method was used to study the adsorption and desorption of Cr(III) on IRN77. The performance of the adsorption in continuous operation was carried out by column runs at room temperature. Effect of important parameters viz. flow rates and initial concentrations of Cr(III) were studied. Chromium solutions having an initial concentration of 150–400 mg/L were pumped from the bottom to the top of the column at a flow rate of 10 mL/min by a peristaltic pump until the breakthrough curve was completed, and then elution was conducted. Then, 300 mL 250 mg/L Cr(III) solutions were passed through the bed using a peristaltic pump at the flow rates range of 5.5–10.0 mL/min, and then elution of IRN77 resin was conducted at the corresponding flow rates. Samples were collected from the exit of the column and analyzed for chromium concentrations.

Table 1
Characteristics of IRN77 cation-exchange resin

Number	Characteristics	Values
Physical characteristics		
1	Physical form	Uniform particle size spherical beads
2	Shipping weight	800 g/l
3	Harmonic mean size	650 ± 50 μm
4	Uniformity coefficient	<1.2
5	Particle size	<0.300 mm, 0.2%maximum; >1.180 mm,2.0%maximum
6	Whole beads	95% minimum
7	Breaking weight (average)	>350 g per bead
Chemical characteristics		
8	Matrix	Polystyrene DVB gel
9	Functional groups	Sulfonic acid
10	Ionic form as shipped	H^+
11	Total exchange capacity	>1.9 equiv. l^{-1} (H^+ form)
12	Moisture holding capacity	49–55% (H^+ form)
13	Ionic conversion	99% minimum H^+

2.3. IER successive regeneration study

To assess the extraction capacity of IRN77 resin after successive regeneration, a sequence of four cycles that comprised of a 40 min sorption phase and a 40 min elution phase were conducted with fixed-bed (Bed volume (BV)= 0.71 mL). Distilled water was circulated through the columns for 7 min, between the sorption and elution phases. Hence, filling the column with water prevented undesired reactions between the leachate and elution reagent. During the sorption phase, 150 mg/L Cr(III) synthetic solution was fed into the IRN77 column and the H_2SO_4 (10%) solution was fed into this column during the regeneration phase at a flow rate of 7.5 mL/min. Consequently, the feed solution during one cycle of sorption-elution was as follows: Cr(III) synthetic solution (40 min), water (7 min), elution reagent (40 min), and water (7 min). During the experiments, a total of four successive cycles were carried out. Samples were withdrawn at the outlet of the columns at 4 or 7 min intervals. Furthermore, the sorption phase effluent and the elution phase effluent were kept for calculation of the total metal uptake and release by the sorbent media.

In order to validate the process developed with model waste solution, removal of Cr(III) from actual acid-dissolution water of chromium sludge was also investigated. The acid-dissolution water samples were collected from a local tannery factory in Quanzhou, China, with a pH of 0.49, COD of 3,034 mg/L, Cr^{3+} 5,400 mg/L, and salinity 115 g/kg. The collected acid-dissolution water was diluted 40 times while the pH increased to 1.97. The extraction capacity of IRN77 resin for diluted acid-dissolution water of chromium sludge after successive regeneration was assessed as above. In order to further improve the performance of IRN77 resin, acid-dissolution water of chromium sludge after diluted 40 times was treated using 2.5% NaCLO (*v*/*v*) before it was passed through IRN77 resin, and then, the impact on the removal rate and the performance of resin after successive regeneration were also assessed as above.

2.4. Coagulation–precipitation

Coagulation and precipitation experiments were carried out in duplicate with 270 mL of effluent coming out of IRN77 columns. 1 g NaOH/MgO mixtures with mass ratio of 5:1 was added to the effluent and then stirred at 100 rpm for 30 min using a magnetic stirrer. The mixture was left to stand overnight to allow the solids to settle, and then the liquid phase was analyzed for metal quantification.

3. Results and discussion

3.1. Influence of initial concentrations and flow rates

Commonly, the electrostatic interaction, surface complexation, and ion-exchange mechanisms may be identified as the major adsorption mechanisms that work individually or in combinations for the adsorption of metal ions on the adsorbents [17]. Similar to other unit operations, ion exchange is a process whose performance is affected by a number of operational parameters, including the equilibrium resin adsorption capacity and the mass transfer rate [18]. In sorption processes, the concentrations of the metal ions and sample flow rates played an important role for obtaining high adsorption and desorption capacity.

