



## Removal of Hg<sup>2+</sup> ions from aqueous solution by ETS-4 microporous titanosilicate—Kinetic and equilibrium studies

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### ABSTRACT

Batch stirred tank experiments were carried out to study the application of ETS-4 microporous titanosilicate for Hg<sup>2+</sup> ions removal from aqueous solution. The effect of operational conditions was assessed and it was proved that Hg<sup>2+</sup> uptake (%) increases with increasing contact time, increasing ETS-4 mass and decreasing initial Hg<sup>2+</sup> concentration. It was confirmed that stirring rate does not affect the Hg<sup>2+</sup> removal by ETS-4 as long as it is high enough to break the diffusion resistance.

Two simplified models, the pseudo first-order and the pseudo second-order equations, were used to describe the kinetics of the sorption process and better fittings were obtained by the last one. The Bt versus t plots indicated that film diffusion is the rate-limiting step of the removal of Hg<sup>2+</sup> by ETS-4. Langmuir, Freundlich and Dubinin–Radushkevich isotherm equations fitted quite well the equilibrium data and the Langmuir maximum capacity of ETS-4 was found to be 246 mg g<sup>-1</sup> at 21 °C.

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### 1. Introduction

Water pollution due to mercury trace metal is recognised worldwide as a serious environmental and public problem. The great concern about mercury pollution is due to its persistent character in the environment and biota as well as bioamplification and bioaccumulation along the food chain. Natural inputs resulting from the weathering of mercuriferous areas, degassing from surface water and earth's crust through volcanic eruptions, naturally-caused forest fires and biogenic emissions [1], combined with the global anthropogenic sources (such as production of chloro-alkalis, pharmaceutical and cosmetic preparations, electrical instruments, pulp and paper industries, recovery of gold by artesian miners, fossil-fuel burning, mining, metallurgical processes, fertilizer industries and a wide variety of products of common use, like thermometers, batteries, fluorescent lamps and medical drugs) [1–5] make mercury pollution a planetary-scale problem. However, due to its high toxicity, strict environmental policies have been required on this metal discharges. In the European Union mercury is considered as a priority and hazardous pollutant, its maximum permissible concentration for wastewater discharge being 5 µg L<sup>-1</sup>, while for drinking water is 1 µg L<sup>-1</sup>. Furthermore, under Directive 2000/60/CE, the European Union regulated the cessation or phasing out of dis-

charges, emissions and losses by 2020 [4]. Consequently, the development of efficient new materials and clean-up technologies for removing mercury from effluents is extremely urgent [6–11].

Some studies have demonstrated that titanosilicates are excellent materials to remove Hg<sup>2+</sup> from aqueous solutions [12–15]. Because of their unique structure, these materials display important chemical and physical properties, such as selective sorption, ion exchange and catalytic activity. Titanosilicate ETS-4 (Engelhard titanosilicates number 4, Na<sub>9</sub>Ti<sub>5</sub>Si<sub>12</sub>O<sub>38</sub>(OH)·12H<sub>2</sub>O) is one of the main members of a class of microporous heteropolyhedral transition-metal silicates. The frameworks of this microporous material and mineral zorite are identical, and are highly disordered [16]. Two orthogonal sets of channels are defined by 12-T/O and 8-T atoms rings (T = tetrahedral silicon; O = octahedral titanium) [8]. Its framework comprises corner-sharing SiO<sub>4</sub> tetrahedra, TiO<sub>5</sub> pentahedra and TiO<sub>6</sub> octahedra (Fig. 1). Each titanium ion has an associated –2 charge, which is neutralised by extra-framework cations usually Na<sup>+</sup> and K<sup>+</sup>. The possibility of replacement of those cations by others, such as Hg<sup>2+</sup>, makes ETS-4 a good ion exchange based sorbent.

In this work, the efficiency of ETS-4 for the removal of mercury (II) from aqueous solution was investigated and the effect of operating parameters on the sorption efficiency was assessed. The sorption equilibrium and kinetics of Hg<sup>2+</sup> onto ETS-4 were studied and the experimental results were described by well-known kinetic and equilibrium equations.

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## Nomenclature

$B_t$	mathematical function of $F$ in Eqs. (7)–(9)
$C$	concentration of $\text{Hg}^{2+}$ in bulk solution, ( $\mu\text{g L}^{-1}$ )
CV-AFS	cold vapour atomic fluorescence spectroscopy
$D$	Polanyi potential in Eq. (12)
$E$	mean energy of sorption, ( $\text{kJ mol}^{-1}$ )
$F$	fraction of solute adsorbed at different times $t$ in Eqs. (7) and (8)
$K_F$	Freundlich parameter in Eq. (11), ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )
$K_L$	Langmuir constant in Eq. (10), ( $\text{L} \mu\text{g}^{-1}$ )
$k_1$	first-order rate constant in Eqs. (3) and (4), ( $\text{h}^{-1}$ )
$k_2$	second-order rate constant in Eqs. (5) and (6), ( $\text{g mg}^{-1} \text{h}^{-1}$ )
$M$	dry weight of ETS-4, (mg)
$n$	Freundlich parameter in Eq. (11)
$q$	concentration of $\text{Hg}^{2+}$ in the particle (ETS-4), ( $\text{mg g}^{-1}$ )
$q_D$	theoretical D–R maximum capacity in Eq. (12), ( $\text{mg L}^{-1}$ )
$Q$	maximum Langmuir capacity in Eq. (10), ( $\text{mg g}^{-1}$ )
$V$	volume of solution, (L)

## Greek letters

$\beta_D$	D–R model constant in Eq. (12), ( $\text{mol}^{-2} \text{kJ}^{-2}$ )
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## Subscripts

0	initial condition of experiment
$t$	intermediate condition of the experiment at a certain time
$e$	equilibrium condition of experiment

## 2. Experimental

### 2.1. Chemicals

All chemical reagents used in this work were of analytical reagent grade, obtained from chemical commercial suppliers and were used without further purification. The certified standard stock solution of mercury(II) nitrate was purchased from BDH Chemicals Ltd.

