Chemical Engineering Journal 114 (2005) 105–113

Chemical Engineering Journal

www.elsevier.com/locate/cej

Removal of some chelators from aqueous solutions using polymeric ingredients

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Received 11 March 2005; received in revised form 9 September 2005; accepted 9 September 2005

Abstract

This work tries to throw a light on the removal of thenoyl trifluoroacetone (TTA) and ethylene diamine tetraacetic acid (EDTA) extractants that extensively used in many nuclear facilities. Using Amberlite XAD resins, equilibrium studies were performed to identify the adsorption of these chelatos from aqueous solutions under various experimental conditions. The applied resins exhibit high retention ability for the studied chelators with a maximum adsorption capacity of 23.9 and 38.0 mg g^{-1} for sorption of TTA and EDTA on Amberlite XAD4 and 18.6 and 21.2 mg g^{-1} for their adsorption on Amberlite XAD7. Factors affecting the resin retention ability, such as pH value of aqueous solution and presence of cosolvent have been studied. The kinetics of adsorption behavior, in the applied system, indicate the process to be controlled by more than one diffusion mechanism. Therefore, two diffusion models were utilized to understand and verify the mechanism of adsorption processes; they are the film mass transfer model and the intraparticle diffusion model. The first model, based on film resistance, gave a successful depiction for adsorption of TTA onto Amberlite XAD4 and XAD7. The second one displayed an acceptable prediction for sorption of EDTA onto Amberlite XAD4.

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Keywords: TTA; EDTA; Removal; Amberlite XAD; Diffusion model

1. Introduction

Application of nuclear technology in many fields have undoubtedly accompanied by generation of large quantities of radioactive aqueous wastes. These wastes contain significant amounts of organic materials notably complexants, such as thenoyl trifluoroacetone (TTA) and ethylene diamine tetraacetic acid (EDTA) that extensively used in reprocessing and decontamination processes [1–4]. Safe and effective disposal of radioactive waste containing such organic ingredients are difficult tasks because these chelators form water-soluble complexes with most radionuclides. Environmentally, this complexation enhances the migration of disposed radionuclides in geosphere due to the formation of less adhered water-soluble compounds [5]. Also, certain chelators, in radioactive environment, degrade rapidly creating an organic mixture of unaffected chelators' components along with an array of chelator-related fragments. This degradation changes the speciation of disposed radionuclides causing a variation in their leachability and so depresses the ability of any predictive transport model to intensively predict the retention, transport and fate of these radionuclides. In addition, Chang and Ku asserted that presence of complexing agents inhibits the removal of metal species in treatment of a variety of industrial waste waters [6].

Increasing safety demands and environment quality assurance have prompted development of treatment technologies for the removal of organic solutes, especially chelators, from aqueous waste solutions. Sorption is one of several trends that have been successfully employed to attain this approach [7]. A number of processes, including adsorption on Amberlite XAD resins [8], polyurethane foam [9], activated carbon [10–12], silicate minerals [13] and titanium dioxide [14] offers an efficient removal and produces high quality treated effluents. In addition, metal oxides, such as MnO_2 are used as oxidative substrate in the degradative removal of organic ingredients from aqueous solution through surface redox reactions with the organic ingredient [15].

In aqueous solutions, the kinetics of organic solute adsorption by porous solid adsorbent are concerned with the force field between solute molecules and active sites in adsorbent surface. The mass transfer associated with such processes occurs via three consecutive steps of bulk, film and intraparticle transport

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doi:10.1016/j.cej.2005.09.015

and the predominant rate of adsorption is determined by one or more of these steps. In batch systems, the adsorption involves a sequential progression through four steps: diffusion through bulk liquid, film diffusion, intraparticle diffusion and adsorption on the solid surface. Generally, the bulk liquid diffusion and adsorption steps are rapid and thus not rate-limiting step [16]. Systems with low solute concentration are more likely to have their mass transfer controlled by film diffusion where the film mass transfer coefficient is directly proportional to linear concentration gradient across the film. Intraparticle diffusion is the likely predominant mechanism in systems with high initial solute concentration. In some systems, the two diffusion mechanisms occur in parallel and the slower of the two is the rate controlling one [17]. These diffusions depend on the solute concentration as well as the involved reaction, such as acid dissociation, neutralization and/or complex formation. Snukiskis and Kauspediene clarified that these reactions can affect the sorption kinetics as they affect the equilibria [18].

The purpose of this study is to identify the adsorption of TTA and EDTA from aqueous solutions using Amberlite XAD4 and XAD7 resins under different experimental conditions to assess its affinity towards the studied chelators. Specific objectives included: (a) determining the adsorption rate constant, (b) specifying the mass transfer processes and evaluating film mass transfer and intraparticle diffusion coefficients and (c) describing the chelators adsorption and desorption behaviors in packed column system to confirm the quantitative efficiency of Amberlite resins to be used as an adsorbent for removal of such organic chelators from aqueous media.

2. Experimental

2.1. Materials

Amberlite XAD resins were obtained from Fluka with 725 and 450 $m^2\,g^{-1}$ surface area for XAD4 and XAD7, respectively and 20–60 mesh size. They were equilibrated with a mixture of 50% acetone/water to eliminate the inorganic impurities and the monomeric species. After equilibrium, resins were filtered, dried at 40 °C for 24 h and then kept in a desiccator for further usage. TTA and EDTA were obtained from Merck in an analytical grade form. Stock aqueous solutions, of these chelators (solutes), were prepared by percolating a certain weight of each compound with the desired water volume in presence of appreciate polar organic solvent. The equilibrium concentrations of TTA and EDTA were determined spectrophotometrically by measuring their maximum absorbance at the characteristics wave lengths using double beam UV spectrophotometer of Shimadzu, UV-160 A type, Japan with 1 cm light-path cell. In accordance with Lambert–Beer's law, a calibration curve for each solute was constructed covering a concentration range within the spectrophotometric detection limits. The absorbance of TTA was measured at $\lambda = 320$ nm while the concentration of EDTA was determined using the procedures described elsewhere [19].

