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# Trialkylamine Impregnated Macroporous Polymeric Sorbent for the Effective Removal of Chromium from Industrial Wastewater

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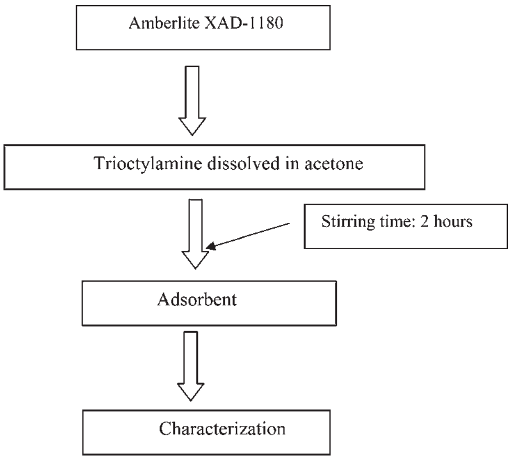
**ABSTRACT:** The universal concern for heavy metal removal demands effective methods for detoxification. Chromium(VI) is one such heavy metal which is recognized to be carcinogenic. In this paper, an efficient approach is proposed for the removal of chromium based on the impregnation of trioctylamine (TOA) on a macroporous Amberlite XAD-1180 polymeric matrix. Chromium(VI) could be quantitatively adsorbed in an acidic medium (pH 2 to 3), while chromium(III) could be retained on the resin matrix at alkaline pH. The adsorbent was characterized using Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and energy dispersive X-ray (EDX) studies. The comprehensively characterized adsorbent showed a high adsorption capacity of 171.82 $\text{mg}\cdot\text{g}^{-1}$ in accordance with the Langmuir isotherm model. The adsorption follows second-order kinetics, and a study of the various thermodynamic parameters such as Gibbs energy, entropy, and the enthalpy changes showed that the adsorption decreases with an increase in temperature. Column studies and regeneration data validated the performance efficiency of the adsorbent with large sample volume tolerance (1 L) and high preconcentration factor (100). The resin column could be regenerated using NaOH after the removal of total chromium without any loss in the performance efficiency for nearly 15 cycles. Chromium could be effectively separated from a synthetic mixture of various ions, thus making it a viable proposition for the detoxification of chromium from industrial effluents.

## 1. INTRODUCTION

The universal concern for heavy metal pollution has led to the development of newer and more environment friendly techniques for their removal from various sources. The two major species of chromium(III, VI) originate mainly from tannery, electroplating, and dyeing effluents.[1] Since Cr(VI) is a potential carcinogen, the safe disposal of Cr(VI) containing effluents requires considerable attention. Even though the literature reveals an upswing in the number of methods for the detoxification of chromium,[2−5] there is a need to seek more efficient and improved methods for its removal from various sources. Low-cost adsorbents such as activated carbon,[6] lignocellulose,[7] wheat residue derived black carbon,[8] seaweed,[9] sawdust,[10] agricultural biowaste,[11] and so forth are known for the solid phase extraction and speciation of chromium. More recently, functionalized nanoporous silica[12] and thermo-responsive polymeric resin[13] have been reported as potential adsorbents for heavy metal detoxification. Dowex M4195 chelating resin,[14] functionalized pyridine copolymer with amine groups,[15] and hybrid inorganic/organic adsorbents[16] have proved their excellent utility in the removal of chromium. In this context, chemically modified polystyrenedivinylbenzene resins have been utilized for the preconcentration of many metal ions including chromium.[17−20] Amberlite XAD-1180 belongs to one such class of resins known to have high surface area and excellent physical, thermal, and chemical stability. The chelation of Cr(VI) with diphenyl carbazide and the subsequent adsorption on Amberlite XAD-1180 has been reported.[21] Amine impregnated Amberlite XAD-4 has been utilized for the collection of precious metals such as platinium and palladium from water.[22] However, a literature survey reveals that XAD-1180 resins impregnated with long-chain amines have not been explored for the removal of chromium. The present work proposes an improved approach for the adsorption of chromium using a long-chain amine (trioctylamine) impregnated in an Amberlite XAD-1180 resin matrix. The polymeric sorbent before and after the adsorption was thoroughly characterized using various analytical techniques followed by a detailed study of the kinetics, thermodynamics, regeneration of sorbent, and other factors that affect the adsorption. The feasibility of the method has been

**Scheme 1. Adsorbent Preparation**



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successfully demonstrated for the removal of chromium in synthetic effluents and in real industrial wastewater samples.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Analytical grade reagents were used throughout. Milli-Q water (MQW) (Elix 3, conductivity 0.12 $\mu S \cdot cm^{-1}$) was used in the preparation of aqueous solutions. Synthetic solutions of Cr(VI) were prepared from potassium dichromate (Merck, India) by appropriate dilution with Milli-Q water. Sulfuric acid and sodium hydroxide were procured from Qualigens Fine Chemicals, India. Amberlite XAD-1180 (Fluka, 20−50 mesh) was used as the adsorbent. Acetone (Merck, India) was used as such without further purification. Trioctylamine (Spectrochem, India) of 0.05 $mol \cdot L^{-1}$ was prepared using acetone as the diluent.

