



## An efficient ultrasound assisted approach for the impregnation of room temperature ionic liquid onto Dowex 1 × 8 resin matrix and its application toward the enhanced adsorption of chromium (VI)

S. Kalidhasan<sup>a</sup>, A. Santhana Krishna Kumar<sup>a</sup>, Vidya Rajesh<sup>b</sup>, N. Rajesh<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Birla Institute of Technology and Science (BITS), Pilani-Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, R. R. Dist 500 078, AP, India

<sup>b</sup> Department of Biological Sciences, Birla Institute of Technology and Science (BITS), Pilani-Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, R. R. Dist 500 078, AP, India

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### ABSTRACT

The work discussed in this paper is based on the utilization of ultrasound in conjunction with an ionic liquid (Aliquat 336) impregnated Dowex 1 × 8 resin for the effective adsorption of chromium. Ionic liquids are known for their selectivity toward metal extraction and ultrasonic medium offers efficient energy transfer for impregnating the ionic liquid in the resin matrix. The molecular interaction between the ionic liquid impregnated resin and chromium was studied through various physicochemical and spectroscopic techniques. The influence of various analytical parameters on the adsorption of Cr(VI) such as pH, adsorbent dosage, temperature and interference of foreign ions was studied in detail. Chromium (VI) was quantitatively adsorbed in the pH range of 3.5–4, with a high adsorption capacity of 230.9 mg g<sup>-1</sup> in conformity with the Langmuir isotherm model. The study of thermodynamic parameters showed that the adsorption process is exothermic and spontaneous. The adsorbent could be regenerated using 1 mol L<sup>-1</sup> HCl–0.28 mol L<sup>-1</sup> ascorbic acid mixture. Chromium could be effectively detoxified from an industrial effluent and finally the developed method was validated with the analysis of a certified reference material (BCR-715). The obtained results indicated that the ultrasonic assisted impregnation of the room temperature ionic liquid significantly enhances and improves the removal efficiency of Cr(VI).

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### 1. Introduction

The release of chromium from industries such as chrome tanning and electroplating [1–3], is an important issue that needs to be addressed. The discharged chromium exists in two important oxidation states, +3 and +6 respectively and the toxicity of Cr(VI) is much higher than Cr(III) [4–6]. According to the United States Environmental Protection Agency (USEPA), the permitted concentration of Cr(VI) and total chromium discharged to surface water should be less than 0.05 mg L<sup>-1</sup> and 0.1 mg L<sup>-1</sup> respectively [7]. Hence, it is of paramount importance to treat the Cr(VI) containing wastewater before it is discharged into the environment. Several treatment methods have been studied to remove chromium from wastewater. These include reduction [8], chemical precipitation [9], ion exchange [10,11], membrane separations [12,13], electrochemical precipitation [14], nanofiltration [15], flotation [16], electrocoagulation [17], solvent extraction [18], sedimentation [19], reverse osmosis [20] and adsorption [21,22]. Although these methods are quite satisfactory in removing chromium,

production of solid residue is a major environmental concern. Moreover, when the concentration of chromium in the wastewater is low, its removal efficiency by chemical reduction is poor [23]. As an alternative, physico-chemical treatments such as ion exchange [24] have also been utilized to treat chromium-laden wastewater. Ion exchange using synthetic resins is an interesting methodology for removing toxic contaminants from aqueous phase at various concentration levels. The main advantages of ion exchange resins include high degree of metal recovery and selectivity. The anion exchange processes can be used for the removal of chromium from wastewater at varying pH in the presence of high concentration of anions such as chloride, sulfate, bicarbonate and nitrate [25,26]. Various anion exchangers have been studied for the removal of heavy metal ions [27]. Similarly, the selectivity of the commercially available strong or weak base anion exchangers for chromate anion has been studied in the pH range 3–8 [28–35]. Modifying the anion exchangers by impregnation, functionalization etc. offers higher affinity toward chromium adsorption [36]. The selectivity of these strongly basic anion exchangers is influenced by the concentration of chromium, the ionic form of the resin and the substituents. These features are well satisfied by Dowex 1 × 8 resin, a styrene-divinyl benzene polymeric resin containing quaternary ammonium functional group with chloride (Cl<sup>-</sup>)

\* Corresponding author. Tel.: +91 40 66303503; fax: +91 40 66303998.

E-mail address: [nrajesh05@gmail.com](mailto:nrajesh05@gmail.com) (N. Rajesh).

and a total exchange capacity of 1.2 mequiv. mL<sup>-1</sup>, Dowex M4195 chelating resin [37], functionalized pyridine copolymer with amine groups [38] and hybrid inorganic/organic adsorbents [39]. Wang et al. [40] used Dowex 1 × 8 resin to remove radioisotopes from aqueous solution. Raji and Anirudhan [41] have made a comparative study of polyacrylamide grafted sawdust adsorbent for the removal of chromium with Dowex resin. A relative assessment of the removal efficiency of Dowex 1 × 8 and Amberlite IRA96 resins for heavy metal remediation has been reported [42]. Ionic liquids exhibit good selectivity, sensitivity and reproducibility toward metal extraction [43]. Recently, various ionic liquids have been explored for the removal of metal ions [44]. Aliquat 336 is a room temperature ionic liquid (RTIL), which has been utilized for the extraction of chromium (III) [45] with high degree of metal recovery. Konczyk et al. [12] have reported the competitive transport of Cr(III) and Cr(VI) by polymer inclusion membranes with D2EHPA and Aliquat 336. At pH 1.0 Cr(VI), oxo-anions were removed with a recovery factor of 90%. Herein, Aliquat 336 plays the role of a plasticizer and an ion carrier. Recently, Kalidhasan et al. [46] have reported an effective method for chromium with an adsorption capacity of 38.94 mg g<sup>-1</sup> using ultrasound assisted impregnation of Aliquat 336 in a cellulose matrix. Solvent impregnation of metal extractants in various matrices is also known for their efficacy [47] toward the removal of heavy metals.

