Chemical Engineering Journal 168 (2011) 1163–1173

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of Hg(II) from aqueous solutions using a novel impregnated resin containing 1-(2-thiazolylazo)-2-naphthol (TAN)

Ahmad Hosseini-Bandegharaei[a,*], Mohammad Saeid Hosseini[b], Yousef Jalalabadi[a], Masoud Sarwghadi[a], Mehdi Nedaie[a], Akram Taherian[a], Ahmad Ghaznavi[a], Ahmad Eftekhari[a]

[a] *Department of Engineering, Islamic Azad University-Kashmar Branch, Kashmar, P.O. Box 102, Iran*
[b] *Department of Chemistry, Faculty of Science, University of Birjand, Birjand, P.O. Box 414, Iran*

ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form 31 January 2011
Accepted 1 February 2011

Keywords:
Extractant-impregnated resins
Hg(II) sorption
1-(2-Thiazolylazo)-2-naphtol
Amberlite XAD-4
Langmuir model
Kinetic study

ABSTRACT

A novel efficient Hg(II) adsorbent was prepared by impregnating 1-(2-thiazolylazo)-2-naphtol (TAN) onto Amberlite XAD-4 resin beads. Batch sorption experiments were carried out for the removal of Hg(II) from aqueous solutions using the new extractant-impregnated resin, EIR. The influences of various experimental parameters like pH, initial concentration, EIR dosage, contact time and the effect of temperature were evaluated. Optimum conditions for Hg(II) removal were found to be pH range of 5–6, EIR dosage 0.5 g L^{-1} and equilibrium time 55 min. The equilibrium sorption isotherm was better described by Langmuir sorption isotherm model. The maximum sorption capacity (q_{max}) of EIR for Hg(II) ions in terms of monolayer sorption was 450.45 mg g^{-1}. Increase of temperature increased the sorption. The obtained negative values of Gibbs free energy (ΔG°) indicated feasible and spontaneous nature of the sorption process at different temperatures. The change of entropy (ΔS°) and enthalpy (ΔH°) were estimated. Results of the kinetic studies showed that the sorption process follows Bangham's kinetic model, and the pore diffusion is the rate-controlling step. The pore diffusion coefficients, D_p values, were of the order of 10^{-12} m^2 s^{-1}. The new EIR could be successfully recycled for several consecutive cycles without significant loss in its sorption capacity.

1. Introduction

Heavy metals are widely distributed in the environment as a result of numerous industrial processes and cause toxic effects to human beings. Mercury is one of the most toxic heavy metals with known negative impacts on both human health and ecological functions. Mercury compounds are strongly able to bioconcentrate in organisms and to biomagnify through food chains. This ability leads to brain damage, chromosome breakage and dysfunction of liver, kidney, gastrointestinal tract and central nervous system. The toxicity of mercury depends strongly on its redox state. The most toxic form of mercury is the highly reactive Hg^{2+} which binds to the amino acids in proteins and it mainly affects the renal and nervous systems. In contrast, the danger of elemental mercury and organomercury compounds lies in their transport routes [1–3]. Industries mainly responsible for the dispersion of mercury are chlor-alkali, paint, pulp and paper; oil refining, electrical, rubber processing and fertilizer [4]. Removal of mercury ions from water and wastewater, before its discharge into the environment, is very important. A range of different technologies for mercury ion removal from the water and wastewater, such as chemical precipitation, coagulation, membrane technologies, sorption, etc., have been investigated extensively [5–7]. Among them, sorption has been found to be superior to other techniques for effective mercury emission control in terms of cost, simplicity of design, ease of operation and reusability [8–13].

In the recent decades, chelating ion exchange resins has been reported to be effective solid adsorbents for removal of metal ions, including Hg(II), from their aqueous solutions [10–20]. For providing chelating ion exchange resins, appropriate extractant molecules can be chemically bonded to or impregnated onto macroporous polymeric matrixes such as Amberlite XAD series resins. The XAD series resins are of immense value for designing desired chelating resins and many previous studies have been reported for various XAD resins in which an inert support is chemically bonded or physically impregnated with a selective organic extractant to produce a chelating adsorbent for the sorption of metal ions from aqueous solutions [15–20]. However, direct bonding of chelating ligands to a polymeric matrix is very difficult and time consuming due to relative inertness of polymeric surface in the ground state and, hence, requiring surface activation. But the impregnation technique is the most convenient method of preparing chelating resins, since it is exceedingly easy to perform, merely

---

* Corresponding author. Tel.: +98 532 8250550; fax: +98 532 8250525.
E-mail addresses: ahoseinib@yahoo.com, ahoseinib@iaukashmar.ac.ir (A. Hosseini-Bandegharaei).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.02.004

Nomenclature

a	Bangham's constant (<1)
b	Langmuir constant related to the free energy of sorption ($L\,mg^{-1}$)
b_M	Langmuir constant related to the free energy of sorption ($L\,mol^{-1}$)
C_e	the equilibrium concentration of Hg(II) ion in the bulk solution ($mg\,L^{-1}$)
D_p	pore diffusion coefficient ($m^2\,s^{-1}$)
k	pore diffusion constant (s^{-1})
K_0	Bangham's constant ($mL\,g^{-1}\,L^{-1}$)
K_F	Freundlich constant indicative of the relative sorption capacity of the adsorbent ($mg^{1-(1/n)}\,L^{1/n}\,g^{-1}$)
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$)
m	weight of EIR per liter of solution ($g\,L^{-1}$)
N	number of measurements
n	Freundlich constant indicative of the intensity of the sorption
q_t	the amount of Hg(II) ion sorbed at any time t ($mg\,g^{-1}$)
q_e	the amount of Hg(II) ion sorbed per unit weight of EIR at equilibrium ($mg\,g^{-1}$)
q_{max}	Langmuir constant; theoretical maximum sorption capacity ($mg\,g^{-1}$)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
R^2	correlation coefficient
$R\%$	removal percentage (%)
R_L	dimensionless separation factor
t	time (min or s)
T	temperature (K)
V	solution volume (L or mL)
X_t	fractional attainment to equilibrium at time 't'
Greek letters	
ΔG°	Gibb's free energy change ($J\,mol^{-1}$)
ΔH°	enthalpy change ($J\,mol^{-1}$)
Δq	normalized standard deviation (%)
ΔS°	entropy change ($J\,mol^{-1}\,K^{-1}$)
α	Elovich constant; initial sorption rate ($mg\,g^{-1}\,min^{-1}$)
β	Elovich constant; desorption constant ($g\,mg^{-1}$)

requiring stirring of the extractant and the polymeric support. Subsequently, impregnating methods have been more developed in the last decade, because the impregnation methods are free from difficulties encountered in chemically linking a chelating reagent to a polymeric matrix [19–22]. By using the impregnation methods, chelating ion exchange resins can be simply prepared by immobilization of a desired complexing reagent, extractant, within the matrix structure of polymeric adsorbents by physical contact. In addition, there is a wide choice of extractants for desired selectivity [22–25].

In the last years, our research group has been involved in the study of EIRs containing different extractants impregnated onto adequate Amberlite XAD resins [24–28]. In continuation of these studies, the present work was focused on designing an adequate chelating ion-exchange support for the sorption and removal of Hg(II) from the waters and wastewaters. For this purpose, 1-(2-thiazolylazo)-2-naphtol (TAN) was impregnated onto the surface of Amberlite XAD-4 resin beads to prepare a new extractant-impregnated resin, EIR. The effectiveness of new EIR for the sorption of Hg(II) ion was examined by batch sorption experiments. Varying the extractant concentration, impregnated resin samples of different impregnating ratios were prepared. To evaluate the effects of solution pH, contact time, initial concentration of mercury, adsorbent dosage, temperature, and ionic strength, batch sorption experiments were carried out using the optimum EIR sample. Sorption isotherms, kinetics and thermodynamic parameters were also evaluated for the sorption of mercury(II) onto the new chelating cation-exchange resin. In addition, the kinetic and equilibrium studies were used to gain insight on the potential sorption mechanism of Hg(II) by EIR beads.

2. Experimental

2.1. Chemicals and apparatus

All chemicals used were of analytical grade and purchased from Merck (Darmstadt, Germany). A stock Hg(II)) solution ($1000\,mg\,L^{-1}$) was prepared by dissolving the appropriate amounts of $HgCl_2$ in deionized water (conductivity $0.5\,\mu S\,cm^{-1}$ and pH 6), acidified with small amount of HNO_3, and all the working solutions were prepared by diluting this stock solution with deionized water. Buffer solutions of pH 1–3, 4–6, and 7–9 were prepared by mixing appropriate ratios of 0.1 M HCl and KCl, 0.5 M acetic acid and ammonium acetate, and 0.5 M ammonia and NH_4Cl solutions, respectively. 1-(2-thiazolylazo)-2-naphtol (TAN) and Amberlite XAD-4 (surface area of $750\,m^2\,g^{-1}$, average pore diameter 10.0 nm and bead size 20–60 mesh) were obtained from Fluka, Germany. The surface area, pore diameter and mesh size of the resin were quoted by the supplier. The pH measurements were made on a digital inoLab pH level I pH-meter. A Gallenkamp automatic shaker model BKS 305-010, UK, was used for the batch experiments. A Shimadzu model AA 6800 atomic absorption spectrometer was used for the determination of Hg(II) in solutions.

