

UPTAKE OF Hg²⁺ FROM AQUEOUS SOLUTIONS BY MICROPOROUS TITANO- AND ZIRCONO-SILICATES

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Being mercury one of the most toxic heavy metals present in the environment, it is of major concern to develop cleanup technologies to remove it from wastewater and recover mercury polluted ecosystems. In this context, we study the potential of some microporous titanosilicates and zirconosilicates for taking up Hg²⁺ from aqueous solutions. These materials have unique chemical and physical properties, and here we are able to confirm that they readily remove Hg²⁺ from aqueous solutions. Moreover, the presence of the competitive Mg²⁺ and Na⁺, which are some of the dominant cations in natural waters, does not reduce the uptake capacity of some of these materials. Thus, several inorganic materials reported here may have important environmental applications, efficiently removing Hg²⁺ from aqueous solutions.

Keywords: mercury; titanosilicates; zirconosilicates.

INTRODUCTION

Heavy metals are well known by their toxicology (*e.g.* they accumulate in living organisms) and their concentration in the environment has been increasing steadily¹. Mercury is one of the most toxic heavy metals present in the aquatic systems, exhibiting a complex behaviour in the environment where it remains for a long time after even the pollutant source is interrupted. The persistence of mercury in the aquatic environment, its toxicity, bioaccumulation and bioamplification along the food chain, motivate the study of the phenomena regulating its transfer among different environmental compartments and encourage the development of techniques for removing this metal from the aquatic systems.

Several processes have been proposed for removing heavy metals from aqueous solutions^{1,2}, however, these technologies are not entirely satisfactorily. They are expensive and often originate secondary problems. Adsorption is probably the most attractive process because its application is simple and efficient², although the cost of the substrate and its regeneration are limiting factors¹. Therefore, it becomes important to search low cost substrates, which may replace activated carbons and resins. Some attention has been focused on biopolymers, zeolites, clays, natural oxides and industrial wastes, which exhibit the capacity of removing heavy metals from contaminated waters, at relatively low cost³. Zeolites are perhaps the most promising of such materials because they have high ion-exchange capacity, selectivity and environmental compatibility, since the exchangeable ions (Na⁺, Ca²⁺ and K⁺) are relatively harmless^{1,4}.

Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional structures built of SiO₄ and AlO₄ tetrahedra linked to each other by sharing all the oxygens to form regular intracrystalline cavities and channels of molecular dimensions^{5,6}. Silicon-oxygen tetrahedra are electrically neutral when connected together in a three-dimensional network as in quartz (SiO₂), however

the replacement of Si⁴⁺ by Al³⁺ in such structure creates an electrical imbalance and, to preserve the overall electrical neutrality, each AlO₄ tetrahedron needs a balancing positive charge that is provided by exchangeable cations held electrostatically within the zeolite⁶. Due to their structure, these type of materials exhibit remarkable physical and chemical properties, such as selective sorption, ion exchange and catalytic activity⁶ and due to these properties they present considerable potential for environmental and industrial applications⁷. Of special importance for environmental uses is their ability to uptake and retain heavy metals species from aqueous media. Some work is already available on the adsorption and removal of heavy metals such copper, arsenic, cadmium, nickel and zinc by zeolites^{4,8-10}.

