



## Kinetics, equilibrium and thermodynamic study of Cr(VI) sorption into toluidine blue o-impregnated XAD-7 resin beads and its application for the treatment of wastewaters containing Cr(VI)

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### ABSTRACT

The paper presents a novel support for Cr(VI) sorption and its removal from wastewaters. The support is a new extractant-impregnated resin, EIR. Toluidine blue o as an extractant was impregnated onto/into Amberlite XAD-7 beads, and kinetics, equilibrium and thermodynamic aspects of Cr(VI) sorption were investigated. An eluent solution having concentration of 0.1 M respect to  $\text{NH}_3$  and NaCl was used for regenerating new EIR and the concentration of Cr(VI) was measured spectrophotometrically. The maximum adsorption of Cr(VI) on/in TBO-impregnated XAD-7 occurs at pH range of 3.0–4.0. The results obtained from equilibrium adsorption studies were fitted in Langmuir model of adsorption. The thermodynamic parameters of Cr(VI) adsorption onto/into EIR beads were estimated. The kinetic studies were showed that  $t_{1/2}$  was less than 5 min and equilibrium could be obtained in 50 min. The pseudo-second-order kinetics model fitted with kinetic data. It also was observed that after rapid saturation of surface and big pores, the intra-particle diffusion is the only mechanism of Cr(VI) sorption into new EIR. The performance of new EIR under flow conditions was also studied and the results indicate that columns packed with TBO-impregnated XAD-7 beads can be effectively used for treating wastewaters containing Cr(VI).

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### 1. Introduction

Heavy metals, including chromium, are widely distributed in the environment as a result of numerous industrial processes that include galvanization, steel, paints, textiles, oxidative dyeing, cooling water towers, leather tanning, corrosion inhibitors, electroplating and batteries. Such processes add heavy metals, such as chromium, to industrial wastewater, thereby posing a great hazard to humans, animals and plants through their incorporation in the food chain and the bioaccumulation effect [1–3].

Chromium can exist in the form of several oxidation states, however, from the environmental point of view only the trivalent and hexavalent forms are important [4]. Chromium(VI) can be toxic as it can diffuse as  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$  through cell membranes and oxidize biological molecules [5]. The maximum permissible levels of Cr(VI) in potable water, inland surface water and industrial wastewater are 0.05, 0.1 and 0.25  $\text{mg L}^{-1}$ , respectively [4]. Cr(VI) is ingested beyond the maximum concentration, it can cause health

disorders, such as vomiting and hemorrhage [6]. Therefore, treatment of wastewater containing Cr(VI) prior to discharge is essential.

Among the various presented methods for the treatment of wastewaters, solid phase extraction has been more developed in the last decade [7–11]. Impregnating appropriate solid supports, such as Amberlite XAD series, is one of the well-known and effective solid sorbent preparation methods for treatment purposes [12–16]. In the recent years, a variety of extractant-impregnated resins, EIRs, have been developed for their high capacity to remove toxic metal ions [17–20]. The impregnation method is free from difficulties encountered in chemically linking a chelating reagent to a support matrix. In addition, there is a wide choice of reagents for desired selectivity [21–23].

In the application of impregnated support systems in industrial scale equipment using fixed column or fluidized bed technology the knowledge of the kinetics and equilibrium of the removal extraction processes and the operating hydraulic behavior is necessary [24]. The physico-chemical characterization EIR and determination of the kinetic parameters has two objectives:

- (i) to approach, as accurately as possible, the real physical-chemistry of the metal extraction process and

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### Nomenclature

$C_0$	initial concentration of Cr(VI) in solution ( $\text{mg L}^{-1}$ )
$C_e$	liquid phase concentration of Cr(VI) at equilibrium ( $\text{mg L}^{-1}$ )
$I$	constant that gives an idea about the initial portion of Cr(VI) ions that adsorb by the surface and big pores of EIR beads
$k_f$	rate constant of pseudo-first-order adsorption model ( $\text{min}^{-1}$ )
$k_{id}$	intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$k_s$	rate constant of pseudo-second-order adsorption model ( $\text{g mg}^{-1} \text{min}$ )
$b$	constant of Langmuir isotherm ( $\text{L mg}^{-1}$ )
$m$	mass of EIR per liter of solution ( $\text{g L}^{-1}$ )
$q_e$	equilibrium Cr(VI) concentration of EIR ( $\text{mg g}^{-1}$ )
$q_{e,cal}$	calculated value of solid phase concentration of Cr(VI) at equilibrium ( $\text{mg g}^{-1}$ )
$q_{e,exp}$	experimental value of solid phase concentration of Cr(VI) at equilibrium ( $\text{mg g}^{-1}$ )
$q_{max}$	maximum adsorption capacity of EIR ( $\text{mg g}^{-1}$ )
$q_t$	amount of Cr(VI) adsorbed by EIR at time $t$ ( $\text{mg g}^{-1}$ )
$R$	universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$t$	time (min)
$T$	absolute temperature (K)
$v$	volume of the solution (L)
$\Delta G$	Gibbs free energy of adsorption ( $\text{kJ mol}^{-1}$ )

(ii) to get empirical or semiempirical equations for the design of the equipment.

In the light of the requirements for the search of a simple and effective method for removal of Cr(VI) from the wastewaters and in the following of our previously group works in the context of EIRs application on removal, separation and preconcentration of metal ions [25–28], this work has been designed to prepare a selective anion-exchange resin containing TBO via the impregnation into high surface macroporous supports of Amberlite XAD-7, a copolymer backbone for the sorption of Cr(VI) from weakly acidic solutions. The present work is aimed to study the Cr(VI) removal kinetics and equilibrium between the Cr(VI) ions present in the aqueous solution and TBO into Amberlite XAD-7. Subsequently, enabling to effective Cr(VI) removal from the wastewaters by a simple method has targeted to use a column packed with this new EIR. The experimental procedures, data collection, graphical and numerical treatments of kinetic data used in the study of extractions kinetics by EIRs are based on the procedures developed for the study of ion exchange resins as described later.