### 2.2. Equipment

Mercury analysis were performed by cold vapour atomic fluorescence spectroscopy (CV-AFS), on a PSA cold vapour generator, model 10.003, associated with a Merlin PSA detector, model 10.023 and using  $\text{SnCl}_2$  as reducing agent.

### 2.3. Material

The synthesis of ETS-4 was performed as follows [12]: an alkaline solution was made by dissolving 33.16 g of metasilicate (BDH), 2.00 g NaOH (Merck), and 3.00 g KCl (Merck) into 25.40 g  $\text{H}_2\text{O}$ . 31.88 g of  $\text{TiCl}_3$  (15% m/m  $\text{TiCl}_3$  and 10% m/m HCl, Merck) were added to this solution and stirred thoroughly. The gel, with a molar composition 5.9  $\text{Na}_2\text{O}$ : 0.7  $\text{K}_2\text{O}$ : 5.0  $\text{SiO}_2$ : 1.0  $\text{TiO}_2$ : 114  $\text{H}_2\text{O}$ , was transferred to a Teflon-lined autoclave and treated at 230 °C for 17 h under autogenous pressure without agitation. The product was filtered off, washed at room temperature with distilled water, and dried at 70 °C overnight, the final product being an off-white microcrystalline powder. Main relevant properties of ETS-4 related to its sorption capacity have been shown elsewhere [12].

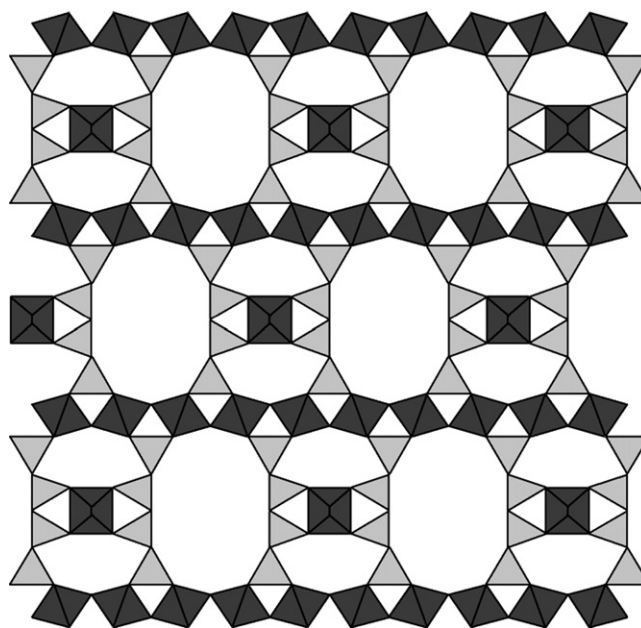


Fig. 1. Schematic representation of ETS-4 structure [13]. The centres of black octahedra and grey tetrahedra are occupied by Ti and Si atoms, respectively. Extra framework cations and water molecules have been omitted for clarity.

### 2.4. Sorption studies: effect of stirring velocity, contact time, mass of titanosilicate and initial concentration of $\text{Hg}^{2+}$

All batch experiments were performed by contacting under agitation 2 L of  $\text{Hg}^{2+}$  solution and ETS-4 in volumetric flasks at  $21 \pm 1$  °C. The effect of each parameter on the ETS-4 sorption capacity was studied individually, by changing the study parameter and keeping all the others constant. The stirring rate effect on  $\text{Hg}^{2+}$  removal by ETS-4 was studied for four different values (60, 500, 900 and 1400 rpm), using 8 mg of ETS-4 and an initial  $\text{Hg}^{2+}$  concentration of  $50 \mu\text{g L}^{-1}$ . The ETS-4 mass effect was evaluated at 1400 rpm, using nine different masses of ETS-4 (0.573, 0.851, 1.639, 2.220, 3.450, 5.055, 8.024, 12.201 and 16.233 mg) and an initial  $\text{Hg}^{2+}$  concentration of  $50 \mu\text{g L}^{-1}$ . For assessing the effect of initial  $\text{Hg}^{2+}$  concentration, 8 mg of ETS-4 were stirred at 1400 rpm together with  $\text{Hg}^{2+}$  solutions of different concentrations in the range of 50–250  $\mu\text{g L}^{-1}$ . The pH of the solution kept between 4 and 5 along all the experiments carried out. For each experiment, in order to evaluate the time necessary for solution–solid equilibrium, stirring was kept until  $\text{Hg}^{2+}$  concentration in solution remained constant.

$\text{Hg}^{2+}$  solutions were prepared daily by diluting the stock solution to the desired concentration, in high-purity water ( $18.2 \text{ M}\Omega \text{ cm}$ ). The experiments started at the time when known masses of ETS-4 were added to  $\text{Hg}^{2+}$  solutions and stirring was initiated. Aliquots (25 mL) were collected at increasing times, filtered through an acid-washed 0.45  $\mu\text{m}$  Millipore membrane, adjusted to pH <2 with  $\text{HNO}_3$   $\text{Hg}$  free and then analysed by CV-AFS.

All glassware used in the experiments was acid-washed prior to use and a blank experiment (without ETS-4) was always run as a control, to check that the  $\text{Hg}^{2+}$  removal occurred essentially by uptake onto the adsorbent particles and not by (e.g.) adsorption on the vessel walls.

