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Effect of pH and temperature on Hg^{2+} water decontamination using ETS-4 titanosilicate

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ABSTRACT

Batch stirred tank experiments were carried out to study the effect of pH (range 2–10, at 294 K) and temperature (277, 294 and 313 K, at pH 5) on the uptake of Hg^{2+} ions by ETS-4 microporous titanosilicate. Changes in the pH have a significant effect on the ETS-4 uptake efficiency, the optimal range being 4–6. Due to competition effects, the chemical used to adjust the pH of the Hg^{2+} solution also influences the uptake efficiency. Thermodynamic parameters for the uptake of Hg^{2+} ions were calculated. For the temperature range studied, the Hg^{2+} sorption increased with decreasing temperature.

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1. Introduction

Mercury's persistent character in the environment and biota, as well as bioamplification and bioaccumulation along the food chain, make mercury one of the most toxic pollutants present in the environment. Under the Water Framework Directive, the European Union regulated the cessation or phasing out of discharge emissions and losses by 2020 and, thus, it is appropriate to develop efficient new materials and clean-up technologies for removing mercury ions from solutions.

In the last few years, many studies have been published assessing different types of materials in the removal of metals from water and/or effluents. However, most of these studies deal with materials that are able to remove metals from very concentrated solutions but the final residual concentrations are relatively high. In fact, this is one of the major limitations of most of these materials since metals such as mercury are toxic even at very low levels.

It has been shown that the application of microporous titanosilicates for removing priority pollutants such as Hg^{2+} and Cd^{2+} ions from water may lead to the development of efficient clean-up technologies [1–4]. Among these microporous materials, the most promising for Hg^{2+} ions removal is titanosilicate ETS-4 ($Na_9Ti_5Si_{12}O_{38}(OH)\cdot 12H_2O$) a prominent member of the class of microporous heteropolyhedra transition-metal silicates. The framework of this material consists of two orthogonal sets of channels defined by 12-T/O and 8-T atoms rings (T-*t*etrahedral silicon; O-octahedral titanium) [5], and comprising corner-sharing SiO_4 tetrahedra, TiO_5 pentahedra and TiO_6 octahedra (Fig. 1). The presence of tetravalent sixfold Ti generates two negative charges balanced by ion-exchangeable alkali cations, usually Na^+, and affords ETS-4 excellent ion-exchange capacity for divalent heavy metals, such as Hg^{2+}. Unlikely other ion-exchangers, ETS-4 has such a high affinity for Hg^{2+} ions that only a few milligrams of the solid in aqueous suspension are able to attain such low residual concentrations that, after treatment, the water is suitable for drinking [6]. This evidences the enormous potential that this microporous titanosilicate has for the treatment of polluted effluents, in order to achieve "Zero Discharge or Totally Effluent Free" that will be required for mercury by the Water Framework Directive in the next 10 years. Moreover, on one hand, ETS-4 seems to be harmless for human health and the environment and, on the other hand, only a relatively small amount of ETS-4 is required for the complete removal of Hg^{2+} ions from polluted waters, which significantly reduces the application costs.

Although it has already been shown that ETS-4 is an ion-exchanger with a high Hg^{2+} sorption capacity [3,6], it is important to assess how this capacity depends on pH and temperature, which, due to their effect on the sorbent material and/or on the metal speciation, are known to highly affect the removal of heavy metals [7–11]. For example, pH determines the surface charge of the

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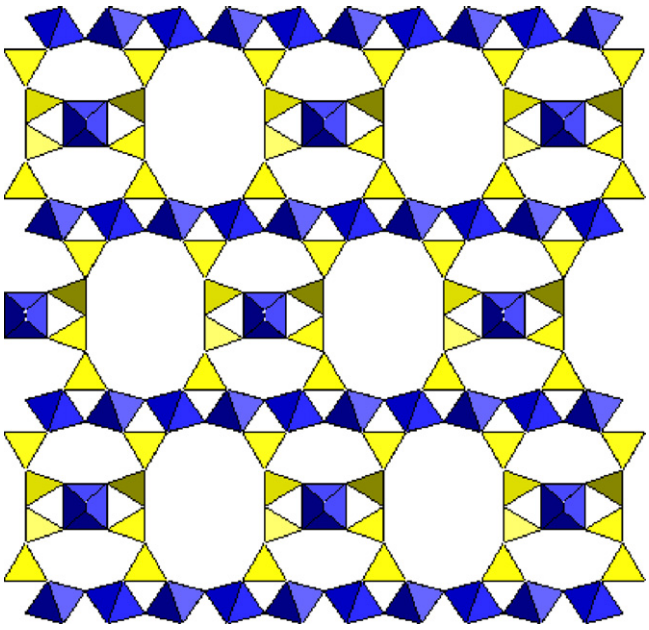