Microporous crystalline titanosilicates and zirconosilicates constitute novel zeotype families and the ion exchange properties of these materials have attracted a considerable attention during the last decade since they are stable, have large pore sizes, remarkable selectivity and consist of a variety of framework structures¹¹. The framework of these microporous oxides are built up of interconnected octahedra, pentahedra and tetrahedra. ETS-10 (Engelhard TitanoSilicate material number 10), [(Na,K)₂TiSi₅O₁₃·4H₂O] is the most important microporous titanosilicate known, possessing a three-dimensional 12-ring pore system (Figure 1), and exhibiting considerable potential for being used as ion-exchanger, especially for divalent cations⁶. ETS-4 [Na₉Ti₅Si₁₂O₃₈(OH)·12H₂O], the synthetic analogue of mineral zorite, AM-2 (Aveiro-Manchester material number 2), [K₂TiSi₃O₉·H₂O], the titaneous analogue of mineral umbite and synthetic titaneous pharmacosiderite [HK₃Ti₄O₄(SiO₄)₃·4H₂O] are other examples of microporous titanosilicates studied here (Figure 1). Petarasite and its synthetic analogue (AV-3), [Na₅Zr₂Si₆O₁₈(Cl,OH)·nH₂O] (Figure 1) is a microporous zirconosilicate consisting of an open three-dimensional framework built of corner-sharing SiO₄ tetrahedra and ZrO₆ octahedra⁶. AV-13 (Figure 1) is yet another microporous zirconosilicate with formula Na_(2+x)ZrSi₃O₉Cl_x·2H₂O¹².

The aim of this work is to evaluate the ability of microporous titanosilicates (ETS-10, ETS-4, AM-2 and synthetic titaneous

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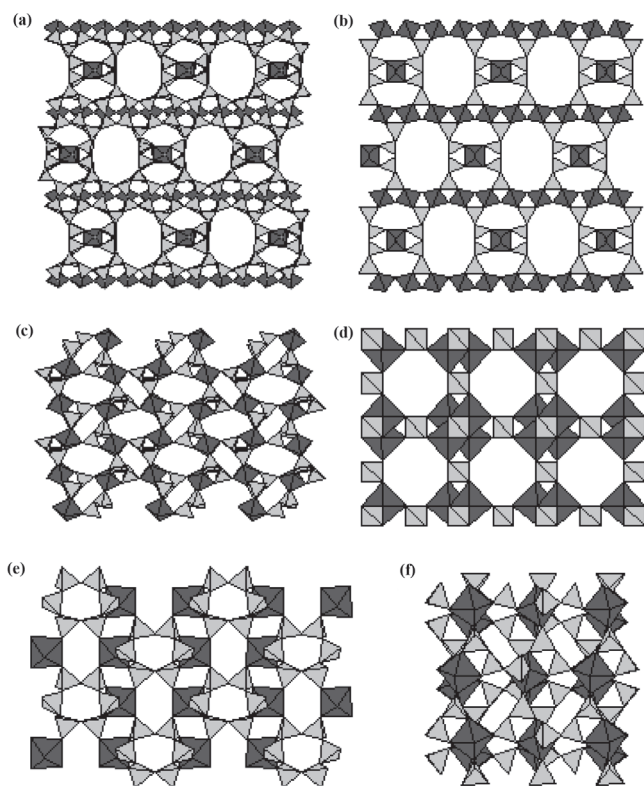


Figure 1. Schematic representation of the structures of: (a) ETS-10 $[(Na,K)_2TiSi_3O_{13} \cdot 4H_2O]$; (b) ETS-4 $[Na_9Ti_5Si_{12}O_{38}(OH) \cdot 12H_2O]$; (c) AM-2 $[K_2TiSi_3O_9 \cdot H_2O]$; (d) pharmacosiderite $[HK_3Ti_4O_4(SiO_4)_3 \cdot 4H_2O]$; (e) petarasite $[Na_5Zr_2Si_6O_{18}(Cl,OH)_n \cdot nH_2O]$; (f) AV-13 $[Na_{(2+x)}ZrSi_3O_9Cl_x \cdot 2H_2O]$. The centres of black octahedra and grey tetrahedra are occupied by Ti (or Zr) and Si atoms, respectively. Extra framework cations and water molecules have been omitted for clarity

pharmacosiderite) and zirconsilicates (synthetic petarasite and AV-13), to uptake Hg^{2+} from aqueous solutions, assessing their potential for natural waters Hg^{2+} decontamination. We, thus, report on the uptake of Hg^{2+} at low contamination levels (similar concentrations as those found in natural waters) and study the effect of the presence of competitive Mg^{2+} and Na^+ ions on this process.