The quantity of  $\text{Hg}^{2+}$  removed by ETS-4 at a given time  $t$  ( $q_t$ ,  $\text{mg g}^{-1}$ ) was deduced from the mass balance between initial concentration in solution and concentration after stirring during a time  $t$ :

$$q_t (\text{mg g}^{-1}) = (C_0 - C_t) \times \frac{V}{M} \quad (1)$$

where  $V/M$  is the batch factor, i.e. the volume of solution ( $L$ ) to dry weight of ETS-4 ( $mg$ ) ratio,  $C_0$  ( $\mu g L^{-1}$ ) is the initial  $Hg^{2+}$  concentration and  $C_t$  ( $\mu g L^{-1}$ ) is its concentration at time  $t$ . Upon mercury (II) removal,  $q_t$  increases and  $C_t$  decreases along time until equilibrium values ( $q_e$  and  $C_e$ ) are attained.

The results were also compared by uptake percentage, which at time  $t$  is defined by:

$$\text{Uptake}(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)$$

The kinetic of the sorption process was studied at several initial conditions (different ETS-4 masses and different initial  $Hg^{2+}$  concentrations) and the experimental results interpreted by two simple kinetic models commonly used: the semi-empirical pseudo-first order and the pseudo-second order kinetic equations [17–25].

The first order equation, firstly applied by Lagergren and Handlinger [17], is mathematically expressed by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

or after integration:

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

where  $k_1$  ( $h^{-1}$ ) is the rate constant. Accordingly, the validity of the model is shown by the linear trend observed when graphing experimental  $\log(q_e - q_t)$  as a function of  $t$ . The rate constant may be determined from the slope of the linear regression, as well as the intercept should match the  $q_e$  value previously introduced. However, it is well known that Lagergren model may not represent the sorption evolution along full time range [19,23].

The pseudo second-order equation may be also applicable and, in contrast with the previous model, usually correlates the behaviour over the whole range of sorption [18,20,23]. The kinetic rate equation is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where  $k_2$  ( $g mg^{-1} h^{-1}$ ) is the rate constant. By applying the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_e$ , the integrated form of Eq. (5) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

For the applicability of the model, the plot of  $t/q_t$  versus  $t$  should be linear so both  $k_2$  and  $q_e$  may be found from the corresponding intercept and slope.

In order to determine the actual rate-controlling step involved in the  $Hg^{2+}$  removal process, the adsorption data were further analyzed using Eq. (7):

$$F = 1 - \frac{6}{\pi^2} \exp(-B_t) \quad (7)$$

where  $F$  is the fraction of solute adsorbed at different times  $t$  and  $B_t$  is a mathematical function of  $F$  and  $F$  can be expressed as:

$$F = \frac{q_t}{q_e} \quad (8)$$

Substituting Eq. (8) into Eq. (7), the kinetic expression becomes:

$$B_t = -0.4977 - \ln \left( 1 - \frac{q_t}{q_e} \right) \quad (9)$$

Thus, the value of  $B_t$  can be calculated for each value of  $F$  using Eq. (9). If a plot of  $B_t$  versus  $t$  is a straight line passing through the origin, adsorption is most probably governed by a particle-diffusion mechanism, otherwise governed by film diffusion.

The equilibrium data fittings to the Langmuir (Eq. (10)), Freundlich (Eq. (11)) and Dubinin–Radushkevich (D–R) (Eq. (12)) isotherm equations were found:

$$q_e = \frac{Q K_L C_e}{1 + K_L C_e} \quad (10)$$

where  $K_L$  ( $L mg^{-1}$ ) and  $Q$  ( $mg g^{-1}$ ) are the Langmuir sorption equilibrium constant and maximum capacity of ETS-4, respectively;

$$q_e = K_F C_e^{1/n} \quad (11)$$

where  $K_F$  ( $mg^{1-1/n} L^{1/n} g^{-1}$ ) and  $n$  are the Freundlich parameters.  $n$  is usually between 1 and 10, which points out favourable adsorption, and is related to the non-linearity of the model.

$$q_e = q_D \exp(-\beta_D \varepsilon_D^2) \quad (12)$$

where  $q_D$  is the theoretical maximum capacity ( $mg L^{-1}$ ),  $\beta_D$  is the D–R model constant ( $mol^{-2} kJ^{-2}$ ),  $D^2$  is the Polanyi potential and is equal to:

$$\varepsilon_D = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (13)$$

The  $\beta_D$  is related to mean energy of sorption,  $E$  ( $kJ mol^{-1}$ ), which may be calculated by the following equation:

$$E = \frac{1}{\sqrt{2\beta_D}} \quad (14)$$

Fittings of experimental data to the above isotherms and the corresponding parameters were obtained by nonlinear regression analysis using GraphPad Prism 5 program, using the least-squares method and the Marquardt and Levenberg algorithm for minimizing the function.