Fig. 1. Schematic representation of ETS-4 structure. Blue—TiO_6 octahedra and yellow—SiO_4 tetrahedra. Extra framework cations and water molecules are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

sorbent and the degree of ionisation and speciation of the species to be removed [10]. As a continuation of a previous work [6], the present study assesses the influence of pH and temperature on the ETS-4 efficiency in order to ascertain the optimal conditions for using this material in the treatment of water effluents.

2. Materials and methods

2.1. Chemicals and materials

All reagents used in this work were of analytical grade. They were obtained from chemical commercial suppliers and were used without further purification. Mercury (II) nitrate standard solution ($1000 \pm 2\,mg\,dm^{-3}$) was purchased from BDH Chemicals Ltd., and all working solutions were obtained by diluting the corresponding stock solution.

ETS-4 (Engelhard titanosilicates number 4) is the synthetic analogue of the mineral zorite and it was produced and used as cation exchanger to remove Hg^{2+} ions from water. The synthesis of ETS-4 was performed according to Lopes et al. [1]. Although the production costs of ETS-4 will obviously depend on the scale and amount produced, according with Otero et al. [12] at an industrial scale they can be estimated to be 400–600 $ per ton. Table 1 depicts relevant information on ETS-4 titanosilicate. Particle size was estimated from SEM images (Hitachi S-4100), density and pore size were calculated from crystallographic data and theoretical cation exchange capacity (CEC) was calculated from molecular weight and exchangeable cations.

Table 1
Features of ETS-4 titanosilicate synthesized and used for pH and temperature studies.

Titanosilicate	ETS-4
Formula	$Na_9Ti_5Si_{12}O_{38}(OH)\cdot 4H_2O$
Physical form	White powder
Density ($kg\,m^{-3}$)	2200
Particle diameter (10^{-6} m)	0.5–0.9
Pore diameter (10^{-10} m)	3–4
Theoretical CEC ($meq\,g^{-1}$)	5.54

2.2. Analytic procedures

Mercury concentration in solution was measured by atomic fluorescence spectroscopy (AFS), which allows its detection at very low levels ($1\,ng\,dm^{-3}$), *ca.* 100 times lower than atomic absorption spectroscopy [13,14]. Analyses were carried out on a cold vapour-atomic fluorescence spectrometer (Hydride/vapour generator PS Analytical Model 10.003, coupled to a PS Analytical Model 10.023 Merlin atomic fluorescence spectrometer) (PS Analytical, Orpington, Kent, England), and using $SnCl_2$ as reducing agent.

All glassware used in this work was acid-washed prior to use (nitric acid 25%, 12 h).

2.3. Sorption studies: effect of pH and temperature

All experiments were carried out in batch conditions in $2\,dm^3$ volumetric flasks. Closed volumetric flasks were used to avoid metal losses. Hg^{2+} solutions were prepared daily by diluting the corresponding stock solution to the desired initial concentrations ($[Hg^{2+}]$ $50\,\mu g\,dm^{-3}$) in high purity water (18 MΩ cm). Known masses of ETS-4 ($4\,mg\,dm^{-3}$) were added to the Hg^{2+} solution and this was considered the starting time of the experiment. The ETS-4 suspension was magnetically stirred (1400 rpm) and samples were withdrawn at increasing times, filtered through an acid-washed Millipore membrane (0.45 μm), adjusted to pH < 2 with HNO_3 *Hg free* and then immediately analysed.

The effect of pH on Hg^{2+} sorption from solution by ETS-4 was studied in the range of 2–10 at 294 ± 1 K, while the effect of temperature was studied at 277, 294 and 313 K for a pH value of 5. The pH of the solution was adjusted with HNO_3 *Hg free* for pH values 2–4 and with NaOH 0.1 M for pH values 6–10. To verify the influence of the chemical used for the pH adjustment, a second set of experiments were performed for pH values 6–10 using KOH 0.1 M. All pH values were measured with a WTW pH meter. The experiments at 277 K were performed in a cold room with controlled temperature while in those at 294 and 313 K the temperature was controlled using a magnetic hotplate stirrer with a water bath and an electronic contact thermometer. A control Hg^{2+} solution was always run in parallel under the same experimental conditions. All experiments were performed in triplicate.

