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Chromic acid recovery from waste acid solution by an ion exchange process: equilibrium and column ion exchange modeling

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Abstract

A four-step ion exchange process for chromic acid recovery from waste acid solution was proposed in the present work. Strong acid anionic (OH-type) ion exchange resin was used in the first step to capture chromic acid (H_2CrO_4) which was converted to sodium chromate (Na_2CrO_4) by sodium hydroxide (NaOH) solution in the second step. Sodium chromate was converted back to chromic acid using strong base cationic (H-type) ion exchange resin in the third step and in the fourth step, the exhausted ion exchange resin was regenerated by hydrochloric acid (HCl) solutions. Batch and column experimental tests were conducted to provide data for theoretical modeling and to verify the system performance of the recovery process. Results of batch equilibrium tests indicated that Freundlich isotherm describes well both chromic acid and sodium chromate adsorption equilibrium. A theoretical column model adopted in this work was found to describe well the ion exchange breakthrough characteristics. The four-step process was proved to be efficient and was capable of providing continuous chromic acid recovery operation.

Keywords: Chromic acid recovery; Four-step ion exchange process; Anionic and cationic resins; Column adsorption; Equilibrium; Isotherms

1. Introduction

Chromic acid (H_2CrO_4) is widely employed in many industries for plating, leather tanning, electrolytic stripping of copper, anodizing of aluminum, passivation of cadmium, magnesium and zinc [1,2]. In more recent development in the printed circuit board manufacturing, strong chromic acid is used as an oxidant in the desmearing operation. In these industries, a large quantity of waste chromic acid solution is commonly generated. The public concerns about this waste acid solution stem from the fact that the chromium in the aqueous solution can be readily adsorbed by marine animals and directly enter the human food chains, thus, presenting a high health risk to consumers [2–4]. Hence, the waste chromic acid solution has been strictly regulated by the government. It must be properly treated before it is allowed for direct discharge to natural water streams.

During the past several decades, many physicochemical methods have been developed for chromium removal from waste chromium acid solution. These methods include chemical coagulation, adsorption, extraction, ion exchange and membrane separation process [3,5–12]. In many industrial practices in Taiwan, a popular method is to reduce the hexavalent chromium (Cr^{6+}) by sodium sulfite (Na_2SO_3) to trivalent form (Cr^{3+}). The trivalent chromium is in turn converted under alkaline condition to $Cr(OH)_3$ which precipitates out of the aqueous solution. Such a process is not easy to operate and generates a significant amount of toxic sludge that entails careful further disposal. Alternatively, ion exchange arn adsorption are becoming a popular method that has received much attention in recent years. Dikshit [13], Santiago et al. [14], Khan et al. [15], Sharma and Forster [16], Zhao et al. [17] and Hamadi et al. [18] were investigators studying chromium removal by ion exchange and various adsorbents. The previous investigations focused primarily on reducing the chromium content in the waste acid solution to the discharge standard. In fact, the chromic acid in the waste solution, if properly dealt with, can be recovered as a raw material and recycled back to the electroplating and other industrial processes for reuse. Relatively little attention has been paid to this aspect in the past.

The objective of the present study is to address this issue by employing a four-step ion exchange process in recovering chromic acid from the waste solution. In this multi-step process, two types of ion exchange resins were used. In the first two steps, chromate was captured and concentrated using a strong base anionic ion exchange resin while in the last two steps, the chromate was converted to chromic acid by a strong acid cationic ion exchange resin. The present

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multi-step process allows continuous operation of chromic acid recovery in a efficient manner and thus has potential practical applications.

2. Ion exchange process for chromic acid recovery

In this section, the basic principle of the two-stage ion exchange process will be illustrated. The process is in essence a four-step operation. In the first step, chromate is adsorbed onto the solid (the OH-type resin) phase by exchange with OH^- which is combined with H^+ in the aqueous solution to form H_2O. In the second step, the adsorbed chromate in the solid phase is replaced under alkaline condition by OH^- and is detached. It combines with Na^+ in the aqueous solution for form Na_2CrO_4. These first two steps of ion exchange can be represented by

$$\text{adsorption}: \quad 2\text{R–OH} + H_2CrO_4 \rightarrow R_2\text{–}CrO_4 + 2H_2O$$

$$\text{desorption}: \quad R_2\text{–}CrO_4 + 2NaOH \rightarrow 2\text{R–OH} + Na_2CrO_4$$

where R–OH represents the OH-type ion exchange resin. It is noted that between the adsorption and desorption steps, chromic acid in the original waste acid solution is significantly concentrated although it form a sodium salt (Na_2CrO_4) after desorption, as shown in the second reaction.