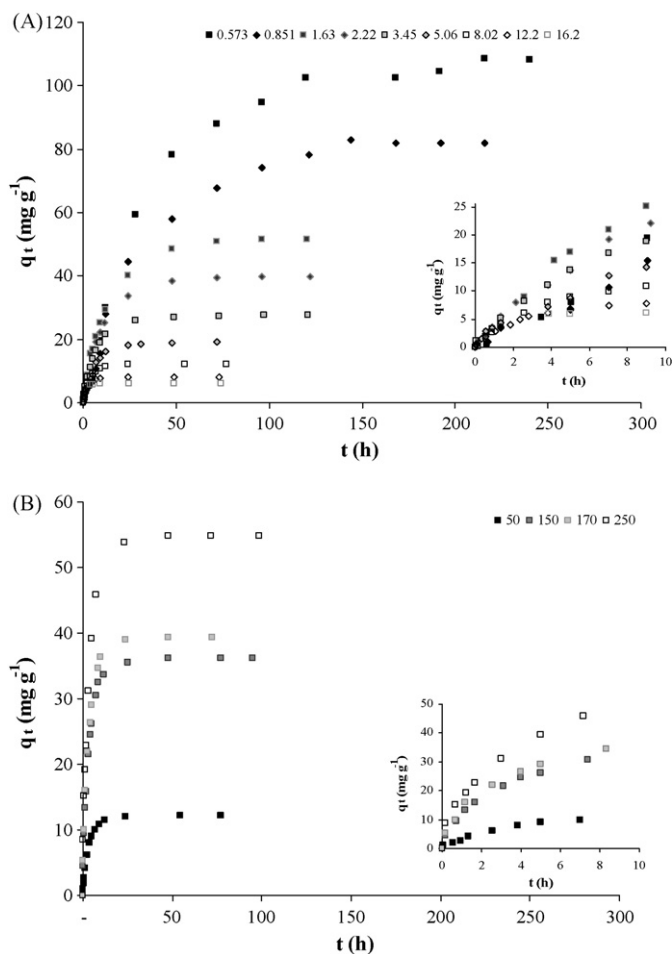
### 3. Results and discussion

#### 3.1. Stirring rate

The results obtained from the stirring rate study (data not shown) indicated that, except for the lowest agitation rate (60 rpm), the quantity of  $Hg^{2+}$  removed by ETS-4 at the equilibrium ( $12.1 \pm 0.1 mg g^{-1}$ ) and the  $Hg^{2+}$  uptake ( $98 \pm 1\%$ ) were not dependent of the stirring rate. However, it must be highlighted that the sorption was relatively slow for the lowest stirring velocity (60 rpm) here considered. At 60 rpm, the equilibrium time was ca. 150 h while for the others stirring rates the equilibrium time was 24 h. These results indicated that the diffusion of  $Hg^{2+}$  ions into the ETS-4 may be a limiting step for the sorption of  $Hg^{2+}$  and thus stirring used in experiments must be high enough to break the diffusion resistance.

#### 3.2. Contact time

Fig. 2 shows the kinetic curves corresponding to the sorption of  $Hg^{2+}$  onto ETS-4: (A) conducted for nine different masses of titanosilicate and for an initial  $Hg^{2+}$  concentration of  $50 \mu g L^{-1}$ ; (B) performed for 8 mg of ETS-4 and for four different concentrations. For all ETS-4 masses and  $Hg^{2+}$  concentrations used, a decrease with time on  $Hg^{2+}$  concentration in the liquid phase was observed, even when starting with a higher concentration ( $[Hg^{2+}] = 250 \mu g L^{-1}$ ). The uptake curves obtained from  $Hg^{2+}$  concentration and from ETS-4 mass effect experiments show that equilibrium is attained in 24 h for all  $Hg^{2+}$  concentrations used and for ETS-4 masses  $\geq 3.450$  mg. However, as long as ETS-4 mass decreases, the time necessary to attain the equilibrium increases. This fact is particularly notorious when comparing the equilibrium time for the lowest and the highest ETS-4 mass: 216 h for the lowest



**Fig. 2.** Variation of  $q_t$  ( $mg g^{-1}$ ) along with time at  $21 \pm 1$  °C. Conditions (A) Initial  $Hg^{2+}$  concentration of  $50 \mu g L^{-1}$  and different masses (mg) of ETS-4; (B) 8 mg of ETS-4 and different initial concentrations of  $Hg^{2+}$  ( $\mu g L^{-1}$ ).

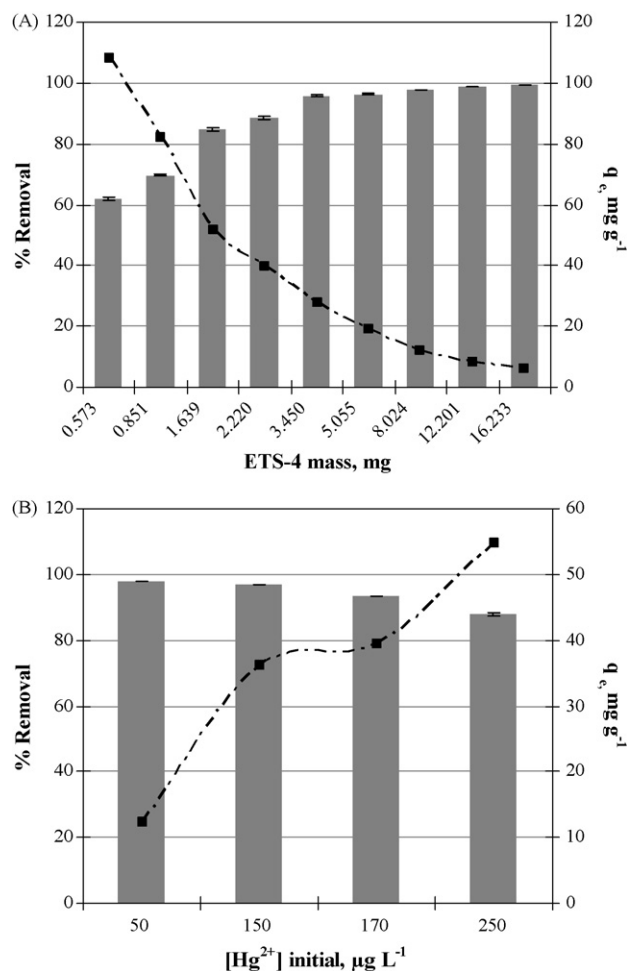
(0.573 mg) and 24 h for the highest one (16.233 mg) (Fig. 2A). On the other hand, full equilibrium time for different  $Hg^{2+}$  concentration is the same for all concentrations (24 h). Those results suggest that equilibrium time can be drastically affected by small variations in ETS-4 mass and not so much by  $Hg^{2+}$  concentration variations. The profile of the curves on the inset Fig. 2A and B reveal that during the first 10 h or so, the  $Hg^{2+}$  removal increased abruptly and then caught up approaching equilibrium.