## 2. Experimental

### 2.1. Materials and chemicals

Amberlite XAD-7 (20–50 mesh, surface area:  $450 \text{ m}^2 \text{ g}^{-1}$ , pore diameter:  $90 \text{ \AA}$ ) was obtained from Fluka (Switzerland). Other chemical reagents were of analytical reagent grade and supplied by Merck (Darmstadt, Germany). Double distilled water was used for making solutions. TBO solutions were prepared by dissolving the appropriate amounts in 100 mL of methanol. Working solutions were prepared by diluting the stock solution. A solution with concentration of 0.1 M with respect to  $\text{NH}_3$  and NaCl was prepared as the eluent. Potassium dichromate was dissolved in water to pre-

pare synthetic wastewater and the pH of the solution was adjusted using  $\text{H}_2\text{SO}_4$  and NaOH.

### 2.2. Apparatus

Spectrophotometric Cr(VI) determinations with quercetin were performed by use of a Shimadzu model UV-1601PC spectrophotometer equipped with quartz cuvettes of 1 cm thickness. A Corning model 130 pH-meter was used for pH measurement. The flow of liquids through the short column was controlled with an EylaSMP-23 peristaltic pump and a 6-port valve (V-451, Upchurch). Nitrogen analysis of the prepared impregnated resin was carried out using a Gerhardt microKjeldahl apparatus. To understand the morphology difference between the XAD-7, EIR and EIR after the adsorption of Cr(VI), the samples beads were gold–palladium sputter coated by using a sputter coater instrument, Model SC 7620. Subsequently, the scanning electron microscopic (SEM) micrographs were taken by using a LEO instrument, Model 1450 VP, at an accelerating voltage of 20 kV. A Sartorius membrane filter of pore size  $0.45 \mu\text{m}$  was used for filtration of the natural water samples.

### 2.3. Preparation of the EIR

In order to remove each type of impurity, which may be found with the fabricated beads, before the impregnation, the Amberlite XAD-7 resin was treated with 1:1 methanol–water solution containing 6 M HCl for 12 h. Then, the resin was thoroughly rinsed with doubly distilled water and placed into a drying oven at  $50^\circ\text{C}$  (323 K) for 30 min. To prepare the impregnated resin, portions of Amberlite XAD-7 (1 g of dry resin) were transferred into a series of glass stoppered bottles containing 200 mL of TBO solutions with different concentrations. The mixtures were slowly shaken for 6 h to complete the impregnation process. After that, they were placed into a drying oven to remove the solvents at the ambient temperature. Each type of the resin beads was then transferred to a porous filter and washed successively with HCl and large amounts of distilled water until none amount of TBO was detected in the filtrate, spectrophotometrically. Finally, the impregnated resins were dried at  $50^\circ\text{C}$  (323 K) and weighed. The amount of TBO impregnated on/in the resin bead was determined from the amount of weight change in resin. To protect the prepared EIR from damage, it was kept in a stoppered dark glass bottle under the distilled water content.

### 2.4. Sorption experiments

The effect of pH on chromium adsorption was studied by varying the pH from 1 to 8. The concentration of Cr(VI) solution used for this study was  $40 \text{ mg L}^{-1}$  at  $298 \pm 1 \text{ K}$ . The volume of Cr(VI) solution was 100 mL. The adsorbent dosage was 0.0500 g dry weight of EIR at various impregnation ratios (g TBO/g dry XAD-7). The shaker speed was 220 rpm and time contact was about 120 min.

The sorption isotherms of Cr(VI) ions on/in the EIR were obtained using the batch technique at the pH of maximum uptake. For this purpose, aliquots of 100-mL of the solutions (pH 3.5) containing Cr(VI) with the different concentrations were placed in a series of conical flasks and 0.0500 g of the EIR was added to each of them. The mixtures were placed in a constant temperature shaker and were shaken at  $298 \pm 1 \text{ K}$  for 2 h. After that, portions of 5-mL of the supernatants were withdrawn and subjected to the determination process of Cr(VI). To obtain thermodynamic data these experiments were performed at various temperatures.

To obtain sorption kinetic data a series of fixed weighed portions (0.0500 g) of the EIRs were immersed into aliquots of 100-mL of Cr(VI) buffered solutions (pH 3.5) with concentration of 10, 20 and  $40 \text{ mg L}^{-1}$  at  $298 \pm 1 \text{ K}$ . The mixtures were stirred mechanically for a pre-determined time interval at a fixed speed (220 rpm). The

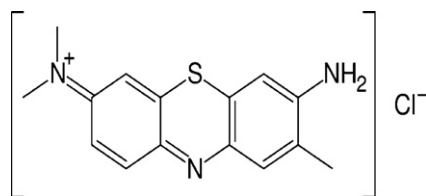


Fig. 1. Molecular structure of TBO.

EIR amount, contact time and temperature of sorption were carefully controlled. At the appointed time, each one of the mixtures was rapidly filtrated using a porous filter and the EIR was treated with 4.5 mL of the eluent solution. After that, the filtrate eluent was acidified with 0.5 mL 1 M HCl and subjected to the determination process of Cr(VI) as discussed at the following. The optimum contact period was taken as the time at which maximum Cr(VI) sorption took place.

### 2.5. Analysis of Cr(VI)

Concentration of Cr(VI) in the aqueous solution was estimated spectrophotometrically by using quercetin as described in our previous work [28].

## 3. Results and discussion

### 3.1. Preparation and characterization of the EIR

Toluidine blue o (TBO) is a heterocyclic aromatic chemical compound, a phenothiazine compound, with molecular formula of  $C_{15}H_{16}N_3S$ . At room temperature it appears as a solid, odorless, dark blue powder, which yields a blue solution when dissolved in water. It is one of the commonly known cationic dye (structure is shown in Fig. 1). It has been used as haemostatic, a biological stain, and a dye for wool and silk. TBO has also been used as a diagnostic aid for oral and gastric neoplasms and in the identification of the parathyroid gland in thyroid surgery. Adsorption of TBO on a series of organic/inorganic substances was characterized for various purposes, e.g. removal of TBO from aqueous solution [29–31], preparation of NADH sensor [32].