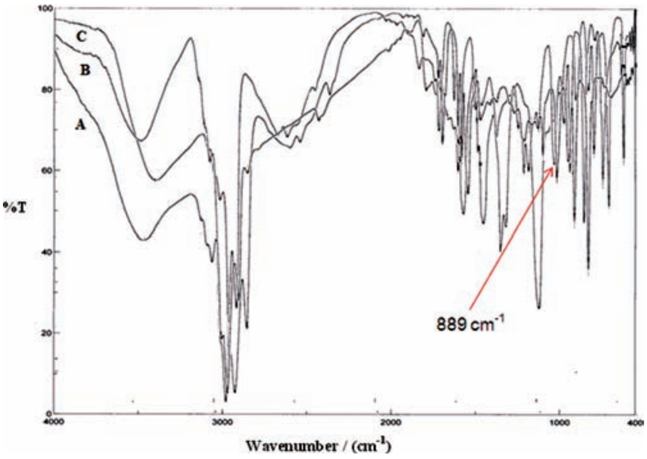
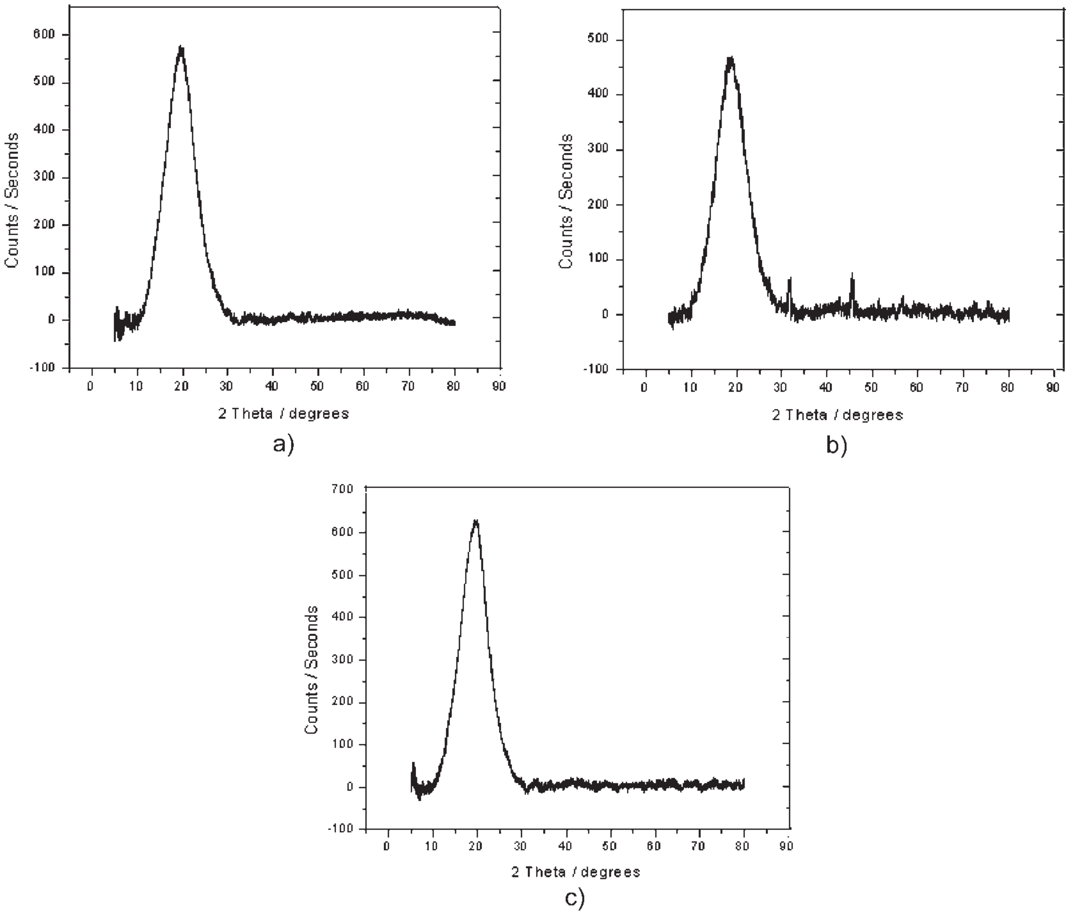


**Figure 1.** FT-IR spectrum of the polymeric adsorbent in various forms: (A) adsorbent, (B) after the adsorption of chromium(VI), and (C) after the desorption of chromium(VI).

**2.2. Instrumentation.** A Jasco V-650 UV−visible spectrophotometer was used for absorbance measurements. One cm matched quartz cells were used for recording the absorbance. An Elico LI 127 model pH meter was used for pH measurement. The IR studies were performed using a Jasco Fourier transform infrared (FT-IR) 460 spectrophotometer. The characterization of the adsorbent was done using X-ray diffraction (XRD; Panalytical) with Cu Kα radiation and energy dispersive X-ray (EDX; Hitachi S-3000H) studies.

**2.3. Impregnation of Amine in the Resin Matrix.** The Amberlite based macroporous polymeric resins are known to have a specific surface area in the range (150 to 900) $m^2 \cdot g^{-1}$ and an average pore diameter of (4 to 9) nm.[23] The 4 g of Amberlite XAD-1180 resin was dispersed in acetone medium and stirred magnetically with 0.05 $mol \cdot L^{-1}$ TOA in acetone for two hours. The dispersion of the resin was uniform with acetone as the medium. The homogeneous dispersion of the amine in the polymeric matrix was attained



a)

b)

c)

**Figure 2.** Powder XRD pattern of the polymeric adsorbent in various forms: (a) adsorbent, (b) after the adsorption of chromium(VI), and (c) after the desorption of chromium(VI).