The sodium chromate obtained from the second ion exchange (desorption) step needs to be converted back to chromic acid. This is accomplished in the third step using the H-type ion exchange resin. In this step, the sodium ion in the aqueous solution is adsorbed by ion exchange with H^+ on the solid phase and the chromic acid is formed according to

$$\text{conversion}: \quad Na_2CrO_4 + 2\text{R–H} \rightarrow H_2CrO_4 + 2\text{R–Na}$$

where R–H is the H-type ion exchange resin. In the final step, the exhausted ion exchange resin (R–Na) is regenerated by hydrochloric acid (HCl) solution with which H^+ is exchanged with Na^+ on the solid phase. This last step is represented by

$$\text{regeneration}: \quad \text{R–Na} + HCl \rightarrow \text{R–H} + NaCl$$

These four steps complete the present chromic acid recovery process. In summary, the multi-step ion exchange works this way: the chromic acid is captured from the waste acid solution in the first step using the OH-type ion exchange resin and converted to sodium chromate in the second using NaOH solution. The second step also serves to regenerate the exhausted OH-type ion exchange resin. The sodium chromate is then converted back chromic acid in the third step utilizing the H-type ion exchange resin and is recovered. Finally, the exhausted H-type ion exchange resin is regenerated in the fourth step using HCl solution. The stepwise process permits continuous and efficient operation for practical purposes. In the following Section 3, the equilibrium adsorption capacities of the ion exchange resins and the performances of the multi-step ion exchange process will be tested and evaluated.

3. Experimental studies

The ion exchange resins employed in this study were the Ambersep 900 and 132 resins, as obtained from Rohm and Haas Co. (Philadelphia, PA). The Ambersep 900 is a strong acid anionic resin (OH-type) and the Ambersep 132 is a strong base cationic resin (H-type). For pretreatment, both Ambersep resins were washed several times first by deionized water, followed by rinsing with acetone to remove all impurities on the resins. They were then rinsed with deionized water several times and dried at 60 °C in an oven for at least 24 h. For experimental batch and column tests, the stock solutions of chromic acid (H_2CrO_4) and sodium chromate (Na_2CrO_4) were prepared by dissolving in deionized water appropriate amounts of reagent grade chromium oxide (CrO_3) and sodium chromate, as obtained from E Merck GmbH (Darmstadt, Germany).

For equilibrium adsorption experimental tests, 250 ml of the stock chromic acid solution were put in a flask and 0.1 g of pretreated Ambersep 900 resin was added. The flask was sealed and placed in a constant-temperature shaker maintained at 25 °C and 120 cycles per minute shaking speed for 24 h to ensure adsorption equilibrium. Aqueous samples were then taken for hexavalent chromium (Cr^{6+}) measurements using a GBC 932 atomic absorption spectrophotometer (GBC Scientific Equipment Pvt. Ltd., Melbourne, Australia). The equilibrium experimental tests were repeated for solutions of different initial chromic acid concentrations to ensure that sufficient data were collected for isotherm identification of Cr^{6+} adsorption by Ambersep 900 resin. Similar experimental tests were performed for Na_2CrO_4 equilibrium adsorption by Ambersep 132 that adsorbed the sodium ion (Na^+) from the aqueous solution. The equilibrium sodium ion concentration in the aqueous solution was measured using a JASCO high performance liquid chromatography (HPLC; Model PU 980i, JASCO, Inc., Tokyo, Japan). Again, sufficient number of equilibrium test runs were conducted for different initial sodium chromate concentrations to gather data for isotherm identification of sodium adsorption by the Ambersep 132 resin. It is noted that the equilibrium and the following column test runs were replicated at least once to ensure the accuracy of the collected data and the average of two data sets was reported. In nearly all instances, the accuracy of data was very good, with the data being deviated from the average in less than 2%.