Prediction of column performance usually involves the resolution of a set of nonlinear partial differential equations, though as an alternative, the Thomas model was selected for describing the breakthrough for the fixed-bed sorption column since it could be written in a simple form allowing a quick and easy interpretation of the results. The Thomas model can be expressed by [19]:

$$\frac{\rho_e}{\rho_0} = \frac{1}{1 + \exp[K_T(q_0 m - \rho_0 V_e)/\theta]} \tag{1}$$

where ρ_0 and ρ_e are metal ion concentrations in the influent and effluent, respectively; m is the total mass of the sorbent loaded in the column; V_e is the volume of metal solution passed through the column; K_T is the Thomas rate constant; and θ is the volumetric flow rate and q_0 is total sorption capacity of metal ion in the column. The linearized form of the Thomas model is

$$\ln\left(\frac{\rho_0}{\rho_e} - 1\right) = \frac{K_T q_0 m}{\theta} - \frac{K_T \rho_0}{\theta} V_e \tag{2}$$

The kinetic coefficient K_T and the sorption capacity of the bed, q_0, could be determined from a plot of $\ln[(\rho_0/\rho_e) - 1]$ against t at a given inlet metal concentrations and flow rates (Figs. 1 and 2), whereas the estimated parameters for IRN77 adsorption of Cr(III) were listed in Table 2. The Thomas model was found in a relatively good fitness with breakthrough curves for adsorption of Cr(III) on IRN77 resin with the high R^2 value (>0.9), and the theoretical q_0 value was very close to the experimental one.

Using the estimated parameters, the breakthrough curves for various inlet concentrations and flow rates could be predicted for Cr(III) adsorption. Figs. 3 and 4 compared the predicted and experimental data for various inlet Cr(III) concentrations and flow rates, respectively. It could be observed that the model predictions compared reasonably well with the experimental data. Therefore, the Thomas model could be used for convenient representation of the column ion exchange process under the present experimental conditions.

The removal of Cr(III) by adsorption on adsorbents by column method has been shown in Fig. 3 and Table 2. On changing the initial concentration of Cr (III) solution from 400 to 150 mg/L, the efficiency of adsorption and desorption both increased significantly. The adsorption efficiency increased from 26 to 58%, the time of ρ_e/ρ_0 values reached 90% was 15, 20, and 30 min, respectively. At the same time, the efficiency of desorption also increased from 81 to 95% (charts not shown). As shown in Table 2, the distribution coefficients or Thomas rate constants for Cr(III) ions were very high in the low concentrations in favor of sorption and desorption. The observed ρ_e/ρ_0 increase was quite obvious as on increasing the concentrations of solute (Fig. 3). At very high concentration, adsorbed chromium ions were decreased due to saturation of all adsorbent surfaces [20]. This was a common finding and has been largely reported in the literature [21–23]. Therefore, the best adsorption capacity at 10.0 mL/min flow rates were obtained at low concentration of 150 mg/L Cr(III) solution.

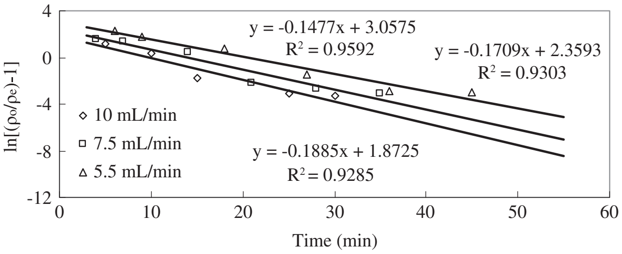

Fig. 1. Linear plots of $\ln[(\rho_0/\rho_e) - 1]$ vs. time for Cr(III) adsorption for different flow rates by application of Thomas model (resin 400 mg, ρ_0 = 250 mg/L).

