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Enhancing the adsorption of chromium(VI) from the acidic chloride media using solvent impregnated resin (SIR)

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HIGHLIGHTS

- Both polymeric support and extractant of SIR enhanced its adsorption capacity for chromium(VI).
- Adsorption of chromium on SIR followed Freundlich isotherm and Thomas model.
- Chromium from chromium-loaded SIR was eluted effectively by 0.1 M NaOH solution.
- The SIR can be used for adsorption of chromium at least in three cycles.

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ABSTRACT

In this study, the solvent impregnated resin (SIR) based on impregnation of Cyanex 923 in Amberlite XAD-7HP resin was used to remove hazardous chromium(VI) from the acidic chloride media. The results showed that SIR adsorbed chromium effectively when the solution pH was low (acidity of solution; 0.3–2.0 M). The adsorption mechanism of the SIR for chromium(VI) could be explained taking into account the interaction between the protonated oxygen atoms of polyacrylate (ester group) in the resin and the solvation of Cyanex 923 with trioxochloromate (CrO_3Cl^-) complexes. The involvement of both the polymeric support and extractant for chromium adsorption enhanced uptake capacity of SIR to 28.2 mg Cr/g SIR (1.0 g SIR contained 0.375 g the extractant) compared to that of 16.9 mg Cr/g resin. Freundlich isotherm was more suitable than Langmuir isotherm and Thomas model described well the adsorption behavior of chromium in column. Chromium was eluted effectively from chromium-loaded SIR by 0.1 M sodium hydroxide solution, and elution efficiency reached 92% in the first stage. The regenerated SIR when reused for adsorption of chromium showed almost the same level of efficiency at least in three cycles.

1. Introduction

In electronic manufacturing industries, chromium is widely used as a plating material (in chromate conversion coatings) to inhibit the corrosion of electronic parts, fasteners and sheet metal and as pigments in plastics used for printed circuit boards (PCBs). The waste effluents of these processes contain hazardous chromium(VI) with the concentration exceeding the local discharge limit. E-waste is reported to be a fastest growing solid waste stream and therefore, recycling of e-waste is considered to be a major issue in conserving resources and reducing environmental pollution. Hydrometallurgical technology is an alternative method to the traditional pyrometallurgy for recycling of e-waste because of its advantages such as low capital cost with suitability for small scale application, reduced environmental degradation and high metal recoveries [1]. In hydrometallurgy, leaching is a fundamental process using lixiviants such as acids, cyanide, thiosulfate or alkaline solutions, to dissolve desired metals. Electro-generated chlorine has been used as a potential method for leaching metals from electronic waste [2,3]. The solutions obtained from leaching process contain valuable metals and hazardous chromium(VI). It is known that chromium(VI) is a highly toxic element to humans and causes lung cancer, liver, kidney and gastric damage [4,5]. Therefore, chromium(VI) must be removed from waste solutions before discharging to the environment because chromium(VI) is soluble and easily transported in water resources [6]. Chromium(VI) ions contaminate the surface and underground water due to the migration of hexavalent chromates. The limit for discharge of Cr(VI) into the land surface waters is 0.1 mg/L [7].

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The common methods such as reduction–precipitation, solvent extraction and adsorption/ion exchange resin have been used for recovery and removal of chromium(VI) from aqueous solutions [8–10]. The disadvantages of reduction–precipitation are large quantity of chemical consumption and generation of sludge which needs costly disposal procedure for landfill. The use of solvent extraction is also not effective for the separation of metals from dilute solutions because of the loss of extractant, third phase formation and use of inflammable diluents [10]. Adsorption/ion exchange resin is effective for dilute metal solutions but it often has low adsorption capacity and less selectivity towards metals than solvent extraction. Chelating resin is highly selective but it is expensive and eluting metal is difficult from the loaded resin [11,12].

The combination between solvent extraction and ion exchange resin has given a solvent impregnated resin technology for separation and purification of metals from aqueous solutions. Solvent impregnated resin (SIR) has several advantages over normal extraction systems such as the selectivity characteristics of dissolved extractants with operational simplicity of solid ion exchange equipment (fixed bed columns and fluidized beds), the ease of phase separation (due to the elimination of problems dealing with the formation of stable emulsions), the ease of SIR preparation, the easy recovery of the loaded substance in the desorption step, and wide diversity of extractants that can be selected [13]. The SIRs based on impregnating various types of extractants in different polymeric support resins have been used for recovery and removal of metals from aqueous solutions such as Cd [13,14], Hg [15] and Pb [16]. The removal of chromium(VI) has been investigated using Aliquat 336 impregnated in Amberlite XAD-7 resin [17,18]. Chromium(VI) was preferably removed (89%) from the mixture of metals including Cu, Co, Pb, Zn and Cd by polysulfone microcapsules containing Cyanex 923 [7]. For the synthesis of SIR materials, selection of polymeric support and extractant is of paramount importance as their properties essentially contribute to the capability of SIR for adsorption of target metals. Usually, resin acts as a supporting matrix to retain extractant inside itself. There are very limited reports available to investigate the adsorption of metals by polymeric support in SIR. In this study, Amberlite XAD-7HP resin is selected as a polymeric support because of its large surface area and high porosity. Among available extractants, Cyanex 923 has shown promise to extract chromium(VI) effectively through solvation mechanism, and loaded metal on the extractant is easy to strip and regenerate. The involvement of both polymeric support and extractant in SIR is considered key to the research on the adsorption of chromium.

The present study aims at removing hazardous chromium(VI) from the acidic chloride solution using solvent impregnated resin based on the impregnation of Cyanex 923 in Amberlite XAD-7HP resin. The synthetic solutions containing chromium(VI) used for adsorption by SIR are similar to that of the leach liquor of electronic scraps obtained from electro-generated chlorine leaching process [10]. The adsorption mechanism of chromium by SIR is determined, and structure of resin and SIR, besides loaded SIR is ascertained by FTIR. The parameters such as contact time, pH of solution and capacity of SIR. are investigated, and the optimized condition will be used for removal of chromium from the real acidic chloride leach liquor.