### 3.3. Mass of titanosilicate

The amount of adsorbent is an important parameter to obtain quantitative metal removal, since it influences the contact time necessary to reach equilibrium and the sorption capacity.

Although the  $Hg^{2+}$  concentration in the liquid phase decreases with time for all ETS-4 masses used, the achieving of clean water, of drinking quality ( $[Hg^{2+}] \leq 2 \mu g L^{-1}$ ) [26] it was only possible with the employment of ETS-4 masses higher or equal than 3.45 mg.

As it was shown in Fig. 2A, the smaller the mass of ETS-4 titanosilicate used, the higher the amount of  $Hg^{2+}$  removed per gram of ETS-4 at the equilibrium. Thus, under the experimental conditions here used, the minimum  $q_e$  was 6.13 (for 16.2 mg of ETS-4) and the maximum was  $108 mg g^{-1}$  (for 0.573 mg of ETS-4). However, in absolute terms, mercury (II) uptake (%) decreases with decreasing ETS-4 mass (Fig. 3A), from 99.5% (16.2 mg) to 61.9% (0.573 mg). These results were expected because for an invariable initial  $Hg^{2+}$  concentration, increasing ETS-4 mass provides greater



**Fig. 3.** Effect of ETS-4 mass (A) and initial  $Hg^{2+}$  concentration (B) on the  $Hg^{2+}$  removal (%) (columns) and ETS-4 sorption capacity ( $mg g^{-1}$ ) (line).

surface area and increases the number of available sorption sites [27].

The rate constants ( $k_1$  and  $k_2$ ) and the  $q_e$  values in Eqs. (4) and (6) are presented in Table 1 for the different masses of ETS-4 together with the correlation coefficient ( $R^2$ ) corresponding to linear fittings. Both rate constants increase with the increasing of ETS-4 mass (Table 1), which mathematically reinforces that the higher is the mass used, the faster equilibrium is reached. The theoretical curves of  $q_t$  along time were calculated by the application of each kinetic equation and using the related parameters (Table 1). Fig. 4 shows the experimental results corresponding to the sorption of  $Hg^{2+}$  onto different masses of ETS-4 together with the fittings to the considered first-order and second-order kinetic equations. Comparing the experimental and fitted  $q_t$  values in Fig. 4, it may be said that the sorption of  $Hg^{2+}$  ions is better described by the pseudo-second order kinetic model. Furthermore, the first-order kinetic model underestimates the  $q_t$  values during almost full time range, while the second-order kinetic model fits the  $Hg^{2+}$  removed during the first quick stage of sorption and also when equilibrium is achieved.

### 3.4. $Hg^{2+}$ initial concentration

The initial metal concentration is also an important parameter because influences the metal uptake mechanism [28] since at increasing metal concentrations ETS-4 capacity gets saturated. In the range of concentrations studied, a noticeably increase in the