2.2. EIR synthesis

Before impregnation process, Amberlite XAD-4 resin beads were treated with 1:1 methanol–water solution containing 6 M HCl for 24 h, in order to remove remained monomers and other types of impurity which may be found with the fabricated beads. Then, the resin was thoroughly rinsed with doubly distilled water and placed into a drying oven at 50 °C for 30 min. To prepare the impregnated resin, portions of Amberlite XAD-4 (1 g of dry resin) were transferred into a series of glass stoppered bottles containing 200 mL of TAN 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 solvent at 60 °C. 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 TAN was detected in the filtrate, spectrophotometrically. Then the EIR samples were subjected to 15 Hg(II) sorption–desorption cycles, using 100 mL-aliquots of Hg(II) solution of $500\,mg\,L^{-1}$, followed by washing with HCl and distilled water. Finally, the impregnated resins were dried at 50 °C and weighed. The amount of TAN impregnated on/in the resin beads was determined from the amount of weight change of polymeric resin. To protect the prepared EIR from damage, it was kept in a stoppered dark glass bottle under the distilled water content.

2.3. Hg(II) sorption experiments

TAN impregnated XAD-4 (at maximum impregnation ratio of 1.13 g TAN/g XAD-4) was evaluated for Hg(II) removal from synthetic solutions. The operating variables studied were pH, adsorbent dosage, initial metal ion concentration, ionic strength and temperature. Stock solutions of Hg(II) (1000 mg L^{-1}) were prepared from mercury chloride in double distilled-deionized water. Experimental solutions of Hg(II) having known initial concentrations were prepared by diluting the stock solution in 250-mL stoppered conical flasks. Aliquots of 100 mL of the experimental solutions were mixed with certain amounts of EIR and the mixtures were shaken at a fixed temperature using a temperature controlled shaker set at 220 rpm for a period of desired time at desired pHs. After that, the mixtures were filtered and the Hg(II) loaded EIR beads were washed with distilled water to remove any unadsorbed Hg(II). In the next step, the Hg(II) loaded EIR beads were eluted using HCl as a desired desorption regent. Then, the filtrates, or the eluted solutions, were analyzed for the determining the amount of Hg(II) adsorbed onto EIR using atomic absorption spectrometer (Shimadzu model AA 6800). Control experiments showed that no sorption occurred on either glassware or filtration systems. The amounts of metal ions adsorbed per gram of the EIR beads were calculated at various time 't' (q_t) and at equilibrium (q_e) by the difference between the initial and the final readings using the following equations.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_t is the amount of the mercury sorbed onto the EIR beads at time 't' (mg g^{-1}), $q_{e,}$ the amount of the mercury sorbed onto the EIR beads at equilibrium (mg g^{-1}), C_0, the initial concentration of Hg(II) in the aqueous solutions (mg L^{-1}), C_t, the Hg(II) concentration remaining in the solutions at time 't' (mg L^{-1}), C_e, the equilibrium concentration of Hg(II) in the solutions (mg L^{-1}), V, the volume of the solutions used (L), and m, the weight of the EIR beads used in g. Also, the removal percentage at equilibrium (R%) was calculated by Eq. (3):

$$R\% = \frac{(C_0 - C_e)}{C_e} \times 100 \quad (3)$$

Keeping the other parameters fixed, one parameter was varied at a time. For pH studies, 100-mL solutions of 100 mg L^{-1} metal ion were adjusted to various pHs ranging from 1 to 9. The pH-adjusted solutions were kept for a contact time of 1 h at an agitation speed of 220 rpm at 298 ± 1 K. EIR samples of different impregnation ratio were used to study the effect of impregnation ratio on the Hg(II) removal under the optimum sorption conditions. Different EIR doses ranging from 10 to 50 mg were used to study the effect of adsorbent on the removal of Hg(II) at 100 mg L^{-1} initial Hg(II) concentration.

The sorption isotherms of Hg(II) ion onto the EIR were obtained at the pH of maximum uptake. For this purpose, aliquots of 100-mL of the solutions (pH 5.5) containing Hg(II) with the different concentrations were shaken at 298 ± 1 K for 1 h. 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 Hg(II) buffered solutions (pH 5.5) with concentration of 25, 75, 125 and 175 mg L^{-1} at 298 ± 1 K. The mixtures were stirred mechanically for a pre-determined time interval at a fixed speed (220 rpm).

All the batch experiments were carried out in triplicate and showed differences less than 2%. The values reported are average of three readings.

2.4. Desorption studies

Desorption studies were carried out as follows: after sorption experiments with 100 mg L^{-1} Hg(II) at 0.050 g of EIR in 100 mL, the Hg(II) loaded EIRs were separated by filtration and washed with distilled water to remove any unadsorbed Hg(II). The EIR beads loaded with mercury were placed in a solution of interested mineral acid and stirred at 220 rpm for 1 h at 298 K. After that, the suspension was filtered and the filtrate was analyzed for Hg(II). A comparison of the value with those observed in the initial sorption step was used to compute the percentage recovery values. To test the reusability of the EIR, the sorption–desorption cycles were repeated 25 times.

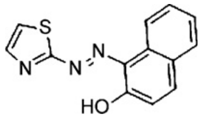

Fig. 1. Molecular structure of TAN.

3. Results and discussions

3.1. Preparation and characterization of TAN-impregnated resin

1-(2-Thiazolylazo)-2-naphtol (TAN) is a chromogenic reagent (structure is shown in Fig. 1). It has been used for the pre-concentration and determination of metallic elements, including mercury, iron, nickel, copper and zinc [29–34]. At the pH range of 2.3–9.5 and 25 °C, TAN is present as a neutral species which is almost water-insoluble. Because of the protonation of functional groups in the acidic media, the regent is present as cationic species (at pHs < 2.3) which cause a high solubility TAN. Also, deprotonation cause to form the anion (at pH > 9.5) and high solubility of TAN at the high pHs.

The aim of presented work was to develop an adequate chelating ion-exchange support for the sorption and removal of Hg(II) from the waters and wastewaters. For this purpose, TAN was impregnated onto/into Amberlite XAD-4, which has been often used as a solid polymeric adsorbent to prepare ligand-loaded resins. Amberlite XAD-4 is a cross linked polymer which derives its sorptive properties from its macroreticular structure and higher surface area. This structure imparts excellent physical, chemical and thermal stability and is a very good choice for preparing extractant-impregnated resins. Recently, the XAD-4 resin, impregnated with many compounds as extracting agents, has been used for sorption, extraction and pre-concentration of some heavy metals [35–38].

TAN-impregnated XAD-4, TAN/XAD-4, was efficiently synthesized by the impregnation method described at our previous study [28]. To investigate the optimum pH for impregnating Amberlite XAD-4 resin beads by TAN, impregnation process was carried out at various pHs using 200-mL aliquots of aqueous mixture of 1.40% (w/w) TAN with different pHs from 1 to 8. The EIR beads were then transferred to a porous filter and washed successively with HCl and large amounts of distilled water. Then the EIR samples were subjected to several Hg(II) sorption–desorption cycles (15 cycles) followed by washing with HCl and distilled water. The result showed that pH 2.0 was the most suitable one for impregnation process. Also, the required time needed for completing the impregnating process was found to be at least 5 h.

To prepare the appropriate form of the EIR, the impregnation process was carried out at various impregnation ratios (g TAN/g dry polymer adsorbent). The impregnation of macroporous matrices leads to the immobilization of the extractant both in pores and in the gel regions of the polymer beads. The impregnating extractant located in the pore volume is weakly retained by the polymer (mainly due to the capillary forces) and can be easily leached out from the freshly prepared EIR samples during the first days of its use (unstable part of EIR capacity). The impregnating

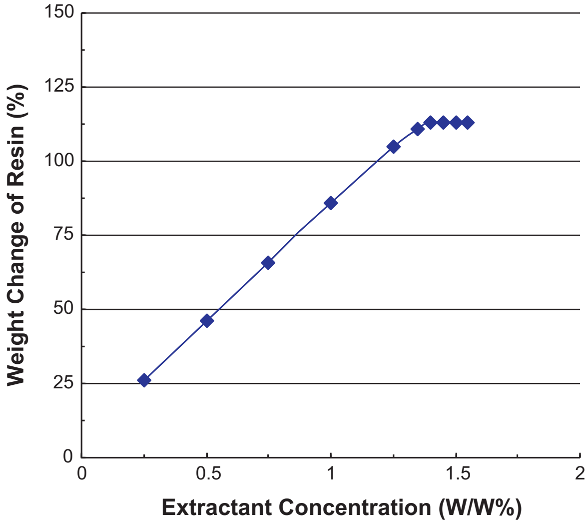

Fig. 2. Effect of TAN concentration on the EIR preparation at the conditions that portions of 1 g of the dry polymer beads of Amberlite XAD-4 were subjected to the impregnation process.