Table 1
Characteristic properties of Amberlite XAD-7HP resin.

Matrix	Macroreticular aliphatic crosslinked polymer
Physical form	White translucent beads
Moisture holding capacity	61–69%
Specific gravity	1.06–1.08
Harmonic mean size	0.56–0.71 mm
Uniformity coefficient	$\leqslant$2.0
Fines content	<0.3 mm: 7% max
Coarse beads	>1.18 mm: 8% max
Surface area	$\geqslant$380 m^2/g
Porosity	$\geqslant$0.5

Table 2
Typical properties of Cyanex 923.

Trialkylphosphine oxides	93%
Appearance	Colorless mobile liquid
Specific gravity	0.88 at 25 °C
Freezing point	−5 to 0 °C
Viscosity	40.0 centipoise at 25 °C
Flashpoint	13.7 centipoise at 50 °C 182 °C
Vapor pressure	0.09 mmHg at 31 °C
Boiling point	310 °C at 50 mmHg
Solubility in water	10 mg/L

Table 3
Impregnation of resin with varying amount of extractant.

Amberlite XAD-7HP resin (g)	Acetone (mL)	Extractant (g)	SIR weight (g)	Extractant in 1 g of SIR (g)
2	10	0.5	2.30	0.130
2	10	1	2.56	0.218
2	10	2	2.96	0.324
2	10	3	3.20	0.375
2	10	4	3.48	0.425
2	10	6	3.54	0.435

2. Experimental

2.1. Materials

In order to carry out the adsorption/extraction studies, the synthetic solutions containing chromium(VI) 5–400 mg/L were prepared by dissolving the calculated amounts of potassium chromate in distilled water, and adding a known amount of hydrochloric acid to maintain the desired pH (acidic) of solutions. The chemicals viz. potassium chromate, hydrochloric acid, sodium hydroxide, acetone, etc. were laboratory reagent grade.

Amberlite XAD-7HP resin supplied by Rohm and Hass was treated with 1.0 M HCl to remove any impurities and organics. The resin was washed several times with de-ionized water and then dried for 12 h in an oven at 50 °C before use. Its properties are given in Table 1. Cyanex 923 extractant is a mixture of four trialkyl phosphine oxide with general formula R_3PO ($R = CH_3(CH_2)_7$ or $CH_3(CH_2)_5$). The principal advantage of Cyanex 923 is its very low solubility in water and easy to strip the loaded metal. Cyanex 923 is supplied by Cytec company (USA), and the typical properties of Cyanex 923 are shown in Table 2.

2.1.1. Preparation of solvent impregnated resin beads

Two most conventional approaches for preparation of SIR materials are dry and wet impregnation methods. In this study, the dry impregnation method has been used for preparing SIR material beads because it is simple and easy to determine the amount of extractant loaded in resin. The dilute Cyanex 923 was prepared by mixing a known amount of extractant and acetone. The exact amount of Amberlite XAD-7HP resin was put in dilute extractant, and the mixture was shaken for 24 h at 25 °C. The solid beads were then separated by using Bunchner filter. The SIR beads were put in vacuum oven at 60 °C for 12 h to evaporate acetone. The dry SIR materials were weighed to record increase of weight after impregnation.

2.2. Methods

The experimental studies for the adsorption and elution of chromium using SIR were performed in both batch and continuous modes. The batch experiments were carried out using a conical flask in a water bath shaker under atmospheric conditions using the resin.

The adsorption in continuous mode was made in a column of pyrex glass with diameter of 10 mm and length of 200 mm. The flow rate of solution in the column was controlled by the adjustment of a stopcock. The bed volume (BV) of the resin was determined by adding a weighed amount of resin in a 25 mL cylinder and then immersing it in water. The chromium content of the samples was analyzed by UV–visible Spectrophometer (UV-1601, Shimadzu Inc., Japan) after complexing with diphenyl carbazide. Atomic Absorption Spectrometry (A Analyst 400, Perkin Elmer, USA) was also used to determine chromium concentration of the samples for comparing the results of both analytical procedures. The structure of the original and chromium-loaded resin and SIR was determined by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 380, USA).

3. Results and discussion

3.1. The investigation of extractant/resin ratio

The effect of extractant amount for impregnation process was investigated. A 2.0 g of fresh dry Amberlite XAD-7HP resin was placed in 10 mL acetone containing varied amount of Cyanex 923 from 0.5 to 6.0 g following impregnation procedure. From table 3 it can be seen that weight of SIR increased with increasing the amount of extractant. It implies that the impregnation of extractant in polymeric support increases with increasing amount of extractant. Because of the limitation of void space in polymeric support, the saturation loading of extractant in resin was found at extractant/resin ratio of 3 (g/g).

Due to the saturation of extractant in the resin causing the loss of extractant in the extraction process, the amount of extractant impregnated in the resin needs to be selected. The amount of extractant should be in the range 0.35–0.4 g in 1.0 g of SIR as suggested [13]. At extractant/resin ratio of 1 (g/g), the SIR was obtained with 0.375 g of extractant in 1.0 g SIR which was chosen throughout the course of study. Both the resin and solvent impregnated resin (0.375 g Cyanex 923/1 g SIR) were characterized using Micromeristics Tristar 3000 instrument (USA) to find out the change in surface area and porosity. The surface area of 390 and 305 m^2/g was obtained for the resin and SIR, and porosity was found to be 0.52 mL/g and 0.15 mL/g for the resin and SIR, respectively. After impregnation, the surface area and porosity of the SIR decreased by ∼22% and 71%, indicating the presence of the extractant in the resin.