In each study, the Hg^{2+} concentration $C = C(t)$ was determined along the time for the residual ion in solution. The amount of Hg^{2+} sorbed by the titanosilicate at a given time, q_t ($\mu g\,mg^{-1}$), was calculated by the mass balance:

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

where C_0 ($\mu g\,dm^{-3}$) is the initial concentration of metal in the liquid phase, and confirmed by the control solution, where C_t ($\mu g\,dm^{-3}$) is the instantaneous liquid-phase concentration, V the volume of the solution (dm^3) and W the titanosilicate dry weight (mg). Hg^{2+} sorbed at the equilibrium, q_e ($\mu g\,mg^{-1}$), was calculated as:

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

where C_e ($\mu g\,dm^{-3}$) is the metal concentration in the liquid phase at the equilibrium.

The uptake degree, α (%), at time t, was defined by:

$$\alpha(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Thermodynamic parameters, Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) change for the system Hg^{2+}/ETS-4 were

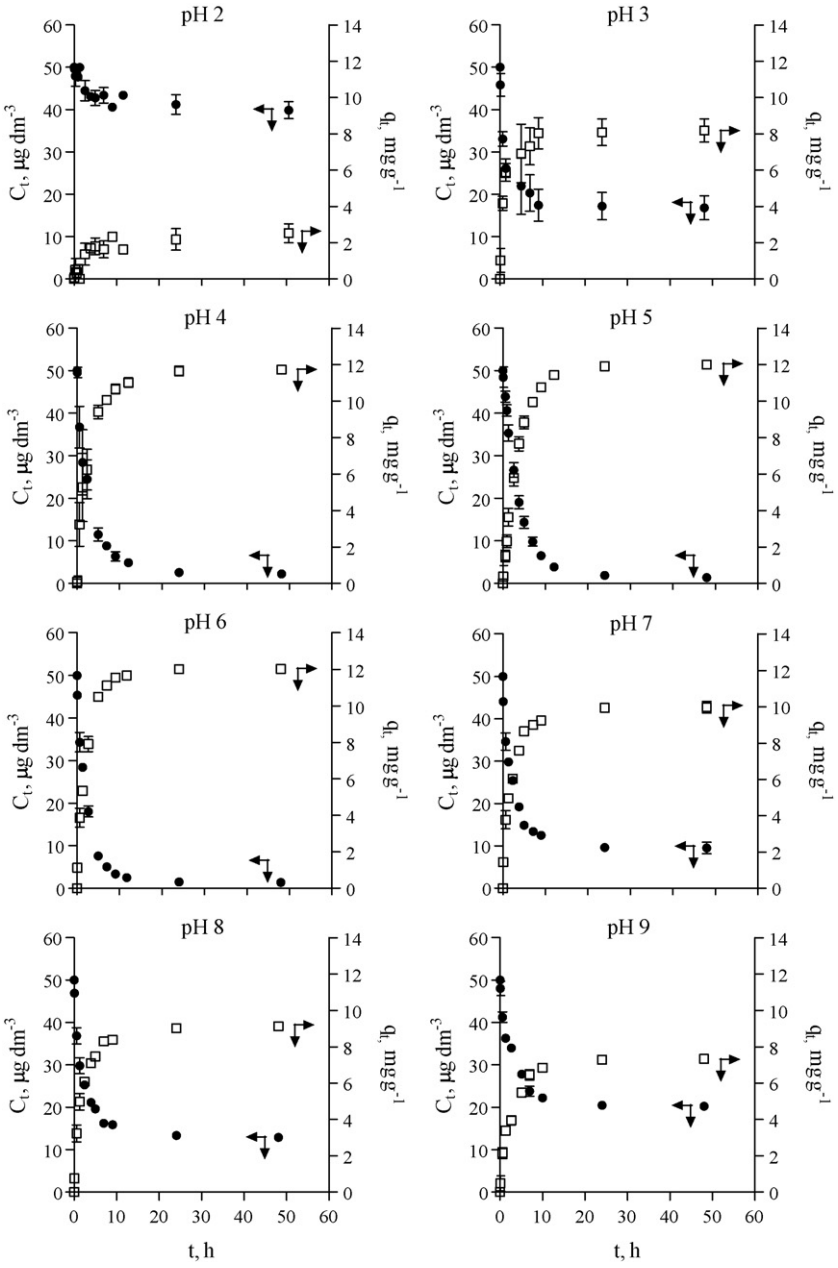

Fig. 2. Hg^{2+} concentration in the liquid phase (C_t—black symbols) and sorbed on ETS-4 (q_t—white symbols) as a function of time, for different pH values.