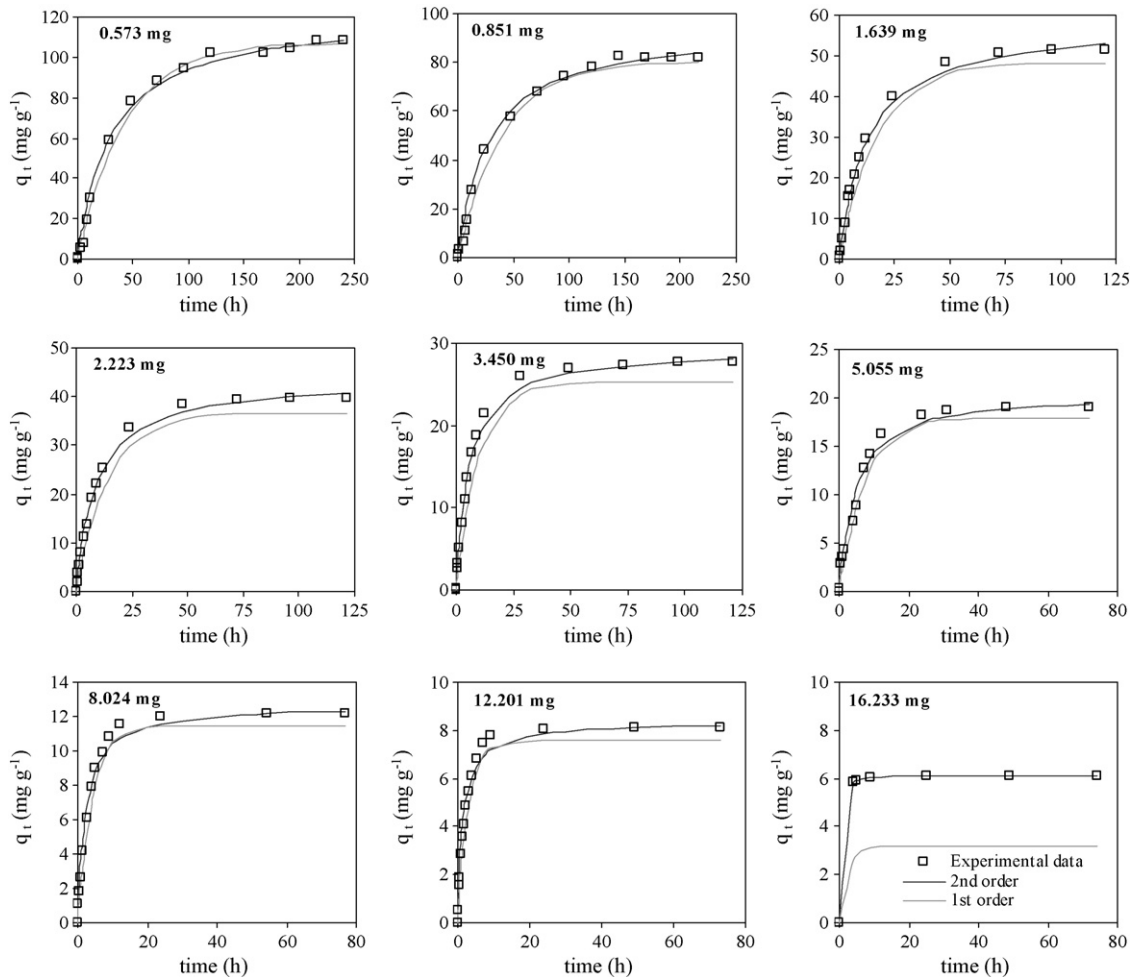
**Table 1**

Kinetic sorption rate constants,  $k_1$  (pseudo first-order Lagergren) and  $k_2$  (pseudo second-order), together with experimental  $q^{\text{-exp}}$  and calculated  $q^{\text{-fitted}}$   $q_e$ , and the corresponding correlation coefficients ( $R^2$ ) of the fittings.

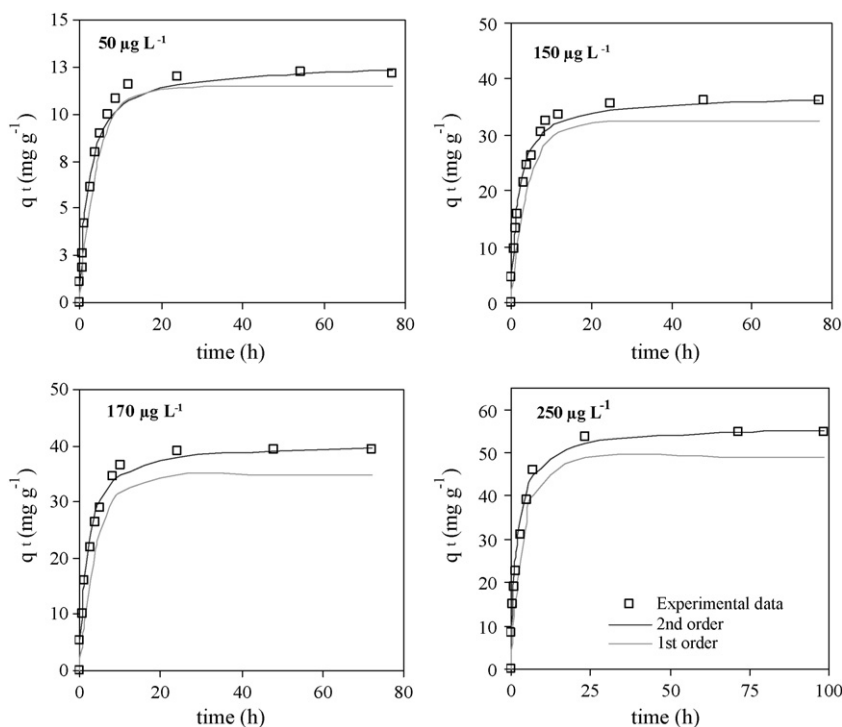
	$q_e^{\text{-exp}}$ (mg g <sup>-1</sup> )		First-order kinetics		Second-order kinetics			
			$k_1$ (h <sup>-1</sup> )	$R^2$	$q_e^{\text{-fitted}}$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	$R^2$	$q_e^{\text{-fitted}}$ (mg g <sup>-1</sup> )
Adsorbent (mg)	0.573	108.09	0.024	0.992	107.05	0.0003	0.998	121.95
	0.851	81.90	0.025	0.995	80.46	0.0004	0.998	94.34
	1.63	51.68	0.058	0.995	48.29	0.0014	0.997	58.48
	2.22	39.89	0.070	0.994	36.70	0.0025	0.999	43.67
	3.45	27.77	0.102	0.984	25.26	0.0061	0.999	29.33
	5.06	19.07	0.136	0.988	17.96	0.0105	0.997	20.66
	8.02	12.19	0.240	0.997	11.49	0.0366	0.999	12.63
	12.2	8.115	-0.351	0.998	7.57	0.0839	1.000	8.33
Adsorbate (μg L <sup>-1</sup> )	16.2	6.127	0.436	0.828	3.18	0.8708	1.000	6.15
	50	12.19	0.238	0.995	11.46	0.0366	0.999	12.63
	150	36.13	0.247	0.994	32.42	0.0160	1.000	36.90
	170	39.38	0.245	0.995	34.84	0.0148	1.000	40.49
	250	54.77	0.237	0.993	48.99	0.0098	1.000	56.18

amount of Hg<sup>2+</sup> removed per gram of ETS-4 was observed to occur with the increase of the initial Hg<sup>2+</sup> concentration (Fig. 2B). The equilibrium  $q_e$  values ranged from 12.2 to 54.8 mg g<sup>-1</sup>, corresponding to initial Hg<sup>2+</sup> concentrations of 50 and 250 μg L<sup>-1</sup>, respectively. In contrast, the Hg<sup>2+</sup> uptake (%) increases with decreasing initial Hg<sup>2+</sup> concentration. This may be related to the fact that there are more available sites when there is a relatively fewer number of Hg<sup>2+</sup> ions [29]. The uptake is higher (98%) for the lower initial concentrations and the lowest value (88%) is reached for an initial concentration of 250 μg L<sup>-1</sup> Hg<sup>2+</sup> (Fig. 3B).