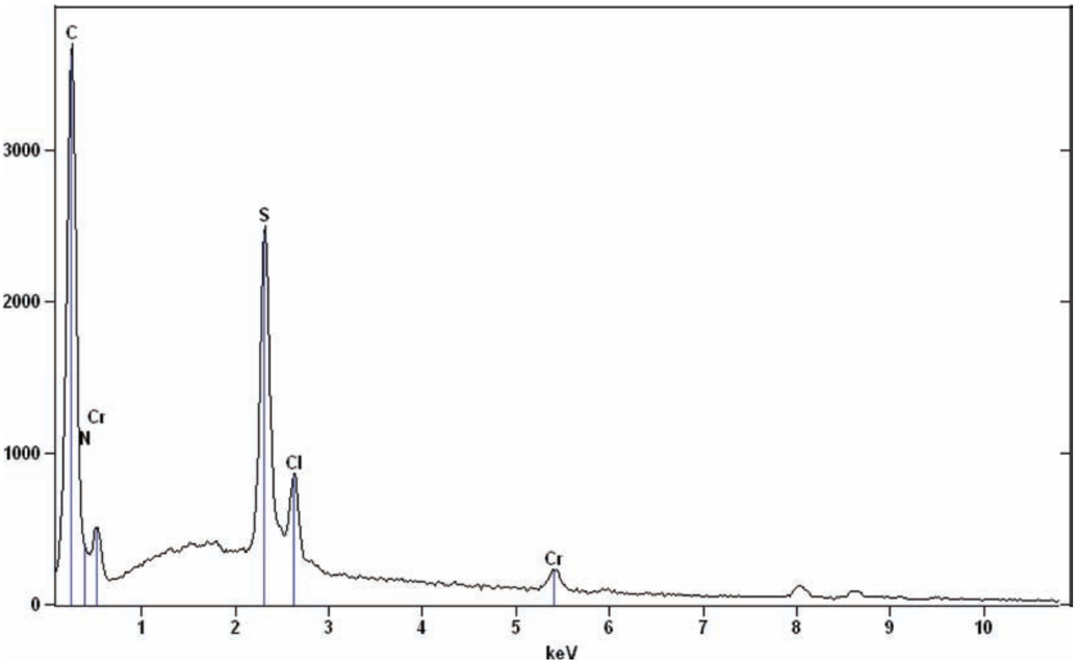
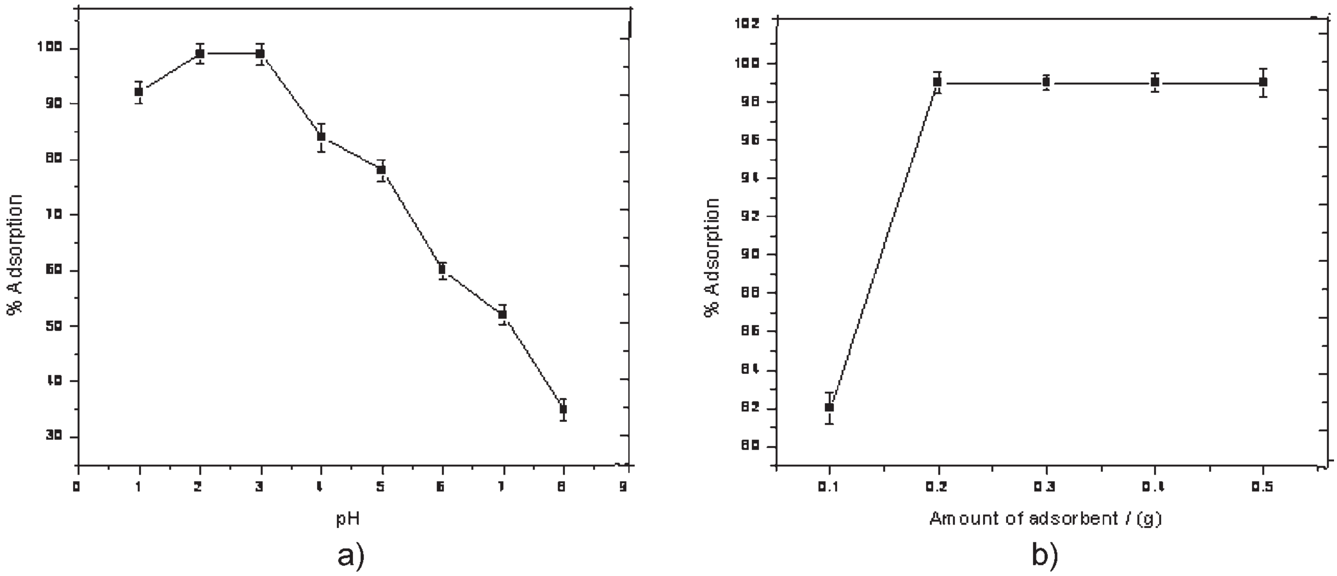


**Figure 3.** EDX spectrum of the adsorbed Cr(VI) on the resin matrix.



a) b)

**Figure 4.** Effect of (a) pH and (b) amount of adsorbent.

in two hours. The preparation of the adsorbent is given as a flowchart in Scheme 1. The adsorbent was separated by filtration, dried, and characterized through various analytical techniques.

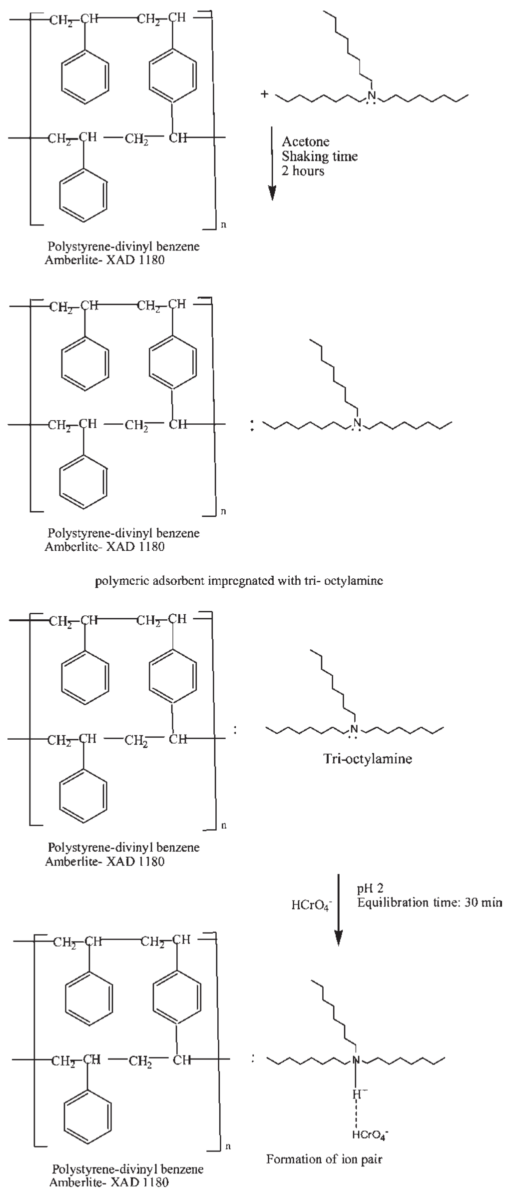
**2.4. Batch Studies.** The batch study was performed by equilibrating 0.2 g of the adsorbent containing 25 mL of chromium(VI) solution (100 $\mu$g·mL$^{-1}$) at pH 3 in a conical flask at room temperature for the desired time interval in an orbital incubator shaker (Biotechnic, India). The concentration of chromium after adsorption was analyzed spectrophotometrically using the standard diphenyl carbazide method.[24] The amount of chromium(VI) adsorbed at equilibrium ($q_e$) is calculated using the relation

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where $V$ is the volume of the solution (L), $W$ is the weight of the adsorbent used (g), and $C_o$ and $C_e$ are the initial and equilibrium liquid phase concentrations of the chromium(VI) (mg·L$^{-1}$), respectively. The adsorption process was studied using first-order and second-order kinetics, and the isotherm was evaluated using the Langmuir and Freundlich models.

**2.5. Column Dynamic Study.** A glass column 1.5 cm in diameter and 25 cm in length was used for the dynamic studies.

**Scheme 2. Impregnation of the Resin with Amine and Formation of Ion Pair**



The 3.0 g of the adsorbent was dispersed with 25 mL of Milli-Q water to form a slurry and then poured into the column. Cotton was placed at the bottom of the column for the resin to settle properly and packed up to a height of 2 cm. A 1 L volume of an aqueous solution containing 100 $\mu$g$\cdot$L$^{-1}$ chromium(VI) solution was adjusted to pH 3 and loaded on the column filled with the resin. The flow rate was maintained at 5 mL$\cdot$min$^{-1}$, and the concentration of chromium(VI) in the aqueous phase was measured spectrophotometrically. The adsorbed chromium could be quantitatively recovered using 10 mL of 3 mol$\cdot$L$^{-1}$ NaOH, and the column could be reused for the adsorption study.