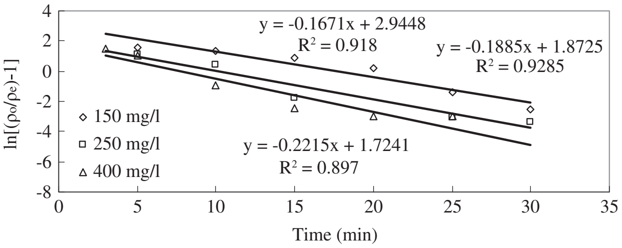

Fig. 2. Linear plots of $\ln[(\rho_0/\rho_e) - 1]$ vs. time for Cr(III) adsorption for different inlet metal concentrations by application of Thomas model (resin 400 mg, flow rate 10 mL/min).

The influence of the sample flow rates on sorption and desorption of Cr(III) was examined in the flow rates range of 5.5–10.0 mL/min at 250 mg/L Cr(III) solution and are shown in Figs. 4 and 5. As the flow rate increased, metal concentrations in the effluent increased in sorption process and decreased in desorption process. This behavior may be due to insufficient residence time of the solute in the column and the diffusion limitations of the solute into the pores of the sorbent [24]. On changing the sample flow rates from 10 to 5.5 mL/min, the efficiency of adsorption and desorption both also increased slightly. The adsorption efficiency increased from 32.6 to 36.5%, the time of ρ_e/ρ_0 values reached 90% was 20, 28, and 36 min, respectively. At the same time, the efficiency of desorption also increased from 89 to 95%.

Table 2
Parameters of Eq. (1)

Flow rate (mL/min)	Inlet concentration (mg/L)	K_T (mL/(min mg))	Theoretical q_0 (mg/g)	Experimental q_0 (mg/g)
10	250	0.75	62.4	60.4
7.5	250	0.68	65.1	64.3
5.5	250	0.59	79.3	67.4
10	400	0.55	78.4	76.1
10	150	1.11	66.3	63.8

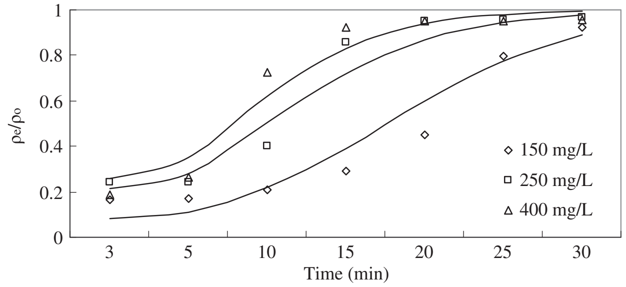

Fig. 3. Comparison of predicted (lines) and experimental (symbols) Cr(III) adsorption breakthrough curves of IRN77 for different inlet metal concentrations (Resin 400 mg, flow rate 10 mL/min).

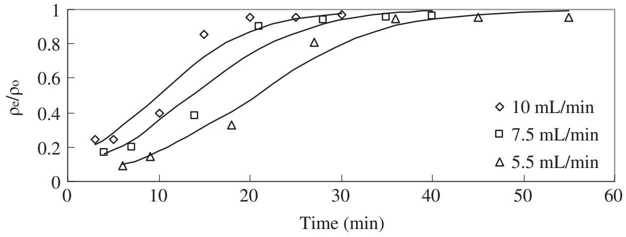

Fig. 4. Comparison of predicted (lines) and experimental (symbols) Cr(III) adsorption breakthrough curves of IRN77 for different flow rates (Resin 400 mg, $\rho_0 = 250$ mg/L).

It was found that the best adsorption and desorption capacity were obtained at 7.5 mL/min flow rate from the point of view of time and efficiency.

Desorption curve (Fig. 5) was obtained by plotting the effluent concentration (ρ_e) vs. time at the flow rates range of 5.5–10.0 mL/min. Less desorption flow rate indicated that the volume of elution was decreased which helped for easy handling and the concentration was high so that economical metal recovery was possible. It was observed that the total volume of eluent was 300 mL, and further desorption was negligible. Therefore, 300 mL 10% H_2SO_4 could help for easy handling and recovering of Cr(III) absorbed by 400 mg IRN77 resin.