The conventional methods followed in the preparation of solvent impregnated resins are quite time consuming and hence an alternative green and economic process involving ultrasonication is proposed for the impregnation of the metal extractant. In this work, we report an enhanced method for the adsorption of chromium by impregnation of Aliquat 336 in Dowex 1 × 8 resin matrix using ultrasonication. The resin before and after the adsorption was thoroughly characterized using various analytical techniques followed by the optimization of vital experimental parameters. The feasibility of the method has been successfully demonstrated in the detoxification of chromium from industrial wastewater samples and validated with the analysis of chromium in a certified industrial wastewater effluent sample (BCR-715).

## 2. Experimental

### 2.1. Reagents

All reagents were of analytical grade. Milli-Q water (MQW) was used in the preparation of solutions. An appropriate amount of potassium dichromate (S. d. Fine Chemicals, Mumbai, India) was diluted to 100 mL with MQW to give 1000 mg L<sup>-1</sup> chromium (VI) solution. Working solutions were prepared by appropriate dilution. 1 mol L<sup>-1</sup> sulfuric acid (S. d. Fine chemicals, Mumbai, India) was prepared by appropriate dilution with MQW. Dowex 1 × 8 resin was procured from Merck, India. Sodium hydroxide, ascorbic acid, sodium nitrite, sodium sulfite, methylisobutylketone (MIBK), hydrochloric acid, thiourea, and Aliquat 336 were procured from S. d. Fine Chemicals, Mumbai (India). MIBK was used as the diluent for the ionic liquid, Aliquat-336. BCR-715 (certified industrial wastewater effluent) was used for the validation of the method.

### 2.2. Instrumentation

A Branson (model 1510) ultrasonic bath with frequency 40 kHz was utilized in the adsorbent preparation. The morphological changes in the adsorbent were obtained from JSM-840 scanning electron microscope (SEM). The surface area of the adsorbent was determined using Micromeritics porosimeter model ASAP2020 analyzer in a nitrogen atmosphere, and this was out gassed at 150 °C for 12 hr. The solid state <sup>13</sup>C NMR spectra were recorded in

Bruker DSX-300 NMR spectrometer at ambient temperature. The characteristic changes in the vibrational frequency of the adsorbent before and after the adsorption of chromium were recorded using Jasco-4200 FT-IR spectrometer. X-ray diffraction pattern was recorded in XPERT-PRO X-ray diffractometer using Cu K $\alpha$  radiation. The Energy Dispersive X-ray spectrum (EDX) was recorded with Hitachi S-3000H spectrometer and the removal efficiency of chromium was estimated quantitatively using a Jasco V-650 UV-visible spectrophotometer. The pH of the reaction medium was adjusted using an Elico LI-127 (India) model pH meter.

### 2.3. Adsorbent preparation

A known amount of Dowex 1 × 8 resin was washed with a mixture of ethanol, hydrochloric acid and water in the ratio 2:1:1. It was dried in hot air oven for 5 h at 60 °C and kept in desiccator for further use. 5 g of the resin was sonicated for 3 h with 30 mL of 1.01 mol L<sup>-1</sup> Aliquat 336 in MIBK medium for effective impregnation. The resin adsorbent was dried at 60 °C and used for further study. The prepared adsorbent was well characterized using various analytical techniques.

### 2.4. Adsorption studies

Adsorption experiments were performed by equilibrating 0.25 g of adsorbent containing 10 mg L<sup>-1</sup> Cr(VI) solution for 30 min in rotatory orbital incubator shaker (Biotechnics, India) at room temperature (27 ± 1 °C). The pH was adjusted to 3.5 using sodium hydroxide and sulfuric acid. After 30 min, the reaction mixture was filtered and the percentage of chromium adsorbed was estimated by measuring its concentration in the supernatant by the standard diphenylcarbazide method at  $\lambda_{\max}$  540 nm [22]. The uptake of chromium by the adsorbent was calculated from the following equation,

$$q_e = C_0 - C_e \times \frac{V}{W} \quad (1)$$

where  $q_e$  is the chromium uptake (mg g<sup>-1</sup>),  $C_0$  and  $C_e$  are the initial and equilibrium Cr(VI) concentrations in the aqueous phase (mg L<sup>-1</sup>),  $W$  is adsorbent dosage (g) and  $V$  is the solution volume (L). The desorption could be done using 5 mL of 0.1 mol L<sup>-1</sup> HCl–0.28 mol L<sup>-1</sup> ascorbic acid mixture in 1:1 ratio wherein the adsorbed chromium (VI) is reduced to Cr(III) and this brings out the greener aspect in the rejuvenation of the adsorbent.

## 3. Results and discussion

### 3.1. Characterization of adsorbent

Increasing the effective adsorption sites along with the existing active adsorption center without any functionalization was achieved by simple impregnation through ultra-sonication. The ultrasound assisted impregnation results in an effective mass transfer with enhanced sorption and desorption kinetics [48]. The generation of pressure waves in liquids leads to the creation and breakdown of tiny bubbles and the energy released during this process ensures homogenous dispersion and impregnation of the ionic liquid in the Dowex resin matrix. In this method, isobutylmethylketone (MIBK) was used as a diluent for the ionic liquid [46,49]. MIBK is known to be a good diluent for Aliquat 336 [50] in the extraction of aliphatic acids from aqueous solutions. The extractant is impregnated into the polymeric backbone by van der Waals force of attraction and  $\pi$  interaction with the phenyl ring of the resin. The impregnation of ionic liquid in the Dowex resin matrix and its application toward the adsorption of chromium is shown schematically in Fig. 1. The molecular interaction before and after

