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Sorption on natural solids for arsenic removal

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Abstract

Steady state experiments were conducted on arsenic sorption from aqueous solutions by natural solids to test the feasibility of these materials to act as concentrator for arsenic removal from groundwater and drinking water. The solids considered were natural zeolites, volcanic stone, and the cactaceous powder CACMM. The arsenic species studied were As(III), As(V), dimethylarsinic acid (DMA) and phenylarsonic acid (PHA). The arsenic removed was determined from the data obtained by measuring the concentration diminution of the arsenic species in the liquid phase at equilibrium before and after the adsorption experiment by means of ICP-AES for the total concentration of arsenic and IC-ICP-MS to determine the arsenic species. The latter method allowed the detection of As(V) additionally formed as a result of the oxidation of As(III) on some of the zeolites. The sorption of the arsenic species onto zeolites was studied on both non-activated and activated zeolites, as well as on zeolites hydrogenated or modified with iron, and with respect to varying pH. The kinetics and the ability to desorb and readsorb the arsenic species were investigated for selected zeolites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Natural solids; Arsenic; Sorption; Zeolites

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1. Introduction

Arsenic is ubiquitous in the environment and is a notoriously toxic element for the general population, which is mainly exposed to arsenic via drinking water and marine food. While organic arsenic species like dimethylarsinic acid (DMA), for example, with a median lethal doses in animals $LD^{50}(DMA)=1200\,mg\,kg^{-1}$, are found as non-toxic compounds, the inorganic arsenite with $LD^{50}(As^{3+})=4.5\,mg\,kg^{-1}$ and arsenate $LD^{50}(As^{5+})=14\,mg\,kg^{-1}$ which makes no great difference, should be considered to be rather toxic. Most of the international drinking water standards are in the range of 0.04–0.05 $mg\,l^{-1}$ arsenic which was lowered in Germany in 1996 to 0.01 $mg\,l^{-1}$. Consequently there is growing interest in using low-cost materials to remove arsenic from water. One promising method appears to be adsorption from solution. In the study stage this removal technique is carried out in batch experiments, columns or fixed bed reactors, and offers remarkable advantages. Trivalent and pentavalent arsenic species in aqueous solutions were adsorbed onto activated carbon impregnated with silver and copper [1], while the adsorption of organic species has been studied on classical carbonaceous adsorbents [2]. The adsorption of arsenic, both as As(III) and as total arsenic, has also been studied using a variety of natural materials including sand, clay, kaolinite, bentonite, montmorillonite, goethite [3], spodic [4] and aquifer material from mining areas [5]. The removal of As(III) and As(V) has been studied in detail using antimony pentoxide and manganese dioxide [6], as well as lanthanum compounds [7], iron hydroxides [8,9] and iron-coated catalyst [10]. However, comparatively few published papers deal with ion exchange for arsenic elimination [11].

Over the last 40 years, zeolites have attracted ever-increasing interest from academic and industrial laboratories. They represent an important group of materials due to their catalytic, sieve and exchange properties. Natural zeolites present additionally low cost and have high occurrence in some countries. However, metal ion exchange has chiefly been viewed as a procedure in the preparation of metal zeolites for reaction promotion. Although the fast application of the cation exchange phenomenon for heavy metal removal has been described in the literature in the last few years, in the case of arsenic, where arsenious and arsenic acid remain undissociated depending on the pH, a molecular complex sorption mechanism can be expected.