2.2. Methods

2.2.1. Batch experiments

Adsorption studies were performed by shaking, in tightly closed glass bottles, a certain weight of XAD resins with 10 mL aqueous solution of organic solutes having initial concentration amounted to 50 and 700 $mg\,L^{-1}$ for TTA and EDTA, respectively. At the end of each predetermined time period, shaking was stopped, samples were centrifuged and supernatants were separated and subjected to spectrophotometric measurements. In clarifying their cosolvent effect, volumes in the range 1–10 mL of ethyl alcohol or chloroform were added to a set of mother chelators aqueous solutions and equilibrated with XAD resins. After equilibrium, samples were centrifuged and aliquots were subjected to spectrophotometric analysis. The adsorbed amount (q) of organic solute, at equilibrium, was calculated using the following formula:

$$q = (C_0 - C_e)V/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of the organic solute ($mg\,L^{-1}$), V the aqueous phase volume (L) and W is the weight of applied resin (g).

2.2.2. Column experiment

A glass column has an inner diameter of 1.5 and 3 cm height was packed with a weighted amount of Amberlite XAD4 and treated with bi-distilled water. Aqueous solution of TTA has 60 $mg\,L^{-1}$ initial concentration and pH ∼ 2 was pumped upward and the feed rate was maintained at 0.5 mL/min using peristaltic pump. The break through percentage was calculated using the formula:

$$\text{break through}\,(\%) = (C_f/C_0) \times 100 \tag{2}$$

where C_0 is the initial concentration of TTA in feed solution ($mg\,L^{-1}$) and C_f is the final concentration of TTA in effluent after passing through the column ($mg\,L^{-1}$). The column adsorption capacity (q_c) was determined by applying the following equation:

$$q_c = (V_{50} \times C_0)/W \tag{3}$$

where V_{50} is the effluent volume (mL) corresponding to 50% break through and W is the weight of XAD4 resin in grams. Elution experiment was performed using 10% ethyl alcohol as an eluant for TTA loaded on XAD4. The volume of eluant was collected at a flow rate of 1 $mL\,min^{-1}$ and the elution percentage (E%) was determined as:

$$E\% = (C_E/C_L) \times 100 \tag{4}$$

where C_e and C_L are the concentrations of TTA ($mg\,L^{-1}$) in collected eluant and that loaded on XAD4 resin, respectively.

3. Results and discussion

3.1. Adsorption studies

All adsorption experiments were performed, as described above, at room temperature under different experimental conditions to assess the main factors controlling the adsorption of TTA and EDTA, in addition to Co-EDTA, on Amberlite XAD4 and XAD7 resins. The influence of factors considered to play a significant role on adsorption process is discussed below.

3.1.1. Equilibrium time

Adsorption of TTA and EDTA from aqueous solution at different time intervals using Amberlite XAD4 and XAD7 resins is illustrated in Fig. 1. The plots imply that the uptake percentages increase with elapsed time till reaching equilibrium after about 3 h of contact. The uptake of TTA and EDTA onto Amberlite XAD4 attained the values of 94 and 32%, respectively while these values was decreased to 82 and 10% for their sorption onto Amberlite XAD7. Also, the plots show that Co–EDTA complex is weakly adsorbed where only 16% uptake was achieved for sorption onto Amberlite XAD4. The high adsorbability of Amberlite XAD4 comparing to Amberlite XAD7 may be referred to the surface properties of XAD4 that has a surface area of 725 $m^2 g^{-1}$ relative to 450 $m^2 g^{-1}$ for XAD7.

Based on the former batch equilibrium data, the maximum adsorption capacity of Amberlite resins, for the investigated organic chelators, was determined at room temperature and values are given in Table 1. The results exhibit a high sorption capacity of Amberlite XAD4 for the studied organic chelators asserting a high affinity for the quantitative removal of these chelators from aqueous solutions.

Table 1
The maximum sorption capacity of Amberlite XAD resins for the investigated organic chelators

Species	Sorption capacity ($mg g^{-1}$)	
	XAD4	XAD7
TTA	23.9	18.6
EDTA	38.0	21.2
Co–EDTA	43.1	–

3.1.2. pH effect

Equilibrium adsorption of TTA and EDTA onto XAD4 and XAD7 from aqueous solution of various pH values is displayed in Figs. 2 and 3. The figures show that adsorption of TTA and EDTA increases with decreasing pH values upto ∼3. This behavior can be explained on the basis of acid–base dissociation interactions. At low pH values, chelators molecules are highly retended electrostatically to the oppositely charged sites on the protonated resin surface. Subsequently, coordination interactions at resin–solution interface may participate in promoting the extent of their adsorption.