As pointed out above, there is no report referring to use TBO as an extractant for Cr(VI) ion removal. In the current study, TBO was impregnated into Amberlite XAD-7, which is an inert polymeric substance based on acrylic ester, hydrophobic, continuous pore phase with a weak dipole moment of 1.8. It is used for removal of organic pollutants from aqueous wastes, groundwater and vapor streams. It has been also used in the impregnation procedures for preparation of various impregnated resin employed for selective separation of certain metal ions [33,20,34,35].

To investigate the optimum pH for impregnating Amberlite XAD-7 resin beads by TBO, impregnation process was carried out at various pHs using 200-mL aliquots of solution of 0.90% (w/w) TBO with different pHs from 1 to 11. The results show (Fig. 2.) that pHs greater than 3.5 are suitable for impregnation process. Also, the required time for completing the impregnating process was studied; and experiments represented that impregnation process needed at least 4 h to complete.

To prepare the appropriate form of the EIR, the impregnation process was carried out at various impregnation ratios (g TBO/g dry polymer adsorbent). Fig. 3 depicts the weight change obtained against the TBO concentration. As it is shown, a maximum weight change (106.9%) was found at the concentrations more than 0.85% TBO, which was used for the EIR preparation.

The chemical stability of the EIR was examined by sequentially suspending a portion of 0.5-g of the EIR in different pHs and shaking

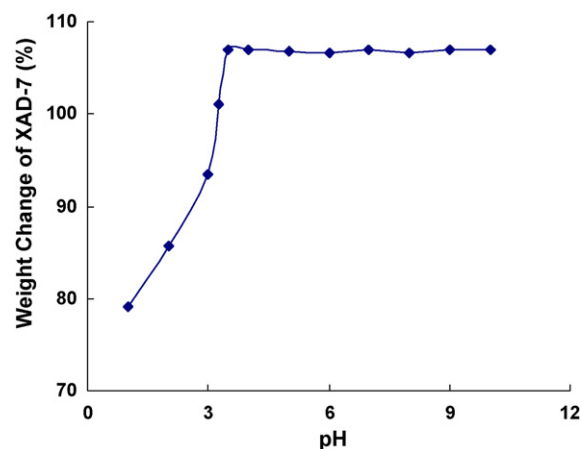


Fig. 2. Effect of pH on the impregnation process at the conditions that 200-mL aliquots of TBO solution (in different pHs) were used for impregnating 1 g of Amberlite XAD-7 beads.

for 2 h. After filtering the solution and rinsing the EIR with distilled water, the released amount of TBO in the rinsed solutions was examined by absorbance measuring at  $\lambda_{max}$  of TBO (640.4 nm). It was found that the EIR benefited from a high stability since no considerable quantity of TBO was observed in the solutions. In another experiment, the nitrogen content of 0.5 g of the EIR, used continuously for 150 runs of column sorption/desorption processes, was determined by Kjeldahl method. The result obtained was 4.91 mmol N/g dry EIR, which was in agreement with that obtained from the nitrogen analysis of 0.5 g fresh EIR (5.03 mmol N/g dry EIR). This observation confirmed reuse stability of the EIR, satisfactorily.

To observe surface morphological change of Amberlite XAD-7 resin beads following their impregnation by TBO and after loading with Cr(VI), SEM micrographs were taken. The SEM micrographs are widely used to observe the morphological features and surface characteristics of the adsorbent materials [36]. Fig. 4 shows the surface morphology of nonimpregnated XAD-7 resin, TBO/XAD-7 (EIR) and EIR after adsorption of Cr(VI).

### 3.2. Effect of pH on the sorption of Cr(VI)

Adsorption of Cr(VI), which exists in aqueous medium as  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$ , takes place through ion exchange mechanism involving positively charged amino group and negatively charged chromate or dichromate ion depending on the conditions. The