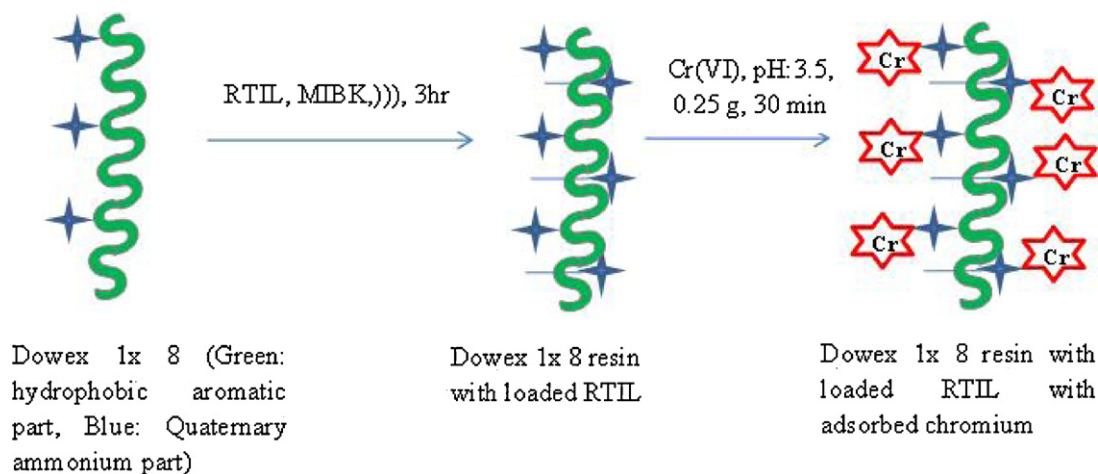


Fig. 1. Schematic representation of the interaction of the adsorbent with chromium.

the adsorption was well studied by various analytical techniques. The surface morphology of the prepared adsorbent was analyzed using SEM (Fig. 2) which shows the presence of broken resin beads with a dark surface. After the adsorption of Cr(VI), the morphology is distinctly different with a polished surface. The surface area of the sorbent was found to be  $1.9687 \text{ m}^2 \text{ g}^{-1}$ . The XRD (Fig. 3) pattern of the adsorbent shows changes after the impregnation of the ionic liquid and the characteristic peaks corresponding to  $2\theta$  values  $32^\circ$  and  $45^\circ$  indicates the presence of chromium (VI) [51]. After the adsorption of chromium, the XRD pattern sharpens which indicates the increase in the size of the adsorbent. This increase is attributed to the adsorption of chromium as  $\text{HCrO}_4^-$  on the resin surface. The monotonic asymptotic trend in the later part of the curve disappears after the adsorption of chromium. This is manifested a small hump (indicated in the spectrum after adsorption) in the  $2\theta$  range  $32^\circ$  and  $45^\circ$ , which is characteristic of chromium, in accordance with the reported value in the literature. The presence of chromium after adsorption was also confirmed by the energy dispersive X-ray spectrum (Fig. 4A) which clearly indicates the presence of chromium [35,52]. Further, the changes in the functionalities were also analyzed through FT-IR and CP-MAS  $^{13}\text{C}$  NMR spectroscopy respectively. The FT-IR study (Fig. 4B) showed characteristic bands at  $2948 \text{ cm}^{-1}$  (C–H, aliphatic),  $3050 \text{ cm}^{-1}$  (C–H, aromatic),  $1615 \text{ cm}^{-1}$  (C=C aromatic), and  $1255 \text{ cm}^{-1}$  (C–N) respectively. There is a considerable change in the FT-IR spectrum after the adsorption of chromium (VI) and a prominent new peak

appears at  $889 \text{ cm}^{-1}$  corresponding to the stretching vibration of Cr=O in  $\text{HCrO}_4^-$  [18,35,53]. The  $^{13}\text{C}$  NMR spectrum of the ionic liquid impregnated Dowex  $1 \times 8$  resin before and after the adsorption of the chromium (VI) is shown in Fig. 5. The characteristic chemical shifts corresponding to the aromatic carbon, quaternary carbon attached to the backbone,  $\text{CH}_2$ ,  $\text{CH}_3$ , in the resin were observed at 127.9 ppm, 145.11 ppm and 10–40 ppm respectively in accordance with the reported literature values [54,55]. The splitting of the peak in the range 10–40 ppm is due to the ion-pair formation of  $\text{HCrO}_4^-$  ion with the Dowex  $1 \times 8$ -resin containing ammonium ion. The  $\text{HCrO}_4^-$  anion changes the chemical/electronic environment near the ammonium cation of the Dowex  $1 \times 8$  resin. A distinct variation is observed in the NMR spectrum after the adsorption of Cr(VI) in the C–N chemical shift value from 68.7 to 61.5 ppm and this indicates the association of the quaternary ammonium ion in the ionic liquid ( $\text{N}^+$ ) as an ion pair with the hydrogen chromate anion on the surface of the resin.

### 3.2. Optimization of analytical parameters

#### 3.2.1. Effect of pH on adsorption

The existence of Cr(VI) in various forms such as chromate, hydrogen chromate or dichromate oxo-anion species is dependent on the pH of the reaction medium. Under alkaline conditions, the yellow chromate oxo-anion is the major species, whereas in acidic medium, the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$  oxo-anions are the predominant