3.2. Effect of contact time

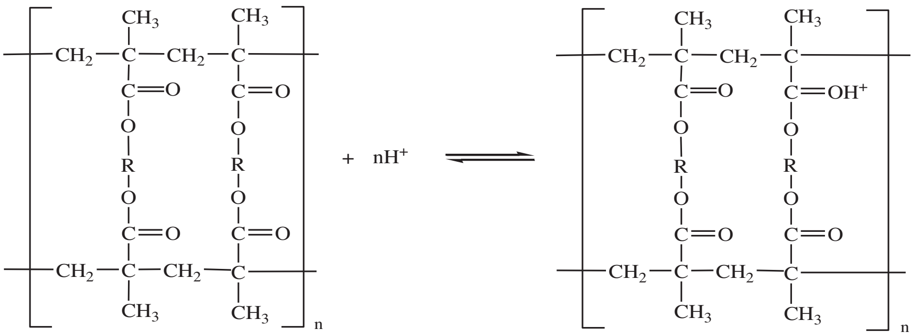
Solvent impregnated resin (1.0 g SIR containing 0.375 g Cyanex 923) was used to examine the effect of time on adsorption of hexavalent chromium. The liquid/solid ratio (A/R) was 25 mL/g and the acidity of solution being around 2.0 M. The flasks were shaken at 120 RPM for different time intervals and at 25 °C with different concentration of chromium (5–400 mg Cr/L). The results given in Fig. 1 showed the increase in adsorption of Cr(VI) with time and the amount of Cr(VI) adsorbed, q (mg/g) increased from 0.107, 1.028, 1.980 and 6.200 mg Cr to 0.124, 1.238, 2.440 and 9.198 mg Cr for aqueous concentrations of chromium of 5, 50, 100 and 400 mg/L, respectively. The equilibrium for adsorption of chromium on SIR was attained in 30 min.

3.3. Effect of pH

pH of a solution is an important factor affecting the adsorption because it involves both the aqueous charge distribution and the surface binding site of the adsorbent. The speciation diagram of chromium(VI) is presented in Fig. 2. In this figure, the chromate ions exist in the aqueous phase as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, H_2CrO_4, and CrO_3Cl^-. In an aqueous chloride medium (acidic conditions, pH < 1), the dominant chromium species may be present as the trioxochloromate(VI) ions [4,19] as per following equation:

$$HCrO_4^- + Cl^- + H^+ \Longleftrightarrow CrO_3Cl^- + H_2O \qquad (1)$$

As reported [10], Amberlite XAD-7HP resin can adsorb chromium(VI) effectively through the interaction of the ester group C=O in the resin with the trioxochloromate-complex. Cyanex 923 has been found to extract chromium(VI) by the solvation of extractant molecules with trioxochloromate-complex [9,19]. Therefore, the adsorption of chromium using SIR includes two mechanisms which are as follows (Eqs. (3) and (4)):



(2)

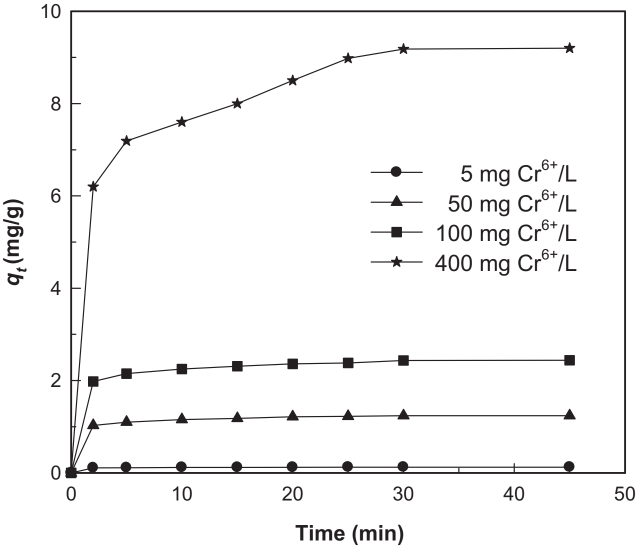


Fig. 1. Effect of contact time on adsorption of chromium(VI) using SIR (SIR, 1.0 g; volume of solution, 25 mL; acidity of solution, 2.0 M; mixing speed, 120 RPM; temperature, 25 °C).

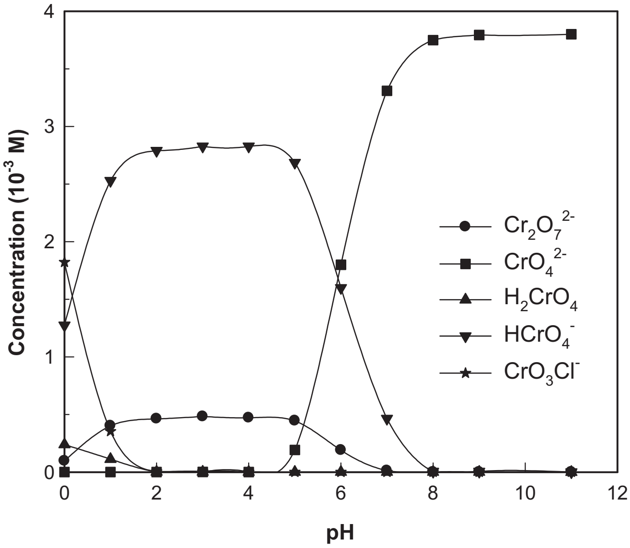
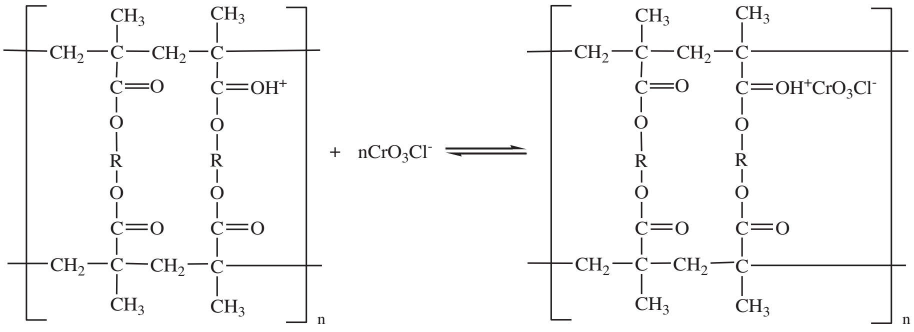