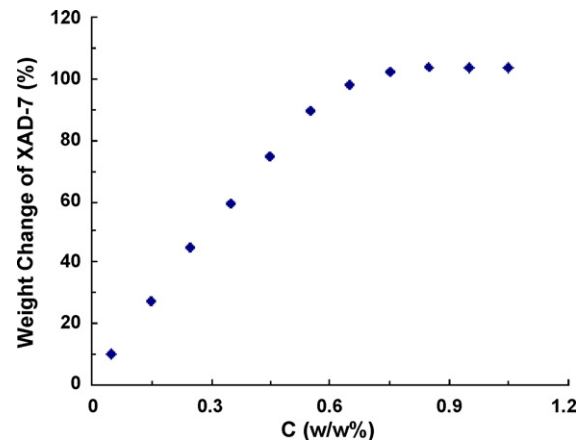
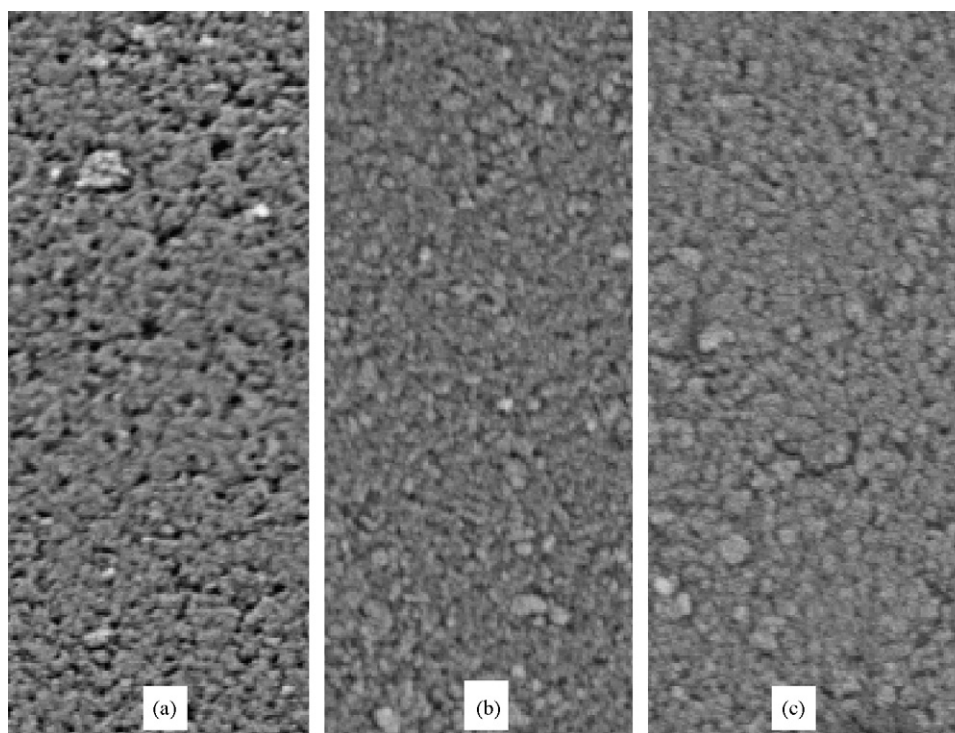
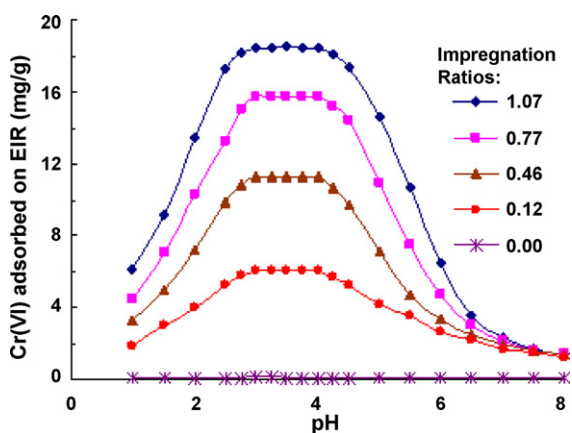


Fig. 3. Effect of TBO concentration on the EIR preparation at the condition that portions of 1 g of the dry polymer beads of Amberlite XAD-7 was subjected to the impregnation process.



**Fig. 4.** Scanning electron microscopy (SEM) micrographs of polymeric support samples (10,000 $\times$ ): nonimpregnated XAD-7 (a), TBO-impregnated XAD-7 (b) and TBO-impregnated XAD-7 after adsorbing Cr(VI) (c).

adsorption of Cr(VI) on new EIR was studied by shaking 100-ml aliquots of Cr(VI) solution with 0.05-g portions of new EIR samples (at impregnation ratios of 1.07, 0.77, 0.46, 0.12 and 0.00 g TBO/g XAD-7) at various pHs for 2 h. The amount of Cr(VI) adsorbed ( $\text{mg g}^{-1}$ ) as a function of pH is shown in Fig. 5. The results show that maximum adsorption of Cr(VI) on EIR samples occurs at pH range of 3.0–4.0 and beyond pH 8 no significant adsorption is observed. As mentioned earlier, adsorption of Cr(VI) on EIR takes place by ionic interaction therefore; at pH above 7, where EIR exists in the neutral form not much interaction occurs between Cr(VI) and TBO on the resin and hence observed adsorption is lower. Below pH 3.0, the decrease in the amount of Cr(VI) adsorbed on EIR is due to change in the form of Cr(VI) in this pH range. Below pH 2 Cr(VI) exists as  $\text{H}_2\text{CrO}_4$  and hence cannot interact with TBO on EIR through ion exchange mechanism. In addition, Fig. 5 shows that sorption capacity of nonimpregnated XAD-7 beads is very small; and the



**Fig. 5.** Effect of pH on the removal capacity of various EIR samples (EIRs with different impregnation ratio) using 100 mL of model solutions of  $40 \text{ mg L}^{-1}$  Cr(VI) containing 0.0500 g of the EIR.

various plots in Fig. 5 depict that greater impregnating ratios lead to greater amounts of Cr(VI) adsorbed on EIR samples, and the maximum sorption capacity belong to EIR sample that has the maximum impregnation ratio (1.07 g TBO/g XAD-7).

### 3.3. Equilibrium adsorption isotherms

In a two-component system consisting of sorbent and solution, a plot of the solute concentration in the solid phase,  $q_e$  ( $\text{mg g}^{-1}$ ), as function of the solute concentration in the solution,  $C_{\text{eq}}$  ( $\text{mg L}^{-1}$ ), at equilibrium gives an adsorption isotherm. In a solid liquid system, the adsorption results in the removal of solute from the solution onto/solid matrix until the remaining solute in the solution is in dynamic equilibrium with solute on the solid surface. At equilibrium there is a finite distribution of the solute between the liquid and solid phases, which can be described by many isotherms and adsorption models can be used to fit the observed experimental data and determining the model parameters. We have tried to fit our experimental data in various models.

For the purpose of investigating the best model of adsorption, the EIRs prepared at an impregnation ratio of 1.07 g TBO/g polymer adsorbent were contacted with a series of solutions containing Cr(VI) over the concentration range of 5–120  $\text{mg L}^{-1}$  at the pH of 3.5. The Langmuir isotherm given in Eq. (1) gave the best fit of the experimental data [37].

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}b} + \frac{C_e}{Q_{\text{max}}} \quad (1)$$

where  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $Q_e$  is the amount of Cr(VI) sorbed at equilibrium ( $\text{mg g}^{-1}$ ), and  $Q_{\text{max}}$  and  $b$  are the Langmuir constants related to sorption capacity and energy of sorption, respectively. The linear regression equation obtained is  $C_e/Q_e = 0.0485C_e + 0.1355$  with regression coefficient ( $r^2$ ) equal to 0.9993 (Fig. 6). Isotherm parameters of  $Q_{\text{max}}$  and  $b$  calculated from this equation are 20.6186  $\text{mg g}^{-1}$  and 0.3579  $\text{L mg}^{-1}$ , respectively.