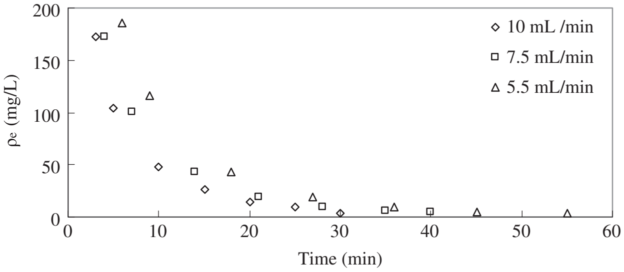

Fig. 5. Dynamic desorption curve of IRN77 for different flow rates.

3.2. Sorption and elution cycles in synthetic and acid-dissolution water

In Fig. 6, chromium showed the same sorption and elution pattern in the four sequences. As expected, the chromium outlet concentration in IRN77 column was very low during the sorption phases but was sharply eluted during desorption phases. A fraction of chromium was not retained by IRN77, whereas the extracted chromium exited the column during strong acid elution. Both trivalent metals were scattered onto the resin until the column was fed with a strong acid when both metals were solubilized. Therefore, the chromium profile was noteworthy. This explained why chromium concentration in the elution effluent was high. With the number of cycles increased, the elution outlet concentration at first-point increased gradually which may be due to the residue caused by the last elution cycle.

Furthermore, the cyclic experiments were designed to assess the resins performances evolution during several sorption and elution sequences. As a result, IRN77 resin did not show any signs of performances diminution over the four cycles (Fig. 7), the adsorption efficiency remained above 60%, and elution efficiency remained above 95%. Incomplete adsorption was due to insufficient adsorption time and adsorbent dosage, while complete elution could be achieved by extending the elution time. Moreover, the rinsing with

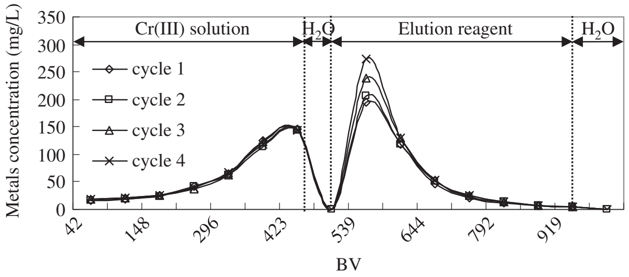

Fig. 6. Sorption and elution profile of chromium from IRN77 resin (BV = 0.71 mL; flow rate = 7.5 mL/min; feed (IRN77)=150 mg/L Cr(III) solution, H_2O and 10% H_2SO_4).

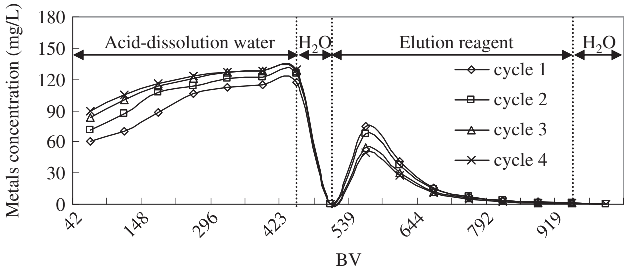

Fig. 8. Sorption and elution profile of chromium from IRN77 resin (BV = 0.71 mL; flow rate = 7.5 mL/min; feed (IRN77)=135 mg/L Cr(III) acid-dissolution water, H_2O and 10% H_2SO_4).

water between the elution and sorption steps did not cause the release of chromium, meaning Cr recovery could not be improved by the rinsing with water.

In order to validate the process developed with synthetic solutions, removal of Cr(III) from actual acid-dissolution water of chromium sludge was also investigated. The cyclic experiments about acid-dissolution water of chromium sludge were designed to assess the resins performances evolution during several sorption and elution sequences and, more especially, to look for dissolved organic matter (DOC) negative impact on the resin sorption capacities. As a result, metals removal and elution by IRN77 resin did not stay stable over the four cycles, meaning the DOC affected severely the performance of IRN77 resin (Fig. 8). With the number of cycles increased, the chromium outlet concentration in IRN77 column increased gradually during the sorption phases, and the adsorption efficiency decreased from 29 to 14%. The adsorption efficiency was lower than the theoretical value of the synthetic solution (60%), because of the refractory chromium fraction and competitive salinity impurities in acid-dissolution water. Cr(III) might be complexed by sulfate and carboxyl ligands available in acid-dissolution water produced from the sulfuric acid used during the acid-dissolution step. Dabrowski et al. [25] also reported that sulfates might cause difficulties because trivalent chromium complexes were not sorbed by sulfonic cation exchangers. But DOC was also responsible for the decreased adsorption efficiency gradually over the four cycles. The elution outlet concentration decreased gradually which may be caused by the reduction of the adsorption capacity, but elution efficiency remained above 95%. The results showed that DOC had little effect on the elution phases.