Fig. 2. Speciation diagram for chromium in chloride media (chromium, 3.8×10^{-3} M). *Source*: visual MINTEQ program



(3)

$$CrO_3Cl^- + H^+ + pCyanex\ 923 \iff [HCrO_3Cl \cdot pCyanex\ 923] \quad (4)$$

The mechanism for adsorption of chromium by SIR is thought to be combining both the behaviors of adsorption by Amberlite XAD-7HP (resin) and extraction by Cyanex 923. In Fig. 3, the adsorption of chromium increases when the acidity of solution increases. The adsorption of chromium using both adsorbent and extractant was high at high acidity of the solution (around 2.0 M HCl). The simultaneous adsorption of chromium on polymeric matrix and impregnated extractant occurs through the interaction of both with trioxochloromate (CrO_3Cl^-).

3.4. Effect of SIR dose

The ratio of liquid/solid was examined using aqueous feed containing 100 and 200 mg Cr^{6+}/L at the acidity of 2.0 M. The quantity of SIR was varied from 0.1 to 3.0 g (8.33–250 mL solution/g of SIR) maintaining the solution volume of 25 mL. The results presented in Fig. 4 indicated that percentage of chromium adsorption increased with increasing SIR dose for both the solutions containing 100 and 200 mg Cr/L. The fraction of metal removed from the aqueous phase increased with an increasing adsorbent dose in the batch experiments with a fixed initial metal concentration. As expected, increasing the resin dose provides more active sites or a greater adsorption area, thereby increasing chromium adsorption. The liquid/solid ratio of 25 (mL/g) was found suitable for adsorption of chromium(VI).

3.5. Effect of temperature

The effect of temperature on the adsorption of chromium(VI) using SIR was investigated from 25 to 55 °C (298–328 K). The experiments were carried out with 1.0 g of SIR in contact time of 30 min and liquid/solid ratio of 25 (mL/g). The equilibrium constant is expressed by the equation:

$$K_c = \frac{C_{Ae}}{C_e} \quad (5)$$

where K_c is equilibrium constant, C_{Ae} is the equilibrium concentration (mg/L) of the metal on the resin and C_e is the equilibrium concentration in solution.

Thermodynamic parameters such as free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) can be calculated by following equations:

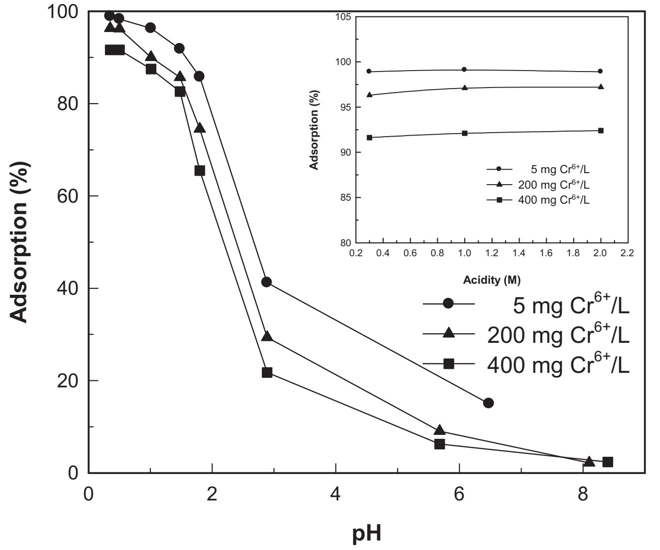


Fig. 3. Effect of pH of solution on adsorption of chromium by SIR (SIR, 1.0 g; volume of solution, 25 mL; contact time, 30 min; mixing speed, 120 RPM; temperature, 25 °C).

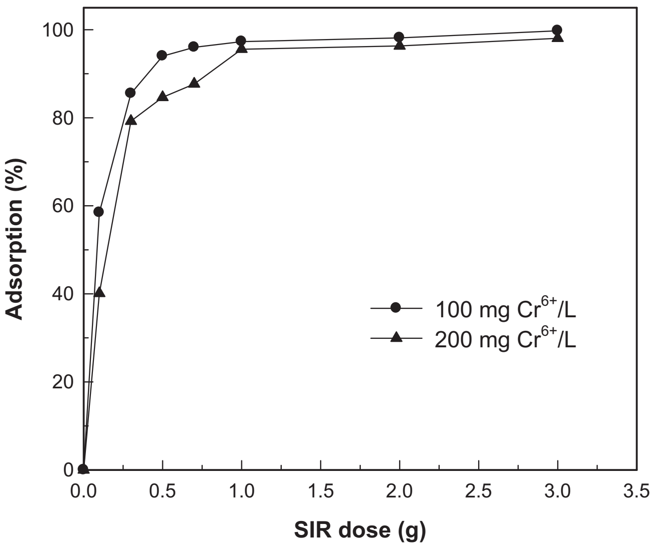


Fig. 4. Effect of SIR dose on adsorption of chromium (acidity of solution, 2.0 M; contact time, 30 min; mixing speed, 120 RPM; temperature, 25 °C).

$$\Delta G^o = -RT \ln K_c \tag{6}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

$$\log K_c = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \tag{8}$$

T is absolute temperature (K), R is the gas constant (8.314 J/mol K).

As presented in our previous report [10], the adsorption of chromium on Amberlite XAD-7HP resin decreased with increasing temperature. The relationship between $\log K_c$ and $1/T$ was found to follow linear equation: $y = 288.5x - 0.021$ with coefficient of determination 0.986 and $y = 407.2x - 0.083$ with coefficient of determination 0.981 for resin and SIR, respectively. ΔG^o, ΔH^o and ΔS^o were determined from the linear equations obtained above. The calculated values of ΔG^o, ΔH^o and ΔS^o are listed in Table 4. The negative values of ΔG^o indicate that the process is thermodynamically feasible and spontaneous adsorption of chromium on resin and SIR takes place. Negative ΔH^o values suggest the exothermic nature of adsorption and ΔS^o can be used to describe the randomness at the solid–solution interface during the sorption. The values of ΔG^o, ΔH^o and ΔS^o for SIR were found to be lower than that of resin resulting in higher value of $\log K_c$ for SIR than $\log K_c$ for resin, indicating that the adsorption of chromium by SIR is more efficient than the resin.