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Arsenic in solution has a complex and interesting chemistry with redox reactions also taking place. It can occur in four oxidation states in nature, but in natural waters it is found only as As(III) and As(V) oxidation states. As an anion it presents acid characteristics whose stability and dominance depend directly on the pH of the solution. Trivalent arsenic is stable at pH 0–9 as neutral H_3AsO_3, while $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} exist as stable species in the pH intervals 10–12, 13 and 14, respectively. For pentavalent arsenic the corresponding stability of species pH values are: H_3AsO_4 (pH 0–2), $H_2AsO_4^-$ (pH 3–6), $HAsO_4^{2-}$ (pH 7–11) and AsO_4^{3-} (pH 12–14). It can be then presumed that the following processes are involved in adsorption at the basic and acid Brönsted sites:

$$\text{Z–O}^{\ominus} + \text{(ads) H–OAs(OH)}_2 \quad \text{for As(III) at pH 4 and 7}$$

$$\text{Z–O}^{\ominus}\text{H}^{\oplus} + \text{(ads)}^{\ominus}\text{O–As(OH)}_2 \quad \text{for As(III) at pH 11}$$

$$\text{Z–O}^{\ominus}\text{H}^{\oplus} + \text{(ads)}^{\ominus}\text{O–AsO(OH)}_2 \quad \text{for As(V) at pH 4}$$

Just one report concerning arsenic removal using the natural zeolites clinoptilolite and chabazite can be found in the literature [12]. The aims defined in our investigation were to test the feasibility of diverse zeolites to remove for the first time arsenic as species As(III), As(V), DMA and phenylarsonic acid (PHA), the sorption kinetics, the pH dependence and desorption ability of the investigated arsenic species. Primary attention was paid to clinoptilolite – the most common naturally occurring zeolite – and other solids were studied in comparison.

2. Experimental

The natural solids used in this work were natural Mexican and Hungarian zeolites and synthetic mordenite with mesh sizes of 60 and 20 and are described in Table 1, Mexican volcanic stone, and the cactaceous powder CACMM [13–15] with a particle size of 420 μm. They were properly analyzed and their characterization will be described separately. Their activation comprised acid wash with 2 M HCl with agitation at 50°C for 2 h, keeping them for 24 h in the acid solution, decantation and washing with water until a pH of 5 was obtained and the $AgNO_3$ chloride test proved negative, followed by drying at 200°C for 2 h. The ferrous forms of each zeolite were prepared by equilibrating a defined mass of the solid with Fe^{2+} solution of various concentrations and one set with 1.5 mM Pb^{2+}. Following equilibration for 72 h, the samples were filtered and the zeolite subsequently washed with water. The iron intake was determined by ICP-AES. The sorption experiments were carried out at 22°C using glass containers as batch reactors. In all the trials the solid-to-solution ratio was maintained at 1:10. The solutions were equilibrated for 7 days or more and were initially shaken in an ultrasonic bath. After equilibration, the final pH was measured and 2 ml of the supernatant was used for species analysis by IC-ICP-MS (ion chromatography separation coupled with ICP-MS detection) in adsorption experiments or for total As analysis by ICP-AES in desorption experiments. The desorption of As(V) was carried out by immersing the dry solid sample with an amount of sorbed arsenic in water or 1 M HCl and determining the quantity of arsenic going into solution after a period equal to the time allowed for sorption. Afterwards the zeolites were dried and put in contact again with a new As(V) solution to determine the readsorption capacity. In experiments in the absence of oxygen, the adsorption system was purged with He and kept stoppered until analysis. In the kinetic experiments, a 1000 ml batch system was analyzed daily by extracting a 2 ml sample and taking into account in calculations the volume removed in the solid/solution ratio. Iron hydroxide FeO(OH) and iron oxide Fe_2O_3 (both from Aldrich) were used for comparison, since the adsorption of As(V) on iron has a strong nature [5,8,16,17] and the precipitation-coagulation with ferric salts is used as conventional method for arsenic removal from aqueous systems. Arsenic adsorbed onto iron oxy-hydroxides surface can yield the following complex [5]:

$$>\text{FeOH} + H_3AsO_3 \rightarrow >\text{FeH}_2\text{AsO}_3 + H_2O$$

Stock solutions of the arsenic compounds with different concentrations were prepared from arsenic trioxide (Fluka), arsenate solution (Titrisol, Merck), dimethylarsinic acid trihydrate (Merck) and phenylarsonic acid (Fluka). The concentration of the arsenic species is always given as the concentration of elemental arsenic. The pH of the solutions was adjusted by adding 1×10^{-4} M HCl or 1×10^{-4} M LiOH. Iron and lead solutions were prepared from $FeSO_4\cdot7H_2O$ (Fluka) and $Pb(ClO_4)_2\cdot3H_2O$ (Aldrich), respectively. Deionized water (Milli-Q, Millipore) was used in every solution. The ICP-AES equipment was a Spectroflame P/M (Spectro A.I.) with pneumatic nebulization using a cross-flow nebulizer. The IC-ICP-MS system consisted of an LC 250 binary pump (Perkin-Elmer) coupled with an Elan 5000 ICP-MS (Perkin-Elmer) via a cross-flow nebulizer. A volume of 200 μl was always injected. The guard and separation columns used were Ion Pac AG7 and Ion Pac AS7 (Dionex), respectively. The mobile phase was nitric acid

Table 1
Studied zeolites, their type and composition

Zeolites	Origin	Type	Other components
ZMA		Clinoptilolite+erionite	Tosudite
ZME	Mexico, natural	Mordenite+clinoptilolite	Calcite, feldspars, quartz, mica
ZMS		Clinoptilolite	Feldspars, quartz, cristobalite
ZMT		Clinoptilolite	Calcite, feldspars, quartz, mica
ZH	Hungary, natural	Clinoptilolite	
ZS-M	Synthetic	Mordenite	

with the ion-pairing modifier benzene-1,2-disulfonic acid in accordance with [18]. The chromatograms were quantitatively evaluated by integrating the peaks corresponding to As(III), As(V), DMA and PHA, applying the peak fitting module of the software Microcal Origin 4.1. The sorbed amount a ($\mu g\,g^{-1}$) was calculated as the difference between the initial concentration C_0 and the equilibrium concentration C_f, as $a=V(C_0-C_f)/m$, where V is the volume of the batch solution and m is the mass of the solid. Sorption efficiency is considered in percent as $\varepsilon=100-100C_f/C_0$.

3. Results and discussion

3.1. Sorption kinetics

The concentration variation of arsenite and arsenate was measured daily for a period of 12 days with two of the studied zeolites described in Table 1 and an initial As(III)+As(V) solution concentration of 100 and 20 $\mu g\,l^{-1}$, respectively. After 24 h, the arsenite concentration considerably decreased in the batch solution containing ZH as compared to zeolite ZME, and sorption was faster, i.e. equilibrium was achieved after approximately 4 days. Arsenate concentration variation was referred to the initial 20 $\mu g\,l^{-1}$ concentration. The discontinuity of the As(V) curves in Fig. 1 is especially striking. An abrupt increase in the As(V) content was observed after 48 h for the mordenite-type zeolite ZME, indicating the formation of additional amounts of As(V) as a result of contact with the zeolite. In connection with this result, the possibility of the donation or removal of protons by the Brönsted sites in zeolites during interaction with molecules must be considered. Electron density from the interacting molecule may be transferred to the electron acceptor sites of the zeolite, represented by various cations coordinated at the cation positions of the zeolite, or by the protons in the hydrogenated forms as in the case of the acid–base catalysis.