In order to eliminate the influence of DOC on the resin properties, acid-dissolution water of chromium sludge after diluted 40 times was treated using 2.5% NaCLO (*v*/*v*) before passing IRN77 resin. As a result, removal of the metals and elution by IRN77 resin stayed stable over the four cycles, meaning 2.5% NaCLO (*v*/*v*) could mitigate effectively the impact of DOC on the resin properties (Fig. 9). At the same time, the adsorption efficiency increased from 29 to 37% after 2.5% NaCLO pretreatment which could

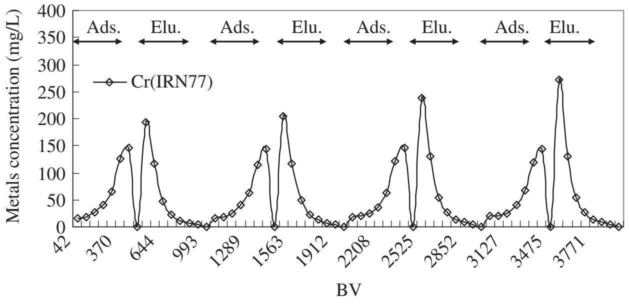

Fig. 7. Successive sorption and elution profile of IRN77 resin (sequence = adsorption (Ads.) 40 min, rinsing 7 min, elution (Elu.) 40 min and rinsing 7 min; adsorption feed = 150 mg/L Cr(III) solution; elution feed = H_2SO_4 10%; flow rate = 7.5 Ml/min; BV = 0.71 mL).

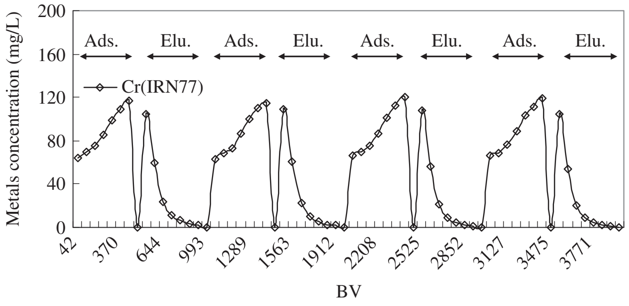

Fig. 9. Successive sorption and elution profile of IRN77 resin (sequence = adsorption (Ads.) 40 min, rinsing 7 min, elution (Elu.) 40 min and rinsing 7 min; adsorption feed = 2.5% NaCLO-treated acid-dissolution water of 135 mg/L Cr(III); elution feed = H_2SO_4 10%; flow rate = 7.5 mL/min; BV = 0.71 mL).

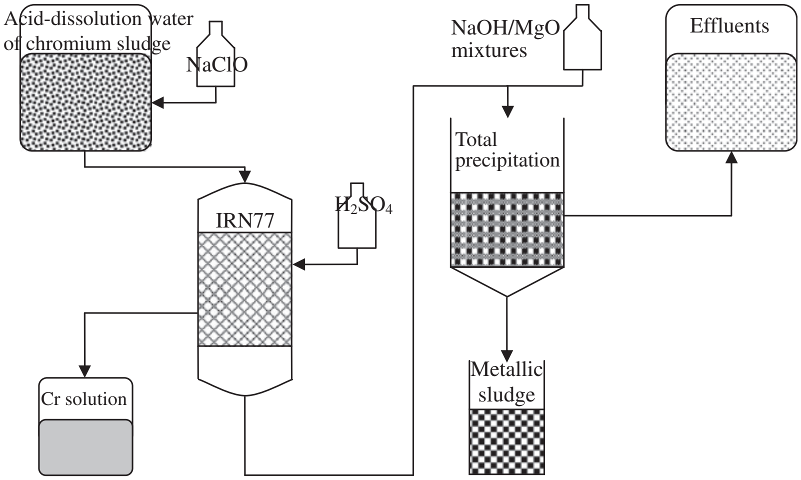

Fig. 10. A scheme for the process of successive IRN77 resin and precipitation for treatment of acid-dissolution water of chromium sludge.