Table 4
Thermodynamic parameters for adsorption of Cr(VI) on the resin and SIR.

Adsorbent	ΔH^o (J/mol)	ΔS^o (J/K mol)	ΔG^o (J/mol)			
			298 K	308 K	318 K	328 K
Amberlite XAD-7HP resin	−5522.1	−0.4	−5402.7	−5398.8	−5394.2	−5390.7
SIR	−7796.7	−1.6	−7319.9	−7303.9	−7287.7	−7271.9

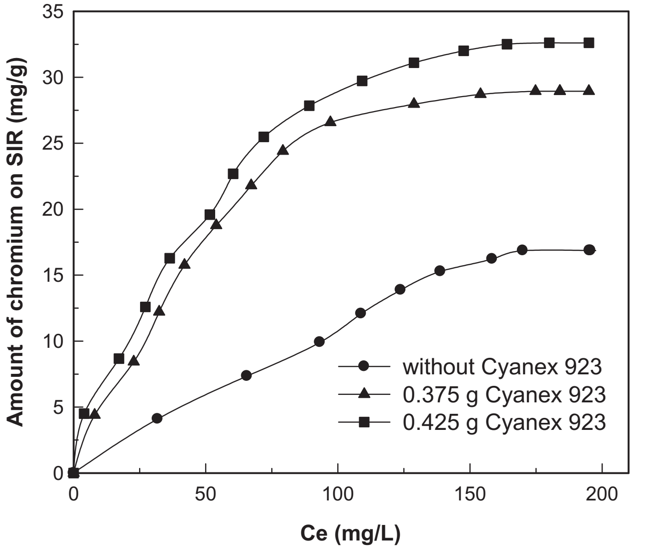


Fig. 5. Loading capacity of SIR for adsorption of chromium (SIR, 1.0 g; acidity of solution, 2.0 M; mixing speed, 120 RPM; temperature, 25 °C).

3.6. Loading capacity of SIR

The loading capacity of the polymeric support (Amberlite XAD-7HP) and SIR was determined using 1.0 g sample of adsorbents which was contacted with 25 mL aqueous feed solution containing 200 mg Cr/L for 30 min at 25 °C. The acidity of the feed solution was around 2.0 M. The repeated contacts with the same chromium-loaded resin and SIR were made with fresh aqueous solutions until a maximum adsorption of chromium was achieved. The loading of chromium on the resin and SIR increased with each contact at an aqueous to adsorbent ratio of 25 mL/g, and the results are presented in Fig. 5. The loading capacity of the resin and SIR was found to be 16.9 and 28.2 mg Cr/g adsorbent, respectively. The loading capacity of SIR is higher than Amberlite XAD-7HP because in the SIR, both polymeric support (Amberlite XAD-7HP resin) and extractant (Cyanex 923) could react with chromium. Compared to the capacity of the resin, the capacity of SIR (1.0 g SIR containing 0.375 g Cyanex 923) for chromium increased approximately 11.3 mg Cr/g.

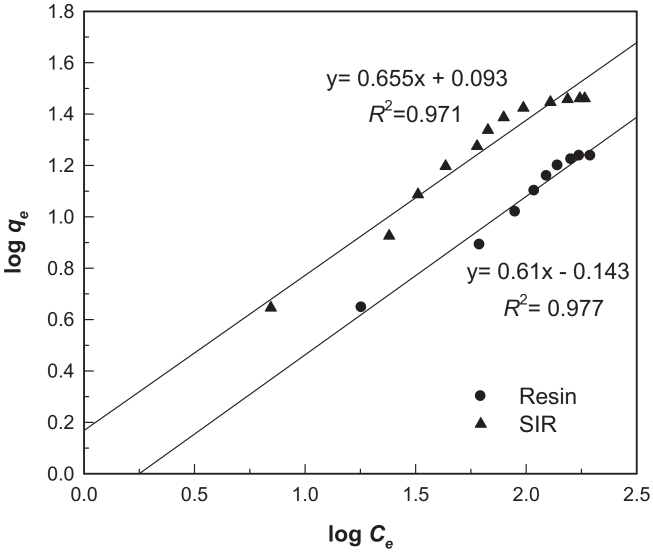


Fig. 6. Freundlich isotherm for adsorption of chromium using SIR (SIR, 1.0 g; acidity of solution, 2.0 M; mixing speed, 120 RPM; temperature, 25 °C).

3.6.1. Adsorption isotherms

Langmuir and Freundlich isotherms are commonly used to describe the relationship between the amount of metal adsorbed on the adsorbent and the equilibrium metal ion concentration in the raffinate. In the Langmuir model, the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ions. The model can be presented in a linear form as follows [20]:

$$\frac{1}{q} = \frac{1}{k_1 q_m} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{9}$$

where C_e is equilibrium concentration of metal in solution (mg/L), q is amount of metal adsorbed on the resin at equilibrium (mg/g), k_l is equilibrium constant related to the affinity of the binding sites for the metals or the Langmuir constant, and q_m is the resin capacity (possible maximum amount of metal ions adsorbed per unit mass of adsorbent, mg/g).

The Freundlich model assumes that the adsorption of metal ions occurs on a heterogeneous surface by monolayer adsorption. The model is given by the general form [20–22]:

$$q = k_f C_e^{1/n} \tag{10}$$

$$\log q = \frac{1}{n} \log C_e + \log k_f \tag{11}$$

where k_f and n are the Freundlich constants for adsorption capacity and adsorption intensity, respectively.