## 3. RESULTS AND DISCUSSION

**3.1. Characterization of the Amine Impregnated Resin.** The FT-IR study (Figure 1) showed characteristic bands at 3046 cm$^{-1}$ (aromatic C—H stretching), 2924 cm$^{-1}$ (aliphatic C—H stretching), 2368 cm$^{-1}$ (protonated nitrogen),[25] 1605 cm$^{-1}$ (aromatic C═C stretching), and 1267 cm$^{-1}$ (C—N stretching). There is a considerable change in the spectrum after the adsorption of chromium(VI), and a prominent new peak appeared at 889 cm$^{-1}$ corresponding to the stretching vibration of Cr═O in $HCrO_4^-$.[26] This indicates that the nitrogen of the amine is protonated and forms an ion pair with $HCrO_4^-$ in the acidic medium. The adsorbent was also characterized by X-ray diffraction, and the pattern is depicted in Figure 2. A characteristic new peak which shows the presence of the hexavalent chromium was observed at a 2$\theta$ value corresponding to 31.7° and 45° which is in near accordance with the reported value in the literature.[27] The EDX spectrum (Figure 3) clearly indicates the presence of chromium observed in the range (5 to 6) keV[5] after the adsorption on the amine impregnated resin along with the other elemental constituents such as carbon, oxygen, sulfur, and nitrogen. The sulfur peak arises from the sulfuric acid medium used for chromium adsorption.[28]

**3.2. Optimization of pH and Mechanism of Adsorption.** It is well-known that the predominant species of chromium(VI) in acidic media are $HCrO_4^-$ and $Cr_2O_7^{2-}$.[29] The optimum pH for the maximum recovery of chromium was observed in the pH range 2 to 3, and the species $HCrO_4^-$ is associated as an ion pair with the protonated amine. This was also substantiated from the FT-IR study as mentioned before. The variation of pH against the adsorption of chromium is shown in Figure 4a. It is evident that, above pH 3, there is a considerable decrease in the adsorption of chromium. The proposed mechanism of adsorption represented in Scheme 2 shows the impregnated resin and the subsequent ion-pair formation associated with the polymeric adsorbent.

**3.3. Amount of Adsorbent.** The amount of adsorbent used in batch study was varied in the range (0.05 to 0.5) g. The results are presented in Figure 4b. The adsorption capacity was found to be a maximium when the amount of adsorbent was in the range (0.2 to 0.5) g in 25 mL of sample volume used for the batch experiments.

**3.4. Adsorption Isotherms.** The Langmuir (Figure 5a) and Freundlich (Figure 5b) isotherm models[30,31] were used to study the adsorption behavior of chromium(VI) on amine impregnated Amberlite XAD-1180. A higher regression coefficient was obtained using the Langmuir isotherm, and the results (Table 1) were consistent with the experimental data. The Langmuir isotherm can be mathematically represented as

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \qquad (2)$$

where $q_e$ is the amount adsorbed (mg$\cdot$g$^{-1}$), $q_o$ is the maximum adsorption capacity (mg$\cdot$g$^{-1}$), $C_e$ is the equilibrium concentration of the adsorbate (mg$\cdot$L$^{-1}$), and $b$ (L$\cdot$mg$^{-1}$) is the Langmuir constant. The Freundlich equation can be represented as

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (3)$$

where $q_e$ is the amount adsorbed (mg$\cdot$g$^{-1}$), $C_e$ is the equilibrium concentration of the adsorbate (mg$\cdot$L$^{-1}$), and $K_f$ and $n$ are the Freundlich constants which indicate the adsorption capacity and the adsorption intensity, respectively. The value of the constants $K_f$ and $n$ in the Freundlich equation were found to be 22.2 mg$^{1-1/n}\cdot$g$^{-1}\cdot$L$^{1/n}$ and 1.8045, respectively. These

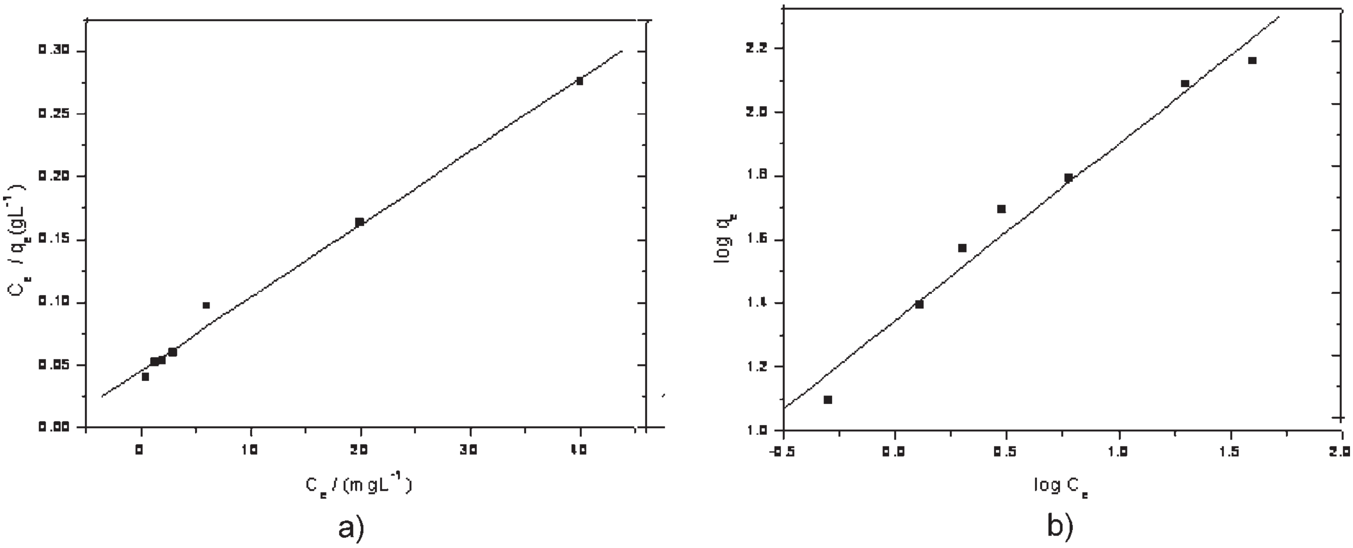


**Figure 5.** Adsorption isotherms: (a) Langmuir and (b) Freundlich.

**Table 1. Langmuir and Freundlich Isotherm Parameters for the Adsorption of Chromium(VI)**

| Langmuir | | | | Freundlich | | |
|---|---|---|---|---|---|---|
| $q_o$/ $(\mathrm{mg \cdot g^{-1}})$ | $R_L$ | $b$/ $(\mathrm{L \cdot mg^{-1}})$ | $r^2$ | $K_f$/ $(\mathrm{mg^{1-1/n} \cdot g^{-1} \cdot L^{1/n}})$ | $n$ | $r^2$ |
| 171.82 | 0.072 | 0.1278 | 0.99 | 22.2 | 1.8045 | 0.97 |

parameters indicate good uptake and affinity of the metal ion toward the adsorbent.