reach 62% of the theoretical adsorption efficiency in synthetic solutions and elution efficiency remained above 95%. The adsorption capacity improved effectively may be due to the organic removal (100%). Therefore, 2.5% NaCLO (*v*/*v*) could improve effectively adsorption efficiency and cyclic characteristic.

3.3. Process design

After passing 2.5% NaCLO-treated acid-dissolution water of chromium sludge through IRN77 columns, the effluent contained 85 mg Cr /L. In order to enhance chromium removal, a coagulation–precipitation step was conducted using NaOH/MgO mixtures. A previous study showed that raising the pH in presence of ferric chloride enables chromium removal from CCA-treated wood leachate [26]. Hence, duplicate tests were conducted with IRN77 effluent using NaOH/MgO mixtures to raise the pH. The filtered effluent, issuing from the coagulation–precipitation step, contained concentrations of 0.5 mg Cr/L in average. Therefore, the precipitation seemed to be an efficient finishing treatment for chromium removal after using an ion exchange resin. Fig. 10 showed a schematic drawing of the set-up of the overall process that could be used for treatment of acid-dissolution water of chromium sludge. Moreover, the IRN77 treatment of 2.5% NaCLO-pretreated acid-dissolution water of chromium sludge followed by coagulation and precipitation treatment with NaOH/MgO mixtures allowed for high Cr concentration reduction to values, in the final effluent, underneath the permitted guidelines for effluent discharge in the industrial wastewater which was 1.5 mg Cr/L.

4. Conclusions

Under dynamic conditions, the increase in the metal concentration and the flow rate caused a decrease of the breakthrough performance. The model with its model parameters properly identified was observed to predict reasonably well the experimental breakthrough curves. IRN77 showed lower extraction capacity in acid-dissolution water of chromium sludge than in synthetic solutions in four sorption and elution cycles, because of the refractory chromium fraction and competitive salinity impurities in acid-dissolution water. After passing 2.5% NaCLO-treated acid-dissolution water of chromium sludge through IRN77 columns, IRN77 resin did not show any signs of performances diminution over the four consecutive sorption and elution cycles. IER effluents were efficiently treated by NaOH/MgO mixtures coagulation and precipitation. Final effluents contained less than 0.5 mg/L of chromium which met the effluent discharge in industrial wastewater in china (1.5 mg Cr/L). H_2SO_4 (10%) was efficient elution solutions for IRN77 resin and 95% of the chromium could be recovered from the column. In this case, the combination of oxidation/resin and coagulation–precipitation could make the advanced reuse of acid-dissolution water become a reality.

Acknowledgments

This work was financially supported by State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (Grant No. 2010DX06), National Natural Science Foundation of China (No. 51178136), and State Environmental Protection Key Laboratory of Microorganism Application and Risk Control (No. MARC2012D009). The authors are grateful to Key Lab of Groundwater Resources and Environment, Ministry of Education, Jilin University for the support.

References

[1] G. Calvanese, R. Cioffi, L. Santoro, Cement stabilization of tannery sludge using quaternary ammonium salt exchanged bentonite as pre-solidification adsorbent, Environ. Technol. 23 (2002) 1051–1062.

[2] C.Z. Yu, C.B. Zhang, S.L. Ding, The present conditions of tannery sludge and prospect of composting with sludge, China Leather 29 (2000) 4–7.

[3] L.X. Zhou, A.T. Hu, N.F. Ge, Study on utilization of municipal sewage sludge in farmland and forest land, Acta Ecologica Sinica 9 (1999) 185–193.

[4] S.G. Zhou, S.M. Wang, S.P. Yu, L.X. Zhou, Isolation of Thiobacillus ferrooxidans and its application on heavy metal bioleaching from sewage sludge, Huanjing Kexue 24 (2003) 56–60.