The above equilibrium adsorption tests permitted determination of the equilibrium amounts of chromate and sodium ions adsorbed by the Ambersep 900 and 132 ion exchange resins, respectively, for various initial chromic acid and sodium chromate concentrations. However, the performance of the multi-step adsorption/regeneration process outlined in the previous section needs to be evaluated in column tests.

For the column ion exchange test runs, a pyrex tube of 2 cm i.d. and 30 cm height was used. The column was equipped with an external water jacket for temperature control. Ten grams of pretreated Ambersep 900 was randomly packed in the column to a bed volume (BV) of 22 cm^3. The stock chromic acid solution with a Cr^{6+} concentration between 250 and 750 mg/l was fed to the top of the resin column by a feed pump at a desired rate between 10 and 30 ml/min. Samples were taken periodically at the bottom of the resin column for Cr^{6+} concentration measurement using the GBC 932 atomic absorption spectrophotometer. As a test run was started, the exit Cr^{6+} concentration was initially nil and after a certain time had elapsed, it began to rise. The run continued until the exit Cr^{6+} concentration became close to the inlet. For the Cr^{6+} desorption (the second step), 10 wt.% NaOH solution was fed to the top of column at one half of the adsorption feeding rate. The same GBC 932 AA was used to determine the Cr^{6+} concentration in the exit samples. A desorption run was terminated when the exit Cr^{6+} concentration was close to nil.

For conversion of sodium chromate to chromic acid, the stock sodium chromate solution was fed to the top of the column randomly packed with 12 g of Ambersep 132 ion exchange resin. The feed flow rate was chosen between 5 and 15 ml/min. The sodium ion (Na^+) concentration in the aqueous solution exiting the column was detected using the JASCO PU 980i HPLC. A test run was terminated when the exit Na^+ concentration was close to the inlet. Finally, the exhausted Ambersep 132 column was regenerated by feeding 5 wt.% HCl solution at a flow rate between 5 and 15 ml/min. The sodium ion concentration in the exit stream was monitored periodically by the JASCO HPLC. A regeneration run was completed when no more sodium ion was detected in the exit solution.

4. Results and discussion

4.1. Equilibrium ion exchange isotherms

Two general isotherms commonly employed to describe the equilibrium ion exchange relation between the liquid and solid phases are the Langmuir and the Freundlich models [9] which are represented by

$$Q_e = \frac{abC_e}{1 + bC_e} \tag{1}$$

$$Q_e = KC_e^{1/n} \tag{2}$$

where Q_e and C_e are the equilibrium ion exchange capacity of Ambersep 900 (or 132) and the equilibrium Cr^{6+} (or Na^+) concentration in the aqueous solution, respectively, and a, b, K and n are the constant isotherm parameters. The observed data of the equilibrium ion exchange tests are shown in Fig. 1(a) for Ambersep 900 adsorption of Cr^{6+} and in Fig. 1(b) for Ambersep 132 adsorption of Na^+. These two graphs also show the model fit using the two isotherms. The model fit reveals that the Freundlich isotherm represents Ambersep 900 adsorption of Cr^{6+} better the Langmuir isotherm. However, for Ambersep 132 adsorption of Na^+, both isotherms represent the observed data equally well. The isotherm parameters obtained by the model fit are listed in Table 1, noting that the values of r^2 for the model fit are greater than 0.98. These isotherm parameters allow easy determination of the equilibrium ion exchange capacities of both ion exchange resins for different initial concentrations.