EXPERIMENTAL

Chemicals and materials

All chemicals reagents used in the work were of analytical reagent grade and obtained from chemical commercial suppliers, without further purification. The certified standard stock solution of mercury (II) nitrate, 1 mL \equiv 1.00 mg Hg^{2+} was purchase from BDH Chemicals Ltd.

ETS-10 titanosilicate was synthesised according to the procedure described by Rocha *et al.*¹³, while the synthesis of ETS-4 was performed as describe follows: 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 H_2O . 31.88 g of $TiCl_3$ (15 % m/m $TiCl_3$ and 10% m/m HCl, Merck) were added to this solution and stirred thoroughly. This gel, with a molar composition 5.9 Na_2O :0.7 K_2O :5.0 SiO_2 :1.0 TiO_2 :114 H_2O , 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 micro-

crystalline powder. AM-2 titanosilicate was prepared by the procedure reported by Lin *et al.*¹⁴ and the synthesis of pharmacosiderite titanium silicate was carried out according to the following procedure: an alkaline solution was made by dissolving 15.00 g of sodium silicate solution (27% m/m SiO_2 , 8% m/m Na_2O , Merck), 11.20 g KOH (85% m/m, Merck) into 15.00 g H_2O . 4.00 g anatase (98% m/m, Merck) was added to this alkaline solution. This gel, with a molar composition 0.4 Na_2O :1.7 K_2O :1.4 SiO_2 :1.0 TiO_2 :30 H_2O , was transferred to a Teflon-lined autoclave and treated at 200°C for 4 days under autogenous pressure without agitation. Synthetic petarasite (AV-3) and AV-13 zirconsilicates were synthesised according to the methods reported by Lin *et al.*¹⁵ and Ferreira *et al.*¹², respectively. Table 1 depicts selected data on the titanosilicates and zirconsilicates used in this work. The particle sizes were obtained from scanning electron microscope images on a Hitachi S-4100 microscope. The pore sizes were calculated from their framework data.

Sorption studies

All studies were carried out in batch conditions, at room temperature (20 °C \pm 1). The work was performed in such a way as intended to simulate the conditions prevalent in poorly-polluted estuarine systems: because in estuarine waters the concentration of mercury rarely exceeds a few hundred ng L^{-1} , a concentration of 500 ng L^{-1} was then used.

A mass of 0.5 g microporous materials was used in each test. Hg^{2+} solution (500 ng L^{-1}) was prepared daily by dilution of a standard Hg^{2+} solution (1000 mg L^{-1}). 50 mL of this Hg^{2+} solution were added to each microporous material and this was considered the starting point of the adsorption experiment. Titanosilicates and zirconsilicates powders and aqueous solutions were maintained in contact for 60 h with stirring. The pH of the solution was ca. 4 measured by a WTW 538 pH meter and was kept constant for all materials. After this period of time, each solution was filtered through a 0.45 μm filter, adjusted to pH<2 with HNO_3 Hg free, stored at 4 °C and then analysed. Mercury analysis was 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 $SnCl_2$ as reducing agent. This analytical methodology is usually a hundred times more sensitive than atomic absorption, allowing the measurement of 1 ng L^{-1} of mercury.

The major problem encountered in these experiments is the low mercury concentration (500 ng L^{-1}) because the adsorption processes and contaminations may seriously compromise the results. For this reason, all glassware used in the experiments was acid-washed prior to use and in order to quantify the amount of Hg^{2+} that was lost due to adsorption to the vessels and during the filtration process, blank experiments were always carried out.