[5] A. Lopez, T. Rotunno, F. Palmisano, R. Passino, G. Tiravanti, P.G. Zambonin, Simultaneous determination of chromium (III), aluminum (III), and iron (II) in tannery sludge acid extracts by reversed-phase high-performance liquid chromatography, Environ. Sci. Technol. 25 (1991) 1262–1266.

[6] S.B. Shen, R.D. Tyagi, J.F. Blais, Extraction of Cr(III) and other metals from tannery sludge by mineral acids, Environ. Technol. 22 (2001) 1007–1014.

[7] G. Macchi, M. Pagano, M. Pettine, M. Santori, G. Tiravanti, A bench study on chromium recovery from tannery sludge, Water Res. 25 (1991) 1019–1026.

[8] S.G. Zhou, L.X. Zhou, S.M. Wang, D. Fang, Removal of Cr from tannery sludge by bioleaching method, J. Environ. Sci. 18 (2006) 885–890.

[9] E. Kilic, J. Font, R. Puig, S. Colak, D. Celik, Chromium recovery from tannery sludge with saponin and oxidative remediation, J. Hazard. Mater. 185 (2011) 456–462.

[10] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard. Mater. 100 (2003) 231–243.

[11] S. Kocaoba, G. Akcin, Removal of chromium (III) and cadmium (II) from aqueous solutions, Desalination 180 (2005) 151–156.

[12] S.A. Cavaco, S. Fernandes, M.M. Quina, L.M. Ferreira, Removal of chromium from electroplating industry effluents by ion exchange resins, J. Hazard. Mater. 144 (2007) 634–638.

[13] J.A.S. Tenorio, D.C.R. Espinosa, Treatment of chromium plating process effluents with ion exchange resins, Waste Manage. 21 (2001) 637–642.

[14] S. Kocaoba, G. Akcin, Chromium(III) removal from wastewaters by a weakly acidic resin containing carboxylic groups, Adsorpt. Sci. Technol. 22 (2004) 401–410.

[15] S. Rengaraj, K.H. Yeon, S.Y. Kang, J.U. Lee, K.W. Kim, S.H. Moon, Studies on adsorptive removal of Co(II), Cr(III) and Ni (II) by IRN77 cation-exchange resin, J. Hazard. Mater. 92 (2002) 185–198.

[16] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. 102 (2003) 257–275.

[17] S.B. Deng, R.B. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: Performance and mechanisms, Water Res. 38 (2004) 2424–2432.

[18] P. Malakul, K.R. Srinivasan, H.Y. Wang, Metal adsorption and desorption characteristics of surfactant modified clay complexes, Ind. Eng. Chem. Res. 37 (1998) 4296–4301.

[19] M. Tabakci, M. Yilmaz, Sorption characteristics of Cu(II) ions onto silica gel-immobilized calix 4 arene polymer in aqueous solutions: Batch and column studies, J. Hazard. Mater. 151 (2008) 331–338.

[20] M.A. Farajzadeh, A.B. Monji, Adsorption characteristics of wheat bran towards heavy metal cations, Sep. Purif. Technol. 38 (2004) 197–207.

[21] J. Bajpai, R. Shrivastava, A.K. Bajpai, Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary biopolymeric beads of cross linked alginate and gelatin, Colloid Surf. A-Physicochem. Eng. Asp. 236 (2004) 81–90.

[22] O. Gezici, H. Kara, M. Ersoz, Y. Abali, The sorption behavior of a nickel-insolubilized humic acid system in a column arrangement, J. Colloid Interface Sci. 292 (2005) 381–391.

[23] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J. 84 (2001) 95–105.

[24] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of cobalt(II) and nickel(II) by seaweeds: Batch and column studies, Sep. Purif. Technol. 44 (2005) 53–59.

[25] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.

[26] A. Janin, F. Zaviska, P. Drogui, J.F. Blais, G. Mercier, Selective recovery of metals in leachate from chromated copper arsenate treated wastes using electrochemical technology and chemical precipitation, Hydrometallurgy 96 (2009) 318–326.