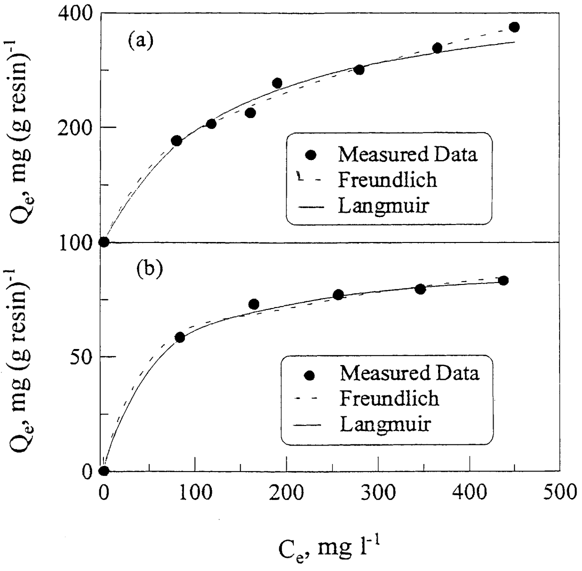

Fig. 1. Isotherm model fits of observed equilibrium ion exchange data of Ambersep 900 (a) and Ambersep 132 (b) with 0.1 g of ion exchange resin and at 25 °C.

4.2. Results of column tests

Like other unit operations, adsorption is a process whose performances are affected by a large number operating factors. Among these factors, the equilibrium resin adsorption capacity and the mass transfer rate are very important ones [8,9]. A process performance parameter of practical importance to process design is the exit Cr^{6+} (or Na^+) concentration from the column. Prediction of this exit concentration is not easy. Usually it involves solving a set of nonlinear partial differential equations by sophisticated numerical schemes

Table 1
Parameters of the Freundlich and Langmuir Isotherms

Ambersep	Langmuir		Freundlich	
	a	*b*	*K*	*n*
900	451.3	0.0075	25.65	2.28
132	92.1	0.0021	24.56	4.91

with proper identification of a number of system parameters [9]. As an alternative, a macroscopic version was developed from the original microscopic model by Bohart and Adams [19] and Thomas [20] for describing the solute breakthrough behavior of a column adsorber. The main advantages of this model are its simplicity and reasonable accuracy in predicting the breakthrough curves (times) under various operating conditions. The macroscopic model is represented by

$$\ln\left(\frac{C_0 - C}{C}\right) = \ln\left[\exp\left(\frac{k_1 Q_e M}{F}\right) - 1\right] - k_1 C_0 t \qquad (3)$$

where C is the solute concentration in the exit aqueous stream at time t (mg/l), C_0 the inlet solute concentration (mg/l), k_1 the rate constant of adsorption (l/(mg h)), Q_e the equilibrium solid-phase concentration of sorbed solute (gram of solute per gram of adsorbent), M the mass of adsorbent (g), F the flow rate (l/h) and t the time (h). Due to relatively larger value of $\exp[(k_1 Q_e M)/F]$ than 1 in most instances, Eq. (3) can be rewritten as:

$$\ln\left(\frac{C}{C_0 - C}\right) = k_1 C_0 t - \frac{k_1 Q_e M}{F} = k_1 C_0\left(t - \frac{Q_e M}{C_0 F}\right) \qquad (4)$$

The equation was also adopted by Hutchins [21] for the design of activated carbon adsorption system. According to Eq. (4), the left-hand quantity, $\ln[C/(C_0 - C)]$, is a linear function of time (t) for a given set of system and operating conditions. Hence, a linear plot of $\ln[C/(C_0 - C)]$ versus t yields a slope and intercept for estimation of the model parameters. In fact, the above equation is essentially the same as the simplified logistic function that describes the biological or population growth and distribution [22]:

$$\ln\left(\frac{C}{C_0 - C}\right) = k(t - \tau) \qquad (5)$$

Comparison of Eqs. (4) and (5) reveals that $k = k_1 C_0$ and $\tau = Q_e M/(C_0 F)$. It is noted that $Q_e M/(C_0 F)$ in Eq. (4) or τ in Eq. (5) represents the time when $C = C_0/2$.