For each material, is displayed the residual Hg^{2+} concentration, the amount of Hg^{2+} sorbed by the materials at equilibrium, q_e (ng g^{-1}) and the uptake efficiency (% uptake). The amount of Hg^{2+} sorbed is calculated by the mass balance:

$$q_e \text{ (ng } g^{-1}\text{)} = (C_0 - C_e) \frac{V}{M} \quad (1)$$

where C_0 (ng L^{-1}) is the initial Hg^{2+} concentration and C_e (ng L^{-1}) is the concentration of Hg^{2+} in the liquid-phase after equilibrium, V M is the batch factor [volume of the Hg^{2+} solution (L) to initial dry weight of titanosilicate or zirconsilicate (g) ratio].

The uptake efficiency is given by:

Table 1. Selected data on the titanosilicates and zirconosilicates, synthesized and used for Hg²⁺ removal from aqueous solution

	ETS-10	ETS-4	AM-2	Pharmacosiderite	Petarasite	AV-13
Formula	(Na,K) ₂ TiSi ₅ O ₁₃ ·4H ₂ O	[Na ₉ Ti ₅ Si ₁₂ O ₃₈ (OH)·12H ₂ O]	K ₂ TiSi ₃ O ₉ ·H ₂ O	HK ₃ Ti ₄ O ₄ (SiO ₄) ₃ ·4H ₂ O	Na ₅ Zr ₂ Si ₆ O ₁₈ (Cl,OH)·nH ₂ O	Na _(2+x) ZrSi ₃ O ₉ Cl _x ·2H ₂ O
Physical form	white powder	white powder	white powder	white powder	white powder	white powder
Density (g cm ⁻³)	1.8	2.2	2.7	2.53	2.88	2.65
Particle diameter (μm)	5	0.5-0.9	1-4	0.2-0.4	0.2 plate, aggregated to 5	2
Pore size (nm)	0.49x0.76	0.4	0.27x0.55	0.36	0.19x0.38	0.23x0.32

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

where C_0 (ng L⁻¹) and C_e (ng L⁻¹) are the initial and the equilibrium concentrations of Hg²⁺ in the liquid-phase.

Competitive sorption studies

Due to the low concentration of Hg²⁺ in natural waters relatively to other ions concentrations, it is important to assess the capacity of these materials to remove Hg²⁺ in the presence of potential competitive ions.

To study the competition between Hg²⁺ and other ions present in seawater, sorption experiments were also performed in the conditions described above but using three different support solutions: MgSO₄ solution (6.1 g L⁻¹), NaCl solution (35 g L⁻¹) and synthetic seawater prepared according to Parsons *et al.*¹⁶. The competitive effect on Hg²⁺ sorption by the different ions was determined by the amount of Hg²⁺ sorbed and uptake efficiency compared to those obtain in the absence of competition.

RESULTS AND DISCUSSION

Blank experiments

In all sorption studies, blank experiments were performed and the same experimental procedure was always used. All the results were corrected taking in account the losses due to the laboratory procedures. The blank experiments indicated that the filtration is the major source of Hg²⁺ loss (*ca.* 27% of total), while the adsorption by containers represents *ca.* 10% of total loss.

Hg²⁺ uptake in absence of ionic competition

Figure 2 displays the uptake percentage of Hg²⁺ by the different microporous titano and zirconosilicates, in absence of competing ions. All microporous materials efficiently (uptake > 85%) remove Hg²⁺ from aqueous solutions, but is visible that Hg²⁺ has different affinity for the various materials. Table 2 depicts the experimental Hg²⁺ uptake by the materials, the residual concentration on the liquid-phase and the amount of Hg²⁺ removed per gram of material. Clearly ETS-10, petarasite and AV-13 are the best mercury sorbers, in absence of competing ions, with the highest uptake efficiencies, removing nearly all metal in solution. Although the microporous titanosilicate AM-2 also sorbs efficiently the Hg²⁺ in solution, its performance is slightly lower than the materials mentioned above. The least efficient of all materials are ETS-4 and pharmacosiderite which display the lowest uptake efficiencies, respectively, 86.4 and 87.3%. Titanosilicate ETS-10 and zirconosilicates petarasite and AV-13 are the best microporous