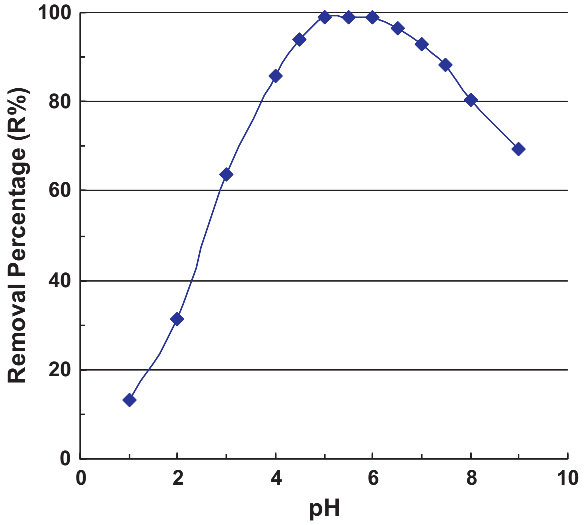

Fig. 3. Effect of pH on the removal percentage of Hg(II) ion by EIR (EIR sample with maximum impregnation ratio; 1.13 g TAN/g XAD-4) using 100 mL of model solutions of 100 mg L^{-1} Hg(II), EIR dose 50 mg, rpm 220 and contact time 1 h at 298 ± 1 K.

extractant taken up by the gel regions of the matrix represents the most stable part of the EIR capacity, which remains practically constant for a long period [39,40]. Thus, for stabilizing the EIR capacity (the amount of extractant impregnated on the resin) 15 cycles of sorption–desorption were carried out by treating the EIR samples with 100-mL aliquots of Hg(VI) solution having high concentration (500 mg L^{-1} at the optimum pH and ionic strengths) and 10-mL aliquots of HCl 4 M solution as eluent. The sorption–desorption cycles lead in fact to the gradual removal of the extractant molecules from the pore volume of the polymer matrix. Fig. 2 shows the weight changes obtained against the TAN concentration, at optimum pH (2.0), after 15 cycles of sorption and desorption and final washing the EIR samples with HCl and distilled water. Fig. 2 depicts that the maximum weight change is 113.1% which can obtain at the concentrations more than 1.40% (w/w) TAN. This observed high impregnation capacity of XAD-4 resin beads (surface area of 750 $m^2 g^{-1}$) may be attributed to the macroporous texture of XAD resins and the high molecular weight of TAN. The observed value of impregnation capacity is similar to those reported for other extractants and macroporous resins in the literature [15,19,41].

The chemical stability of the EIR was examined by sequentially suspending a 0.20-g portion of the EIR in different pHs and shaking for 10 h. After filtering the solutions and rinsing the EIR with distilled water, the released amount of TAN in the acidified rinsed solutions was examined by absorbance measuring at λ_{max} of TAN. It was found that the EIR benefited from a high stability since no considerable quantity of TAN was observed in the solutions.

3.2. *Effect of pH on Hg(II) removal*

Optimization of pH for sorption medium plays important role in the sorption studies. Thus, initially batch sorption studies were performed to study the influence of pH on the sorption of Hg(II) onto TAN/XAD-4 from aqueous solutions. The concentration and volume of Hg(II) solutions used for this studies were 100 mg L^{-1} and 100 mL, respectively. The EIR dosage was 0.050 g dry weight of EIR at maximum impregnation ratio (1.13 g TAN/g dry XAD-4). The effect of pH on Hg(II) removal by the EIR was studied over a pH range of 1.0–9.0 at 298 ± 1 K. Fig. 3 shows that as the pH increases the percentage of Hg(II) removal increases up to pH 5.0 and a narrow pH range of 5.0–6.0 is most suitable for the removal of Hg(II) from aqueous solution. Also, Fig. 3 shows that the removal decreases when pH is greater than 6.0. At 100 mg L^{-1} initial Hg(II) concentration, Hg(II) removal increased from 13.23% to 99.05% on increasing the pH from 1 to 5.0, further increase in pH decreased mercury removal beyond the pH 6 and at pH 9 only 69.28% Hg(II) was adsorbed. The variation in the removal of mercury by TAN/XAD-4 with respect to pH can be elucidated by considering the low dissociation constant of TAN and the speciation of mercury (II). Since the sorption process involved the release of H^+ ions to allow the firm complexation of Hg(II) ions to TAN/XAD-4, at low pHs values, where the release of H^+ ions is not carried out well, there is a low efficiency in the sorption process of charged metal ions (Hg^{2+} and $Hg(OH)^+$) onto new EIR beads. Thus, the increase in Hg(II) sorption in the pH range 1–5.0 is due to an increase in concentration of $Hg(OH)^+$ species, and to the fact that the solution pH influences the release of H^+ ions. At the pH range of 5–6, easier deprotonation of TAN at EIR surface and increased formation of $Hg(OH)^+$ species facilitate the exchange of H^+ from functional groups of EIR over mercury species. However, increased formation of $Hg(OH)_2$ species decrease the sorption efficiency of mercury into EIR beads at the range of 6.5–9.0. But despite the considerable precipitation of Hg(II), the sorption efficiency still seems to be too much at the pHs > 6.5. These results can be explained by considering these two facts: (i) both chelating ion exchange and precipitation are reversible reactions and (ii) the sorption of Hg(II) ions onto the EIR is a heterogeneous reaction between solid EIR and solution which can reach equilibrium in the batch conditions. In fact, the sorption efficiency of Hg(II) at higher pHs is determined by the existing equilibrium between $Hg(OH)_2$ and Hg(II)-TAN complex. As a result, increase in the pH values cause increased amounts of $Hg(OH)_2$ species, which finally decrease the equilibrium amounts of Hg(II) adsorbed into the EIR beads. Hence, for all subsequent experiments, the pH was adjusted to 5.5 using ammonium acetate/acetic acid buffer.

3.3. *Effect of impregnation ratio*

With increase in impregnation ratio (in the EIR sample) from 0.45 to 1.13 g TAN/g XAD-4, the removal percentage (R%) increased from 32.79% to 99.05% at fixed EIR dose 0.05 g, pH 5.5, initial Hg(II) 100 mg L^{-1}, volume of solutions 100 mL, temperature 298 K, shaking speed 220 rpm and 1 h contact time (Fig. 4). The increase in the removal with increase in impregnating ratio is due to increase in

Table 1
Thermodynamic parameters for the sorption of Hg(II) ion by TAN-impregnated XAD-4.

T (K)	b_M (L mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
288	15.95×10^4	−28.69	6.62	122.63
298	17.63×10^4	−29.94		
308	19.10×10^4	−31.14		
318	20.90×10^4	−32.39		
328	22.41×10^4	−33.60		

extractant molecules, and chelating ion exchange sites, on the EIR beads. Thus, the optimum impregnating ratio is the maximum one (1.13 g TAN/g XAD-4).

3.4. Effect of EIR dose

The effect of EIR dose was investigated using different EIR doses in 100 mL of 100 mg L^{-1} Hg(II) solution at 298 K, 220 rpm and 1 h contact time. The effect of EIR dose was expressed in terms of both removal percentage (R%) and maximum uptake (q_e; mg Hg(II) ion/g EIR beads). The results showed that the sorption process is dependent largely on the EIR dose. Since at higher dose of EIR more chelating ion exchange sites are available for the ion exchange, the removal percentage of Hg(II) increased from 34.29% to 99.05% on increasing the EIR dose from 10 to 50 mg (Fig. 5). However, the corresponding maximum uptake decreased from 196.04 to 67.97 mg g^{-1}, which is unavoidable for obtaining better results in mercury removal from wastewaters.

3.5. Effect of electrolyte

The presence of salt may interfere with the sorption process. To understand the effect of electrolytes ions on Hg(II) chelating, Na_2SO_4 was added to the aqueous synthetic solutions of mercury and the sorption experiments were carried out at fixed EIR dose 0.05 g, pH 5.5, volume of solutions 100 mL, shaking speed 220 rpm and 1 h contact time. With increase in concentration of Na_2SO_4 from 0.01 to 1.0 M, the equilibrium sorption capacity of EIR decreased from 49.7 to 38.4 mg g^{-1}, 148.8 to 119.9 mg g^{-1}, 247.1 to 196.3 mg g^{-1} and 341.21 to 261.8 mg g^{-1} for different initial concentrations of 25, 75, 125 and 175 mg L^{-1} at 298 K. This effect may be due to the changes in Hg(II) activity or in the properties of the electric double layer. Also, the decrease in the removal on increasing the electrolyte concentration is due to competition between mercury species and ionic species furnished by electrolytes.