The two parameters in Eq. (5) can be readily determined by plotting $\ln[C/(C_0 - C)]$ against t using the observed data. Fig. 2 shows the plot of $\ln[C/(C_0 - C)]$ versus t for various inlet Cr^{6+} concentrations. The linear relation shown here as represented by Eq. (5) is adequate. In Eq. (5), the parameter τ is the adsorption time when $\ln[C/(C_0 - C)]$ is equal to zero (i.e. $C = C_0/2$) and k is determined from the slope. The parameters determined in this fashion for Ambersep 900 adsorption of Cr^{6+} for different inlet concentrations and flow rates and the corresponding ones for Ambersep 132 adsorption of Na^+ are listed in Table 2. Using the estimated parameters, the breakthrough curves for different inlet concentration and flow rate conditions could be reconstructed for Cr^{6+} adsorption. Fig. 3(a) and (b) compare the theoretical and observed breakthrough curves for different inlet Cr^{6+} concentrations and different flow rates, respectively. Similar comparison is displayed in Fig. 4(a) and (b) for Na^+ adsorption (the third or conversion step). It is apparent that the model predictions compare reasonably well with the observed data. Hence the simplified version of the logistic equation, as represented by Eq. (5), can be recommended for convenient representation of the breakthrough curves of the present column ion exchange processes.

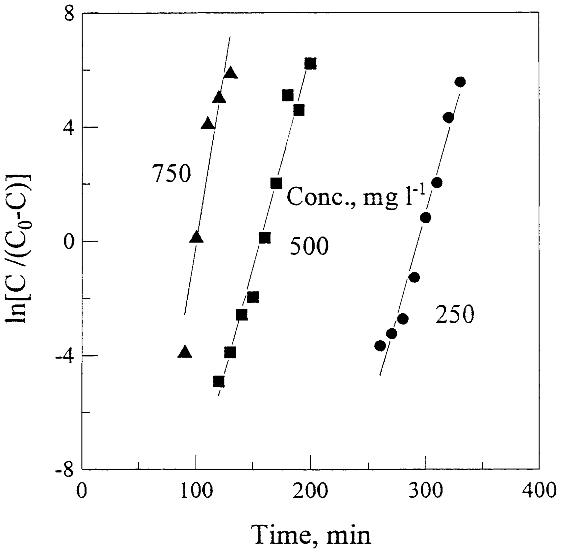

Fig. 2. Plot of $\ln[C/(C_0 - C)]$ vs. ion exchange time (t) for chromate adsorption by Ambersep 900 with 20 ml min^{-1} feed flow rate and at 25 °C.

A practical application of the experimental breakthrough curves is the determination of the breakthrough time. The breakthrough time can help establish the optimum operating conditions of the ion exchange process. However, accurate estimation of the breakthrough time from the experimental curves is not easy especially when the breakthrough concentration is very low. This difficulty can be resolved with Eq. (5). For example, the discharge standard of Cr^{6+} in the

Table 2
Parameters of theoretical breakthrough equations

	k	τ
Ambersep 900 adsorption of chromate		
Flow rate (ml/min)		
10	8.1	317.3
20	6.5	156.6
30	5.5	109.5
Inlet concentration (mg/l)		
250	6.8	293.5
500	6.5	156.6
750	3.6	101.5
Ambersep 132 Adsorption of sodium ion		
Flow rate (ml/min)		
5	12.2	388.4
10	5.9	196.5
15	4.3	117.8
Inlet concentration (mg/l)		
221	12.1	377.7
442	5.9	196.5
663	4.8	122.1

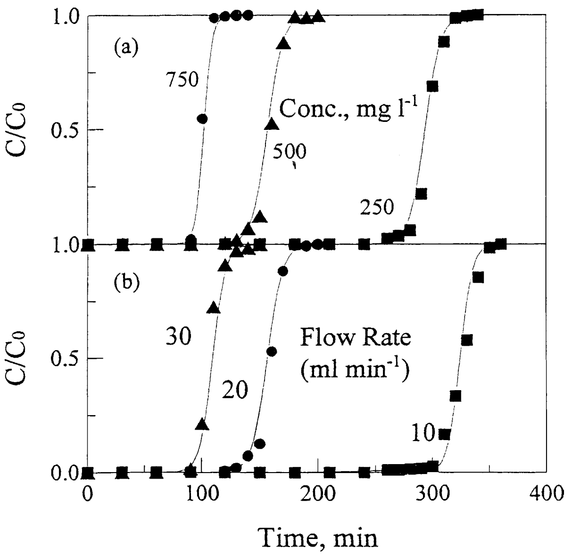

Fig. 3. Comparison of predicted (solid lines) and observed (solid squares, triangles and circles) chromate adsorption breakthrough curves of Ambersep 900 for different inlet chromium concentrations (a) and different feed flow rates (b).