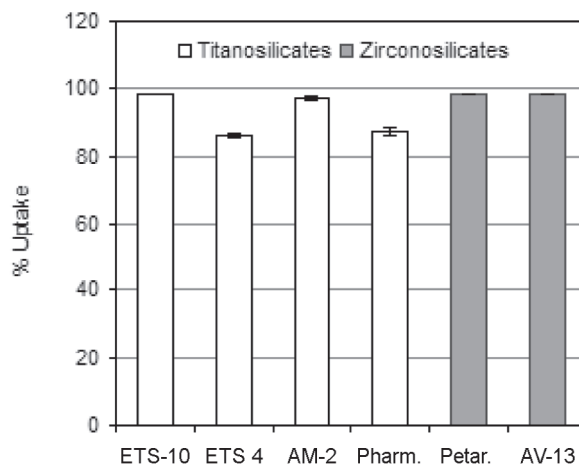


Figure 2. Mean and standard deviation of the uptake percentage of Hg²⁺ by titanosilicates and zirconosilicates, in absence of ionic competition (Milli-Q water adsorption system)

materials for removing Hg²⁺ from aqueous solutions, in absence of ionic competition. Although zirconosilicates seem to perform better than titanosilicates only two examples of the former were studied and, thus, a note of caution is required. Both zirconosilicates have comparable sorption properties, but in contrast, the titanosilicates ETS-10, ETS-4, AM-2 and pharmacosiderite seem to have distinct sorption behaviour.

Hg²⁺ uptake in the presence of ionic competition

Figure 3(a) represents the sorption percentage of Hg²⁺ in the presence of MgSO₄ salt. Zirconosilicates AV-13 and petarasite are the best Hg²⁺ sorbers in presence of Mg²⁺ ion. Their uptake efficiencies remain at almost the same value as when only Hg²⁺ is in solution, even

Table 2. Sorption of Hg²⁺ by microporous materials in the absence of competing ions: available Hg²⁺ concentration after blank correction ([Hg²⁺]_{corr}), residual Hg²⁺ concentration ([Hg²⁺]_{res}), uptake (%) and amount of Hg²⁺ sorbed (q_e)

Microporous material	[Hg ²⁺] _{corr} (ngL ⁻¹)	[Hg ²⁺] _{res} (ngL ⁻¹)	Uptake (%)	q_e (ng g ⁻¹)
ETS-10	362	5.6	98.5	35.72
ETS 4	362	49	86.4	31.30
AM-2	362	10	97.2	35.21
Pharmacosiderite	362	46	87.3	35.70
Petarasite	362	5.5	98.5	35.70
AV-13	362	6.0	98.3	35.61