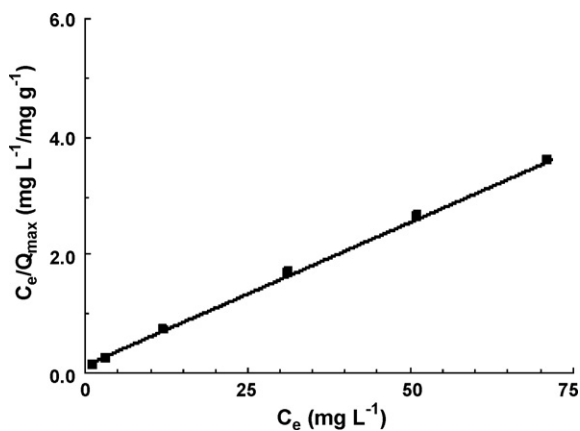


Fig. 6. Langmuir adsorption isotherm for Cr(VI) adsorption on EIR (pH 3.5 and temperature 298 K).

It should be considered that in isotherms obeying the Langmuir isotherm a dimensionless separation factor called the equilibrium parameter,  $R_L$ , has a favorable value and is calculated from equation:

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where  $R_L$  and  $C_0$  are the dimensionless separation factor and initial metal ions concentration, respectively. This equation can be used to predict if an adsorption system is favorable or unfavorable. The value of  $R_L$  indicates the shape of isotherm to be either unfavorable ( $R_L > 1$ ), or linear ( $R_L = 1$ ), or favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). This new EIR is also a favorable sorbent for Cr(VI) since the  $R_L$  value is in the range of  $0 < R_L < 1$ .

### 3.4. Sorption kinetics study

#### 3.4.1. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the rate and the amount of Cr(VI) uptake onto/into new EIR was studied using batch agitation in 250-mL beakers containing Cr(VI) solution of initial concentrations ranging from 10 to 40 mg L<sup>-1</sup>, agitated at 220 rpm and at 298 K. It is clear that the amount of Cr(VI) sorbed at equilibrium increases with an increase in initial Cr(VI) concentration (Fig. 7). The removal of Cr(VI) increased from 13.71 to 18.18 mg g<sup>-1</sup> when the initial Cr(VI) concentration is increased from 10 to 40 mg L<sup>-1</sup> at 298 K and pH 3.5. Increase in concentration

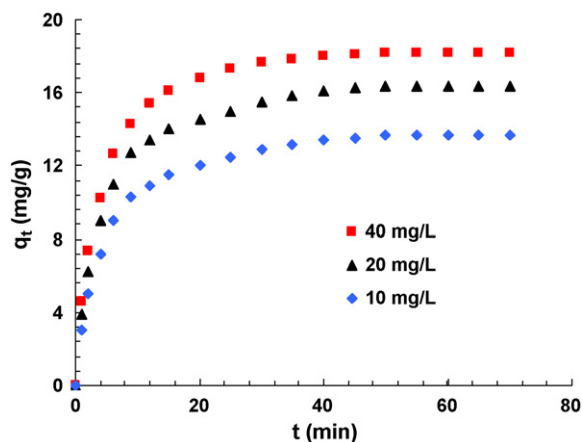


Fig. 7. Variation in the sorption capacity of EIR against time (min) at various initial concentrations of Cr(VI). pH 3.5, EIR dose: 0.50 g L<sup>-1</sup>, agitation: 220 rpm, temp.: 298 K.

up to 120 mg L<sup>-1</sup> showed that the Cr(VI) removal by EIR increases up to 20.62 mg g<sup>-1</sup> and more increase in concentration has not any impact on the amount of Cr(VI) removal. Also the plots in Fig. 7 show that the rates of reaching to equilibrium are almost the same for three different initial concentrations.

#### 3.4.2. Effect of contact time

Effect of contact time for the removal of Cr(VI) by the new EIR at  $C_0 = 10, 20$  and  $40$  mg L<sup>-1</sup> showed rapid adsorption of Cr(VI) in the first 12 min and, thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium in about 50 min as shown in Fig. 7. As illustrated in Fig. 7, the equilibrium half-time for sorption of Cr(VI) was 5 min. The relatively fast sorption of Cr(VI) ions on the EIR probably reflects high accessibility of the Cr(VI) ions to the ion exchange sites in the EIR. Increase in contact time up to 3 h showed that the Cr(VI) removal by EIR was only by about 0.1% over those obtained for 50 min contact time.

### 3.5. Kinetic modeling

Different kinetic models described below were used to describe the chromium(VI) adsorption onto/into the new EIR beads. It should be noted that a relatively high  $r^2$  value for a particular kinetic model does not necessarily mean that this model is the best. A model also cannot be used to definitely determine the mechanism of chromium(VI) adsorption [38].

#### 3.5.1. Pseudo-first-order model

When a single species is considered to adsorb on a heterogeneous surface, the adsorption of a solute from an aqueous solution may follow reversible-first-order kinetics [39,40]. The heterogeneous equilibrium between the solute in solution and the EIR may be expressed as:



where  $k_1$  and  $k_{-1}$  respectively show the forward reaction rate and the backward reaction rate constants. S and E represent solute and EIR.

The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \quad (4)$$

where  $q_t$  (mg g<sup>-1</sup>) is the amount of adsorbate, Cr(VI), adsorbed at time  $t$ ,  $q_e$  (mg g<sup>-1</sup>) the adsorption capacity in equilibrium,  $k_f$  (min<sup>-1</sup>) the rate constant for pseudo-first-order model and  $t$  (min) is the time. After definite integration by applying the initial conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the equation becomes [41]:

$$\log(q_e - q_t) = \log q_e - \frac{k_f t}{2.303} \quad (5)$$

Adsorption rate constants ( $k_f$ ) and adsorption capacity ( $q_e$ ) for the adsorption of Cr(VI) ions by EIR were calculated from the slope and intercept of the plots of  $\log(q_e - q_t)$  against  $t$  (not shown) and are reported in Table 1. The obtained  $r^2$  values indicate that the adsorption process does not obey pseudo-first-order kinetic and particularly  $q_{e,cal}$  values obtained from the intercepts are not in agreement with the  $q_{e,exp}$  values obtained experimentally.