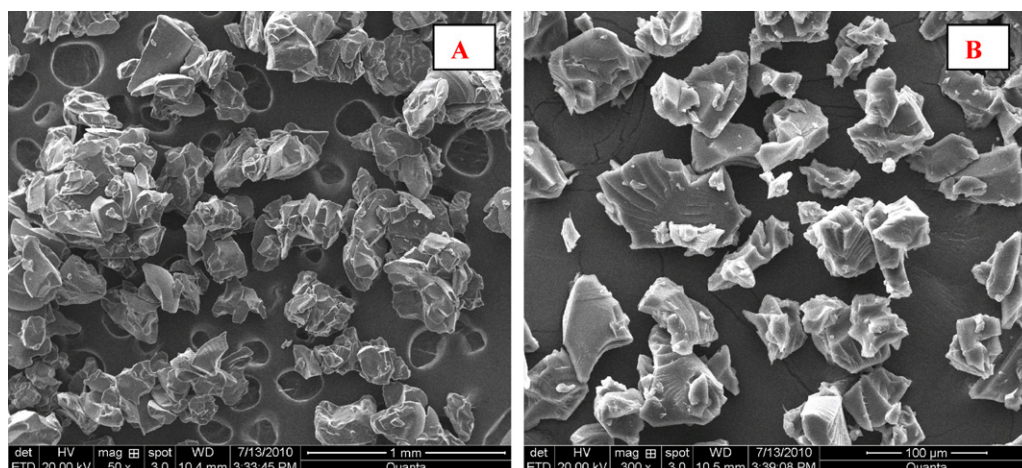


Fig. 2. SEM image of (A) adsorbent and (B) after chromium (VI) adsorption.

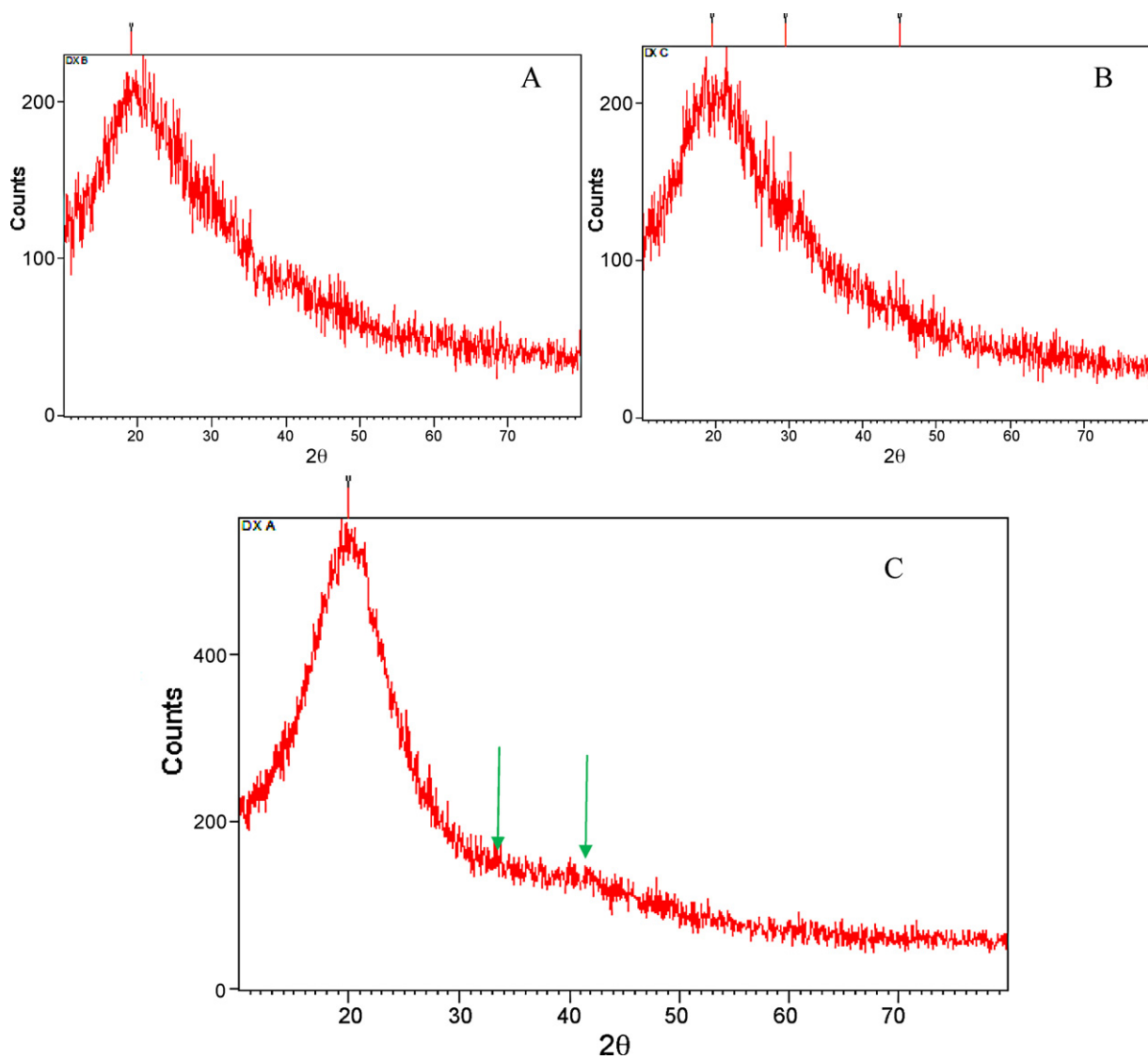


Fig. 3. Powder XRD pattern of (A) Dowex resin, (B) adsorbent, and (C) after chromium (VI) adsorption.