Plot of $\log C_e$ vs. $\log q$ was examined to validate the experimental data with Freundlich isotherms, as presented in Fig. 6. The parameters of the Langmuir and Freundlich isotherms for chromium adsorption on the SIR are summarized in Table 5. The data supported the Freundlich isotherms, as the coefficient of determination R^2 for the Freundlich isotherm is closer to 1 than that for the Langmuir isotherm. The empirical loading capacity of resin and SIR for adsorption of chromium was found to be 16.9 and 28.2 mg Cr/g while the value of loading capacity of resin and SIR obtained from plot of Langmuir isotherm was 22.2 and 35.7 mg Cr/g adsorbent, respectively. The isotherm is compatible with the system because the chromium adsorption by SIR involves both polymeric matrix and the extractant. Therefore, Cr(VI) adsorbed over SIR is the result of heterogeneous adsorption as per definition of Freundlich isotherm itself. Higher loading capacity of the SIR for chromium(VI) in spite of decreased surface area and porosity compared to that of resin (Table 1), may be attributed to the improved chemi-sorption of the metal ions with the modified resin.

Table 5
Parameters of Langmuir and Freundlich isotherm for adsorption of chromium on Amberlite XAD-7HP resin and SIR.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	k_l	R^2	n	k_f	R^2
Amberlite XAD-7HP resin	22.2	0.0134	0.930	1.63	0.72	0.977
SIR	35.7	0.0113	0.941	1.52	1.23	0.971

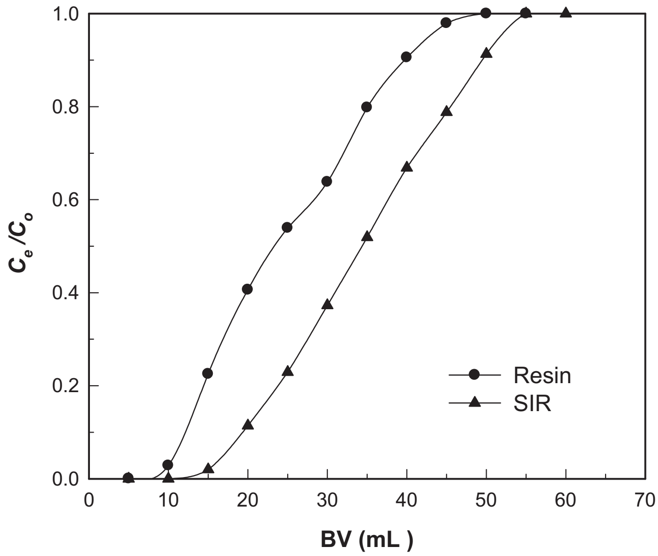


Fig. 7. Breakthrough curve of resin and SIR for adsorption of chromium (BV, 5 mL; aq. feed, 200 mg Cr/L; acidity of solution, 2.0 M; flow rate, 1 mL/min; temperature, 25 °C).

3.7. Thomas model for breakthrough curve in column

The experiments in continuous mode were carried out in glass columns packed resin or SIR. The bed volume of the resin and SIR was fixed with BV = 5.0 mL, and the flow rate of the solutions were maintained at 1 mL/min. The breakthrough curve is used to determine the completion of the adsorption cycle in a continuous process [21,23]. The breakthrough curves of the resin and SIR are presented in Fig. 7. The figure indicates that the breakthrough point of chromium using Amberlite XAD-7HP appeared earlier than that of the SIR, and the sorption capacity of SIR was higher than Amberlite XAD-7HP. The breakthrough point of chromium was observed after 5 BV for Amberlite XAD-7 resin and 10 BV for SIR. The increase in the C_e/C_o ratio can be explained from the fact that the active sites on the resin and SIR were decreased. The sorption of chromium was completed after 50 BV by resin, and 60 BV with SIR, respectively.

In adsorption or ion exchange process, the relationship between concentration of metal and time can be expressed by the equation to predict the change of concentration with time. Traditionally, the Thomas model is widely used to describe the metal breakthrough behavior in column. The main advantages of this model are the simplicity and reasonable accuracy in prediction of the break-

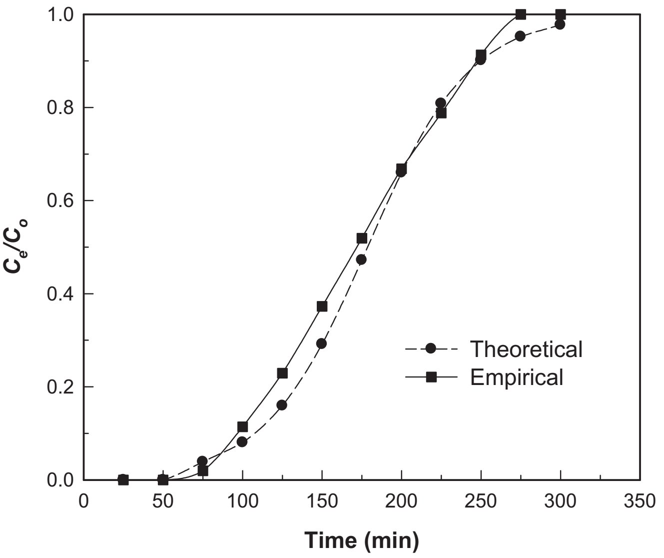


Fig. 8. Thomas model for adsorption of chromium (BV, 5 mL; acidity of solution, 2.0 M; flow rate, 1 mL/min; temperature, 25 °C).