industrial wastewater in this country is 0.5 mg/l. For a given inlet chromate concentration, the breakthrough time meeting this discharge standard would vary with the wastewater flow rate and is easily determined using Eq. (5) and the model parameters in Table 2. The amounts of chromate adsorbed are then computed in terms of the inlet chromate concentration and the feed flow rate. Interestingly, these amounts were found to be essentially independent of both operating variables with an average of 0.1 ± 0.005 g/g resin. The average volume of waste chromic acid solution treated was estimated to be 8.7 BV/g resin. The information obtained in the fashion can facilitate the design and operation of the chromic acid recovery system.

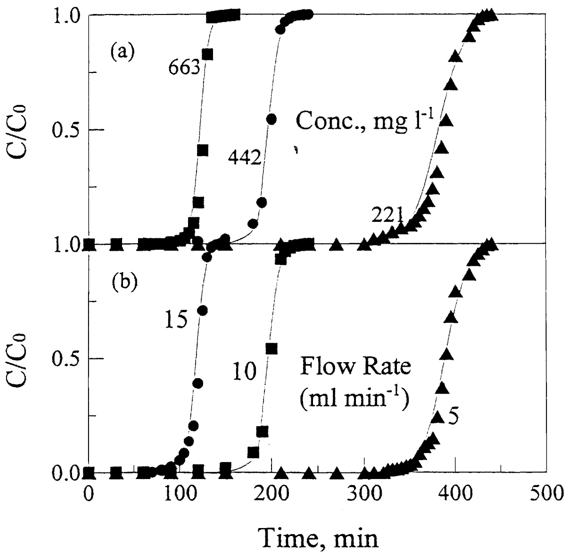

Fig. 4. Comparison of predicted (solid lines) and observed (solid symbols) sodium adsorption breakthrough curves of Ambersep 132 for different inlet chromium concentrations (a) and different feed flow rates (b).

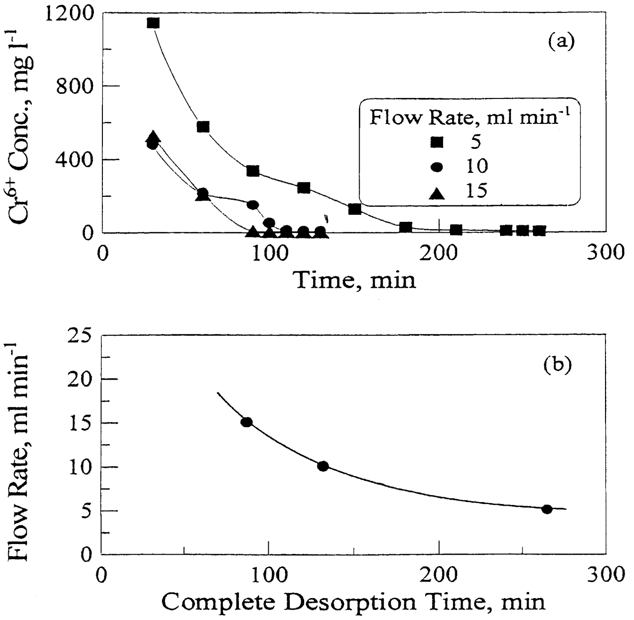

Fig. 5. Chromium concentration in the exit aqueous solution as a function of time for Ambersep 900 regeneration (a) and the relation between the feed flow rate and the desorption time for complete regeneration (b).