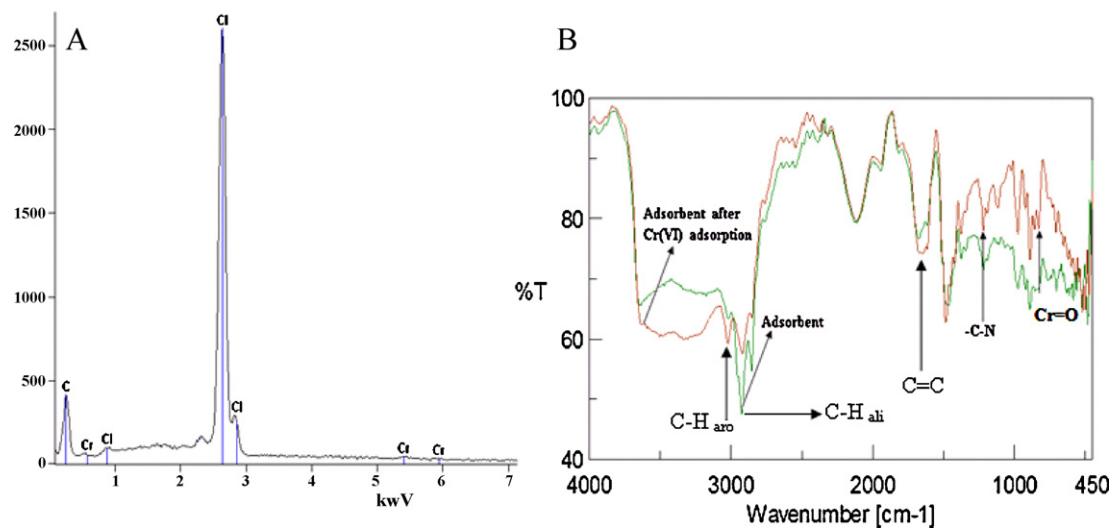


Fig. 4. (A) EDX spectrum of the adsorbed Cr(VI) on the resin matrix. (B) FT-IR spectrum of adsorbent before and after the adsorption of chromium.



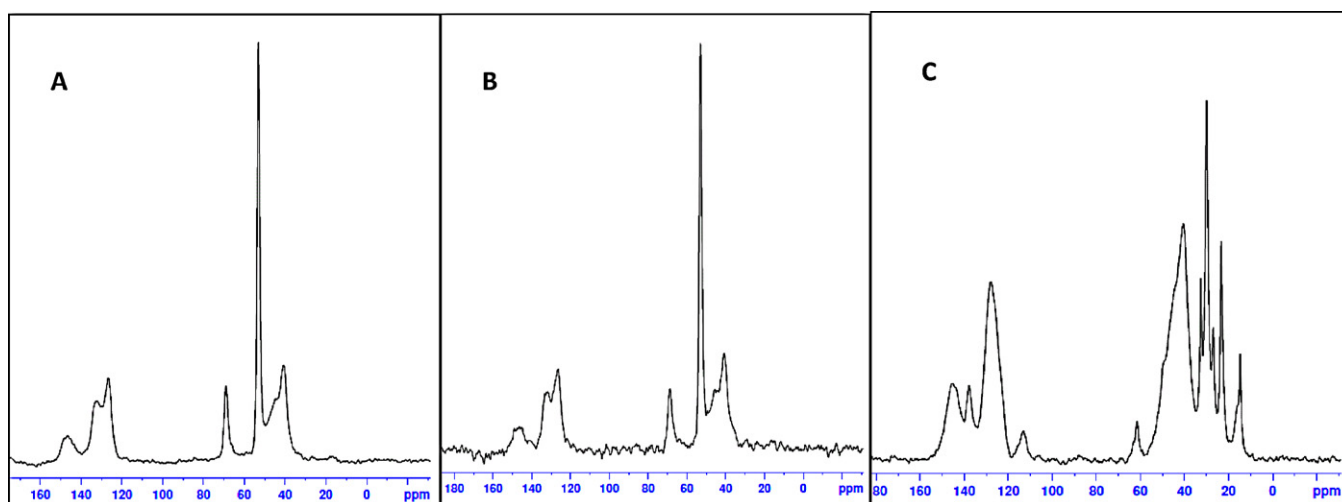


Fig. 5. <sup>13</sup>C NMR spectrum of (A) Dowex resin, (B) the adsorbent, and (C) after the adsorption of Cr(VI).

species [56]. The plot (Fig. 6A) of pH vs % adsorption shows a sharp increase in the amount of chromium adsorbed and reaches a maximum in the range 3–4. Above pH 4, and in the alkaline range, the decrease in the percentage adsorption could be attributed to competition of hydroxide ion along with the  $\text{HCrO}_4^-$  anion for the effective adsorption sites on the resin matrix. In this pH range, it is the hydrogen chromate anionic species, which interacts with the positively charged resin matrix and this fact was confirmed from the characteristic  $\text{Cr}=\text{O}$  peak in FTIR study.

### 3.2.2. Effect of amount of adsorbent and contact time

The amount of adsorbent used in batch study was varied in the range 0.1–0.3 g. The results are presented in Fig. 6B. The adsorption was found to be maximum when the amount of adsorbent is in the range 0.25–0.3 g in 50 mL sample volume used for the batch experiments. The % adsorption increases with time and attains its maximum in 30 min (Fig. 6C) signifying the saturation of the adsorption.

### 3.2.3. Adsorption isotherms

Langmuir [57] and Freundlich [58] isotherm models were used to study the adsorption behavior of chromium (VI) on Aliquat336 loaded Dowex 1 × 8 resin (Fig. 7A and B). The Langmuir isotherm can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (2)$$

where  $q_e$  is the amount of  $\text{HCrO}_4^-$  adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_0$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mg L}^{-1}$ ), and  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant. The values of  $q_0$  and  $b$  in the Langmuir equation were found to be  $230.9 \text{ mg g}^{-1}$  and  $0.3367 \text{ L mg}^{-1}$  respectively with a correlation coefficient value of 0.9943. The dimensionless constant ( $R_L$ ) in the Langmuir model was found to be 0.013 which is indicative of favorable adsorption [59]. The applicability of the monolayer coverage of chromium on the surface of the resin is evident from the Langmuir data. Higher regression coefficient was obtained using Langmuir isotherm and the results (Table 1) were consistent with the experimental data.

The Freundlich isotherm is represented as

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

where  $q_e$  is the amount of  $\text{HCrO}_4^-$  adsorbed ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mg L}^{-1}$ ), 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  $97.7 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$  and 4.08 respectively. The value of  $n$  for this adsorbent indicates that the adsorbent has very good affinity toward Cr(VI) [60].