3.6. Effect of contact time and initial concentration

To study effect of contact time and initial concentration, the sorption of Hg(II) by TAN/XAD-4 was carried out at pH 5.5 and at a temperature of 298 K. The sorption capacity of the new EIR at different time intervals for different initial concentrations varying from 25 to 175 mg L^{-1} is depicted in Fig. 6. The amount of Hg(II) adsorbed onto EIR beads increased with increase in contact time and attained equilibrium at 55 min for all initial concentrations of 25–175 mg L^{-1}. Also, Fig. 6 shows the effect of initial concentration on the sorption of Hg(II) on TAN/XAD-4. The amount of sorption (sorption capacity) increased with increase in initial concentration of Hg(II), but the sorption percentage decreased with increase in initial concentration. At higher initial concentrations, the ratio of the initial number of moles of Hg(II) to the available chelating ion exchange sites is high; hence, the fractional sorption becomes dependent on initial concentration. However, the time required for attaining the equilibrium state is highly independent on initial concentration. The amount of Hg(II) sorption was found to increase from 49.76 to 343.32 mg g^{-1} as the initial concentration increased from 25 to 175 mg L^{-1}. At the same time, the removal percentage decreased from 99.5 to 98.1 as the initial concentration increased from 25 to 175 mg L^{-1}.

3.7. Effect of temperature

The temperature is an effective factor in the context of sorption on solid adsorbent and has two major effects on the sorption process. Increasing the temperature causes to change the equilibrium constant and sorption capacity of the adsorbent for a particular

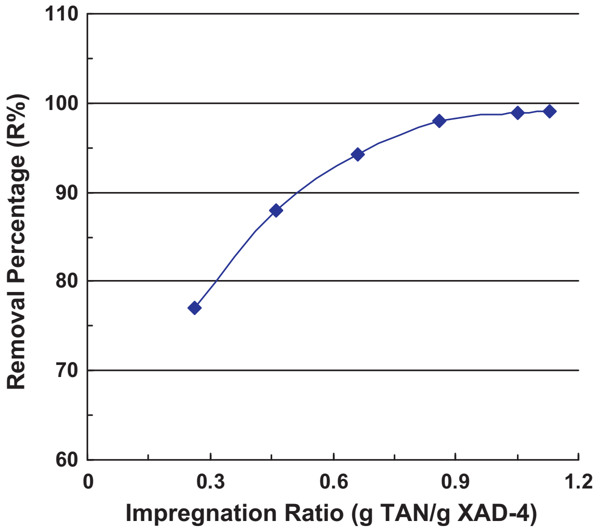

Fig. 4. Effect of impregnating ratio on the sorption of Hg(II) ion by EIR (conditions: Hg(II) concentration 100 mg L^{-1}; solution volume 100 mL; EIR dose 50 mg; contact time 1 h; pH 5.5; stirring speed 220 rpm; temperature 298 ± 1 K).

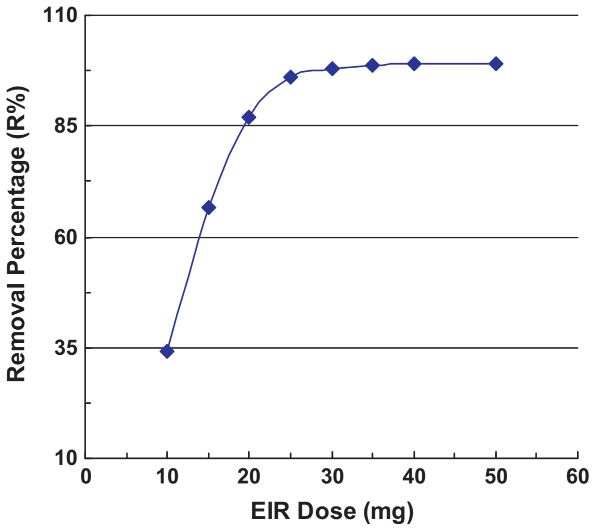

Fig. 5. Effect of adsorbent dosage on the sorption of Hg(II) ion by EIR (conditions: Hg(II) concentration 100 mg L^{-1}; solution volume 100 mL; contact time 1 h; pH 5.5; stirring speed 220 rpm; temperature 298 ± 1 K).

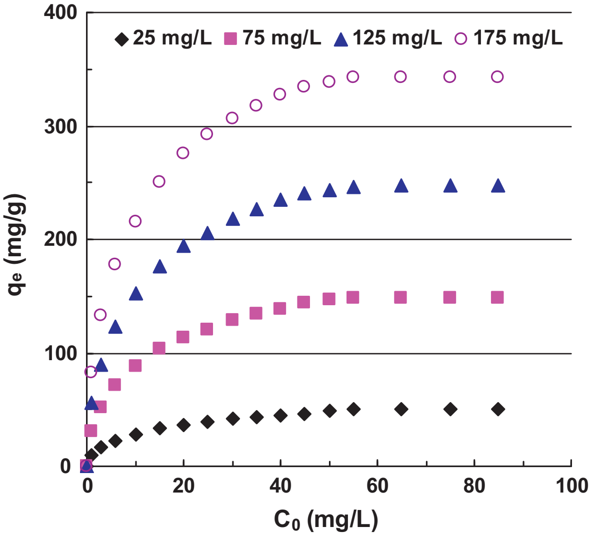

Fig. 6. Effect of time and initial concentration on the sorption capacity of EIR (conditions: solution volume 100 mL; pH 5.5; EIR dose 50 mg; stirring speed 220 rpm; temperature 298 ± 1 K).

solute. In addition, changing temperature will increase the rate of diffusion of the solute molecules, or ions, across the external boundary layer and in the internal pores of the adsorbent particles, owing to decrease in the viscosity of the solution and, also, increase in the solute mobility in the solution. In the present study, the effect of temperature on the sorption was studied in the range of 288–328 K under the selected agitation time (1 h), the volume of solutions (100 mL) and dose of EIR (0.050 g). The sorption capacity of EIR was increased with increasing the temperature. The increase in the sorption capacity may be due to an increased equilibrium constant for sorption at higher temperature. In addition, the increase in the sorption capacity, q_e, with the increase in the temperature, indicates that sorption is endothermic nature.

3.8. Thermodynamic study

The thermodynamic parameters of sorption process were calculated using the following equations [2]:

$$\Delta G^\circ = -RT \ln b_M \tag{4}$$

$$\ln b_M = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

where ΔG° (J mol^{-1}) is change in standard Gibbs free energy, R (J mol^{-1} K^{-1}) is gas constant, b_M (L mol^{-1}) is the Langmuir equilibrium constant, T is the temperature in K, ΔH° (J mol^{-1}) is change in standard enthalpy and ΔS° (J mol^{-1} K^{-1}) is change in standard entropy.

Plotting of $\ln b_M$ versus $1/T$ (Fig. 7) gives straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of thermodynamic parameters were calculated and are reported in Table 1. The positive value of ΔH° (6.62 kJ mol^{-1}) shows the endothermic nature of sorption process. The negative values of (−28.69, −29. 94, −31.14, −32.39 and −33.60 kJ mol^{-1}) ΔG° indicate the feasibility and spontaneous nature of sorption process at 15, 25, 35, 45 and 55 °C for the Langmuir equilibrium constant of b_M (11.98, 12.08, 12.16, 12.25 and 12.32 L mol^{-1}). The positive values of ΔS° (122.63 J K^{-1} mol^{-1}) suggest the increased randomness of the system during the sorption process. These positive values of ΔS° may be related to the liberation of water of hydration, at the solid/solution interface, during the sorption of Hg(II) onto TAN/XAD-4.

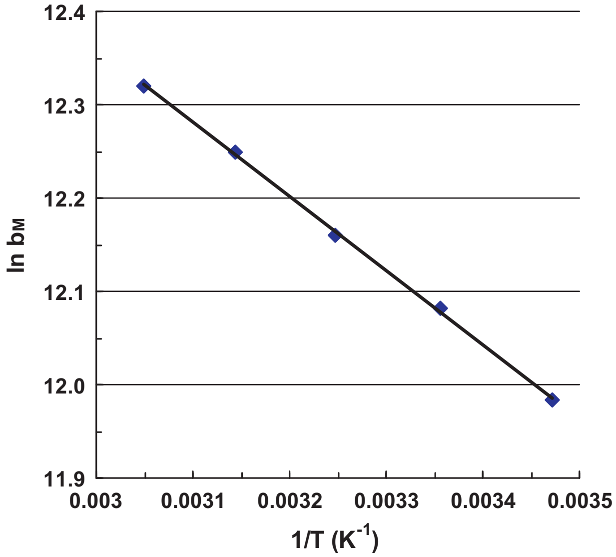

Fig. 7. Plot of $\ln b_M$ versus $1/T$ for the determination of thermodynamic parameters.