Turning the working solution to alkaline range, the investigated chelators dissociate to an array of negatively charged fragments where they have the ionization constants 1.5 and 2.0 for CO_2H and 6.16 and 10.24 for NH of EDTA, respectively and 6.18 for TTA [20,21]. Also, the resin surface being negatively charged and assumed to exhibit a lower affinity towards the species having same charge. Electrostatically and due to the

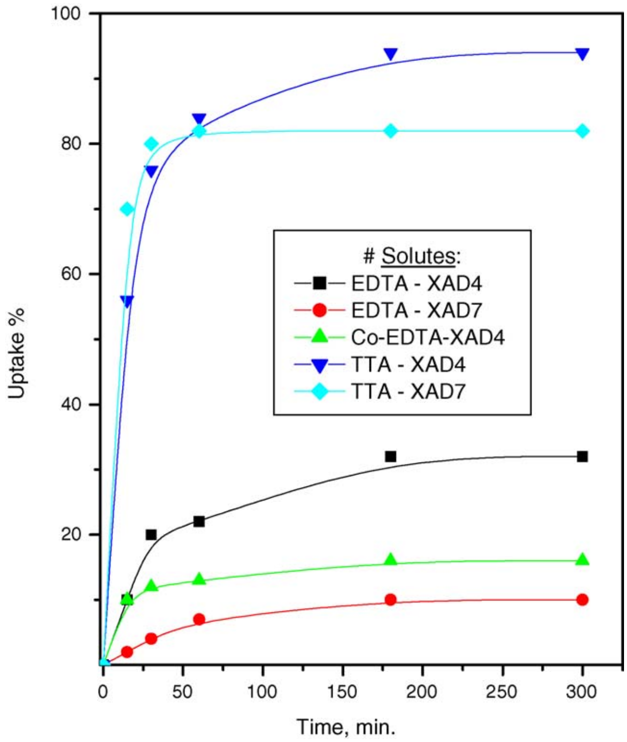

Fig. 1. Effect of contact time on adsorption of some chelators onto Amberlite resins (V/m = 100, pH 2).

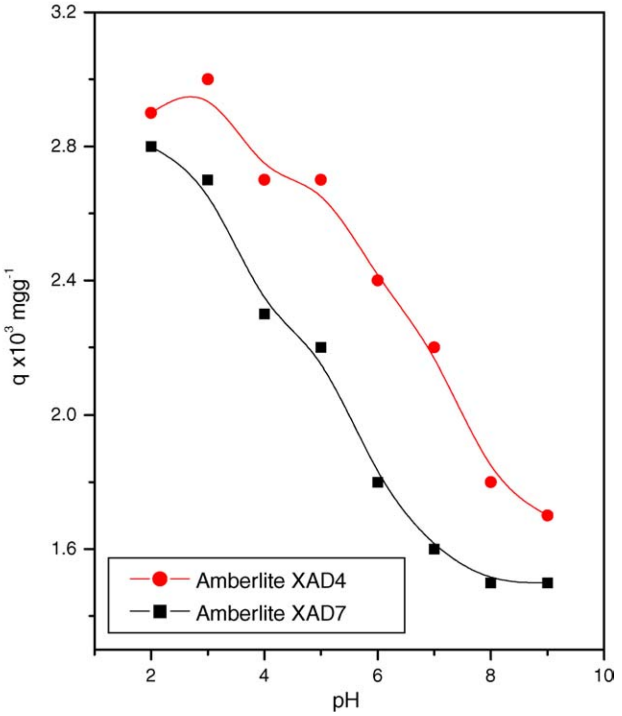

Fig. 2. Adsorption of TTA from aqueous solution of different pH values onto Amberlite resins.

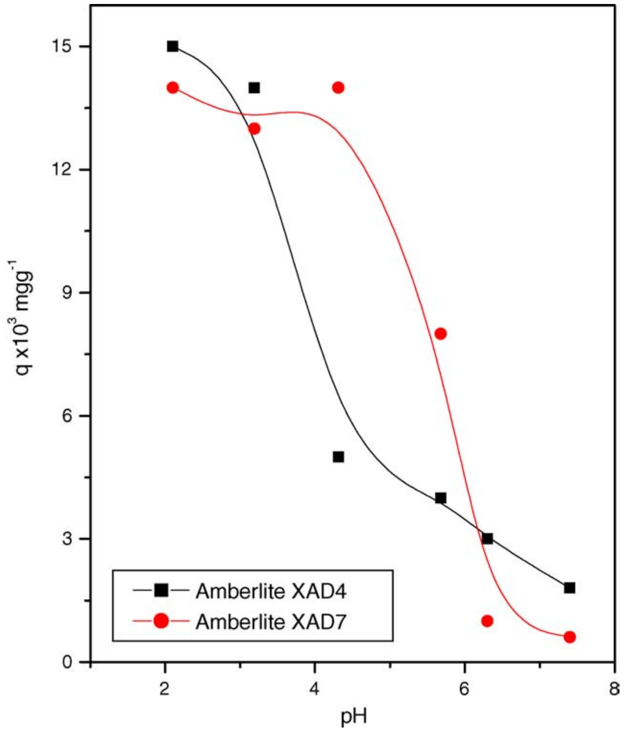

Fig. 3. Adsorption of EDTA from aqueous solution of different pH values onto Amberlite resins.

repulsion force predominating between resin active sites and chelator ions of same charge, the adsorption extent falls sharply with rising pH value.

3.1.3. Cosolvent effect

The change in adsorption of TTA onto Amberlite XAD4 and XAD7 in presence of different volumes of ethyl alcohol or chloroform as cosolvents is depicted in Figs. 4 and 5. The revealed data specify a slight decrease in adsorbed amount with increasing the amount of ethyl alcohol while presence of chloroform has no apparent effect on the extent of sorption.

The tendency of organic solute to be solid-adsorbed might be changed by coexistence of organic cosolvents due to their effect on the aqueous solubility and the solid–liquid partition coefficient of organic solutes. The presence of codissolved organic molecules may influence the hydration shells surrounding the solute of interest changing the energetic cost of forming such shells and the overall dissolution cost decreased [22]. The increase in organic solute solvation maintains it in solution and so lowers its solid–liquid partition coefficient relative to that in absence of cosolvent. The slight decrease in adsorbability of the studied chelators with presence of ethyl alcohol may be implied to the low abundance (molar volume ratio) of ethyl alcohol. This low abundance allow the cosolvent molecules themselves to be hydrated and so play much less influential role of a cosolvent on the aqueous solubility of the solutes of interest [23]. The constant adsorbability depicted with presence of chloroform, as cosolvent, may be ascribed to its aqueous solubility where it is a water insoluble solvent and so has no effect on the solid-partition coefficient.