calculated with the following equations [11,15,16]:

$$\Delta G^{\circ} = -RT \ln K_d \quad (4)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (5)$$

combining Eqs. (4) and (5):

$$\ln K_d = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad (6)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and K_d is the distribution coefficient (dm^3 g^{-1}):

$$K_d = \frac{q_e}{C_e} \quad (7)$$

ΔH° (kJ mol^{-1}) and ΔS° (kJ mol^{-1} K^{-1}) may be obtained from the slope and intercept of ln K_d versus $1/T$ plot, while the free energy ΔG° (kJ mol^{-1}) is, subsequently, calculated from Eq. (5).

3. Results and discussion

3.1. pH

The effect of pH on the Hg^{2+} removal by ETS-4 was studied in the pH range of 2–10. Fig. 2 depicts the Hg^{2+} concentrations in the liquid phase (C_t) and sorbed on ETS-4 (q_t) as a function of time. For the pH values 6, 7, 8 and 9, only the solutions that were adjusted with NaOH 0.1 M are represented. For all pH values, there is a decrease of the Hg^{2+} concentration in the liquid phase and, consequently, an increase with time of the amount of Hg^{2+} sorbed on ETS-4. Even when the equilibrium times are approximately equal at all the pH under study (24 h), it is clear that the removal extent depends strongly on the solution pH. Fig. 3 shows how the q_e and removal percentage (α (%)) increase with increasing pH until they reach a maximum at 4–6 and then decrease. The sorbed concentration at equilibrium and the degree of Hg^{2+} removal increase, respectively,

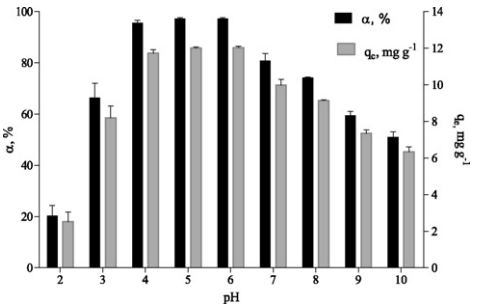

Fig. 3. Effect of pH on the Hg^{2+} uptake degree (black columns) and amount of Hg^{2+} sorbed (grey columns) on ETS-4 at equilibrium.

from 2.52 to 12.0 mg g^{-1} and from 20.3 to 97.2% when the solution pH increases from 2 to 6. Then, the amount of Hg^{2+} sorbed and the Hg^{2+} removal percentage begin to decrease with increasing solution pH and reach almost half of the maximum values at pH 10 (6.34 mg g^{-1} and 51.0%, respectively).

The Hg^{2+} removal efficiency of ETS-4 is lower at low pH values (<4) due to the higher competition between H^+ and free Hg^{2+} ions in solution for the exchange with cations [9,15], namely Na^+, initially present in ETS-4. Moreover, Hg^{2+} removal drastically decreased at the lowest pH value studied (2.0), which may also be a consequence of the partial collapse of the ETS-4 structure. Increasing pH leads to a decrease in the H^+ concentration and consequently the exchange of Hg^{2+} with the cations in the ETS-4 structure is favoured.

As it may be seen in Fig. 3, the optimal pH for Hg^{2+} uptake onto ETS-4 is in the pH range of 4–6. However, the speciation diagram of Hg (II) species in aqueous solution (Fig. 4) indicates that the dominant Hg(II) species at pH > 4 is $Hg(OH)_2$, it has been proved for an initial Hg(II) concentration $\leq$120 mg dm^{-3} in solution that $Hg(OH)_2$ dissolves [10]. Thus, since the Hg(II) concentration used was 50 μg dm^{-3} (<120 mg dm^{-3}), the cation exchange process proceed and it was favoured by the lower H^+ competition. Fig. 3 also shows that, between pH 6 and 10, when pH is adjusted with NaOH 0.1 M, both q_e and α (%) decrease progressively with increasing pH.