#### 3.5.2. Pseudo-second-order model

The pseudo-second-order model can be presented in the following form:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + kt \quad (6)$$

**Table 1**  
Parameters of kinetic models for Cr(VI) sorption into TBO-impregnated XAD-7 beads at different initial concentrations.

Pseudo-first-order model				
$C_0$ (mg L <sup>-1</sup> )	$q_{e,exp}$ (mg g <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$k_f$ (min <sup>-1</sup> )	$r^2$
10	13.7103	9.5170	0.0751	0.9866
20	16.3498	12.1619	0.0774	0.9949
40	18.1797	13.1886	0.774	0.9936
Pseudo-second-order model				
$C_0$ (mg L <sup>-1</sup> )	$q_{e,exp}$ (mg g <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$K_s$ (min <sup>-1</sup> )	$r^2$
10	13.7103	14.4092	0.0160	0.9984
20	16.3498	17.4520	0.0115	0.9971
40	18.1797	20.1207	0.0095	0.9959
Intra-particle diffusion model <sup>a</sup>				
$C_0$ (mg L <sup>-1</sup> )	$k_{id}$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$I$ (mg g <sup>-1</sup> )	$r^2$	
10	1.1854	6.1733	0.9758	
20	1.6284	6.1988	0.9840	
40	2.0405	6.2129	0.9950	

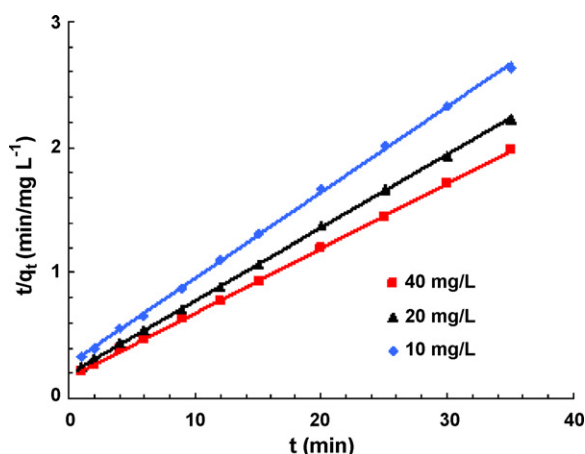
<sup>a</sup> Parameters measured for second portion of sorption (sorption into micropores).

Eq. (6) was reported by Ho to explain the sorption kinetics of divalent metal ions onto peat particles assuming chemisorption [42]. Previously, a similar expression was reported by Blanchard et al. to explain the kinetics of exchange reaction of divalent metallic ions onto NH<sub>4</sub><sup>+</sup> ions fixed zeolite particles [43]. Eq. (6) can be further linearized to:

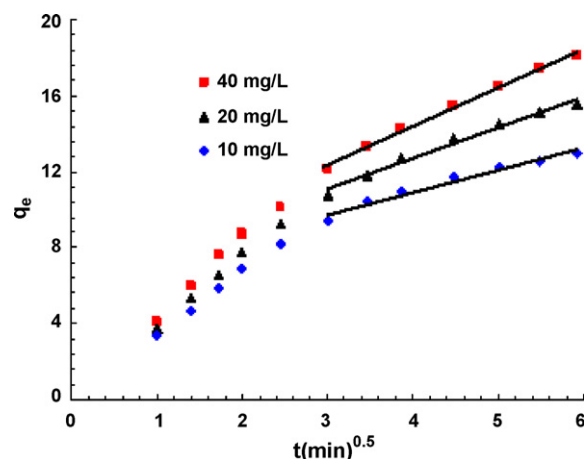
$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (7)$$

where  $q_t$  and  $q_e$  represents the amount of solute adsorbed at any time  $t$  (mg g<sup>-1</sup>),  $k$  is the rate constant of pseudo-second-order sorption (g mg<sup>-1</sup> min<sup>-1</sup>) and  $q_e$  is the amount of solute adsorbed onto adsorbent at equilibrium (mg g<sup>-1</sup>).

Fig. 8 shows that experimental data are in agreement to Eq. (7) and the pseudo-second-order kinetic parameters are reported in Table 1. The calculated adsorption capacities ( $q_e$  values) in different concentrations are in good agreement with experimental adsorption capacities ( $q_{e,exp}$  values). Also correlation coefficients of determinations,  $r^2$ , were found to be more than 0.997 for all initial concentrations.  $q_e$  increased with increasing initial Cr(VI) concentration, while the  $k$  decreased with increasing initial Cr(VI) concentration.



**Fig. 8.** Pseudo-second-order kinetic model in adsorption of Cr(VI) into EIR (pH 3.5 and temperature = 298 K).



**Fig. 9.** Intra-particle kinetic model in adsorption of Cr(VI) into new EIR (pH 3.5 and temperature = 298 K).

### 3.5.3. Intra-particle diffusion model

To confirm the possibility of Cr(VI) ions being transported within pores of EIR, the experimental data was fitted in an intra-particle diffusion plot with the amount of Cr(VI) sorbed per unit mass of sorbent against the square root of contact time [44]:

$$q_t = k_{id}t^{0.5} + I \quad (8)$$

where  $k_{id}$  is the intra-particle diffusion rate constant and values of  $I$  give an idea about the initial portion of Cr(VI) ions that adsorb by the TBO molecules impregnated on the surface of resin beads. The pore diffusion is not the rate-controlling step for adsorption of this initial portion of Cr(VI) ions. In Fig. 9, a plot of  $q_t$  versus  $t^{0.5}$  is presented for adsorption of Cr(VI) ions onto/into EIR. The straight lines are plotted for second portion of Cr(VI) ions into EIR beads. The deviation of straight lines from origin is because of the difference between the rate of mass transfer in the initial and second stages of adsorption. Furthermore, such deviation of straight lines from the origin indicates that the pore diffusion is not the sole rate-controlling step. The intra-particle diffusion parameter,  $k_i$  mg g<sup>-1</sup> min<sup>-0.5</sup>, obtained from the slope of the lines plotted for second portions of the Cr(VI) ions adsorbed into EIR (Table 1). On the other hand, the intercept of the plots reflects the amount of Cr(VI) ions adsorbed by TBO impregnated on beads surfaces and big pores in their surfaces. The values of the intercept,  $I$ , given in Table 1 are almost the same for three initial concentrations, indicating that the pore diffusion initiates after saturation of beads surfaces and their big pores. The rapid surface and big pores sorption causes the rapid fall in Cr(VI) concentration in solution and a  $t_{1/2}$  of smaller than 5 min.

### 3.6. Thermodynamics of sorption

The standard Gibbs free energy change ( $\Delta G^\circ$ ) for sorption process can be calculated using following equation:

$$\Delta G^\circ = -RT \ln K \quad (9)$$

where  $\Delta G^\circ$  and  $T$  are standard Gibbs free energy and absolute temperature, respectively.  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and  $K$  is the equilibrium constant.

At equilibrium, the binding complex formation between Cr(VI) and TBO can be expressed as the following:



where the bar denotes the species in the organic phase of the impregnated resin. Based on Eq. (10), the equilibrium constant ( $K$ )

**Table 2**  
Thermodynamic parameters for the Cr(VI) sorption on the TBO-impregnated XAD-7 beads.

Temperature (K)	$K (\times 10^4 \text{ L mol}^{-1})$	$r^2$	$\Delta H^\circ (\text{kJ mol}^{-1})$	$\Delta S^\circ (\text{kJ mol}^{-1})$	$\Delta G^\circ (\text{kJ mol}^{-1})$
283	2.9891	0.9992	12.9049	0.1313	24.2470
293	3.6006				25.5572
303	4.3240				26.8906
313	5.1544				28.2353
323	5.9000				29.5001
333	6.7797				30.7982

can be expressed as:

$$K = \frac{[\text{Cr(VI)TBO}]}{[\text{Cr(VI)}][\text{TBO}]} \quad (11)$$

where according to the definition of equilibrium constant, [Cr(VI)TBO], [Cr(VI)] and [TBO] must be molar concentrations.

One can calculate  $K$  by using the following equation [45]:

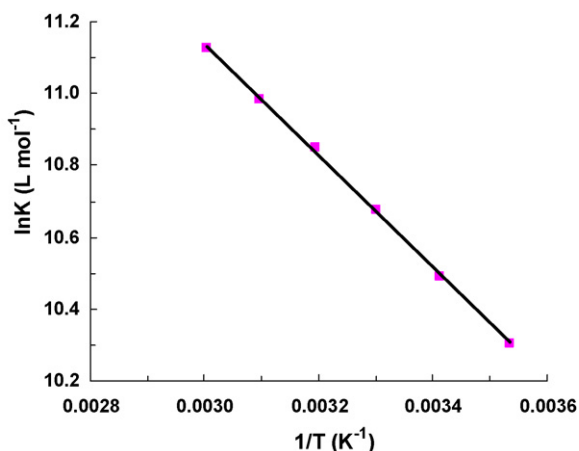
$$K = b \frac{M_{\text{Cr(VI)}} M_{\text{TBO}}}{M_{\text{Cr(VI)TBO}}} \quad (12)$$

where  $b$  is the Langmuir constant ( $\text{L g}^{-1}$ ) and  $M$  represents molar weight.

By using Eqs. (12) and (9), the values of  $K$  and  $\Delta G^\circ$  at room temperature (298 K; 25 °C) for the sorption of Cr(VI) were found to be  $3.9584 \times 10^4 \text{ L mol}^{-1}$  and  $-26.228 \text{ kJ mol}^{-1}$ , respectively, which negative value of  $\Delta G^\circ$  confirms the feasibility and spontaneous nature of the sorption process at 298 K with a high degree of affinity of the Cr(VI) ions for EIR support. The effect of temperature on the equilibrium constant,  $K$ , was studied in the range of 283–333 K (10–60 °C) at optimum conditions. The values of  $\Delta G^\circ$  for the sorption of Cr(VI) at different temperatures were calculated and reported in Table 2. The observed increase in negative values of  $\Delta G^\circ$  with increasing temperature implies that the sorption becomes more favorable at higher temperature.  $\ln K$  was plotted against  $1/T$  ( $T$  in K). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were estimated using the following relationships:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (13)$$

From the slope and intercept of the plot (Fig. 10) the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were estimated and reported in Table 2. The positive values of  $\Delta H^\circ$  indicate the endothermic nature of adsorption process whereas the positive values of  $\Delta S^\circ$  suggest the high degree of freedom of adsorption system at equilibrium due to the interaction between active sites and Cr(VI) ion. The ion exchange of Cr(VI) by the active sites of extractant molecules on the EIR results in the release of one  $\text{Cl}^-$  ion for each Cr(VI) ion.



**Fig. 10.** Effect of temperature on the equilibrium constant.

The data given in Table 2 also showed an increase in the values of  $T\Delta S^\circ$  with increasing temperature and  $|\Delta H^\circ| < |T\Delta S^\circ|$ . This indicates that the sorption process is dominated by entropic rather than enthalpic changes [46].