### 3.2.4. Kinetics of adsorption

The first order and pseudo second order models were used to fit the experimentally obtained adsorption data. The first order [61]

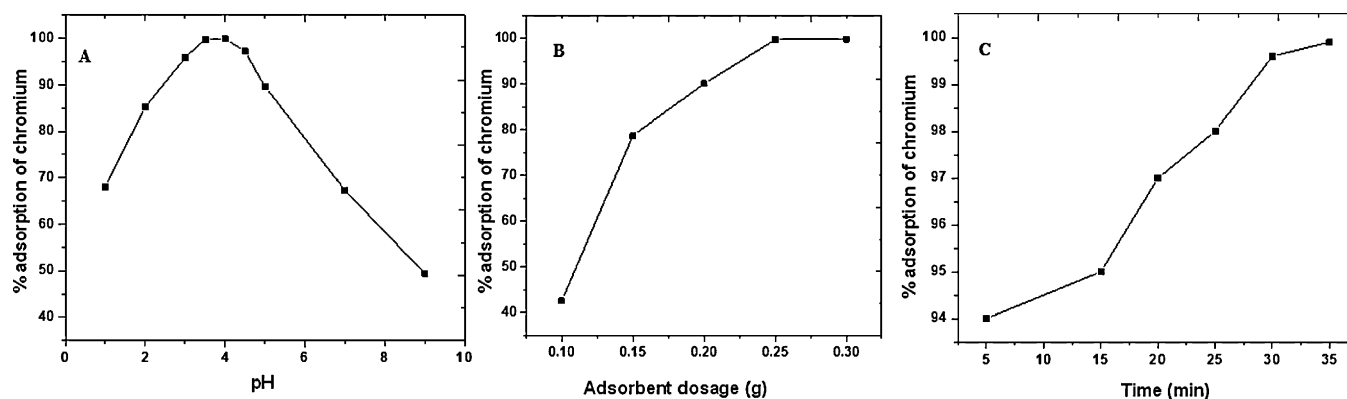


Fig. 6. (A) Effect of pH, (B) amount of adsorbent, and (C) effect of contact time.

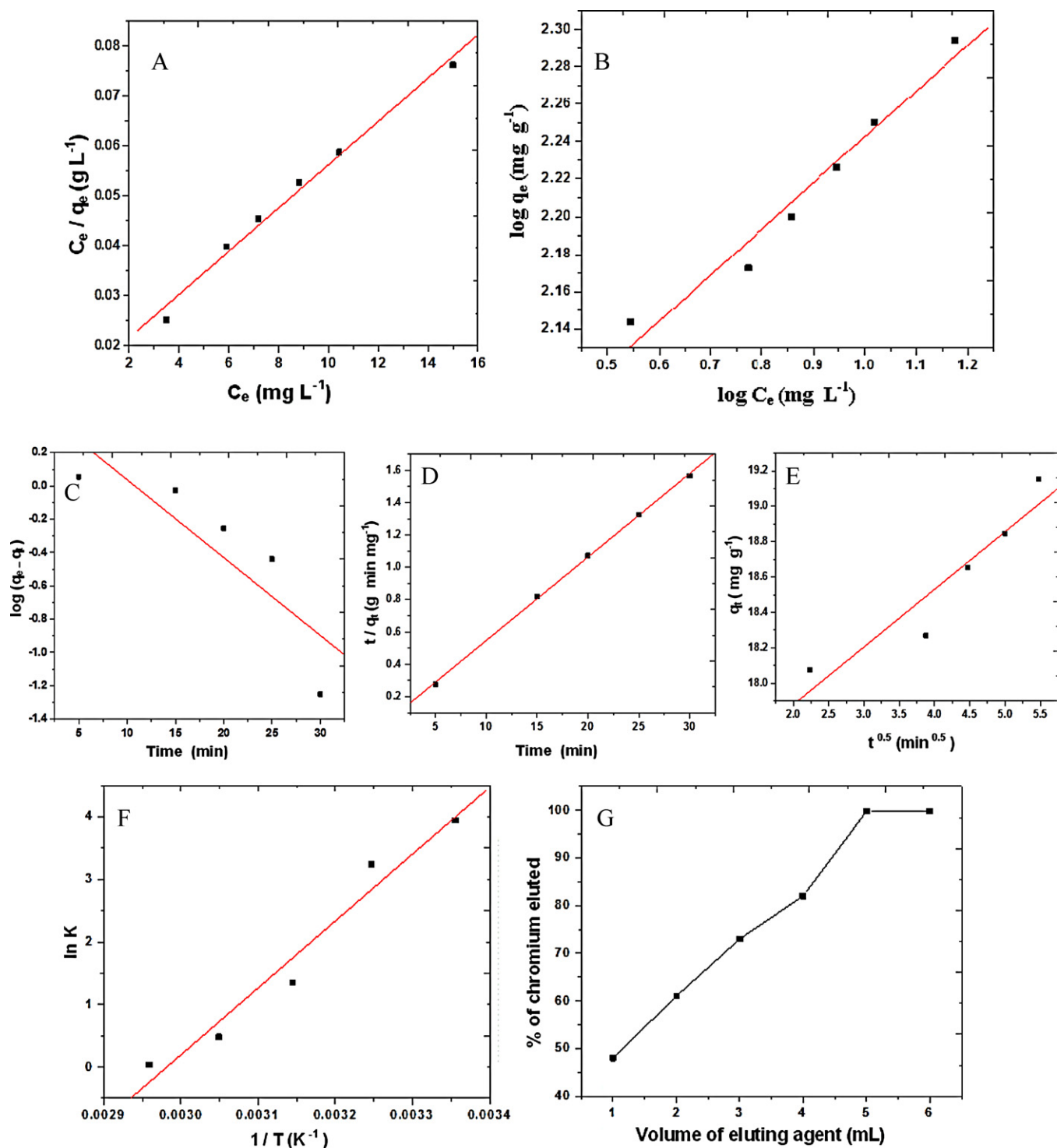


Fig. 7. (A) Langmuir isotherm, (B) Freundlich isotherm, (C) Pseudo first order plot, (D) Pseudo second order plot, (E) Intra particle diffusion, (F) Van't Hoff plot, and (G) Effect of volume of eluting agent.