Figs. 3 and 4 demonstrated the effectiveness aspect of ion exchange of Cr^{6+} and Na^{+} by Ambersep 900 and 132, respectively. However, for continuous operation of the chromic acid recovery system, regeneration of exhausted ion exchange resins plays a crucial role also due to the need of repeated use of the ion exchange resins for cost reasons. Regeneration of exhausted Ambersep 900 and 132 resins was achieved by using 10 wt.% NaOH and 5 wt.% HCl solutions, respectively, as recommended by the manufacturer. In the regeneration of Ambersep 900 resin using 10 wt.% NaOH solution, the chromate on the solid (resin) phase was replaced by exchange with OH^{-} and was detached. The chromate combined with Na^{+} in the aqueous solution to form sodium chromate. Fig. 5(a) demonstrates the Cr^{6+} concentration change in the exit solution as a function of the feed flow rate. The time to reach zero Cr^{6+} concentration (complete desorption of Cr^{6+}) strongly depends on the feed flow rate, varying from 265 min at 5 ml/min to 132 min at 10 ml/min and 87 min at 15 ml/min. Although, regeneration at low flow rate (5 ml/min) took longer to complete, it could be a better choice in practice than those at higher flow rates (10 and 15 ml/min) because the former avoided generating large volumes of dilute solution. The total amounts of solution containing Na_2CrO_4 collected for all feed flow rates remain relatively steady at 1.315±10 ml or about 60 BV which is close to the volume of NaOH solution recommended by the manufacturer for regeneration. For efficient desorption operation, the complete desorption time may be shortened to less than 1 h by a further increase in the feed flow rate, as shown in Fig. 5(b).

In the regeneration of exhausted Ambersep 132 using 5 wt.% HCl solution, the Na^+ in the solid phase was replaced by exchange with H^+. Thus, the released Na^+ was eluted out of the ion exchange resin column. The operation was found to be highly efficient in the experimental tests. For example, for a feed flow rate of 10 ml/min, only 7 min was needed for complete regeneration of exhausted Ambersep 132. Such a short regeneration time was consistently observed for other feed flow rates. Hence, it can be safely said from the test results that using 5 wt.% HCl solution, regeneration of exhausted Ambersep 132 resin can be efficiently accomplished in less than 10 min.

The regenerated Ambersep 900 and 132 resins were tested for chromate and sodium adsorption to compare their performances with those of the virgin ones. The breakthrough curves of the virgin and regenerated resins are demonstrated in Fig. 6(a) for Ambersep 900 and Fig. 6(b) for Ambersep 132. For practical purposes, the two sets of breakthrough curves shown in these figures have little difference. In fact, the test results indicated that the ion exchange capacities of both regenerated resins had decreased only by less than 2% after 10 adsorption/regeneration cycles. Hence, both ion exchange resins are expected to perform well for continuous operation of chromic acid recovery for a long period.

4.3. Flowchart for continuous chromic acid recovery

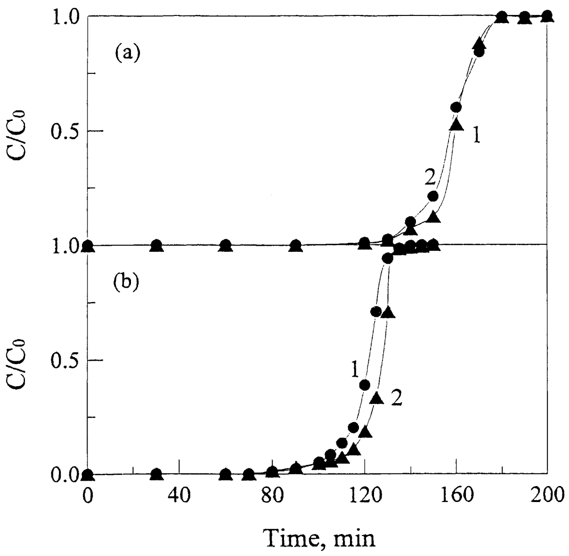

Fig. 6. Comparison of the breakthrough curves of virgin and regenerated Ambersep 900 (a) and Ambersep 132 (b); 1,virgin resin, 2, regenerated resin.

Based on the proposed procedure and according to the test results discussed in the previous section, a feasible flow chart for chromic acid recovery is illustrated in Fig. 7. For continuous operation, two packed columns are required for each of OH- and H-type resins. The recovery process starts with the waste acid solution entering the first OH-type resin column where the chromate is adsorbed onto the solid phase by ion exchange with OH^{-1}. The ion exchange operation continues until the Cr^{6+} concentration in the exit aqueous solution exceeds the direct discharge standard (0.5 mg/l). While the waste acid solution is switched to the second OH-type resin column for continuous operation, regeneration of the first column starts immediately by feeding in 10 wt.% NaOH solution at a rate of 1 BV/min for 60 min. The regenerated first OH-type resin column is ready for the next round operation.