3.9. Sorption isotherm studies

Sorption isotherm model is an important physicochemical feature for the evaluation of basic characteristics of a good adsorbent. Sorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of a solute in bulk solution at a given temperature under equilibrium conditions. In the current study, equilibrium studies were performed to evaluate the best fit isotherm model for explaining the sorption of Hg(II) onto EIR beads. Also, isotherm studies were meant for evaluating the sorption capacity and energy of sorption of EIR.

For sorption of metal ions from the solutions, by solid adsorbents, the most widely used isotherm models are the Langmuir and Freundlich isotherms. Thus, the equilibrium data were analyzed using the Langmuir as well as Freundlich isotherm models. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as the following equation [42]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{6}$$

where C_e is the equilibrium concentration (mg L^{-1}) and q_e the sorption capacity at equilibrium (mg g^{-1}). The Langmuir constants q_{max} (mg g^{-1}) represent the maximum sorption capacity and b (L mg^{-1}) relates the energy of sorption.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed in linear form as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where K_f indicates relative sorption capacity (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) and n is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the adsorbent [43]. The greater the values of the $1/n$, better is the favorability of the sorption.

The equilibrium sorption studies were conducted using various initial concentrations of Hg(II) (25–300 mg L^{-1}) at pH 5.5 and at 298 K. Sorption of Hg(II) by TAN/XAD-4 was modeled by Langmuir (Fig. 8) and Freundlich sorption (not shown) models (Table 2) where the data fitted better to Langmuir isotherm indicating monolayer sorption.

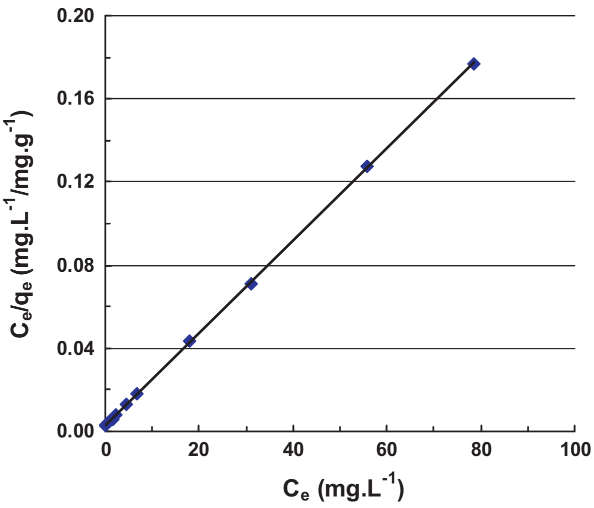

Fig. 8. Langmuir sorption isotherm for Hg(II) sorption by EIR (pH 5.5 and temperature 298 K).

The essential feature of the Langmuir sorption model can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether a sorption system is favorable or unfavorable. R_L is calculated using the following equation [44]:

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where C_0 is the initial Hg(II) concentration (mg L^{-1}). The value of R_L indicates the nature of the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$) and unfavorable ($R_L = 1$). From the experimental data, the values of R_L were found to be between 0 and 1 for all of initial Hg(II) concentrations and there by obeying the Langmuir isotherm model under the conditions used in this study.

The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of extractant molecules, or active chelating sites, on the polymeric surface; since the Langmuir equation assumes that the adsorbent surface is homogenous and the sorption is monolayer.

3.10. Sorption kinetics

The kinetic modeling is helpful for the prediction of sorption rate. Also, the desired kinetic model gives important information for designing the sorption process for wastewater treatment. The sorption process of a metal ion into a macroporous impregnated resin, such as TAN/XAD-4, can be divided into three stages: diffusion through the liquid film surrounding the EIR beads (called external mass-transfer, or film diffusion), diffusion through the particle pores (called pore diffusion), and finally a chemical reaction with the functional groups of extractant molecules. Among them, the last step is assumed to be very fast in most cases. But the first and the second steps can be the rate-controlling step, either singly or in combination. Therefore, kinetic modeling was carried out for investigating the appropriate model for explaining the nature of sorption process. The sorption capacity of Hg(II) at a fixed adsorbent dose of 0.050 g was monitored with time. The kinetics of Hg(II) removal by TAN/XAD-4 indicated rapid binding of Hg(II) to the chelating ion exchange sites of EIR during first few minutes, $t_{1/2} < 8$ min, followed by a slow decrease until a state of equilibrium at 55 min was reached. No change in the sorption capacity was observed with further increase in equilibration time up to 2.0 h. The initial rapid phase may be due to higher number of chelating ion exchange sites available at the initial stage, as a result there was an increased concentration gradient between Hg(II) ions in solution and extractant molecules in the EIR surface. Generally, when sorption involves a surface reaction process, the initial sorption is rapid. Then, a slower sorption would follow as the available chelating ion exchange sites gradually decrease. Kinetics of Hg(II) sorption was modeled by four models, namely the first-order Lagergren model, the pseudo-second-order equation, Elovich model and Bangham equation, at four different initial Hg(II) concentrations (25, 75, 125 and 175 mg L^{-1}).

Table 2
Parameters of the Langmuir and Freundlich isotherm models for the sorption of Hg(II) ion by TAN-impregnated XAD-4.

Isotherm model	Magnitude
Langmuir	
q_{max} (mg g^{-1})	450.45
b (L mg^{-1})	79.86×10^{-2}
R^2	0.9999
Freundlich	
K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1})	163.73
n	3.26
R^2	0.8084

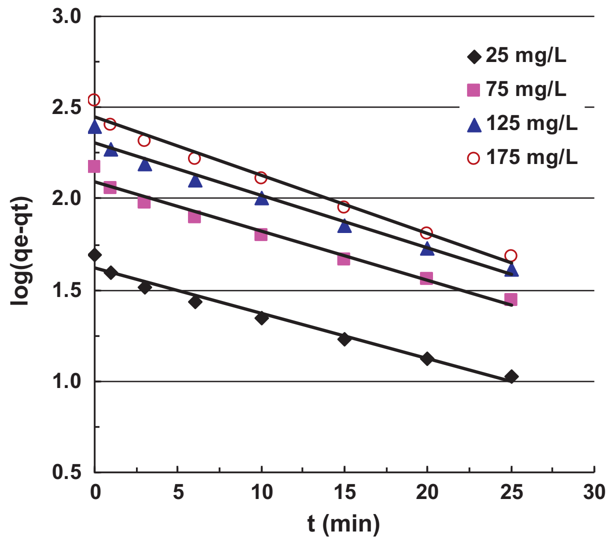

Fig. 9. Lagergren plots for Hg(II) sorption by EIR at different initial Hg(II) concentrations (conditions: solution volume 100 mL; pH 5.5; EIR dose 50 mg; stirring speed 220 rpm; temperature 298 ± 1 K).

The pseudo-first-order Lagergren equation [45] is given as Eq. (9):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

where q_e and q_t (mg g^{-1}) are the amount of Hg(II) adsorbed at equilibrium and at time t (min), respectively and k_1 (min^{-1}) is the rate constant of pseudo-first order sorption.

The pseudo-second-order equation [46] is expressed as Eq. (10):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order sorption and q_e is the sorption capacity at equilibrium (mg g^{-1}).

Elovich model [47] is described as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{11}$$

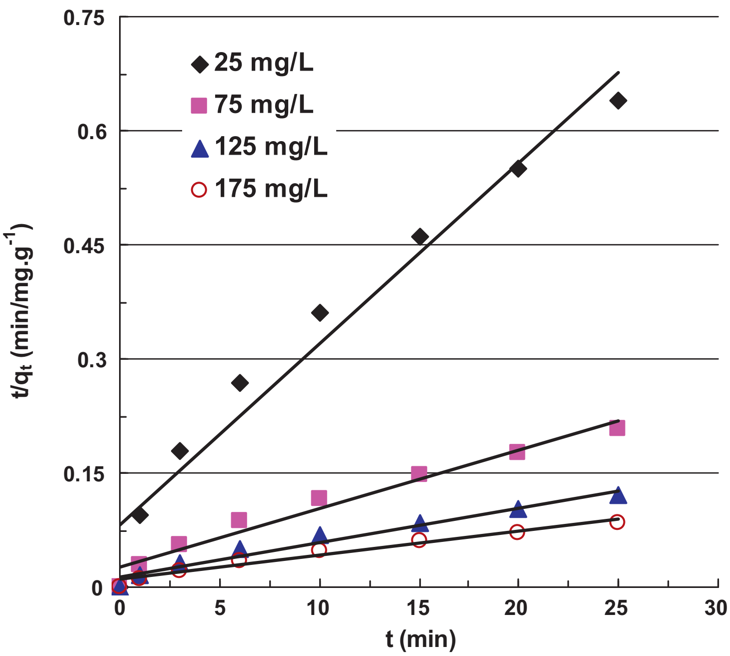

Fig. 10. Pseudo-second-order kinetic model in sorption of Hg(II) onto EIR at different initial Hg(II) concentrations (conditions: solution volume 100 mL; EIR dose 50 mg; pH 5.5; stirring speed 220 rpm; temperature 298 ± 1 K).

where α is initial sorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}).