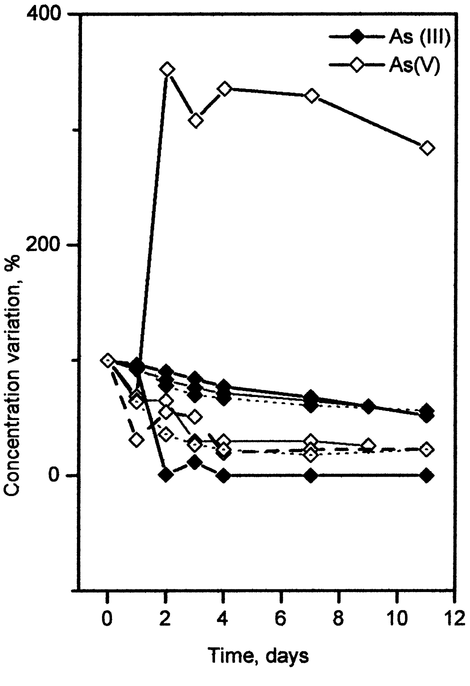

Fig. 1. Effect of time on the As concentration in aqueous solution (pH 4) in contact with activated zeolites ZME (continuous lines) and ZH (discontinuous lines) (activation in 1×10^{-4} M HCl and 1×10^{-4} M H_2SO_4) and without activation (dotted lines). Leaching solution initial concentration 100 $\mu g\,l^{-1}$ As(III) and 20 $\mu g\,l^{-1}$ As(V). Curves for As(V) referred to the initial concentration.

With the clinoptilolite-type zeolite ZH the same effect was observed to a smaller extent, with the sorption of As(V) also starting after 72 h and the corresponding curve reaching a steady-state after 4 days. Arsenate formation on ZH occurred on the zeolite activated with both HCl or H_2SO_4, but not on the initial ZH. The arsenate amount formed on ZME also moderately decreased and did not reach a constant value after 12 days.

When the sorption kinetics in the current study is compared with reported data, in which the adsorption equilibrium for arsenate and arsenite was reached after 1 h on ferrihydrite [9] for example, it must be noted that sorption on zeolites is an essentially more complex process since they exhibit cations and framework acting as two sorption centers and the role of the accompanying materials in natural zeolites cannot be neglected. Thus, the kinetics may be diffusion-controlled, exhibiting the slowest step in the primary and secondary porosity, being the primary considered as the micropores (r=1.5–1.6 nm) present in a specific crystalline zeolite structure, and the secondary as the meso (r=1.6–200 nm) and macropores (r>200 nm) existing between particles and accompanying materials in natural zeolites. Frequently adsorption kinetic curves considered as the increase of the adsorbed amount as well as the decrease of the starting amount of adsorbate with time, follow a first order exponential function. We applied a fitting procedure considering 1–3 order functions and preferred the fit which best described the data. The standard way of defining the best fit is to choose the parameters so that the sum of the χ^2 of the deviations of the theoretical curve(s) from the experimental points for a range of independent variables reaches the absolute minimum. The algorithm, starting from some initial parameter values, minimizes χ by performing a series of iterations on the parameter values computing χ^2 at each stage. For arsenite concentration variation in contact with the clinoptilolite type zeolite ZH, experimental values fitted a first-order exponential decay function whose values are given in Table 2. On ZME consisting of two zeolite types, no data fitting was obtained. Arsenate diminution was also only adjusted to a first-order exponential function in the case of the non-activated ZH zeolite, where only the sorption of As(V) occurs, and not formation and sorption as in the case of the activated zeolites. From the curves it can be seen that the decay of the As(V) concentration is more drastic than that of the As(III) concentration, highlighted by a t coefficient value of 1.4 and 3.0, respectively, while

Table 2
Coefficient values of the first-order exponential function[a] adjusting the data of arsenite and arsenate sorption on zeolites

System	y_0	A	b	(χ^2)[b]
As(III)/ZH (HCl washed)	52	51.2	5.6	14.8
As(III)/ZH (H_2SO_4 washed)	60	41.3	3.2	2.5
As(III)/ZH (not washed)	54.8	47.6	3.0	13.0
As(V)/ZH (not washed)	19.1	82.2	1.4	13.2

[a] $C=C_0+A\exp(-t/b)$, where A and b are constants, t is the time and C_0 and C are the concentrations at $t=0$ and at a given time t, respectively.

[b] χ^2 values of the deviations from the theoretical curve.