Table 1

Various adsorption isotherm (Langmuir and Freundlich) and kinetic parameters for the Cr(VI) adsorption.

Langmuir isotherm				Freundlich isotherm			Pseudo-second order kinetics				Pseudo-first order kinetics		Intra-particle diffusion
$q_0$ ( $\text{mg g}^{-1}$ )	$R_L$	$b$ ( $\text{L mg}^{-1}$ )	$r^2$	$K_f$ ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ )	$n$	$r^2$	$C_0$ ( $\text{mg L}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$r_2^2$	$k_1$ ( $\text{min}^{-1}$ )	$r_1^2$	$k_{\text{int}}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )
230.9	0.013	0.3367	0.99	97.7	4.08	0.98	100	19.368	0.085	0.99	0.108	0.86	0.05163

**Table 2**  
Thermodynamic parameters for the adsorption of chromium.

Temperature (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )
298	-9.77		
303	-8.30		
313	-3.58	-265.1	-88.91
318	-1.31		
328	-0.101		

and the pseudo-second order rate equations [62] are expressed as follows.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_1$  and  $k_2$  refer to the rate constants and the other parameters have their usual significance as mentioned before. The results of adsorption kinetics are shown in Fig. 7C, D and Table 1. It can be seen from Table 1, that the adsorption data is consistent with the pseudo second order model in view of the higher regression coefficients. In general, adsorption processes adhere to one or more of the following features: (i) external mass transfer mechanism, (ii) intra-particle diffusion and (iii) physical and chemical adsorption [63]. Further, the intra-particle rate constant was calculated using the expression [64].

$$q_t = k_{\text{int}} \times t^{0.5} + C \quad (6)$$

where  $k_{\text{int}}$  is the intra-particle diffusion constant and  $q_t$  is the amount of chromium (VI) adsorbed at time  $t$ . The  $k_{\text{int}}$  obtained from the slope of the plot of  $q_t$  vs  $t^{0.5}$  (Table 1 and Fig. 7E) indicates that the mass transfer essentially occurs in the form of diffusion from the bulk solution to the surface of the resin matrix [65]. The plot does not pass through the origin and this could be ascribed to a certain degree of boundary layer control. Hence, the intra-particle diffusion is not the only rate-controlling step and other processes could control the rate of adsorption. Hence, surface adsorption and intraparticle diffusion are likely to occur simultaneously thereby, controlling the kinetics of Cr(VI)-adsorbent interaction.

### 3.2.5. Adsorption thermodynamics

The thermodynamic parameters namely, standard free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) changes were determined from the adsorption studies at various temperatures. These parameters were obtained from the following equations [66] and the graph shown in Fig. 7F.

$$\Delta G^\circ = -RT \ln K \quad (7)$$

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

where  $R$  is gas constant (JK<sup>-1</sup> mol<sup>-1</sup>),  $T$  is the temperature (Kelvin) and  $K$  is obtained from the ratio of the concentration of chromium(VI) in the solid and liquid phase respectively. The negative  $\Delta G^\circ$  values at all temperatures (Table 2) indicate the spontaneity of adsorption. Moreover, the values of  $\Delta G^\circ$  at different temperatures suggest that spontaneity is associated with lower temperatures. A plot of  $\ln K$  against  $1/T$  yields a straight line (Fig. 7F) and the parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept respectively. The negative enthalpy and entropy changes show that the adsorption process is exothermic with decreased randomness at the resin adsorbent-solution interface.

**Table 3**  
Effect of eluting agent on recovery of Cr(VI).

S. No	Eluent	Volume (mL)	% Elution
1	HCl (1 mol L <sup>-1</sup> ) with thiourea	5	60
2	HCl (1 mol L <sup>-1</sup> ) with 0.26 mol L <sup>-1</sup> ascorbic acid	5	99.5
3	0.1 mol L <sup>-1</sup> NaOH	10	20
4	0.1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>3</sub>	10	50
5	0.1 mol L <sup>-1</sup> NaNO <sub>3</sub>	10	53
6	Ascorbic acid (0.28 mol L <sup>-1</sup> )	10	65

### 3.2.6. Column study

After the successful optimization of optimum analytical conditions for the adsorption of chromium in batch studies, the removal of chromium from a larger volume was studied by column method. A glass column 2 cm × 3.5 cm was used for the adsorption studies. 2.0 g of the sorbent was dispersed in 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. The effect of sample volume in the column study for the adsorption of chromium (VI) on the resin was investigated in the range 100–2000 mL maintaining an overall concentration of 100 mg L<sup>-1</sup> Cr(VI). The pH of the solution adjusted to 3.5 and loaded on the column filled with the ionic liquid impregnated resin. The recovery of chromium was found to be quantitative and the column was stable up to 1500 mL sample volume resulting in a high preconcentration factor of 300. The maximum removal efficiency was attained with the flow rate of 2 mL min<sup>-1</sup> and the concentration of chromium (VI) in the aqueous phase was measured spectrophotometrically. At higher sample volumes, the swelling of the resin beads leads to the expansion of the adsorbent column, thereby affecting the quantitative adsorption beyond 1500 mL [35].