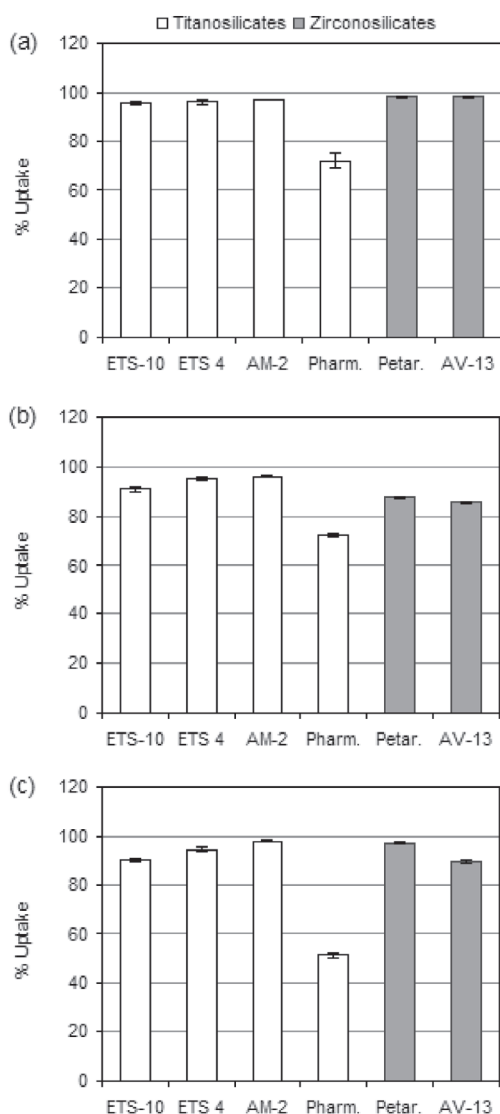


Figure 3. Mean and standard deviation of uptake percentage of Hg^{2+} by titanosilicates and zirconosilicates in three different sorption systems: (a) MgSO_4 solution; (b) NaCl solution; (c) artificial seawater

when the salt concentration is much higher than Hg^{2+} concentration. Between the titanosilicates materials ETS-10, ETS-4 and AM-2 exhibit similar sorption efficiencies, with AM-2 being the best of them (97.0%), while pharmacosiderite is the least efficient (72.4%) material of all in removing Hg^{2+} in presence of Mg^{2+} ion (Table 3). These results show that the presence of a divalent cation, such as Mg^{2+} , does not influence greatly the Hg^{2+} uptake by microporous titano and zirconosilicates, except for the pharma-cosiderite analogue, which has an uptake decrease >10%, relatively to the Hg^{2+} sorption in absence of competing ions. For this competition study zirconosilicates, petarasite and AV-13, exhibited slightly better Hg^{2+} sorption properties than titanosilicates. Once again, a note of caution is required since we only study two examples of the zirconosilicates and the difference in the uptake percentages between the two kinds of materials, if we exclude Pharmacosiderite, is only 2.3%.

Figure 3(b) represents the sorption percentage obtained in the $\text{Hg}^{2+}/\text{Na}^+$ co-adsorption test, showing that the best material for Hg^{2+} uptake in these conditions is AM-2 (96.4%), although ETS-4 and ETS-10 also exhibit higher uptake efficiencies, respectively 95.2 and 90.9% (Table 3).

Table 3. Sorption of Hg^{2+} by microporous materials in the presence of competing ions: available Hg^{2+} concentration after blank correction ($[\text{Hg}^{2+}]_{\text{corr}}$), residual Hg^{2+} concentration ($[\text{Hg}^{2+}]_{\text{res}}$), uptake (%) and amount of Hg^{2+} sorbed (q_e)

Microporous material	Sorption system	$[\text{Hg}^{2+}]_{\text{corr}}$ (ng L ⁻¹)	$[\text{Hg}^{2+}]_{\text{res}}$ (ng L ⁻¹)	Uptake (%)	q_e (ng g ⁻¹)
ETS-10	MgSO_4	178	7.3	95.9	17.1
	NaCl	406	37	90.9	36.9
	Seawater	253	24	90.5	22.8
ETS 4	MgSO_4	178	6.6	96.3	17.1
	NaCl	406	20	95.2	38.7
	Seawater	253	14	94.5	23.9
AM-2	MgSO_4	178	5.3	97.0	17.3
	NaCl	406	16	96.4	39.0
	Seawater	253	5.0	98.0	24.7
Pharmacosiderite	MgSO_4	178	49	72.4	12.9
	NaCl	406	111	72.6	29.4
	Seawater	253	124	50.9	12.9
Petarasite	MgSO_4	178	3.3	98.2	17.4
	NaCl	406	50.0	87.8	35.6
	Seawater	253	7.0	97.2	24.6
AV-13	MgSO_4	178	3.3	98.2	17.4
	NaCl	406	58	85.6	34.8
	Seawater	253	26	89.7	22.7