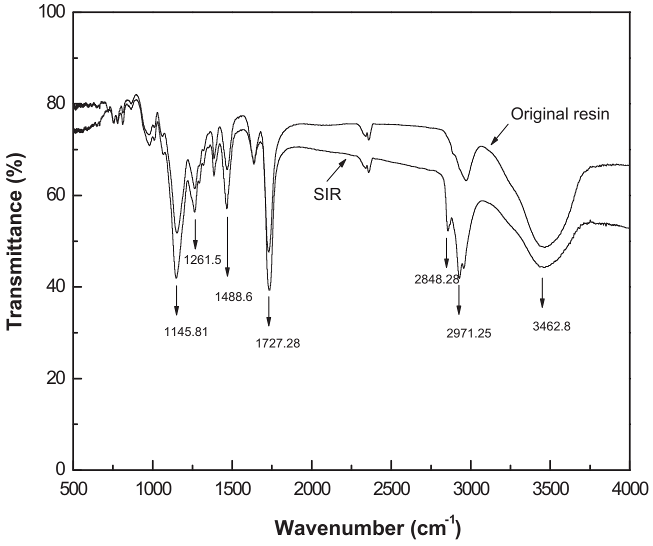


Fig. 9. FTIR characterization for original resin and SIR.

through curves under various operating conditions. The model is expressed by [24,25]:

$$\ln\left(\frac{C_o - C_t}{C_t}\right) = \ln\left[\exp\left(\frac{k_1 Q_e M}{F}\right) - 1\right] - k_1 C_o t \tag{12}$$

where C_t is the solute concentration in the existing aqueous solution at time t (mg/L) and C_o in the feed solution (mg/L); k_1 is the rate constant of adsorption (l/mg h); Q_e is the amount of metal adsorbed on adsorbent (mg/g); M is the mass of adsorbent (g); F is the flow rate (L/h); t is the time (h).

The Eq. (12) can be briefly described as:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = k(\tau - t) \tag{13}$$

where $\tau = \frac{Q_e M}{C_o F}$, $k = k_1 C_o$

The parameter τ is the adsorption time when ln ($C_o/C_t - 1$) is equal to 0, and k is determined from the slope of the figure.

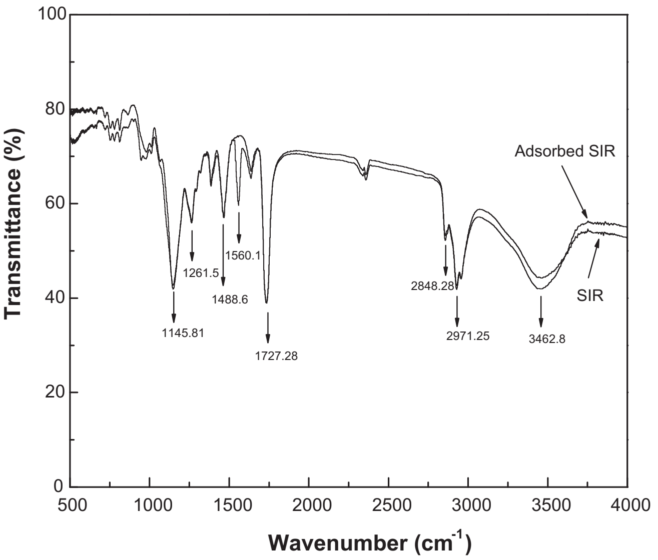


Fig. 10. FTIR characterization for SIR and chromium-loaded SIR.

The relationship between ln ($C_o/C_t - 1$) and t was found to follow linear equation $y = -0.031x + 5.538$ with coefficient of determination 0.97. The theoretical and empirical breakthrough curves have been drawn to find out the difference or resemblance. Fig. 8 shows that the trend of theoretical and empirical breakthrough curve is similar. It is apparent that the model prediction compared reasonably well with the observed data. Therefore, the Thomas model was found suitable to express the change of concentration of chromium with time in continuous column process.

3.8. FTIR characterization for original and adsorbed SIR

The IR spectra of polymeric support were recorded before and after impregnation, and are presented in Fig. 9. Amberlite XAD-7HP is an acrylic ester that contains the ester group O—C=O. All esters have three strong specific infrared bands that appear at approximately 1700, 1200 and 1100 cm^{-1} [26]. The spectrum for the acrylic ester of Amberlite XAD-7HP exhibits a strong band at 1735.10 cm^{-1}, which represents the C=O stretch of the ester group. The band at 1260.70 cm^{-1} may be assigned to the asymmetric stretching of the C—C and C—O bonds attached to the carbonyl carbon. This vibrational C—C—O stretch involves the left side of the ester's functional group. The band at 1145.76 cm^{-1} is due to a vibration involving the ester oxygen and the next two carbons attached to it in the hydrocarbon chain [26]. After the impregnation, some interesting differences in the range 2800–3000 cm^{-1} were observed. The new peaks at 2848.28 and 2971.25 cm^{-1} were found, which are located in the range of C—H stretching [27–29]. These changes give clear proof that the surface of resin is modified after impregnation. The characterization of SIR and chromium-loaded SIR was performed and the results were given in Fig. 10. The difference between the original and the chromium-adsorbed SIR can be seen in terms of a peak at 1561.48 cm^{-1}, which is near the ester group C=O. This might be caused by the interaction between the protonated oxygen atom of the ester group C=O located in the resin with the metal-complex [28,29], demonstrating the attachment of CrO_3Cl^- to the resin.

3.9. Cycles of SIR for adsorption of chromium(VI)

Water and sodium hydroxide solutions were used to elute chromium from the loaded Amberlite XAD-7HP and SIR. A comparison

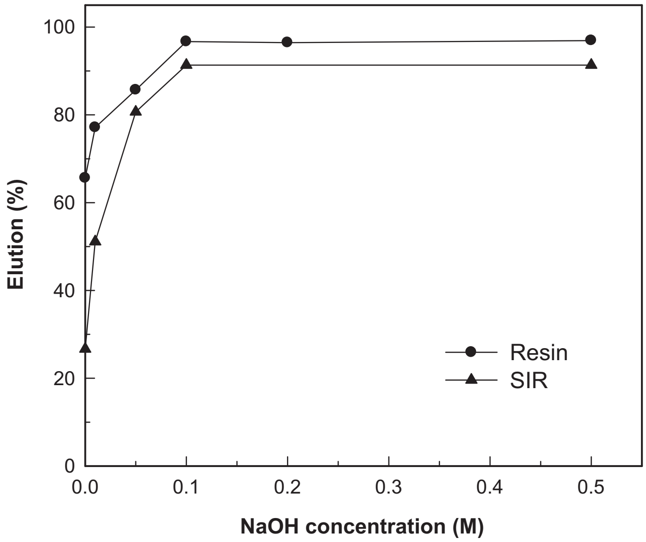


Fig. 11. Elution of chromium using water and various concentration of sodium hydroxide (loadedchromium on resin, 4.25 mg Cr/g resin; loaded-chromium on SIR, 4.5 mg Cr/g SIR; A/R, 25 mg/L; contact time, 30 min; temperature, 25 °C).