Fig. 5 shows the experimental kinetic results corresponding to the sorption of Hg<sup>2+</sup> onto ETS-4 for different initial concentrations together with the fittings corresponding to the pseudo first-order Lagergren and the pseudo second-order equations. The correlation coefficient ( $R^2$ ) corresponding to the fittings (Table 1) indicate that the experimental results are better correlated by second order model, which is also confirmed by the fittings shown in Fig. 5. Furthermore, by comparing the experimental and fitted  $q_t$  values, the first-order kinetic model underestimates the  $q_t$  over almost whole sorption range while the second-order kinetic model gives more



**Fig. 4.** Experimental kinetic results together with fittings corresponding to pseudo-first and pseudo-second-order equations for Hg<sup>2+</sup> sorption using different masses of ETS-4.



**Fig. 5.** Experimental kinetic results together with fittings corresponding to pseudo-first and pseudo-second-order equations for  $\text{Hg}^{2+}$  sorption starting from different initial  $\text{Hg}^{2+}$  concentrations.

comparable fitted  $q_e$  values with respect to the experimental ones (Table 1).

The calculated  $B_t$  values were plotted versus  $t$  as shown in Fig. 6. As it may be observed, plots have not a linear form and do not pass through the origin, which indicates that film diffusion is the main rate-limiting process [30].

### 3.5. Sorption equilibrium

The experimental equilibrium data ( $21 \pm 1^\circ\text{C}$ ) and modelled results using Langmuir, Freundlich and Dubinin–Radushkevich equations are shown in Fig. 7. The isotherms are positive and concave to the concentration axis and in the range of experimental conditions used and, as it may be seen, exist a good agreement between experimental data and the three isotherms considered. The correlation coefficients obtained for fittings to the Freundlich isotherm was ( $R^2 = 0.988$ ), to the Langmuir isotherm ( $R^2 = 0.975$ ) and to the Dubinin–Radushkevich isotherm ( $R^2 = 0.976$ ) confirm the agreement showed in the Fig. 7. Correlation coefficients are used to describe the fitness between experimental data and theoretic models, and the one corresponding to the Freundlich isotherm is slightly higher than those corresponding to fittings by Dubinin–Radushkevich and Langmuir isotherms.

The ETS-4 sorption capacity estimated by the Langmuir isotherm ( $Q$ ) is quite high compared with results found in the literature for the sorption of  $\text{Hg}^{2+}$  by materials such as activated carbon [31] or other adsorbents, as it is shown in Table 2.

Under the experimental conditions here used, according to the Langmuir isotherm,  $K_L = 37.08 \text{ L mg}^{-1}$  and  $Q = 246.3 \text{ mg g}^{-1}$ . The type of isotherm can be given by the separation factor  $R_L$ :

$$R_L = \frac{1}{1 + K_L C_0}$$

The isotherm is irreversible when  $R_L = 0$ ; favourable when  $0 < R_L < 1$ , linear when  $R_L = 1$  and unfavourable when  $R_L > 1$ . The calculated  $R_L$  value is 0.60, indicating that  $\text{Hg}^{2+}$  uptake by ETS-4 is favourable.

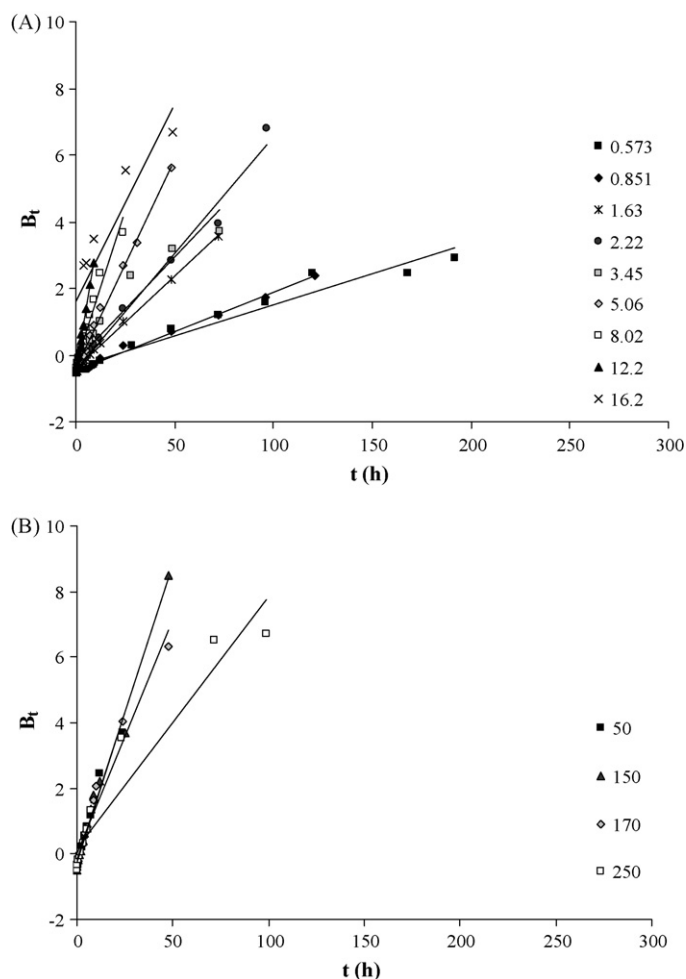
Regarding the Freundlich isotherm, the  $K_F = 1848 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$  and  $n = 1.37$ . Both  $K_F$  and  $n$  are empirical constants, related to adsorption capacity of the adsorbent and adsorption intensity, respectively [24], and their magnitudes indicate easy separation of  $\text{Hg}^{2+}$  from liquid phase and favourable sorption ( $1 < n < 10$ ).