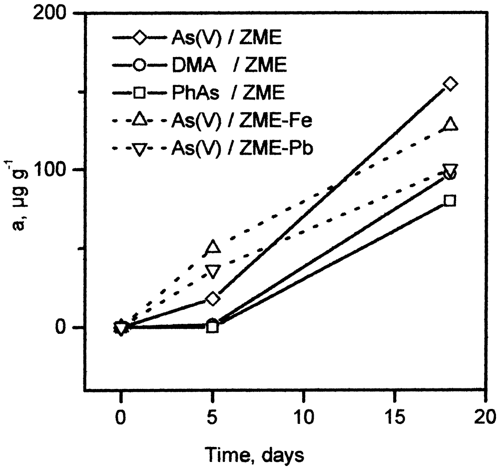

Fig. 2. Time dependence of the sorption of As(V), DMA and PHA on zeolite ZE (initial state) and ZE modified with iron and lead. Start solution concentration: $5\,\mathrm{mg\,l^{-1}}$.

the diminution of arsenite concentration occurs with similar velocity on the primitive and activated ZH.

The sorption of As(V) as species arsenate, dimethylarsinate and phenylarsonate was studied as a function of time on zeolite ZME in the initial state and on iron- and lead-modified forms of ZME. Fig. 2 shows first that equilibrium could not be reached after 20 days' contact in all cases. Secondly it can be seen as expected, that after a given time the sorption of As(V) is greater than that of DMA and PHA. The iron form removes a greater amount of As(V) in comparison to the lead form. It is also apparent that both modified forms seem to reach saturation faster than the unmodified zeolite.

3.2. Dependence of arsenic removal on pH-value

Since the stability and dominance of the arsenic species directly depend on the pH of the solution, the studied zeolites were left in contact with aqueous solution containing $200\,\mu\mathrm{g\,l^{-1}}$ As(III) at different pH values at 23°C for 20 days. Fig. 3 shows the IC-ICP-MS chromatogram of batch solutions at pH 4. It can be clearly seen that on the clinoptilolite type zeolites ZMT, ZMS and ZH, the arsenite concentration drastically decreases, but the formation of arsenate also occurs. Arsenate is promptly formed and subsequently sorbed as was observed in the kinetic studies on ZH. In this way, for example, ZH formed $0.2\,\mu\mathrm{g\,g^{-1}}$ arsenate and 99% arsenite was withdrawn from the $200\,\mu\mathrm{g\,l^{-1}}$ arsenic solution. On the natural mordenite type zeolite ZME, the arsenite concentration vanished and the arsenate formed was sorbed to a smaller extent compared to the clinoptilolites. Since the calibration curves of arsenite and arsenate have slopes whose ratio is 1.04, it is immediately evident from Fig. 3 that almost equal concentrations of both species resulted when synthetic mordenite ZS-M was in contact with As(III) solution.

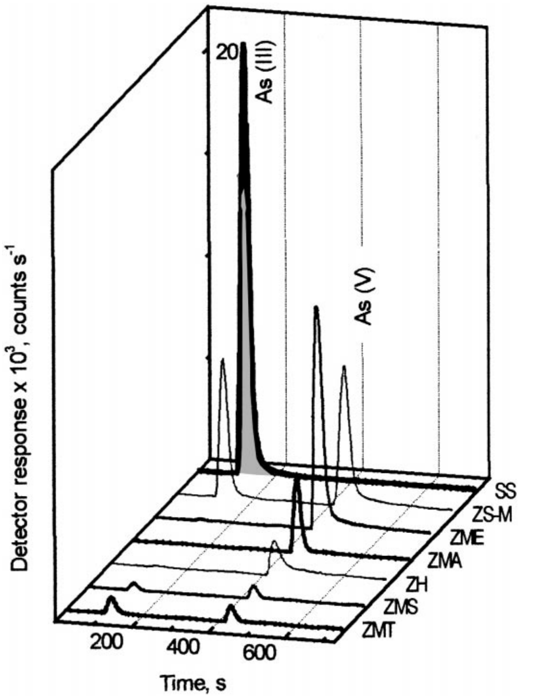

Fig. 3. IC-ICP-MS chromatograms of $200\,\mu\mathrm{g\,l^{-1}}$ As(III) solution pH 4 before (SS) and after 20 days in contact with different zeolites at 23°C.