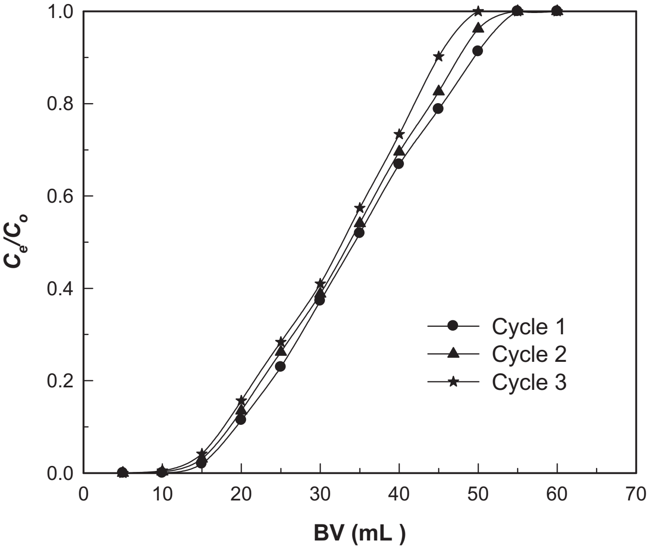


Fig. 12. Breakthrough curve of SIR for adsorption of chromium with the number of cycles (BV, 5 mL; aq. feed, 200 mg Cr/L; flow rate, 1 mL/min)..

of chromium elution using both water and sodium hydroxide solution is given in Fig. 11. As can be seen in the figure, elution efficiency using water (means 0.0 M NaOH) for SIR is lower than that of Amberlite XAD-7HP. Increase in the concentration of sodium hydroxide solution increased elution efficiency of chromium. 0.1 M NaOH solution was found suitable for elution of chromium from chromium-loaded SIR; the elution reached to ~92% in the first stage itself and was ~97% in the next contact. After completing adsorption cycle of chromium(VI), the chromium-loaded on the SIR was eluted by 0.1 M sodium hydroxide solution to remove chromium(VI) and regenerate for using in the next cycle. The cycles of chromium adsorption using regenerated SIR show that the adsorption capacity of SIR for chromium was almost the same in three cycles. The adsorption of chromium in three cycles is presented in Fig. 12. The results presented in Fig. 13 show that in 3 cycles, the elution of chromium was almost similar at the first, second and third cycles.

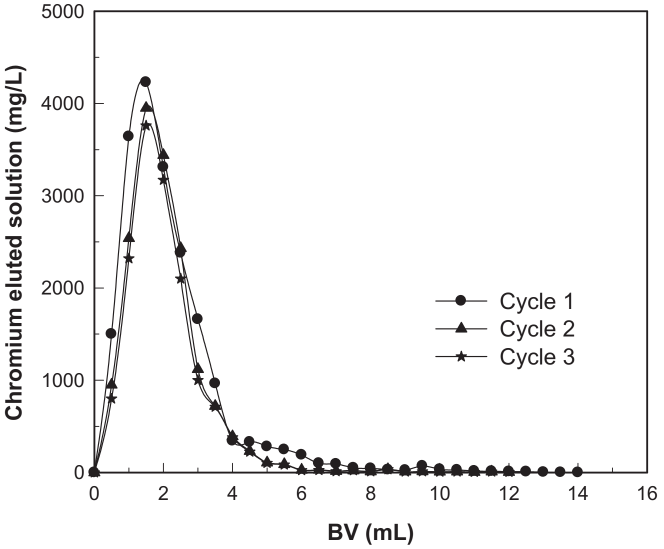


Fig. 13. Elution of chromium in a column test (BV, 5 mL; loaded Cr on SIR, 28.2 mg Cr/g; eluent, 0.1 M NaOH solution; flow rate, 1 mL/min).

The adsorption capacity of the SIR for chromium (VI) slightly decreased in every cycle. This is attributed to several reasons such as the loss of extractant after several cycles, and the incomplete elution of chromium, etc. Some amount of chromium(VI) still existed on SIR, as the hexavalent chromium could be converted to trivalent chromium which was evident from the color of loaded SIR (slight green as compared to yellow color in the beginning). Therefore, the hydrochloric acid was used to elute Cr(III) available on SIR. The washed samples were analyzed by UV and AAS, and it was found that around 3% of hexavalent chromium converted to trivalent chromium.

4. Conclusions

The solvent impregnated resin showed promise for effective adsorption of chromium from a chloride solution. Amberlite XAD-7HP acted as an adsorbent and a polymeric support and therefore, enhanced the adsorption capacity of SIR compared to the resin, Amberlite XAD-7HP itself. The loading capacity of SIR for adsorption of chromium(VI) was found to be 28.2 mg/g (1.0 g SIR containing 0.375 g Cyanex 923). The presence of Cyanex 923 (extractant) in the resin was confirmed by FTIR, and the involvement of polymeric support of SIR for adsorption of chromium was found by appearance of a new peak in SIR characterization which was similar to the new peak found at 1560 cm^{-1} in the resin. The adsorption mechanism of chromium on SIR followed Freundlich isotherm and continuous adsorption of chromium in column was described well by Thomas model. The chromium-loaded on the SIR was eluted effectively by 0.1 M sodium hydroxide solution. The SIR was regenerated and reused for adsorption of chromium at least in three cycles.

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