The Na_2CrO_4 solution collected from the OH-type resin column is fed at a rate of 0.68 BV/min to the first H-type

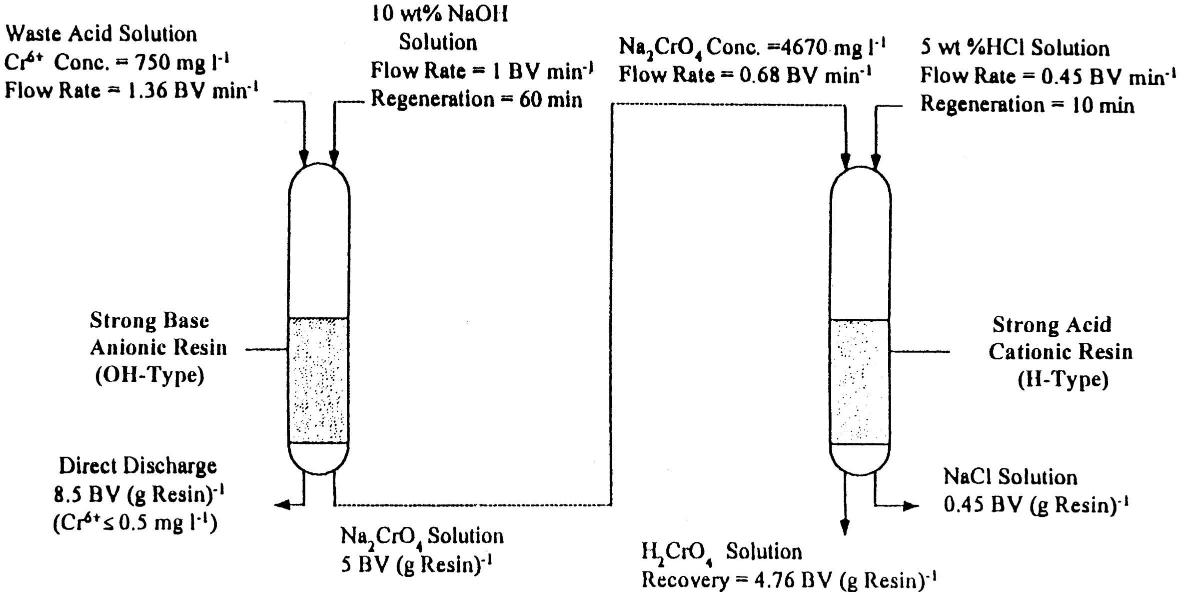

Fig. 7. Process flow chart of chromic acid recovery system.

resin column for conversion in which sodium is adsorbed on the solid phase by ion exchange with H^+. The conversion operation is terminated until the sodium ion appears in the exit aqueous solution and the H_2CrO_4 solution collected from this resin column is recycled for reuse. The Na_2CrO_4 solution is diverted to the second H-type resin column for continuous operation and regeneration of the first column ensues. The regeneration is accomplished by feeding in 5 wt.% HCl solution at a rate of 0.45 BV/min for just 10 min.

5. Conclusions

In the present work, a multi-step ion exchange process was employed for efficient recovery of chromic acid from waste acid solution. The strong base anionic (OH-type) and strong acid cationic (H-type) ion exchange resins were employed in the process. Experimental tests were conducted to determine the equilibrium ion exchange capacities of both resins. The empirical Freundlich isotherm was found to adequately describe the equilibrium relation between the solid (resin) and liquid phases of the ion exchange process. A theoretical model was adopted for representing the column breakthrough. The theoretical model with its model parameters properly identified was observed to predict reasonably well the experimental breakthrough curves. Such a theoretical model can significantly simplify determination of the breakthrough times of the ion exchange process and facilitate the process design by optimizing the operation conditions. Based on the proposed ion exchange procedure and the test results, a flow chart for the chromic acid recovery process is demonstrated. The process allows efficient and continuous operation.

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