Here the total arsenic content was reduced by around 20% by $200\,\mu\mathrm{g\,l^{-1}}$ on $160\,\mu\mathrm{g\,l^{-1}}$, of which 44% corresponded to As(III) and 56% to As(V). This suggests on the one hand that As(III) is not fully transformed into As(V), and on the other hand that a small amount of one species or of both is retained by the zeolite. By contrast, the natural mordenite type zeolite ZME transformed As(III) into As(V) and sorbed the species, leading to a total arsenic decrease of 14%, with the remaining arsenic existing in 94% as arsenate. The zeolite ZMA, which is composed of a mixture of clinoptilolite and erionite, shows similar behavior to the natural clinoptilolites in this study, although the remaining amount of As(V) formed is larger, probably due to the smaller content of the clinoptilolite phase.

At the zeolite surface the following reaction in solution can be proposed:

$$2\mathrm{As(OH)_3} + \mathrm{O_{2,ads}} \xleftrightarrow{\mathrm{Z/H_2O}} 2\mathrm{AsO(OH)_3}, \quad \Delta G = -222\,\mathrm{kJ}$$

It is known that mordenite and clinoptilolite zeolite types can be used for the gas chromatographic separation of a mixture of the gases argon, oxygen and nitrogen at room temperature. Separation selectivity can be affected by modification as well as by decationation and dealumination of the natural zeolites. This indicates that adsorption of oxygen takes place and as it was mentioned in [19], it is even greater on natural than on synthetic samples in the temperature interval 10–40°C. Other factor influencing the oxidation of arsenite can be the presence of Fe^{3+} and Mn^{4+} in the natural zeolite as it can be appreciated for example in the following reaction:

$$4Fe^{3+}+As_2O_3+2H_2O \xleftrightarrow{(ZO^-)_nM^{n+}} 4Fe^{2+}+As_2O_5+4H^+,$$
$$\Delta G=-28\,\mathrm{kJ}$$

Following on from the above results, we then examined two aspects of the removal of the total arsenic, viz. the diminution of the arsenite concentration, and the formation and subsequently sorption of arsenate or the inhibition of the spontaneously formed arsenate at defined pH values when no zeolite is used. At pH 7 the studied zeolites show the same trend in arsenate removal as at pH 4, while at pH 11 the sorption of spontaneously formed As(V) was evidenced. Fig. 4 shows a set of chromatograms. A freshly prepared 200 $\mu g\,l^{-1}$ As(III) solution at pH 11 contained when chromatographed 160 $\mu g\,l^{-1}$ As(III)+40 $\mu g\,l^{-1}$ As(V). The same solution showed 20 $\mu g\,l^{-1}$ As(III)+180 $\mu g\,l^{-1}$ As(V) after 20 days. By way of example, chromatograms of batch solutions in contact with zeolite ZH demonstrate that both arsenite and formed arsenate could be removed in the studied pH interval, producing residual solution concentrations of 0–5 and 30–40 $\mu g\,l^{-1}$, respectively. At pH 11 chromatogram in Fig. 4 stated the rapid transformation of arsenite and almost a total conversion into arsenate with time. When a compound is able to hinder a process, it is usually considered as inhibitor. Here when comparing chromatograms ‘c’ with ‘a’ in Fig. 4 the role of the zeolite will be considered by us primarily as an inhibition in the As(V) formation. Fig. 5 shows the elimination of the species As(III) by the zeolites studied as a function of the pH. The global behavior corresponds to a high total arsenic sorption at low pH and low sorption at high pH, as was observed with aquifer material [5]. The zeolites ZMS and ZME showed low efficiency at pH 11; ZMA, ZMT and ZH displayed high and uniform efficiency in the whole pH interval, and the synthetic mordenite 50% exhibited almost constant efficiency, although a high degree of conversion into As(V) took place, as previously discussed. Table 3 demonstrates in general that the highest amounts of As(V) are formed at pH 7 and that on the Clinoptilolite containing zeolites practically no residual arsenate results at pH 4. When evaluation of resulting arsenate concentration was considered with respect to the spontaneously formed species in absence of zeolite at pH 11, one nearly estimates the inhibition of arsenate production. Here the mixed phase zeolite ZMA presented the lowest inhibition efficiency.