### 3.2.7. Elution of chromium from the adsorbent column

The regeneration of the column was tried various reagents and percentage of chromium eluted is shown in Table 3. The efficacy of these reagents is well illustrated in some of the earlier studies [18,46,67–69] pertaining to the extraction of chromium. The recovery of chromium was found to be maximum (99.5%) with 5 mL of a 1:1 mixture of 1 mol L<sup>-1</sup> of HCl and 0.28 mol L<sup>-1</sup> ascorbic acid as the eluent (Fig. 7G). Although sodium sulfite is a good reducing agent, the results points to the fact that ascorbic acid behaves as a better reductant in eluting the Cr(VI) to the relatively innocuous Cr(III) in solution phase. The column could be used with good precision (2.0% relative standard deviation) for 15 cycles without considerable decrease in the performance efficiency.

### 3.2.8. Recovery of chromium in a synthetic mixture containing various ions

The effects of foreign ions that are commonly present in the real effluents were investigated by preparing a synthetic mixture containing varying concentration of the metal ions. The composition of the various synthetic model effluents is shown in Table 4. After adsorption, the percentage recovery of total chromium follows the order ME1 > ME5 > ME3 > ME4 > ME2 respectively (Fig. 8). The reduction in the recovery of chromium for the samples ME2 and ME4 could be attributed to the presence of redox metal ions present in the mixture. In the presence of halides, the stability of the corresponding metal-halocomplexes could be responsible for the competing adsorption with the hydrogen chromate anion, which leads to a reduction in the recovery of chromium [35].

### 3.2.9. Validation of the method

The validation of the method was performed with tannery effluents, electroplating wastewater and BCR-715, a certified reference material. The total chromium present in the tannery (105.2 mg L<sup>-1</sup>)

**Table 4**  
Recovery of Cr(VI) in various synthetic mixtures.

Sample name	Concentration of ions (mg L <sup>-1</sup> )																Recovery of total Cr(VI) (%)	
	Fe <sup>3+</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	Mg <sup>2+</sup>	Cr <sup>6+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Cr <sup>3+</sup>	Mn <sup>2+</sup>	K <sup>+</sup>	Cu <sup>2+</sup>		Fe <sup>2+</sup>
ME1	250	250	1000	250	500	5000	100	250	500	–	–	–	–	–	–	–	–	99.9
ME2	–	–	–	–	–	–	100	500	500	500	500	1000	100	–	–	–	500	91.4
ME3	–	500	–	–	–	–	100	500	500	–	–	–	–	750	1000	500	–	98.4
ME4	–	1000	–	–	–	–	100	750	–	–	500	–	1000	1000	–	–	150	92
ME5	150	–	–	–	–	–	100	750	500	–	–	–	100	–	1000	–	–	99.8

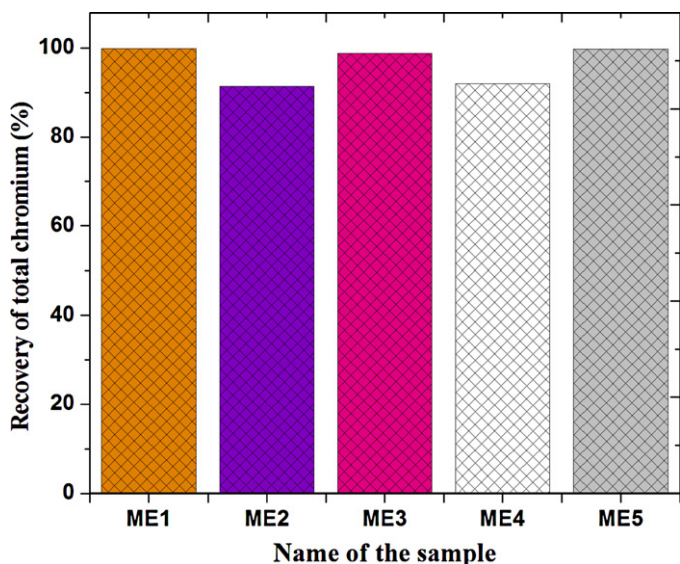


Fig. 8. Recovery of chromium with model synthetic effluents.

and electroplating waste effluent (58.8 mg L<sup>-1</sup>) sample was determined after removing the organic matter by digestion with HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub> mixture followed by alkaline peroxide oxidation [18]. Chromium was quantitatively adsorbed in the column from tannery and electroplating effluents with a recovery of 98.1 ± 0.8% and the 99.6 ± 0.1% respectively. The adsorbed chromium could be effectively desorbed using HCl–ascorbic acid mixture wherein the Cr(VI) is reduced to the relatively innocuous Cr(III). This ensures the process to be economical and ecofriendly. The concentration of chromium was estimated by the standard spectrophotometric method using diphenylcarbazide. The validity of the developed method was also checked by applying it to the extraction and analysis of chromium in a certified material BCR-715 (Industrial effluent wastewater) [18]. The total chromium content in the sample was estimated after oxidation with peroxide–sodium hydroxide mixture [18,35]. The value obtained (0.97 ± 0.07 mg L<sup>-1</sup>) by the developed method was found to be in close concurrence with the certified value (1 ± 0.09 mg L<sup>-1</sup>).

#### 4. Conclusions

In conclusion, the ultrasonic assisted impregnation of the ionic liquid on Dowex 1 × 8 resin matrix has proved to be very efficient for the detoxification of chromium. The efficiency of the process is exemplified by the fast sorption kinetics, quantitative adsorption as well as effective regeneration of the sorbent. The study of thermodynamic parameters showed that the adsorption process is exothermic and spontaneous. The adsorbent could be very well regenerated using 1 mol L<sup>-1</sup> HCl–0.28 mol L<sup>-1</sup> ascorbic acid mixture. The high adsorption capacity (230.9 mg g<sup>-1</sup>) as well as the high preconcentration factor (300) has demonstrated the utility of

the ionic liquid impregnated resin to detoxify chromium in real effluents. The validity of the method has also been illustrated in the analysis of chromium in a certified reference material (BCR-715). Overall, the ultrasound-ionic liquid combination has proved to be economical and greener.

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