The values of $q_o$ and $b$ in the Langmuir equation were found to be 171.82 $\mathrm{mg \cdot g^{-1}}$ and 0.1278 $\mathrm{L \cdot mg^{-1}}$, respectively. The dimensionless constant ($R_L$) in the Langmuir model was found to be 0.072 which is indicative of favorable adsorption.[6] The applicability of the monolayer coverage of chromium on the surface of the resin is evident from the Langmuir data.

**3.5. Kinetics of Adsorption.** The rate of adsorption increased with time and reached its maximum at 30 min. The first-order and pseudosecond-order models were used to fit the experimental data. The first-order[32] and the pseudosecond-order rate equations[33] are expressed as follows.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} \tag{4}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \tag{5}$$

The results of the plots of $t/q_t$ versus $t$ (Figure 6a) and $\log(q_e - q_t)$ versus $t$ (Figure 6b) give the kinetic parameters. It can be seen from Table 2 that the adsorption data is consistent with the pseudosecond-order model in view of the higher regression coefficients. Further, the intraparticle rate constant was calculated using the expression[34]

$$q_t = k_{\mathrm{int}} \cdot t^{0.5} + C \tag{6}$$

where $k_{\mathrm{int}}$ is the intraparticle diffusion constant and $q_t$ is the amount of chromium(VI) adsorbed at time $t$. The $k_{\mathrm{int}}$ and the relevant plot are given in Table 2 and Figure 6c. The plot is indicative of boundary layer control as well as a diffusion-controlled process.[35]

**3.6. Adsorption Thermodynamics.** The thermodynamic parameters such as Gibbs energy, enthalpy, and entropy change were calculated at different temperatures using the following equations.[35,36]

$$\Delta G^0 = -RT \ln K \tag{7}$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{8}$$

The spontaneity of adsorption is ascertained from the equilibrium constant ($K$) and the Gibbs energy values. If $\Delta G^0 < 0$, we can conclude from eq 7 that the adsorption is thermodynamically feasible. Broadly speaking, $K > 1$ implies that the adsorption is effective and spontaneous at a given temperature. The $K$ value is obtained by taking the ratio of the concentration of the metal ion in the adsorbent to that in the solution. The $K$ values were found to decrease with temperature, and this is reflected in the Gibbs energy values obtained at higher temperature. A plot of $\ln K$ against $1/T$ is shown in Figure 6d, and the corresponding thermodynamic parameters are presented in Table 3. The amount of chromium(VI) adsorbed decreased with an increase in temperature from (30 to 55) °C. Lower temperatures are favorable for the adsorption process, which is evident from the $\Delta G^0$ values obtained at different temperatures. In the adsorption process which follows an ion pair mechanism, more energy is released (exothermic), and this is evident from the negative $\Delta H^0$ value. The negative $\Delta S^0$ value indicates less randomness at the adsorbent−solution interface.

**3.7. Regeneration of the Adsorbent Column.** The recovery of chromium(VI) adsorbed onto the column was tried using sodium hydroxide, ascorbic acid, sodium nitrite, and sodium sulfite, respectively.[37,38] Even though ascorbic acid, nitrite, and sulfite were effective in reducing chromium(VI), the desorption was found to be a maximum with 10 mL of 3 $\mathrm{mol \cdot L^{-1}}$ sodium hydroxide as the eluent. The desorption efficiency increases in