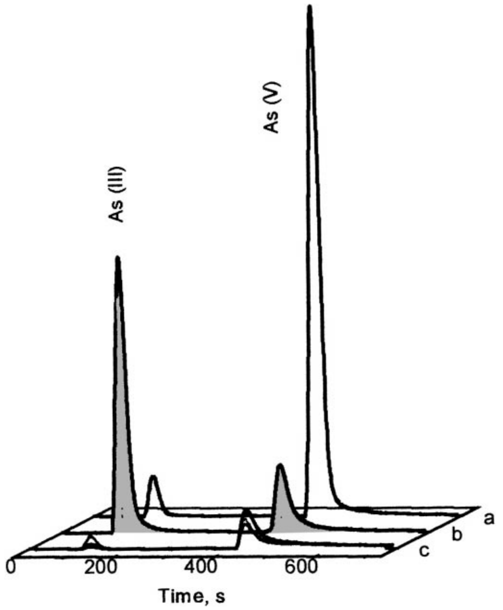

Fig. 4. IC-ICP-MS chromatograms of 200 $\mu g\,l^{-1}$ As(III) solution pH 11 aged 20 days (a), freshly prepared (b) and after contact with zeolite ZH at 23°C, 20 days at pH 4, 7 and 11 as superposed lines (c).

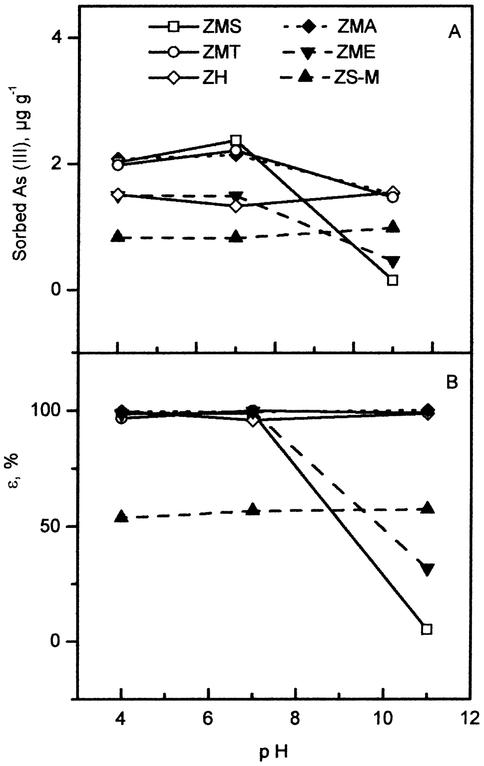

Fig. 5. Dependence of the sorbed amount of As(III) (A) and corresponding removal efficiency (B) on pH value. Continuous lines clinoptilolite type zeolites. Discontinuous lines mordenite type zeolites. Dotted line: erionite+clinoptilolite mixed zeolite.

Table 3
Resulting As(V) in μg l^{-1} after contact with 1 g zeolite at different pH and inhibition of its spontaneous formation from 200 μg l^{-1} As(III) solution at pH 11

Zeolite	pH			Inhibition (%)
	4	7	11	
ZMA	0.5	3.5	2.7	27
ZME	1.2	0.9	0	99
ZMS	0	1.4	0	100
ZMT	0	0.7	1.2	63
ZH	0.2	0.1	0.2	89
ZS-M	1.2	0.8	0.8	73

3.3. Dependence on sorption atmosphere and activation

In order to investigate the role of oxygen in arsenate formation, two experiments were carried out in a helium atmosphere. The chromatograms in Fig. 6 show the almost negligible influence of oxygen on As(V) formation in the case of the clinoptilolite zeolite ZH (Fig. 6B), but a marked effect for the mordenite type natural zeolite ZME (Fig. 6A). In both the presence and absence of oxygen, arsenite concentration diminution occurs for two different zeolite types. Here helium purge of the solution does not effectively displace the adsorbed oxygen and it leads to oxidation of arsenite.