The Bangham's equation [48] can be expressed as the following equation:

$$\log\log\left(\frac{C_0}{C_0 - q_t m}\right) = \log\left(\frac{k_0 m}{2.303V}\right) + a\log t \qquad (12)$$

where C_0 is the initial concentration of Hg(II) in solution (mg L^{-1}), V is the volume of solution (mL), m is the weight of EIR per liter of solution (g L^{-1}), q_t (mg g^{-1}) is the amount of Hg(II) retained at time t, and a (<1) and k_0 (mL g^{-1} L^{-1}) are Bangham's constants.

Kinetic parameters of these models were calculated from the slope and intercept of the linear plots of $\log(q_e - q_t)$ versus t (Fig. 9), t/q_t versus t (Fig. 10), q_t versus $\ln(t)$ (Fig. 11) and double logarithm of $C_0/(C_0 - q_t m)$ versus $\log(t)$ (Fig. 12). The kinetic parameters calculated from the plots are represented in Table 3. The values of k_1 and k_0 were found to be smaller for an initial concentration of 25 mg L^{-1} and increase gradually as the initial concentration increases to 175 mg L^{-1} for the sorption of Hg(II) onto EIR. However, the values of k_2 was found to be greater for an initial concentration of 25 mg L^{-1} and decreases gradually as the initial concentration increases to greater values. The values of rate constant k_1 increase from 5.79×10^{-2} to 7.32×10^{-2} min^{-1}, as the initial concentration increases from 25 to 175 mg L^{-1} for the sorption of Hg(II) onto EIR. Similarly, the values of k_0 were found to increase from 42.50 to 51.90 mL g^{-1} L^{-1}, as the initial concentration increases from 25 to 175 mg L^{-1}. But the values of k_2 were found to decrease from 7.04×10^{-3} to 1.09×10^{-3} g mg^{-1} min^{-1}, as the initial concentration increases from 25 to 175 mg L^{-1}.

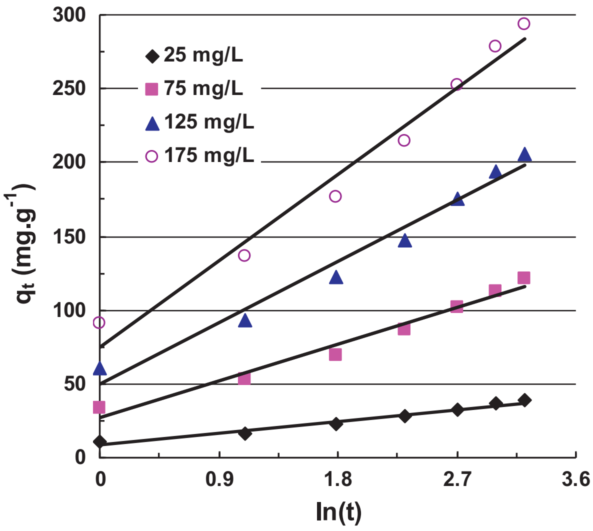

Fig. 11. Elovich kinetic model in sorption of Hg(II) onto EIR at different initial Hg(II) concentrations (conditions: solution volume 100 mL; EIR dose 50 mg; pH 5.5; stirring speed 220 rpm; temperature 298 ± 1 K).

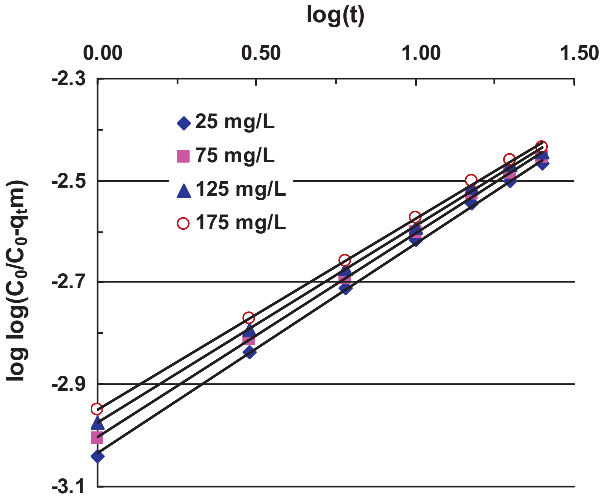

Fig. 12. Bangham plots for Hg(II) sorption by EIR at different initial Hg(II) concentrations (conditions: solution volume 100 mL; pH 5.5; EIR dose 50 mg; stirring speed 220 rpm; temperature 298 ± 1 K).

Table 3
Kinetic parameters for the sorption of Hg(II) ion by TAN-impregnated XAD-4.

Kinetic model	Initial concentration (mg L^{-1})			
	25	75	125	175
Pseudo-first order				
k_1 (min^{-1})	5.79×10^{-2}	6.24×10^{-2}	6.70×10^{-2}	7.32×10^{-2}
$q_{e.cal.}$ (mg g^{-1})	41.74	123.74	203.52	278.36
R^2	0.9749	0.9767	0.9781	0.9798
Δq (%)	7.17	7.09	7.23	7.15
Pseudo-second-order				
k_2 (g mg^{-1} min^{-1})	7.04×10^{-3}	2.37×10^{-3}	1.47×10^{-3}	1.09×10^{-3}
$q_{e.cal.}$ (mg g^{-1})	41.95	129.87	220.26	313.48
R^2	0.9632	0.9657	0.9679	0.9711
Δq (%)	13.06	13.18	13.09	12.84
Elovich model				
α (mg g^{-1} min^{-1})	22.58	74.10	134.97	206.53
β (g mg)	11.08×10^{-2}	3.63×10^{-2}	2.17×10^{-2}	1.54×10^{-2}
R^2	0.9737	0.9739	0.9731	0.9758
Δq (%)	10.56	9.93	9.49	8.61
Bangham model				
k_0 (mL g^{-1} L^{-1})	42.50	45.68	48.87	51.90
α	0.41	0.40	0.38	0.37
R^2	0.9994	0.9994	0.9993	0.9993
Δq (%)	1.18	1.15	1.12	1.16
$q_{e.exp}$ (mg g^{-1})	49.67	148.77	247.09	342.01

To compare the validity of each model, a normalized standard deviation, $\Delta q(\%)$ was calculated using the following equation:

$$\Delta q(\%) = 100\sqrt{\frac{\sum[(q_{t,\mathrm{exp}} - q_{t,\mathrm{cal}})/q_{t,\mathrm{exp}}]^2}{N-1}} \tag{13}$$

where $q_{t,\mathrm{exp}}$ and $q_{t,\mathrm{cal.}}$ are experimental and calculated amount of Hg(II) adsorbed on EIR surface at time 't' and N is the number of measurements made. Table 3 presents the values of $\Delta q(\%)$ and correlation coefficients (R^2). The value of $\Delta q(\%)$ for Bangham kinetic model is very low compared to that for other kinetic models. The values of correlation coefficients for the sorption of Hg(II) onto EIR from all the systems were found to be 0.97 for pseudo-first-order kinetic model, 0.96–0.97 for pseudo-second-order kinetic model, 0.97 for Elovich kinetic model and 0.999 for Bangham kinetic model. Based on correlation coefficients and $\Delta q(\%)$ values (Table 3), it is evident that the sorption of Hg(II) can be best explained using the Bangham kinetic model. Since the double logarithmic plot according to Bangham equation yields the most perfect linear curves for mercury removal by TAN/XAD-4, the diffusion of Hg(II) ion into the pores of the EIR beads is the only rate-controlling step [49]. These results can be elucidated by considering the macroporous structure of the EIR beads and, also, vigorous agitation of the solution in batch experiments, which can eliminate the film mass-transfer resistance. In a fixed-bed reactor, unlike agitated-batch reactor, the external mass-transfer resistance (film diffusion resistant) may distribute in the sorption process and, thus, the above kinetic results can not be used for designing a fixed-bed reactor for the removal of Hg(II) from aqueous solutions.

Since the pore diffusion process can be rigorously described by the Fick's law [50], the validity of pore diffusion, as the rate-controlling step, can be judged again by using this equation. Also, the pore diffusion coefficients of Hg(II) ions, D_p values, can be determined. This equation can describe counter diffusion of two species in a quasi-homogeneous media. If the pore diffusion controls the mass-transfer of ions from a volume of solution into the spherical chelating ion-exchange particle, the relationship between the degree of fractional attainment to equilibrium (X_t) and the reaction time (s) is given as follows [51].