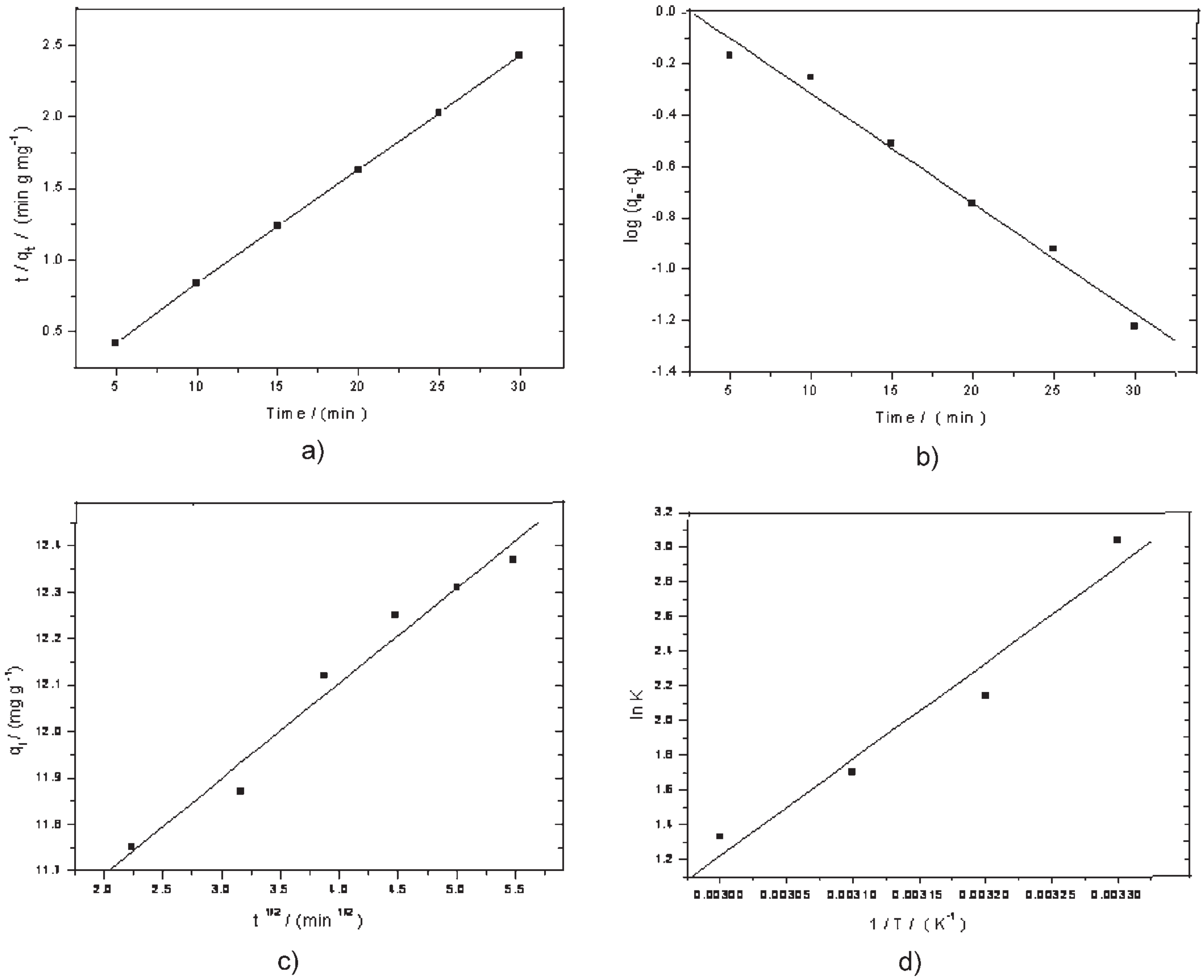


Figure 6. Kinetics and thermodynamics of adsorption: (a) second order kinetics, (b) first order kinetics, (c) intraparticle diffusion study, and (d) van't Hoff plot.

### Table 2. Kinetic Studies and Intraparticle Diffusion Rate Constant for the Adsorption of Chromium(VI)

| $C_o$ | $q_e$ | $k_2$ | | $k_1$ | | $k_{int}$ |
|---|---|---|---|---|---|---|
| $mg \cdot L^{-1}$ | $mg \cdot g^{-1}$ | $g \cdot mg^{-1} \cdot min^{-1}$ | $R_2^2$ | $min^{-1}$ | $R_1^2$ | $mg \cdot g^{-1} \cdot min^{-1/2}$ |
| 100 | 12.43 | 0.1746 | 0.9999 | 0.0988 | 0.9845 | 0.2054 |

the order sodium nitrite (75 %) < ascorbic acid (88.6 %) < sodium sulfite (90 %) < sodium hydroxide (99.5 %), respectively. In this process, the adsorbed chromium(VI) is brought into the aqueous solution as sodium chromate (Scheme 3), and the concentration of the chromium was estimated spectrophotometrically.

The desorption was confirmed through FT-IR (Figure 1) and powder XRD (Figure 2c) studies. The prominent peaks obtained after adsorption showed that the chromium(VI) peak had disappeared after elution using sodium hydroxide and restored the pattern of the original adsorbent, thereby confirming the quantitative desorption.

### Table 3. Thermodynamic Parameters for the Adsorption of Chromium(VI)

| $T$ | $C_o$ | | $\Delta G^0$ | $\Delta S^0$ | $\Delta H^0$ |
|---|---|---|---|---|---|
| K | $mg \cdot L^{-1}$ | $K$ | $kJ \cdot mol^{-1}$ | $J \cdot mol^{-1} \cdot K^{-1}$ | $kJ \cdot mol^{-1}$ |
| 303 | 100 | 20.97 | −7.66 | −128.90 | −46.34 |
| 313 | 100 | 8.51 | −5.57 | | |
| 318 | 100 | 5.49 | −4.50 | | |
| 328 | 100 | 3.78 | −3.62 | | |

**3.8. Effect of Sample Volume.** The effect of sample volume for the adsorption of chromium(VI) on the resin was investigated in the range (100 to 1600) mL maintaining an overall concentration of 100 $\mu g \cdot mL^{-1}$. As can be seen from Figure 7, it is evident that the adsorption of chromium is quantitative up to a 1000 mL sample volume with a preconcentration factor of 100. There are various factors such as bed height, quantity of adsorbent, and diameter of the column which affect the performance efficiency. On loading the column with a known sample volume, the polymeric resin swells, and the adsorbent bed undergoes expansion. In a small diameter column, the effective expanded bed operation is achieved when the expanded bed volume is about twice the volume of the packed bed.[39] At higher sample volume (beyond 1000 mL), the degree of expansion is more, and the distance between the particles in the polymeric sorbent increases. Hence, a smaller amount of Cr(VI) is adsorbed on the column, due to the nonavailability of effective adsorption sites.

**3.9. Optimum Flow Rate and the Amount of Amberlite XAD 1180 Loaded on the Column.** A flow rate of 5 $\text{mL}\cdot\text{min}^{-1}$ was maintained for maximum column efficiency, and the adsorption of chromium was quantitative. At higher flow rates, there was a decrease in the column adsorption efficiency, and this could probably be ascribed to the lesser contact time between the sample solution and the amine impregnated resin matrix. The column adsorption efficiency was a maximum when the resin amount was in the range (2.0 to 3.0) g up to a 1 L sample volume. However, when the resin amount was less than 2.0 g, the column efficiency was found to be good at lower sample volumes.

**3.10. Stability of the Column.** The stability of the Amberlite XAD 1180 column was tested using 100 $\mu\text{g}\cdot\text{mL}^{-1}$ chromium(VI) maintaining a sample volume of 1 L. The adsorbed chromium(VI) was eluted using 10 mL of 3 $\text{mol}\cdot\text{L}^{-1}$ sodium hydroxide. The column could be used with good precision (relative standard deviation 2.0 %) for 15 cycles without a reduction in the performance efficiency.

**3.11. Effect of Diverse Ions.** The effect of various cations and anions that are commonly present in the real effluents were investigated independently at a 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ concentration. Cations such as Fe(II, III) and Mn(II) caused significant reduction (Figure 8a) in the adsorption of chromium(VI). Among the anions, chloride, nitrate, and phosphate caused a marginal decrease in the adsorption efficiency (Figure 8b) of chromium(VI). There is no appreciable interference from Ni(II), Ca(II),