Fig. 5 displays the degree of Hg^{2+} removal at $6 \leq pH \leq 10$, when the solution pH is adjusted with KOH 0.1 M and NaOH 0.1 M. The

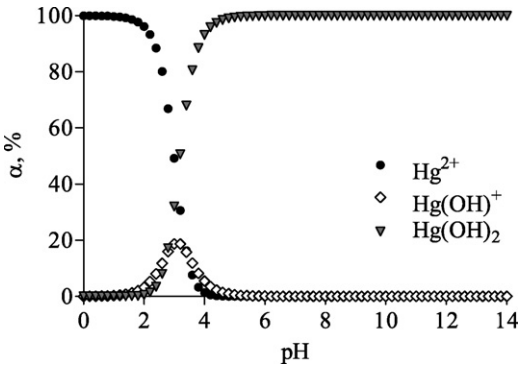

Fig. 4. Speciation diagram for Hg(II) in aqueous solution at 298.15 K (built by using the ionisation fractions, calculated with the K_a values of the Hg^{2+} hydrolysis ($K_{a1} = 10^{-35}$; $K_{a2} = 10^{-27}$ [17])).

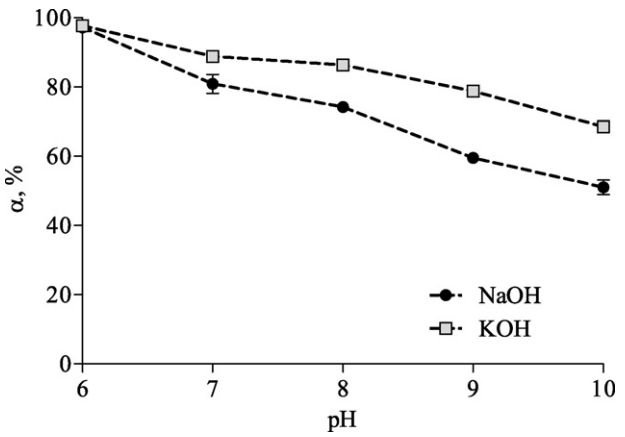

Fig. 5. Effect of NaOH and KOH solutions on Hg^{2+} removal.

results obtained confirm that Hg^{2+} removal decreases with increasing the solution pH, however, the extent to which it occurs depends on the type of solution used to adjust the solution pH. As it may be observed (Fig. 5) the decrease of Hg^{2+} removal for increasing pH (from pH = 6 to pH = 10) is more notorious when NaOH is used instead of KOH. Furthermore, differences increase with rising pH because this implies the addition of higher quantities of base. These results are in agreement with a removal mechanism mainly based on the ion exchange between the metal cations (Hg^{2+}) and the cations (Na^+) present in ETS-4. The increase of the pH refrains the dissolving of $Hg(OH)_2$ and thus the Hg^{2+} exchange. Also, the presence of Na^+ or K^+ cations in solution hinders cationic exchange. This is especially evident in the case of Na^+, as the increase of its concentration in the liquid phase reduces the liquid-solid phase Na^+ concentration gradient.

3.2. Temperature

The effect of temperature on the Hg^{2+} removal by ETS-4 was investigated at 277.15, 294.15 and 313.15 K. Fig. 6 shows the Hg^{2+} concentrations in the liquid phase (C_t) and sorbed on ETS-4 (q_t) as a function of time. The Hg^{2+} concentration in the liquid phase decreases along time at all temperatures. Equilibrium is reached within 24 h and the temperature does not affect the equilibrium time. A very small decrease on the Hg^{2+} removal may be observed for increasing temperature. However, this small decrease is enough to do not obtain clean water of drinking quality (C_e < 1 μg dm^{-3}) at the highest temperature used (313.15 K; C_e = 4.4 μg dm^{-3}).

Fig. 7 shows the small decrease in q_e and degree of Hg^{2+} removal that is observed when increasing the temperature: raising the temperature leads to a decrease of the sorbed concentration at equilibrium from 12.1 to 11.3 mg g^{-1}.

3.3. Thermodynamic studies

The values of ΔH°, ΔS° and ΔG° are collected in Table 2. The negative values of ΔG° indicate the spontaneous nature of the Hg^{2+} sorption on ETS-4 for all temperatures and the increase of their absolute values with decreasing temperature shows that lower temperatures favour Hg^{2+} removal. The negative values of enthalpy

Table 2
Thermodynamic parameters for Hg^{2+} uptake on ETS-4.

ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
		277.15 K	294.15 K	313.15 K
−29.94 ± −11.18	−0.029 ± −0.038	−21.89 ± 15.38	−21.40 ± 15.83	−20.85 ± 16.35

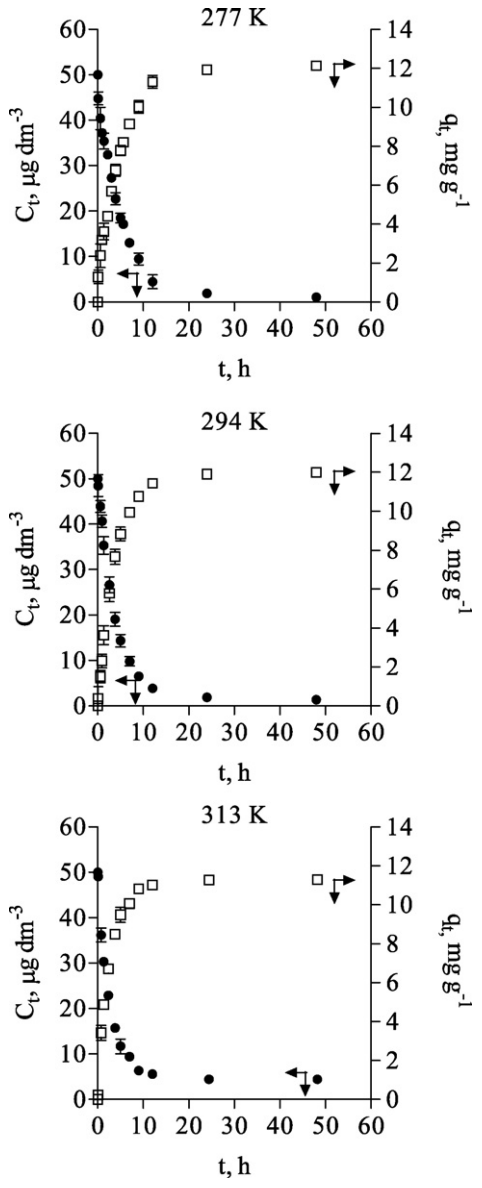

Fig. 6. Hg^{2+} concentrations in the liquid phase (C_t—black symbols) and sorbed on ETS-4 (q_t—white symbols) as a function of time, for different temperatures.

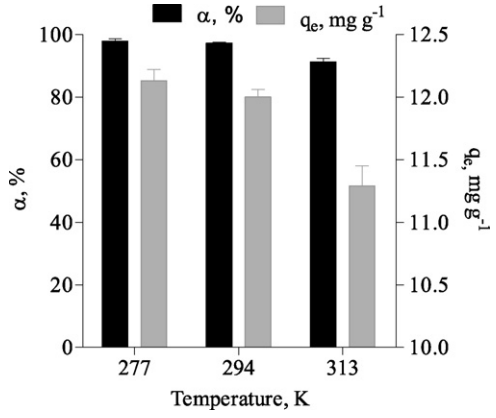

Fig. 7. Effect of temperature on Hg^{2+} uptake degree (black columns) and amount of Hg^{2+} sorbed (grey columns) on ETS-4 at equilibrium.

changes (ΔH°), show that Hg^{2+} sorption on ETS-4 is exothermic, while a negative ΔS° suggests that Hg^{2+} is stable in ETS-4 framework. Thermodynamic parameters show that the uptake of Hg^{2+} ions onto ETS-4 is thermodynamically favourable.

4. Conclusions

In this study, the effect of pH and temperature on the removal of Hg^{2+} from water by ETS-4, a microporous titanosilicate was investigated in a batch mode.

It was concluded that the removal of Hg^{2+} by ETS-4 is an exothermic and thermodynamically favourable process and that the uptake degree of Hg^{2+} by ETS-4 is strongly affected by the solution pH and, to a lesser extent, temperature. Optimal conditions for mercury removal were found to be in the pH range 4–6 and at temperatures under 294 K, at which, ETS-4 is able to remove Hg^{2+} ions from contaminated water (50 μg dm^{-3}) to a very large extent, yielding water of drinking quality, even when only 4 mg dm^{-3} of ETS-4 are used. In these conditions, ETS-4 is able to uptake more than 98%, attaining equilibrium concentrations lower than 1 μg dm^{-3}. However, it must be taken into account that out of this range of pH or at higher temperatures, mercury removal by ETS-4 may diminish and treated water may not fulfil strict requirements for drinking.