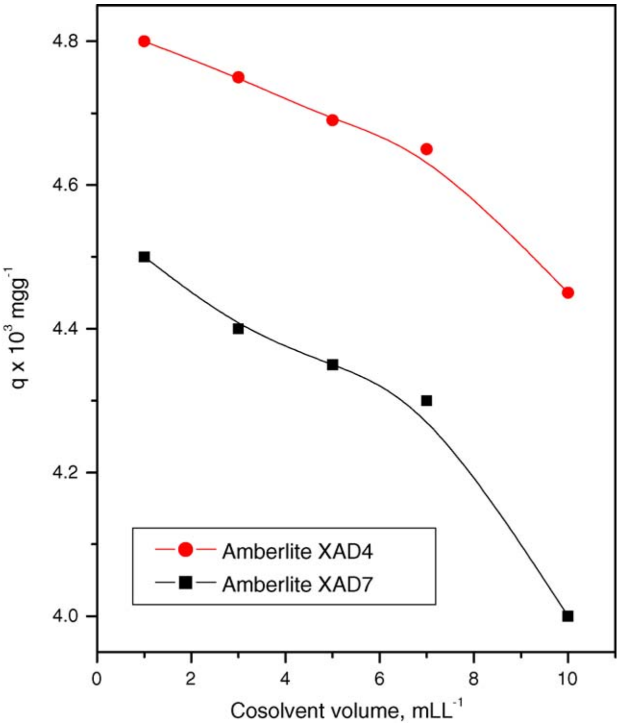

Fig. 4. Effect of ethyl alcohol, as cosolvent, on adsorption of TTA from aqueous solution onto Amberlite resins (V/m = 100, pH 2).

3.2. Adsorption rate

Batch adsorption experiments were carried out to verify the rate of TTA and EDTA adsorption onto Amberlite resins and

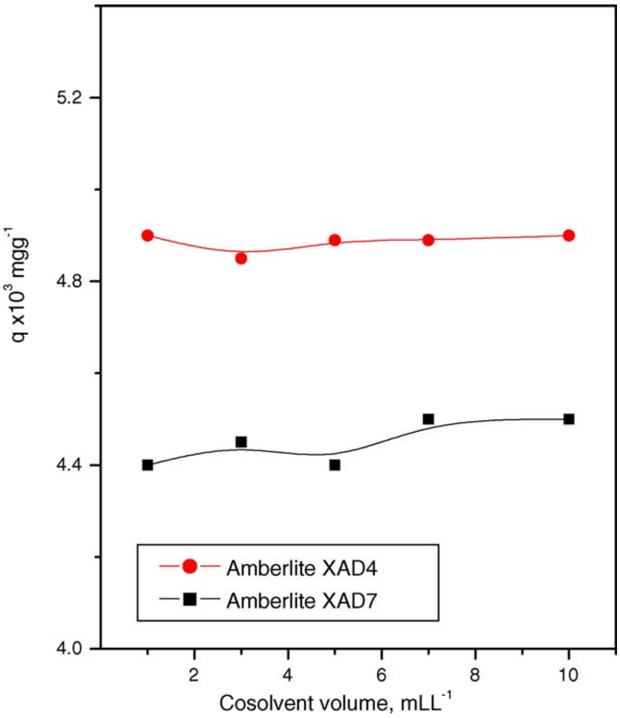

Fig. 5. Effect of chloroform, as cosolvent, on adsorption of TTA from aqueous solution on Amberlite XAD resins (V/m = 100, pH 2).

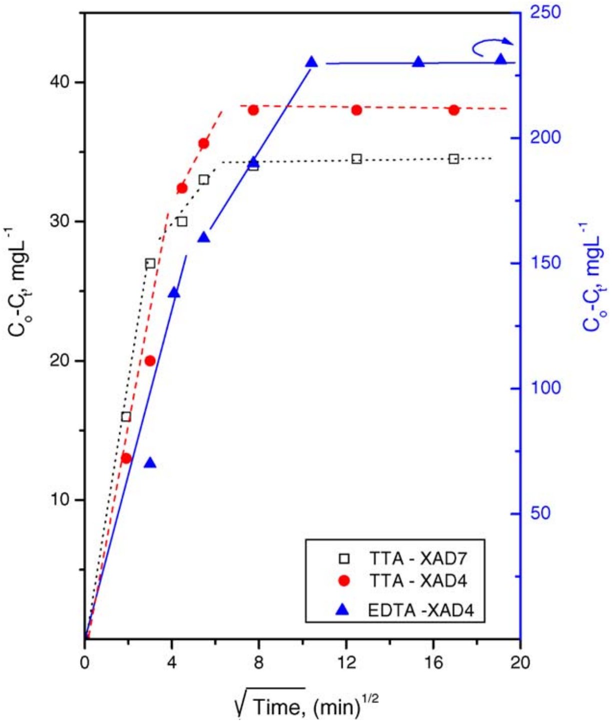

Fig. 6. The change in rate of the studies chelators adsorption onto Amberlite resins.

data obtained were plotted as a function of the square root of contact time and represented in Fig. 6. The results reveal that the initial adsorption step is very high where more than 90% of the starting concentrations are already adsorbed within 30 min and imply three distinguishable sorption stages.