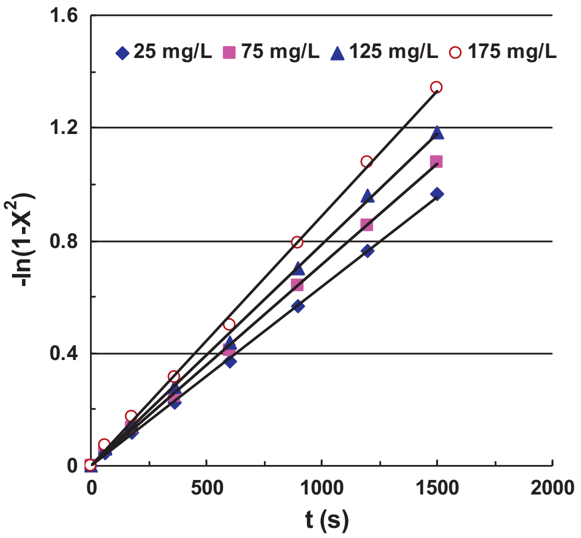

Fig. 13. Linear plots of function $-\ln(1-x_t^2)$ versus time (t; s) at the different initial concentrations.

$$-\ln(1-X_t^2) = kt \quad \text{where} \quad k = \frac{D_\mathrm{P}\pi^2}{r_0^2} \tag{14}$$

In the above equation, r_0 is the average radius of the EIR particles (3.2×10^{-4} m), and X_t values are equal to q_t/q_e at various times. Linear plots based on the above equation are shown in Fig. 13 for different initial concentrations. Also, pore diffusion coefficients, D_p ($m^2\,s^{-1}$) values, were calculated at different initial concentrations using the above equation. The results are present in Table 4. Based on the high correlation coefficients which obtained from the Fick's law (Table 4), it is completely clear that the pore diffusion is the rate-controlling step in the sorption process. The values of D_p increase from 6.62×10^{-12} to 9.22×10^{-12} $m^2\,s^{-1}$, as the initial concentration increases from 25 to 175 mg L^{-1} for the sorption of Hg(II) into the pores of EIR beads.

Table 4
Linear regression analysis of function $-\ln(1-X^2)$ versus time (t) at the different initial concentrations.

Initial concentration ($\mathrm{mg\,L^{-1}}$)	Equation	R^2	D_p ($\mathrm{m^2\,s^{-1}}$)
25	$y = 6.38 \times 10^{-4} \times + 4.73 \times 10^{-7}$	0.9991	6.62×10^{-12}
75	$y = 7.13 \times 10^{-4} \times + 5.35 \times 10^{-7}$	0.9993	7.40×10^{-12}
125	$y = 7.88 \times 10^{-4} \times + 7.61 \times 10^{-7}$	0.9986	8.18×10^{-12}
175	$y = 8.88 \times 10^{-4} \times + 7.04 \times 10^{-6}$	0.9987	9.22×10^{-12}

3.11. *Desorption studies and reusability*

Desorption studies help to regenerate the EIR, as to well as recover Hg (II) from the spent EIR. From the economic point of view, reusability of EIR is of crucial importance and adsorbed Hg(II) should be easily desorbed without destroying the EIR under the suitable conditions. For desorption of Hg(II) ions from the EIR, Hg(II) loaded EIR particles were stirred with three mineral acids including H_2SO_4, HCl and HNO_3. Consequently, a number of experiments with the shaking speed of 220 rpm were carried out in which the recovery of Hg(II) was investigated against the change in volume and concentration of mineral acid solutions as the eluents. Among them, HCl was preferred owing to protect EIR from damage and the recovery results of Hg(II) from spent EIR. By using H_2SO_4 or HNO_3 solution as desorption agent, only partial or incomplete Hg (II) desorption was achieved even in high concentrations. The maximum desorption efficiency (>99%) was obtained by using 10 mL HCl 0.5 M. Therefore, 0.5 M HCl solution (10 mL) was selected as eluent. The higher desorption of Hg(II) by HCl is obviously due to the formation of stable chloride complexes in the eluent solution.

The reusability and stability of the EIR were also tested in 25 successive sorption–desorption cycles. During 25 cycles of operation, only a minor or negligible loss (<1%) in the sorption efficiency of EIR was occurred. Thus, TAN/XAD-4 seems to be stable and can be used repeatedly without significantly loosing the sorption capacity for Hg(II).

4. Conclusions

In this study, TAN impregnated XAD-4 was found to be a suitable adsorbent support for the removal of Hg(II) from water and wastewaters. Batch sorption experiments were carried out for the removal of Hg(II) from aqueous solutions using TAN/XAD-4 at the maximum impregnated ratio. The sorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time temperature, and adsorbent dosages. The removal process was highly pH dependent and best results were obtained at narrow pH range of 5–6. Increase in mass of adsorbent leads to increase in metal ion sorption due to increase in number of chelating ion exchange sites. The equilibrium time for sorption of Hg(II) from aqueous solutions was achieved within 55 min of contact time. The sorption process carries out by chelating ion exchange mechanism. The sorption of Hg(II) onto new EIR was found to increase with increase in temperature. Sorption isotherm and thermodynamic studies indicated monolayer and spontaneous nature of Hg(II) sorption by the EIR. Kinetic sorption data indicate the applicability of Bangham kinetic model than other kinetic models for the sorption process. The diffusion coefficients, D_p values, calculated were found to be in the order of $10^{-12}\,\mathrm{m^2\,s^{-1}}$ under the concentrations and other conditions of studied. The maximum sorption capacity of TAN/XAD-4 for the removal of Hg(II) from aqueous solution was found to be $450.45\,\mathrm{mg\,g^{-1}}$ at 25 °C. Complete removal of Hg(II) from aqueous solutions having initial concentration $100\,\mathrm{mg\,L^{-1}}$ can be achieved by using a minimum of $0.5\,\mathrm{g\,L^{-1}}$ of EIR. The new EIR could be successfully recycled for several consecutive cycles without significant loss in its sorption capacity.

Acknowledgement

The authors wish to take this opportunity to express their sincere thanks to Dr Mohammad Shayegan-Mehr, the president of Islamic Azad University-Kashmar branch, Kashmar, Iran, for his great supports during the experimental works.

References

[1] A. Sigel, H. Sigel, Metal ions in biological systems, in: A. Sigel, H. Sigel (Eds.), Mercury and Its Effects on Environment and Biology, vol. 34, Dekker, NewYork, 1997.

[2] I. Ghodbane, O. Hamdaoui, Removal of mercury(II) from aqueous media using eucalyptus bark: kinetic and equilibrium studies, J. Hazard. Mater. 160 (2008) 301–309.

[3] E.P.C. Lai, B. Wong, V.A. Vandernoot, Preservation of solid mercuric dithizonate samples with polyvinyl chloride for determination of mercury(II) in environmental waters by photochromism-induced photoacoustic spectrometry, Talanta 40 (1993) 1097–1105.

[4] M. Madhava Rao, D.H.K. Kumar Reddy, P. Venkateswarlu, K. Seshaiah, Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste, J. Environ. Manage. 90 (2009) 634–643.

[5] H. Yavuz, A. Denizli, H. Güngünes, M. Safarikova, I. Safarik, Biosorption of mercury on magnetically modified yeast cells, Sep. Purif. Technol. 52 (2006) 253–260.

[6] F.S. Zhang, J.O. Nriagu, H. Itoh, Mercury removal from water using activated carbons derived from organic sewage sludge, Water Res. 39 (2005) 389–395.

[7] D.M. Manohar, K. Anoop Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay, Water Res. 36 (2002) 1609–1619.

[8] Q. Feng, Q. Lin, F. Gong, S. Sugita, M. Shoya, Adsorption of lead and mercury by rice husk ash, J. Colloid Interface Sci. 278 (2004) 1–8.

[9] A.A. Atia, A.M. Donia, K.Z. ELwakeel, Selective Separation of Mercury(II) using a synthetic resin containing amine and mercaptan as chelating groups, React. Funct. Polym. 56 (2005) 267–275.

[10] C. Ji, S. Song, C. Wang, C. Sun, R. Qu, C. Wang, H. Chen, Preparation and adsorption properties of chelating resins containing 3-aminopyridine and hydrophilic spacer arm for Hg(II), Chem. Eng. J. 165 (2010) 573–580.

[11] H. Bessbousse, T. Rhlalou, J.-F. Verchère, L. Lebrun, Mercury removal from wastewater using a poly(vinylalcohol)/poly(vinylimidazole) complexing membrane, Chem. Eng. J. 164 (2010) 37–48.