### 3.7. Column experiments

#### 3.7.1. Performance of EIR under flow conditions

In order to evaluate the performance of EIR under dynamic conditions, adsorption studies were carried using column. For this 6 g of EIR was allowed to swell in water for few hours and the swollen mass was filled in cylindrical glass column of internal diameter 8 mm and height 97 mm. Aqueous solution of  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  was passed through the column to convert TBO into protonated form. The column was washed with water until the effluent was free from  $\text{H}_2\text{SO}_4$ . A solution of potassium dichromate (1 L), having concentration in the range of 20–75  $\text{mg L}^{-1}$ , was passed through the column and effluents were collected. The concentration of Cr(VI) in the effluent after passing through the column against the concentration of Cr(VI) in the feed solution is shown in Table 3. The US Environmental Protection agency (EPA) has allowed maximum permissible discharge limit for Cr(VI) in the industrial effluent as  $0.25 \text{ mg L}^{-1}$ . As can be seen from Table 3, the concentration of Cr(VI) is in the range prescribed by (EPA) for industrial discharge. At higher feed concentration,  $>45 \text{ mg L}^{-1}$ , somewhat high effluent concentration was observed that can be easily overcome by longer column or using multiple columns.

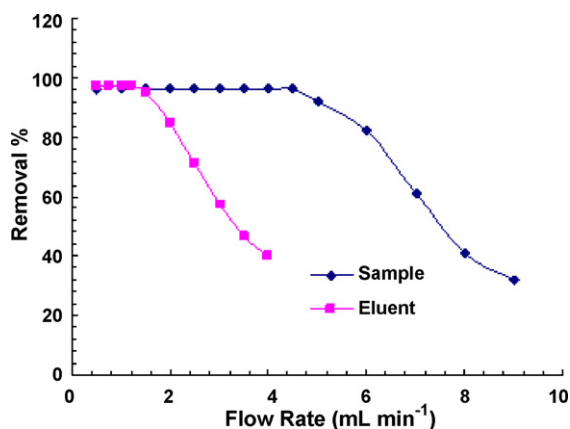
The results show that new EIR is an excellent substrate for treating wastewater containing Cr(VI). Regeneration of column containing EIR loaded with Cr(VI) for reuse is an important feature for using it for industrial applications. Therefore the column loaded with 1 L solution of Cr(VI) was eluted using 10 mL of eluent solution, 0.1 M respect to  $\text{NH}_3$  and NaCl, thus the concentration of Cr(VI) after elution increased by 100 times. The recovered Cr(VI) can be reused thus bringing down the cost of treatment.

#### 3.7.2. Sample and eluent flow rates

The sample and eluent flow rates are important parameters to obtain efficient retention and elution, respectively. The influences of the sample and eluent flow rates on the removal of Cr(VI) ions were separately examined in the flow rates range of 1–9 and 0.5–4  $\text{mL min}^{-1}$ , respectively. A solution of potassium dichromate (1 L), having concentration of  $75 \text{ mg L}^{-1}$ , was passed through the column and in the following the column was eluted with the above

**Table 3**  
Results on column-mod removal of Cr(VI) from aqueous solution by TBO-impregnated XAD-7 beads at different initial concentrations.

S. no	Cr(VI) in feed solution ( $\text{mg L}^{-1}$ )	Cr(VI) in the effluent ( $\text{mg L}^{-1}$ )	Removal (%)
1	75	2.93	96.09
2	65	1.08	98.34
3	55	0.43	99.22
4	45	0.19	99.58
5	35	0.12	99.66
6	25	0.07	99.72



**Fig. 11.** Effect of sample and eluent flow rates on the recovery of Cr(VI) using 1 L of model solution of  $75 \text{ mg g}^{-1}$  Cr(VI) and 10 mL eluent solution of 0.1 M respect to  $\text{NH}_3$  and NaCl.

flow rates. When the influences of flow rates of sample examined, the eluent flow rate was kept constant as  $0.5 \text{ mL min}^{-1}$  and also the flow rate of sample was kept as  $2 \text{ mL min}^{-1}$ , when the effects of flow rates of the eluent. As shown in Fig. 11, the removal percent of Cr(VI) was almost unchanged up to the sample flow rate of  $4.5 \text{ mL min}^{-1}$  and the desorption could be carried out, properly, at the flow rate of  $0.5\text{--}1 \text{ mL min}^{-1}$ .

### 3.7.3. Reuse of the EIR

The stability and regeneration potential of the EIR was also examined. After eluting out the loaded Cr(VI), the column can be regenerated by first washing the column with water till it is free of  $\text{OH}^-$  followed by passing 1 M  $\text{H}_2\text{SO}_4$ . This is important from the point of view of overall economy of the process for treating the wastewater containing Cr(VI) using TBO-impregnated XAD-7 beads. The column can be reused after regenerated with 10 mL distilled water followed by passing 5 mL of 1 M  $\text{H}_2\text{SO}_4$  solution. Column capacity is stable up to 100 runs without appreciable loss of ion exchange sites. The impregnated resin could be stored for at least 6 months and used repeatedly without any appreciable amount of reagent being lost.

## 4. Conclusions

TBO-impregnated XAD-7 beads are very effective in adsorbing Cr(VI) from aqueous medium. On the basis of the studies carried out, the following conclusions can be drawn:

- (i) TBO-impregnated XAD-7 beads have been successfully used for removal of Cr(VI) from aqueous solutions.
- (ii) Time of equilibrium was found to be smaller than 50 min.
- (iii)  $\Delta G$  has been calculated in ambient temperature and indicates that the process of the removal is governed by pseudo-second-order rate kinetics and intra-particle diffusion is the rate-controlling step after rapid saturation of surface and big pores of EIR beads.
- (iv) Maximum removal is obtained at pH 3.5 at 298 K.
- (v) The removal process can be done with a column packed with new EIR.
- (vi) The column-mode removal has a good speed.
- (vii) The new EIR can be easily regenerated and efficiently reused for several times.

The newly impregnated resin exhibited a good capacity to remove Cr(VI) ions as an ion exchange support. This EIR seems promising for rapid and effective removal of Cr(VI) ions as appar-

ent from the column studies. Simple EIR preparation, high capacity, and cost effective removal of Cr(IV) are advantages of the new EIR. The prepared EIR can be successfully regenerated for many cycles of operation in the column. Finally, the data obtained can be successfully used for designing treatment plants for the treatment of Cr(VI) rich water and wastewaters.

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