From a diffusion point of view, this multistage adsorption process reflects that the rate of adsorption is not purely controlled by a certain one diffusion mechanism where the linear relationship between the amount of adsorbed chelators and the square root of contact time, that depicted at the initial stage of adsorption process, is indicative to the possible contribution of intraparticle diffusion in the rate controlling step [24,25]. The breaks comprised in the represented curves emphasize the sharing of a later diffusion mechanism in the rate controlling step too. Under such circumstances of presence of multidiffusion mechanisms, additional experiments were performed to characterize the rate controlling step. This characterization was done by studying the role of solute initial concentration on the rate of adsorption and date are given in Figs. 7 and 8. The curves in the two figures represent a concentration–time profile for adsorption of TTA on Amberlite XAD4 and XAD7 resins. They indicate that the adsorbed fraction obviously increases with increasing the chelator initial concentration. From these plots, the relative adsorption rate constants (K_{arc}) were graphically determined and the values are listed in Table 2. The tabulated values show a linear relationship with very good correlation coefficient (R^2) between K_{arc} and the applied initial concentration. This verified linear proportionality can be considered as an indication that film diffusion, i.e. transport of TTA molecules from bulk solution to the outer surface of resin particles by molecular diffusion, is the prevalent diffusion mechanism under the applied experimental conditions and the working concentration range [26,27].

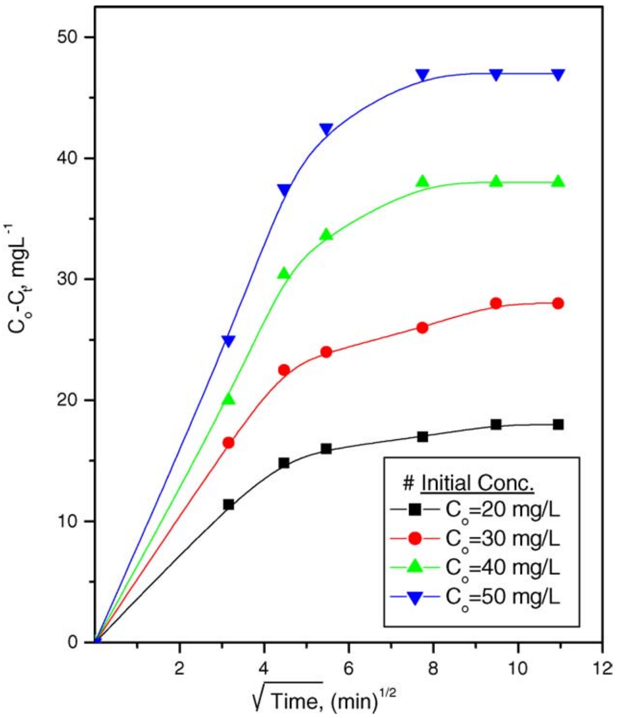

Fig. 7. The variation in rate of TTA adsorption onto XAD4 with its initial concentrations (V/m = 100, pH 2).

The diffusion mechanism predicted to prevail the adsorption of EDTA onto Amberlite XAD4 is tested by construction a graphical relationship between the adsorbed fraction and the

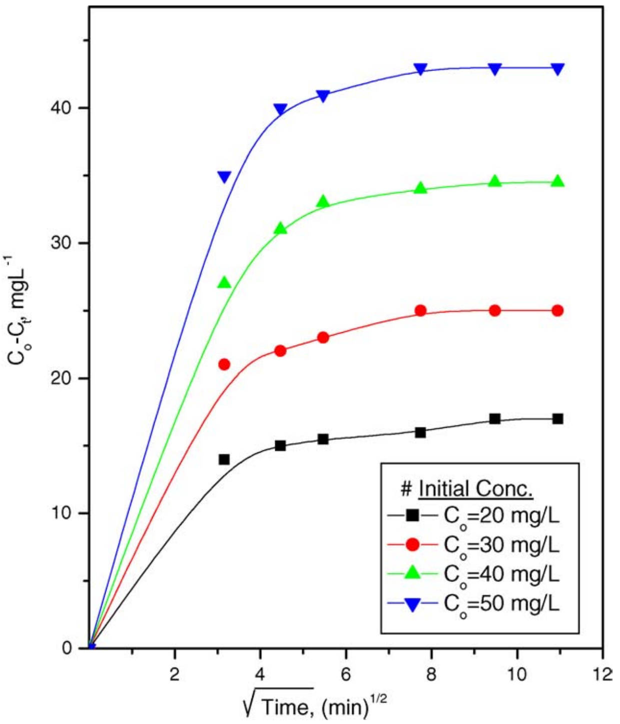

Fig. 8. The variation in rate of TTA adsorption onto XAD7 with its initial concentrations (V/m = 100, pH 2).

Table 2
The relative adsorption rate constants (K_{arc}) and the correlation coefficients (R^2) for TTA adsorption onto Amberlite resins

Co (mg L^{-1})	K_{arc} (mg g^{-1} min$^{-0.5}$)	
	XAD4	XAD7
20	3.03	2.82
30	4.57	4.43
40	6.34	6.30
50	7.96	7.83
R^2	0.996	0.993

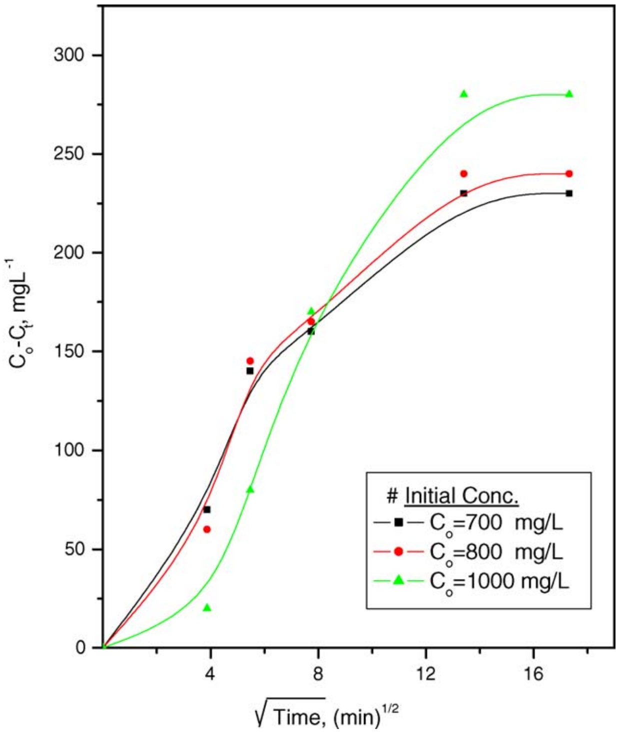

Fig. 9. The variation in rate of EDTA adsorption onto XAD4 with its initial concentrations (V/m = 100, pH 2).