[12] A.A. Atia, Studies on the interaction of mercury(II) and uranyl(II) with modified chitosan resins, Hydrometallurgy 80 (2005) 13–22.

[13] A.A. Atia, A.M. Donia, K.Z. ELwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, J. Hazard. Mater. 151 (2008) 372–379.

[14] C.O. Illanes, N.A. Ochoa, J. Marchese, Kinetic sorption of Cr(VI) into solvent impregnated porous microspheres, Chem. Eng. J. 136 (2008) 92–98.

[15] A.G. Strikovsky, K. Jerábek, J.L. Cortina, A.M. Sastre, A. Warshawsky, Solvent impregnated resin (SIR) containing dialkyl dithiophosphoric acid on Amberlite XAD-2: extraction of copper and comparison to the liquid–liquid extraction, React. Funct. Polym. 28 (1996) 149–158.

[16] S. Seyhan, M. Merdivan, N. Demirel, Use of o-phenylene dioxydiacetic acid impregnated in Amberlite XAD resin for separation and preconcentration of uranium(VI) and thorium(IV), J. Hazard. Mater. 152 (2008) 79–84.

[17] M.T. Draa, T. Belaid, M. Benamor, Extraction of Pb(II) by XAD-7 impregnated resins with organophosphorus extractants (DEHPA, IONQUEST 801, CYANEX 272), Sep. Purif. Technol. 40 (2004) 77–86.

[18] M.S. Hosseini, H. Raissi, S. Madarshahian, Synthesis and application of a new chelating resin functionalized with 2,3-dihydroxy benzoic acid for Fe(III) determination in water samples by flame atomic absorption spectrometry, React. Funct. Polym. 66 (2006) 1539–1545.

[19] E. Metwally, Kinetic studies for sorption of some metal ions from aqueous acid solutions onto TDA impregnated resin, J. Radioanal. Nucl. Chem. 270 (2006) 559–566.

[20] R.S. Juang, J.Y. Su, Sorption of copper and zinc from aqueous sulfate solutions with bis(2-ethylhexy1)phosphoric acid-impregnated macroporous resin, Ind. Eng. Chem. Res. 31 (1992) 2774–2779.

[21] B. Saha, R.J. Gilla, D.G. Baileya, N. Kabay, M. Arda, Sorption of Cr(VI) from aqueous solution by Amberlite XAD-7 resin impregnated with Aliquat 336, React. Funct. Polym. 60 (2004) 223–244.

[22] I. Narin, M. Soylak, The uses of 1-(2-pyridylazo) 2-naphtol (pan) impregnated Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry, Talanta 60 (2003) 215–221.

[23] G.P.C. Rao, S.S. Veni, K. Pratap, Y.K. Rao, K. Seshaiah, Solid phase extraction of trace metals in seawater using morpholine dithiocarbamate-loaded Amberlite XAD-4 and determination by ICP-AES, Anal. Lett. 39 (2006) 1009–1021.

[24] M.S. Hosseini, M. Hosseini, A. Hosseini-Bandegharaei, Solvent impregnated resins containing quinizarin. Preparation and application to the extraction and separation of Cu(II), Cd(II), Ni(II) and Zn(II) prior to the determination by flame atomic absorption spectrometry, Sep. Sci. Technol. 42 (2007) 3465–3480.

[25] M.S. Hosseini, A. Hosseini-Bandegharaei, M. Hosseini, Column-mode separation and preconcentration of some heavy metal ions by solvent impregnated resins containing quinizarin before the determination by flame atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 89 (2009) 35–48.

[26] M.S. Hosseini, A. Hosseini-Bandegharaei, Selective extraction of Th(IV) over U(VI) and other co-existing ions using eosin B-impregnated Amberlite IRA-410 resin beads, J. Radioanal. Nucl. Chem. 283 (2010) 23–30.

[27] M.S. Hosseini, A. Hosseini-Bandegharaei, H. Raissi, F. Belador, Sorption of Cr(VI) by Amberlite XAD-7 resin impregnated with brilliant green and its determination by quercetin as a selective spectrophotometric reagent, J. Hazard. Mater. 169 (2009) 52–57.

[28] A. Hosseini-Bandegharaei, M.S. Hosseini, M. Sarw-Ghadi, S. Zowghi, E. Hosseini, H. Hosseini-Bandegharaei, 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), Chem. Eng. J. 160 (2010) 190–198.

[29] A.M. Starvin, T. Prasada Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, J. Hazard. Mater. B113 (2004) 75–79.

[30] L.S.G. Teixeira, F.R.P. Rocha, M. Korn, B.F. Reis, S.L.C. Ferreira, A.C.S. Costa, Flow-injection solid-phase spectrophotometry for the determination of zinc in pharmaceutical preparations, Anal. Chim. Acta 383 (1999) 309–315.

[31] B.F. Reis, F.R.P. Rocha, L.S.G. Teixeira, A.C.S. Costa, M. Korn, Construction of a flow cell for measurements by solid-phase spectrophotometry, Quim. Nova 23 (2000) 116–118.

[32] L.S.G. Teixeira, F.R.P. Rocha, M. Korn, B.F. Reis, S.L.C. Ferreira, A.C.S. Costa, Nickel and zinc determination by flow-injection solid-phase spectrophotometry exploiting different sorption rates, Talanta 51 (2000) 1027–1033.

[33] L.S.G. Teixeira, J.O.N. Reis, A.C.S. Costa, S.L.C. Ferreira, M.G.A. Korn, J.B. de Andrade, ICP–AES determination of small amounts of zinc in copper-base alloys after separation by adsorption of the zinc–TAN complex on Sep Pak C18 cartridges, Talanta 46 (1998) 1279–1283.

[34] B. Kuswandi, R. Narayanaswamy, Characterisation of Hg(II) ion optrode based on nafion-1-(2-thiazolylazo)-2-7 naphthol composite thin films, J. Environ. Monit. 1 (1999) 109–114.

[35] S. Baytak, A.R. Türker, The use of Agrobacterium tumefacients immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron (II), cobalt(II), manganese(II), and chromium(III), Talanta 65 (4) (2005) 938–945.

[36] Y Liu, X. Chang, S. Wang, Y. Guo, B. Din, S. Meng, Solid-phase spectrophotometric determination of nickel in water and vegetable samples at sub-$\mu g\,L^{-1}$ level with o-carboxylphenyldiazoaminoazobenzene loaded XAD-4, Talanta 64 (1) (2004) 160–166.

[37] A. Uzun, M. Soylak, L. Elçi, Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd, and Bi at trace levels in waste water samples by flame atomic absorption spectrometry, Talanta 54 (2001) 197–202.

[38] E.J.D Santos, A.B. Herrmann, A.S. Ribeiro, A.J. Curtius, Determination of Cd in biological samples by flame AAS following on-line preconcentration by complexation with O,O-diethyldithiophosphate and solid phase extraction with Amberlite XAD-4, Talanta 65 (2005) 593–597.

[39] D. Muraviev, Surface impregnated sulfonate ion exchangers: preparation, properties and application, Solvent. Extr. Ion Exch. 16 (1998) 381–457.

[40] D. Muraviev, L. Ghantous, M. Valiente, Stabilization of solvent-impregnated resin capacities by different techniques, React. Funct. Polym. 38 (1998) 259–268.

[41] N. Kabay, M. Arda, B. Saha, M. Streat, Removal of Cr(VI) by solvent impregnated resins (SIR) containing aliquat 336, React. Funct. Polym. 54 (2003) 103–115.

[42] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[43] H. Freundlich, Adsorption in solution, Phys. Chem. Soc. 40 (1906) 1361–1368.

[44] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[45] S. Lagergren, About the theory of so called adsorption of soluble substance, Kungliga svenska vertenskapsakademiens, Hand linger 24 (1898) 1–39.

[46] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.

[47] S.H. Chein, W.R. Clayton, Application of elovich equation to the biomass of phosphate release and sorption on soil, Soil Sci. Soc. Am. J. 44 (1980) 265–268.

[48] C. Aharoni, S. Sideman, E. Hoffer, Adsorption of phosphate ions by colloid ion-coated alumina, J. Chem. Technol. Biotechnol. 29 (1979) 404–412.

[49] A.K. Jain, V.K. Gupta, S. Jain, Suhas, Removal of chlorophenols using industrial wastes, Environ. Sci. Technol. 38 (2004) 1195–1200.

[50] M. Streat, J.W. Patrick, M.J. Camporro Perez, Sorption of phenol and parachlorophenol from water using conventional and novel activated carbons, Water Res. 29 (2) (1995) 467–472.

[51] M. Hajjaji, S. Kacim, A. Alami, A. El Bouadili, M. El Mountassir, Chemical and mineralogical characterisation of a clay taken from the Moroccan meseta and a study of the interaction between its fine friction and methylene blue, Appl. Clay Sci. 20 (2001) 1–12.