In contrast with the results obtained in the previous adsorption systems (milli-Q water and MgSO_4 solution), in the presence of NaCl , microporous zirconosilicates exhibited Hg^{2+} uptake efficiencies lower than titanosilicates (except pharmacosiderite). The uptake for petarasite reaches 87.8%, while for AV-13 the uptake is 85.6% (Table 3). Pharmacosiderite has again the worst performance of all materials, with the lowest uptake efficiency (72.6%). The comparison of the results obtained on the $\text{Hg}^{2+}/\text{Mg}^{2+}$ and $\text{Hg}^{2+}/\text{Na}^+$ co-adsorption systems leads to the fact that the uptake percentages of titanosilicates only decrease slightly or remain constant (pharmacosiderite) from changing the competitive ion from Mg^{2+} (divalent) to Na^+ (monovalent), whereas for zirconosilicates the uptake percentages decrease >10%. This indicates that petarasite and AV-13 are less selective to (divalent) Hg^{2+} in the presence of monovalent cations.

Figure 3(c) shows the sorption percentage obtained in the $\text{Hg}^{2+}/$ artificial seawater co-adsorption study, which is the most complex adsorption system studied here, because it includes both Mg^{2+} and Na^+ ions in the same concentrations as the previous adsorption systems. In this study, AM-2 is the most efficient material for Hg^{2+} removal. Its uptake efficiency remains at almost the same value as the others studies (only Hg^{2+} , $\text{Hg}^{2+}/\text{Mg}^{2+}$ and $\text{Hg}^{2+}/\text{Na}^+$) (Table 3). Petarasite has also a good performance, its uptake efficiency remains at almost the same value as the studies with only Hg^{2+} and with $\text{Hg}^{2+}/\text{Mg}^{2+}$. The ETS-4 uptake is also high (94.5%) and the sorption results obtained for titanosilicate ETS-10 and zirconosilicate AV-13 are similar, respectively 90.5 and 89.7%. In this adsorption system, pharmacosiderite exhibited the worst sorption results of all with only 50.9% uptake efficiency.

For the Hg^{2+} concentration and batch factor ($V/M=100$) used, the presence of monovalent and divalent cations does not influence greatly the uptake of Hg^{2+} by microporous titanosilicates and zirconosilicates. This probably happens because the concentration of ions in the studied solutions is relatively low and, thus, the full ion-exchange capacity

of the materials is never even approached. The notable exception is pharmacosiderite, since its Hg²⁺ uptake capacity in the presence of competing ions decreases almost 40%. However, the materials performance may be optimised by changing the batch factor and adjusting the Hg²⁺ concentration to be handled^{1, 17-18}.

CONCLUSIONS

It is known that ion-exchange is feasible when an exchanger has a high selectivity for the metal to be removed and the concentration of competing ion is low. The uptake of mercury (Hg²⁺) from aqueous solutions by microporous titanosilicates (ETS-10, ETS-4, AM-2 and pharmacosiderite) and zirconsilicates (petarasite and AV-13) have been measured and compared. In the absence of ionic competition, most microporous materials exhibit efficient sorption ability for removing Hg²⁺ from aqueous solutions, at low concentrations. In the presence of ionic competition, the Hg²⁺ uptake by pharmacosiderite decreases almost 40%, but for the other microporous materials studied, the Hg²⁺ uptake does not change significantly. For these reasons it seems to exist a clearly indication that some of these inorganic materials may have an important environmental application, since they can be used to remove Hg²⁺ from industrial waste effluents.

This preliminary study clearly shows the potential of microporous titanosilicates and zirconsilicates for removing Hg²⁺ from aqueous solutions and future work will concentrate on both, the optimisation of the Hg²⁺ concentration and batch factor, and the investigation of the Hg²⁺ uptake mechanisms. In addition it is also important to optimise the experimental procedure, thus avoiding or minimizing losses of mercury by adsorption on the containers and by filtration.

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