square root of contact time, Fig. 9. The figure shows irregular double nature plots and exhibits a linear increase in EDTA adsorbed amount with the square root of contact time, at the earlier stage of adsorption. This linearity indicates that intraparticle diffusion is a likely occurring rate-determining step, under the applied conditions [28–30]. From these plots, the values of K_{arc} corresponding to different EDTA initial concentrations were determined and given in Table 3.

Closer inspection to the former data, one can observe that K_{arc} is independent on EDTA initial concentrations where it has no certain trend with the applied range of concentration and this can be considered as a deduction for intraparticle diffusion controlled system. This behavior is coincident with the reported by other investigators wherever intraparticle diffusion is expected to be the rate-determining step in stirred systems that have a high adsorbate concentration and high affinity of adsorbate for adsorbent [29,17,27].

Table 3
The relative adsorption rate constant (K_{arc}) for adsorption of EDTA onto Amberlite XAD4 resin

Co (mg L^{-1})	K_{arc} (mg g^{-1} min$^{-0.5}$)
700	21.81
800	19.00
1000	20.43

3.3. Adsorption dynamics

The resistance to mass transfer in film diffusion controlled system can be described using the model developed by McKay et al. [31]. They reported that the rate of concentration variation is related to the film mass transfer by the equation:

$$\frac{\partial C_t}{\partial t} = -\beta S_s (C_t - C_s) \tag{5}$$

where C_t is the concentration of TTA at time t (mg L^{-1}), C_S the concentration in solution at outer surface of Amberlite resin (mg g^{-1}), β the mass transfer coefficient (cm s^{-1}), and S_S is the outer surface of Amberlite resin per unit volume (cm^{-1}). Assuming smooth spherical particles, the surface area for mass transfer S_S can be obtained from the equations:

$$S_s = \frac{6m}{d_r \rho_r (1 - \varepsilon_r)} \tag{6}$$

and

$$m = \frac{W}{V} \tag{7}$$

where d_r is the diameter of resin particles (μm), ρ_r the resin density (g cm^{-3}), ε_r the resin porosity (cm cm^{-1}), m the resin mass per unit volume (mg L^{-1}), W the resin weight (g), and V is the volume of aqueous solution (L). Since C_t approaches C_0 and C_S goes to zero at $t = 0$, substitution of Eqs. (6) and (7) into Eq. (5) and taking the limit $t \rightarrow 0$ yields:

$$\beta = \frac{V}{S_s} \left[\partial \left(\frac{C_t/C_0}{\partial t} \right) \right]_{t=0} \tag{8}$$

The value of β in Eq. (8) can be determined from plotting the term C_t/C_0 versus time. The change film diffusion coefficient (β) with the initial concentration of TTA for adsorption onto Amberlite XAD resins is depicted in Figs. 10 and 11. It was found out that, the adsorbed fraction of TTA is low at high initial concentrations and the initial stage of adsorption is rapid at low initial concentrations. From these plots, the values of β corresponding to the different initial concentrations were determined and listed in Table 4. The revealed values decrease with increasing TTA initial concentration promoting an indirect dependence that may be referred to the driving force for mass transfer from bulk solution to adsorbent surface. Such driving force is based on the difference between the chelator concentrations in bulk solution and at resin surface. This concentration difference, relative to C_0, decreases as the chelator initial concentration increases. Thus, film mass transfer coefficient (β) for adsorption of TTA onto Amberlite resins increases as C_0 decrease.

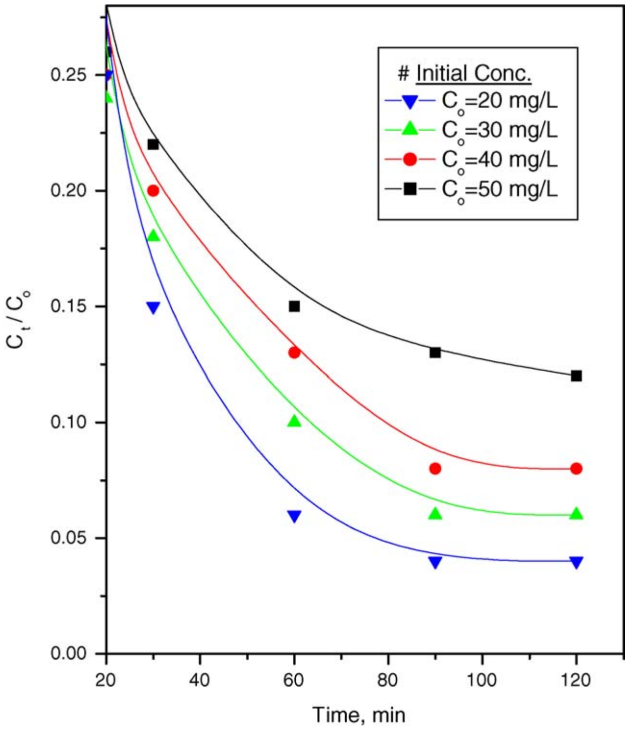

Fig. 10. Plot of C_t/C_0 vs. time for adsorption of TTA onto Amberlite XAD4 at different initial concentrations.