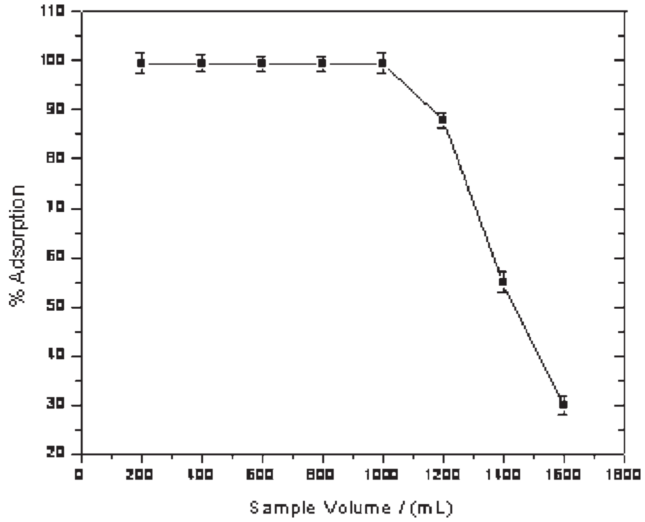
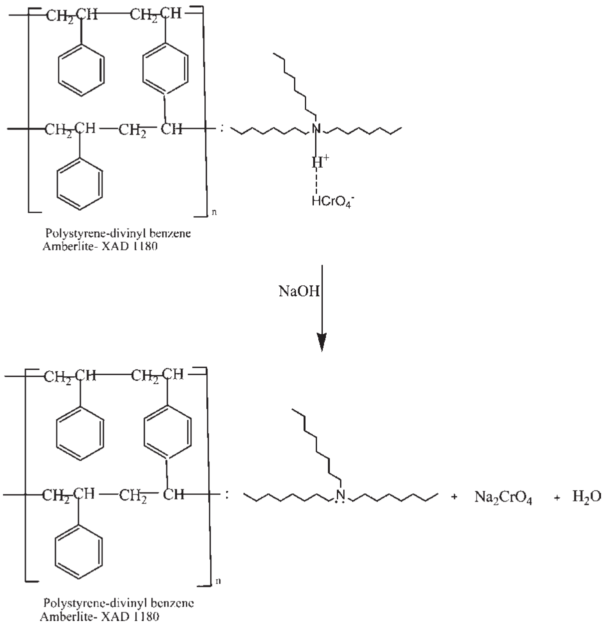


Figure 7. Effect of sample volume in the column study.

**Scheme 3. Recovery of Chromium(VI) with NaOH**



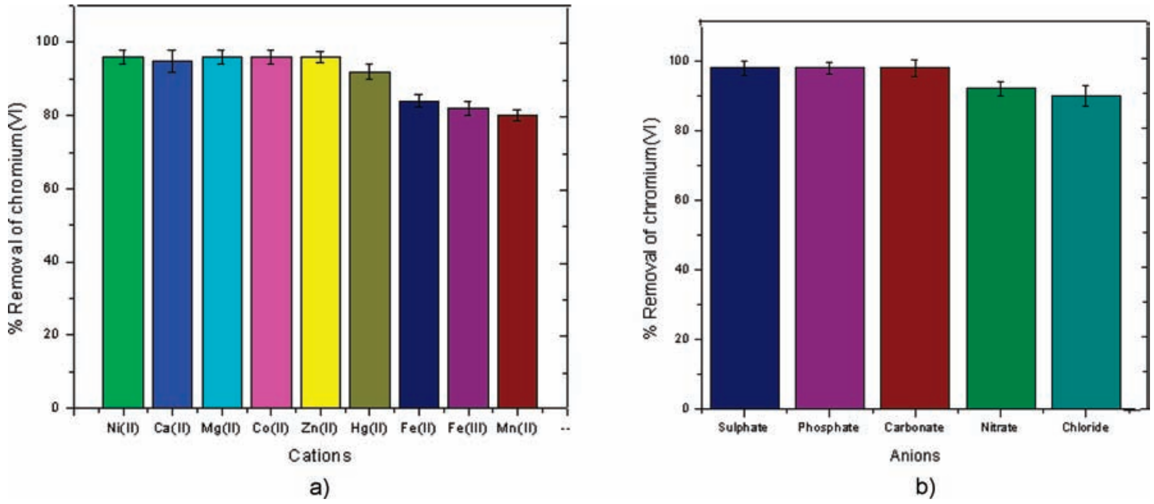


Figure 8. Effect of (a) diverse cations on the removal of Cr(VI) and (b) diverse anions on the removal of Cr(VI).

**Table 4. Recovery of Total Chromium in Various Synthetic Effluents**

| sample | composition in $\mu g \cdot mL^{-1}$ | recovery of total chromium/(%) |
|---|---|---|
| synthetic effluent A | $SO_4^{2-}$(1000), $NO_3^-$(500), $PO_4^{3-}$(1000), $Cl^-$ (1000), $Cu^{2+}$(1000), $Zn^{2+}$(500), $Fe^{3+}$(250), $Mg^{2+}$(1000), $Ca^{2+}$(1000), $Hg^{2+}$ (500), total Cr (100) | 94.3 ± 0.5 |
| synthetic effluent B | $Fe^{3+}$(700), $SO_4^{2-}$(500), $Ca^{2+}$(1000), $Cu^{2+}$(500), $NO_3^-$(250), $Cl^-$(1000), $Mg^{2+}$(1000), $Hg^{2+}$(1000), $Mn^{2+}$ (750), $Zn^{2+}$ (1000), total Cr (700) | 90.1 ± 0.2 |
| synthetic effluent C | $Fe^{3+}$(150), $SO_4^{2-}$(1000), $Ca^{2+}$(1000), $Cu^{2+}$(250), $NO_3^-$(250), $Cl^-$(500), $PO_4^{3-}$(500), $Mg^{2+}$(1000), total Cr (500) | 99.5 ± 0.2 |