On the whole, the obtained experimental results show that ETS-4 is a very promising material, whose application in water decontamination systems for an ultimate/refinement treatment may allow attaining the requirements set by the Water Framework Directive with respect to mercury discharge cease. In this sense, fixed-bed operation and sorption–desorption-reuse cycles are, at present, under study in order to assess the practical interest of ETS-4.

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References

[1] C.B. Lopes, M. Otero, J. Coimbra, E. Pereira, J. Rocha, Z. Lin, A.C. Duarte, Removal of low concentration Hg^{2+} from natural waters by microporous and layered titanosilicates, Micropor. Mesopor. Mater. 103 (2007) 325–332.
[2] C.B. Lopes, J. Coimbra, M. Otero, E. Pereira, J. Rocha, Z. Lin, A.C. Duarte, Uptake of Hg^{2+} from aqueous solutions by microporous titano- and zircono-silicates, Quim. Nova 31 (2008) 321–325.
[3] C.B. Lopes, P.F. Lito, M. Otero, Z. Lin, J. Rocha, C.M. Silva, E. Pereira, A.C. Duarte, Mercury removal with titanosilicate ETS-4: batch experiments and modelling, Micropor. Mesopor. Mater. 115 (2008) 98–105.
[4] T.R. Ferreira, C.B. Lopes, P.F. Lito, M. Otero, Z. Lin, J. Rocha, E. Pereira, C.M. Silva, A.C. Duarte, Cadmium(II) removal from aqueous solution using microporous titanosilicate ETS-4, Chem. Eng. J. 147 (2009) 173–179.
[5] J. Rocha, M.W. Anderson, Microporous titanosilicates and other novel mixed octahedral-tetrahedral framework oxides, Eur. J. Inorg. Chem. 5 (2000) 801–818.
[6] C.B. Lopes, M. Otero, Z. Lin, C.M. Silva, J. Rocha, E. Pereira, A.C. Duarte, Removal of Hg^{2+} ions from aqueous solution by ETS-4 microporous titanosilicate—kinetic and equilibrium studies, Chem. Eng. J. 151 (2009) 247–254.
[7] E. Álvarez-Ayuso, A. Garcia-Sanchez, X. Querol, Purification of metal electroplating waste waters using zeolites, Water Res. 37 (2003) 4855–4862.
[8] A. Walcarius, M. Etienne, C. Delacote, Uptake of inorganic Hg(II) by organically modified silicates: influence of pH and chloride concentration on the binding pathways and electrochemical monitoring of the processes, Anal. Chim. Acta 508 (2004) 87–98.
[9] L. Lv, M.P. Hor, F. Su, X.S. Zhao, Competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on microporous titanosilicate ETS-10, J. Colloid Interface Sci. 287 (2005) 178–184.
[10] 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.
[11] S. Kocaoba, Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals, J. Hazard. Mater. 147 (2007) 488–496.

[12] M. Otero, C.B. Lopes, J. Coimbra, T.R. Ferreira, C.M. Silva, Z. Lin, J. Rocha, E. Pereira, A.C. Duarte, Priority pollutants (Hg^{2+} and Cd^{2+}) removal from water by ETS-4 titanosilicate, Desalination 249 (2009) 742–747.
[13] B. Rood, C. Sanford, Mercury determination in the environment, in: Encyclopedia of Environmental Analysis and Remediation, John Wiley & Sons, New York, 1988.
[14] P. Pichet, K. Morrison, I. Rheault, A. Tremblay, Analysis of Total Mercury and Methyl-mercury in Environmental Samples, Mercury in the Biogeochemical Cycle: Natural Environments and Hydroelectric Reservoirs of Northern Québec (Canada), Springer, Berlin, Germany, 1999.
[15] C.C. Pavel, K. Popa, N. Bilba, A. Cecal, D. Cozma, A. Pui, The sorption of some radiocations on microporous titanosilicate ETS-10, J. Radioanal. Nucl. Chem. 258 (2003) 243–248.
[16] J.H. Choi, S.D. Kim, Y.J. Kwon, W.J. Kim, Adsorption behaviors of ETS-10 and its variant, ETAS-10 on the removal of heavy metals, Cu^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} from a waste water, Micropor. Mesopor. Mater. 96 (2006) 157–167.
[17] B.J. Aylett, Group IIB, in: J.C. Bailar, H.J. Emeléus, Sir Ronald Nyholm, A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, vol. 3, 1973.