Table 4
The film mass transfer coefficients (β) and the correlation coefficients (R^2) for adsorption of TTA onto Amberlite resins

Co (mg L^{-1})	β (cm s^{-1})	
	XAD4	XAD7
20	1.75×10^{-2}	7.50×10^{-3}
30	1.40×10^{-2}	6.00×10^{-3}
40	1.25×10^{-2}	3.75×10^{-3}
50	1.15×10^{-2}	3.45×10^{-3}
R^2	0.994	0.971

The values of β were plotted as log β against log C_0 and shown in Fig. 12. A straight line relationship were observed revealing a definite logarithmic variation and indirect dependence has the correlation coefficients (R^2) values 0.994 and 0.971 for TTA adsorption onto XAD4 and XAD7, respectively. According to β values, the mass transfer is rapid enough to use Amberlite XAD resin in treatment the aqueous solutions enriched with such extractants.

The rate of pore diffusion of EDTA adsorption onto Amberlite XAD4 is related to the rate of concentration variation by the following equation [32]:

$$\frac{C_t}{C_0} = K_p t^{0.5} \tag{9}$$

where K_p is the rate constant for pore diffusion. From this relation, the values of K_p were obtained, at different initial concentrations, from the slopes of C_t/C_0 versus time plots that given in Fig. 13. The figure exhibits a linear variation indicating the system to be pore diffusion controlled. The values of K_p at different initial concentrations were determined from the slops of the respective plots and given in Table 5.

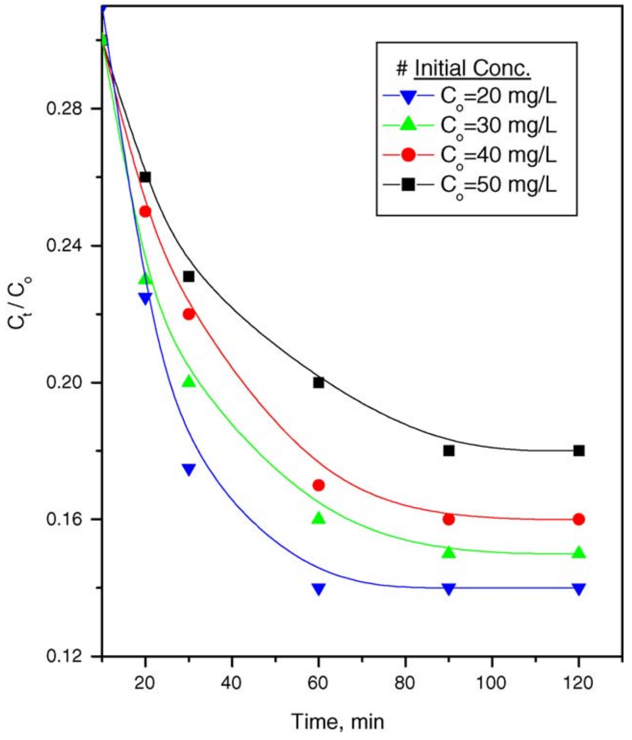

Fig. 11. Plot of C_t/C_0 vs. time for adsorption of TTA onto Amberlite XAD7 at different initial concentrations.

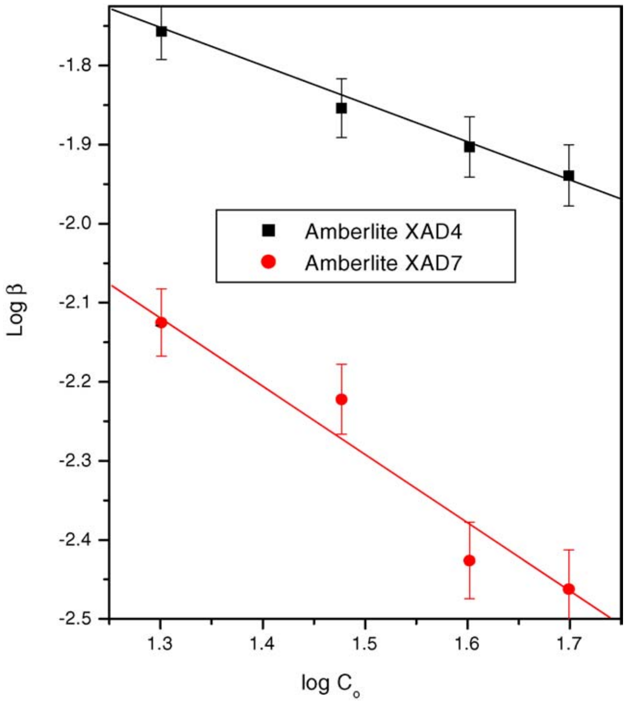

Fig. 12. Plot of log β aganist log C_0 for adsorption of TTA onto Amberlite XAD resins.

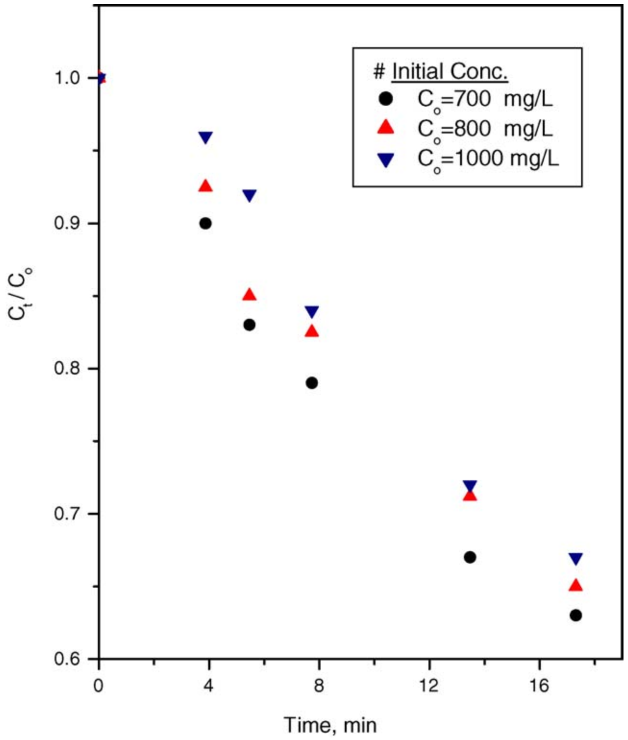

Fig. 13. Plot of C_t/C_0 vs. time for adsorption of EDTA onto Amberlite XAD4 at different initial concentrations.