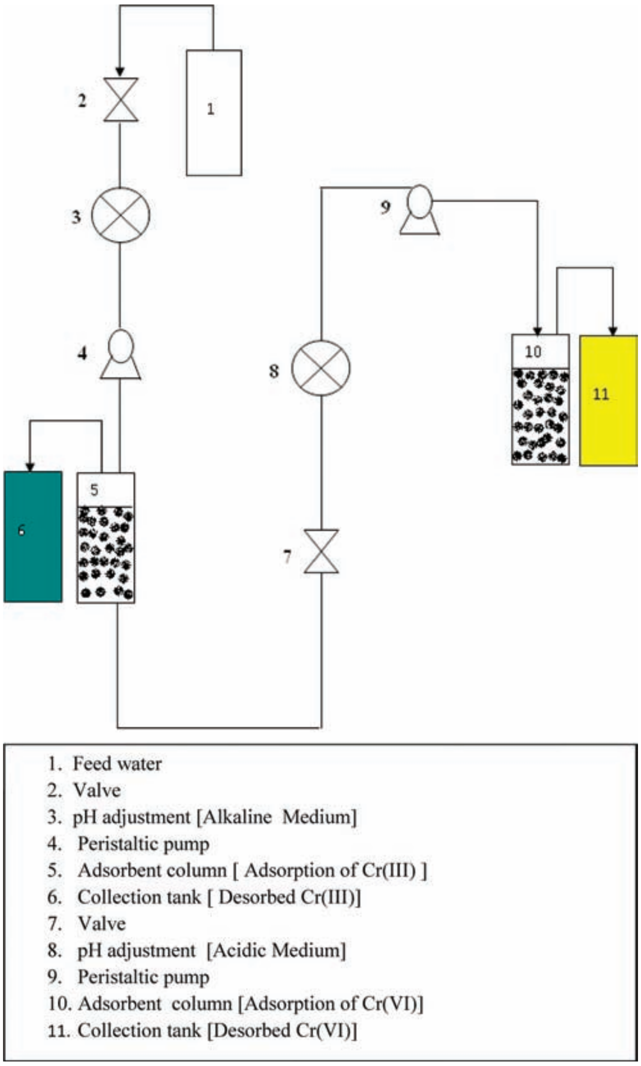


**Figure 9.** Schematic diagram for treating tannery effluent.

Mg(II), Hg(II), and Zn(II) ions. Under the given experimental conditions, these ions do not form any stable ion pair with the protonated amine for competition with the bichromate for the active sites in the adsorbent. However, in the presence of excess chloride concentration, it is possible that Ni(II), Hg(II), and Zn(II) could form tetrahalo complexes which would compete with $HCrO_4^-$ for adsorption causing a decrease in the selectivity. The selectivity decreases in the presence of Mn(II) since manganese in the +2 oxidation state could reduce Cr(VI) to Cr(III) in an acidic medium.

**Table 5. Comparison of Maximum Adsorption Capacity with Other Adsorbents Recently Reported in Literature**

| serial no. | adsorbents | adsorption capacity | refs |
|---|---|---|---|
| | | $mg \cdot g^{-1}$ | |
| 1 | Dowex M4195 chelating resin | 29.7 | 14 |
| 2 | *p-tert*-butylcalix[8]areneoctamide impregnated Amberlite resin | 87.7 | 18 |
| 3 | ion exchange resins 1200H | 84.0 | 41 |
| 4 | Dowex resin | 109.3 | 42 |
| 5 | *N*-methylimidazolium functionalized strongly basic anion exchange resin | 135.0 | 43 |
| 6 | Amberlite XAD-7 resin impregnated with Aliquat 336 | 50.44 | 44 |
| 7 | D314 anion-exchange resins | 120.48 | 45 |
| 8 | Lewatit MP 500 (anion exchange resin) | 21.32 | 46 |
| 9 | glycidyl methacrylate resin bearing quaternary ammonium chloride | 48.0 | 47 |
| 10 | trioctylamine impregnated Amberlite XAD 1180 | 171.82 | present work |

**3.12. Recovery of Total Chromium in Synthetic Effluents.** The applicability of the proposed method was tested in synthetic effluents of three different compositions. The synthetic samples were prepared in such a way so as to match the approximate composition of real effluents. Cr(III) was also one of the constituents in the synthetic mixture; it was oxidized to Cr(VI), and the total chromium concentration was maintained in the level (100 to 700) $\mu g \cdot mL^{-1}$. The results are presented in Table 4. In the presence of chloride, cations such as Hg(II), Zn(II), Mn(II), and Fe(III) caused a reduction in the recovery of total chromium. This may be ascribed to the fact that all of these ions can form stable chloro complexes, which might vie with the oxo-anion chromate for ion-pair formation with the protonated amine.

**3.13. Removal of Chromium from Real Tannery and Electroplating Wastewater Effluents.** The applicability of the method was finally tested for the removal of chromium from a real tannery wastewater sample collected from Tamil Nadu, India. The sample was green in color at alkaline pH and stored in a polythene bottle. It is well-known that the major constituent of tannery effluent is Cr(III), since it is the species used in leather tanning. Trace amounts of Cr(VI) are also likely to be present due to some oxidizing agents used in the tanning process. The organic matter is destroyed using an appropriate amount of a $HNO_3-H_2SO_4$ mixture.[1] A known volume of the effluent was taken and loaded onto the adsorbent column under alkaline conditions where Cr(III) is selectively retained. At higher pH, Cr(III) exists as $Cr(OH)_2^+$ and $Cr(OH)^{2+}$ species, respectively.[40] In an alkaline medium, the amine acts as an electron donor and facilitates effective interaction with the above-mentioned positively charged Cr(III) species. Hence, Cr(III) is effectively retained at higher pH. The resulting solution is acidified to pH 3 and passed through another column containing the amine impregnated resin where Cr(VI) is selectively retained. The process is illustrated schematically in Figure 9. The separated Cr(III) and Cr(VI) could be eluted using $H_2SO_4$ and NaOH, respectively. The total chromium concentration was determined spectrophotometrically. An overall removal efficiency of 99.3 % could be attained by the proposed method.

An electroplating wastewater sample was obtained from a small scale electroplating unit near Bangalore, India. The sample was brown in color and stored in a polythene bottle. The chromium present in the electroplating wastewater sample was oxidized to Cr(VI) with alkaline peroxide and then loaded onto the adsorbent column.[38] The pH was maintained at 2, and the adsorbed chromium was eluted quantitatively using NaOH. An overall removal efficiency of 98.5 % could be attained by the proposed method.

**3.14. Comparison of the Adsorption Capacity with Other Adsorbents.** The effectiveness of trialkylamine impregnated adsorbent was compared in terms of the adsorption capacity with some recently reported adsorbents. The results are given in Table 5. It is evident that the adsorption capacity of the proposed sorbent compares favorably with these adsorbents, and it is also noteworthy to mention that it is quite high compared to some of these adsorbents.

## 4. CONCLUSIONS

The proposed method illustrates the high potential of a polystyrene-divinyl benzene based sorbent impregnated with a long-chain amine for the removal of chromium. The polymeric sorbent is efficient and could endure the treatment in both acidic and alkaline media. The adsorption kinetics is fast, follows a pseudosecond-order model, and is also in accordance with the Langmuir adsorption isotherm model with an adsorption capacity of $171.82\ mg \cdot g^{-1}$. The study of the thermodynamic parameters showed that the adsorption process decreases with an increase in temperature. Column studies proved that the system could tolerate a large sample volume (1 L) with effective separation from a synthetic mixture of various ions. Cr(VI) could be effectively removed at acidic pH based on the electrostatic attraction of the bichromate anion with the protonated amine, whereas Cr(III) was retained in the column at alkaline pH due to the interaction of the amine with $Cr(OH)_2^+$ and $Cr(OH)^{2+}$ species. The adsorbed chromium in the respective oxidation states could be recovered from the column using sulfuric acid and sodium hydroxide, respectively, without any appreciable loss in the performance efficiency for 15 cycles. The validity of the proposed method is very well illustrated for the separation of chromium in real effluent samples with an average removal efficiency greater than 98 %.

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