With respect to the Dubinin–Radushkevich isotherm,  $q_D = 318.2 \text{ mg g}^{-1}$  and  $\beta_D = 0.0123 \text{ mol}^{-2} \text{ kJ}^{-2}$ . The calculated  $E = 6.38 \text{ kJ mol}^{-1}$ , which represents the free energy change when 1 mol of  $\text{Hg}^{2+}$  is transferred to the surface of the solid from infinity in solution. Although no absolutely sharp distinction can be made and intermediate cases exist, the magnitude of  $E$  is useful for estimating the type of adsorption reaction occurring so typically,  $E$  lies within  $8\text{--}16 \text{ kJ mol}^{-1}$  for ion-exchange mechanisms [40] and it is  $< 4 \text{ kJ mol}^{-1}$  in physisorption based processes [41]. As the term chemisorption is used in presence of adsorption energies comparable to the chemical bond energies, the ETS-4/ $\text{Hg}^{2+}$  system is in an energy range where chemical reactions can probably be heavily contributing to the process.

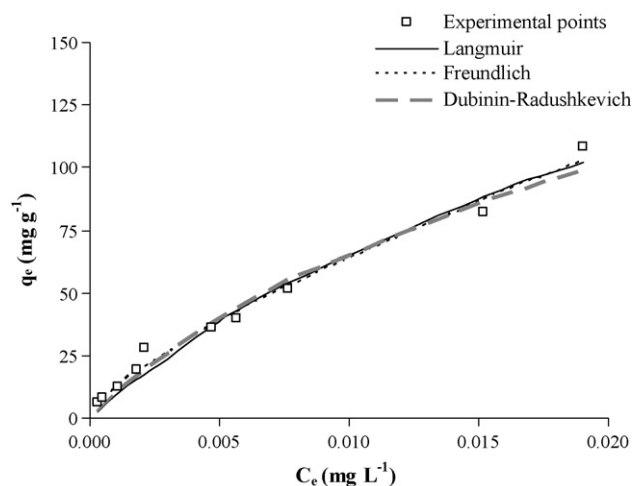
**Table 2**

Data on the Langmuir parameters available in the literature for the sorption of  $\text{Hg}^{2+}$  onto different materials.

Adsorbent	$Q$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	Temperature ( $^\circ\text{C}$ )	Reference
Rice husk ash	6.72	0.016	30	[32]
<i>Bacillus</i> sp.	7.94	1.120	25	[1]
Zeolitic mineral	10.1	0.238	–	[33]
Fly ash	13.4	0.083	–	[6]
Activated carbon	25.8	0.450	–	[34]
Eucalyptus bark	33.1	$13.9 \times 10^3$	–	[35]
Carbon aerogel	34.9	0.483	–	[8]
Activated carbon	43.8	0.239	30	[36]
Seaweed biomass	84.7	1.044	25	[37]
Yeast cells	93.4	0.158	25	[38]
Algal biomass	122.4	–	25	[39]
Papaya wood	155.6	0.004	30	[10]
Furfural carbon	174.0	–	–	[2]
Activated carbon	188.7	0.028	30	[31]



**Fig. 6.**  $B_t$  versus  $t$  plot for the ETS-4/ $Hg^{2+}$  system ( $21 \pm 1^\circ C$ ). (A) Initial  $Hg^{2+}$  concentration of  $50 \mu g L^{-1}$  and different masses (mg) of ETS-4; (B) 8 mg of ETS-4 and different initial concentrations of  $Hg^{2+}$  ( $\mu g L^{-1}$ ).



**Fig. 7.** Experimental equilibrium data together with fittings corresponding to the Langmuir, Freundlich and Dubinin–Radushkevich isotherms ( $21 \pm 1^\circ C$ ).

#### 4. Conclusions

The removal of  $Hg^{2+}$  from aqueous solution by ETS-4 microporous titanosilicate was investigated in batch mode under different experimental conditions. It was confirmed that as long as the

ETS-4/ $Hg^{2+}$  system is stirred highly enough to break the diffusion resistance, the  $Hg^{2+}$  is not affected by stirring rate. On the contrary, the batch experiments performed revealed that  $Hg^{2+}$  sorption by ETS-4 is strongly dependent on contact time, ETS-4 mass and initial  $Hg^{2+}$  concentration.

The  $Hg^{2+}$  uptake (%) from aqueous solutions increases with increasing contact time, with increasing ETS-4 mass and with decreasing initial  $Hg^{2+}$  concentration. After stirring during 24 h, total removal of  $Hg^{2+}$  was attained when using  $4 mg L^{-1}$  of ETS-4 for an initial  $Hg^{2+}$  concentration  $\leq 150 \mu g L^{-1}$ .

The kinetics of the removal of  $Hg^{2+}$  from aqueous solution by ETS-4 is well predicted by the pseudo-second order kinetic model and film diffusion is the rate-controlling step, according with the  $B_t$  versus  $t$  plot. Under the experimental conditions used in this work, the equilibrium results are well described by the Langmuir, Freundlich and Dubinin–Radushkevich isotherms, although the Freundlich one last gave slightly better fittings according with the correlation coefficients ( $R^2$ ). The maximum ETS-4 capacity ( $Q$ ) for  $Hg^{2+}$  ions predicted by Langmuir equation is  $246 mg g^{-1}$  at  $21 \pm 1^\circ C$ , which is quite high compared with the Langmuir capacities found in the literature for other materials, and the separation factor ( $R_L = 60$ ) indicate favourable  $Hg^{2+}$  sorption on ETS-4. The mean energy of sorption ( $E$ ,  $kJ mol^{-1}$ ), which was calculated from the Dubinin–Radushkevich isotherm parameters, indicated that chemical interactions are mostly responsible for the removal of  $Hg^{2+}$  by ETS-4.

On the whole, these results allow predicting mercury (II) removal from aqueous solution by ETS-4 and prove that this microporous titanosilicate has a great potential for mercury (II) purification from wastewater. Apart from ETS-4, other different titanosilicates and possible surface modifications are being studied so to be able to reach the desirable zero mercury levels in effluents by their use.

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