3.4. Column studies

The adsorption behavior of TTA from aqueous solution of pH ~ 2 onto Amberlite XAD4 packed column was investigated at 0.5 mL min^{-1} flow rate and the obtained break through is shown in Fig. 14. The curve displays that the break through begins at effluent volume amounted to 200 mL. The column adsorption capacity was evaluated and found to have the value 27 mg g^{-1} exhibiting Amberlite XAD4 as a good resin for retention of such chelators.

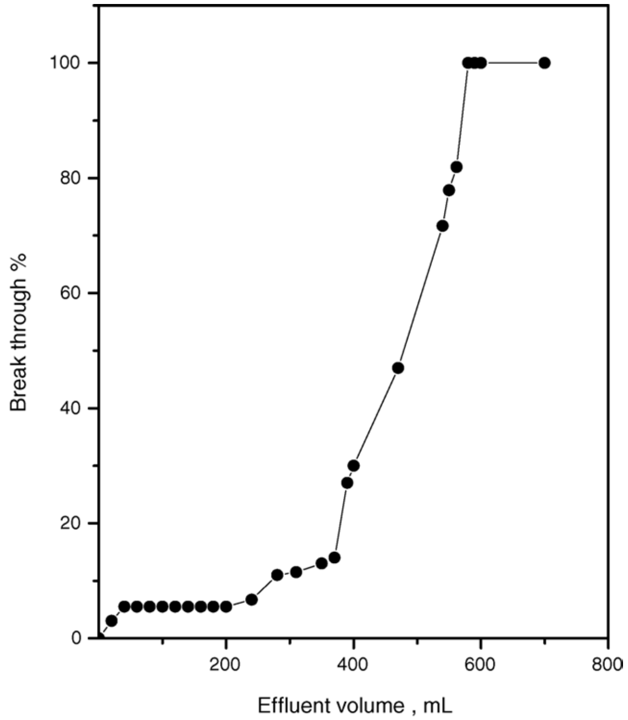

Fig. 14. The break through curve for adsorption of TTA onto XAD4 (r = 1.5 cm, h = 3 cm, rate = 0.5 mL min^{-1}).

Table 5
The pore diffusion coefficients (K_p) for adsorption of EDTA onto Amberlite XAD4

Co (mg L^{-1})	K_p (min$^{-0.5}$)
700	21.14×10^{-2}
800	2.02×10^{-2}
1000	1.93×10^{-2}

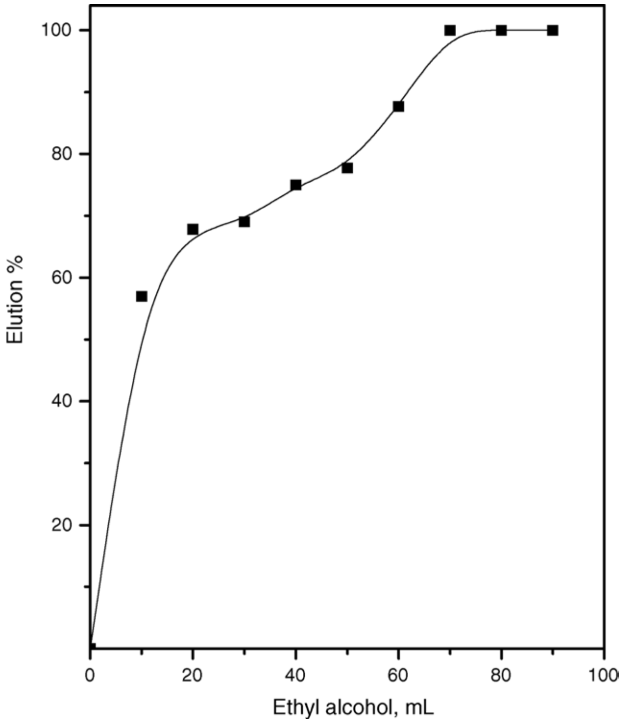

Fig. 15. The elution of TTA from Amberlite XAD4 loaded column using ethyl alcohol as eluant.

Elution the loaded TTA was achieved using 10% ethyl alcohol, as an eluant, at 1 mL min^{-1} flow rate and the relation between elution percentage (E%) and eluant volume was illustrated in Fig. 15. The plot shows a complete elution (~100%) of TTA by ethyl alcohol implying the possibility of applying the handled system for a second recovery.

4. Conclusion

It can be concluded that Amberlite resins are suitable for removal and immobilization of some organic extractants from aqueous solutions. They are successfully used in removal of TTA and EDTA, resulting from different decontamination processes, from high acidic medium, conditions where other conventional resins may not efficient. The resins, especially XAD4, have high sorption capacity implying quantitative removal efficiency with fast adsorption rates. The adsorbability of these chelators decreases with presence of organic cosolvents and their adsorption behavior is controlled by a diffusion mechanism. The loaded chelator can be completely recovered using ethyl alcohol implying the possibility of applying the handled system for a second recovery.

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