When the same 170 μg l^{-1} As(III) batch solutions were activated in an ultrasonic bath and measured after 1 h contact, mordenite zeolite ZME readily transformed 86% As(III) into As(V), showing no difference compared to the non-activated system (Fig. 7A). With the clinoptilolite type zeolite ZH (Fig. 7B), the effect on arsenite concentration was 80% diminution when ultrasonic treatment was applied, in contrast with 20% without activation. The final arsenate concentrations were 30 and 10 μg l^{-1}, respectively. An equilibrium displacement originated by ultrasonic heating, during which the temperature rises from 22 to 27°C, can be added at this point to the sorption process.

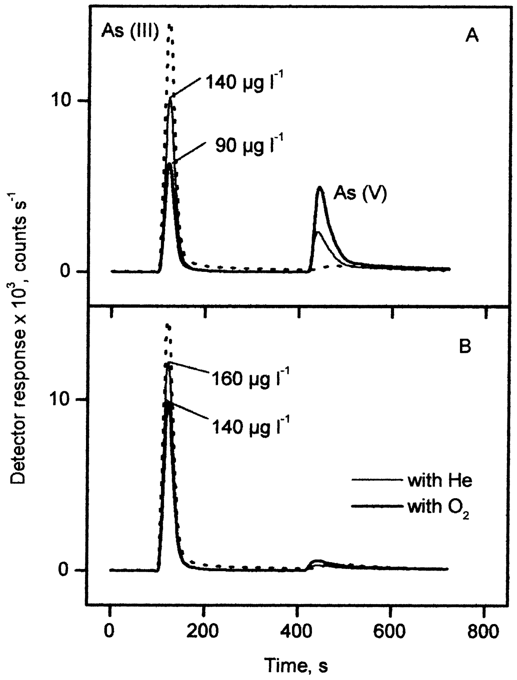

Fig. 6. IC-ICP-MS chromatograms of 170 μg l^{-1} As(III) solution before (dotted line) and after 20 days in contact with zeolites ZME (A) and ZH (B) at 23°C and pH 7 in the presence and absence of oxygen.

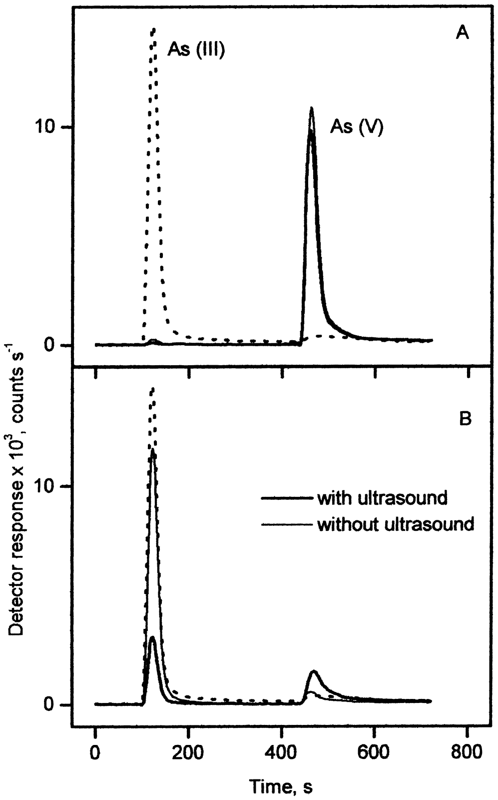

Fig. 7. IC-ICP-MS chromatograms of 170 μg l^{-1} As(III) solution before (dotted line) and after 1 h in contact at 23°C and pH 7 with zeolites ZME (A) and ZH (B) applying ultrasound activation.

Since treatment with HCl can lead to the dealumination of clinoptilolites, we measured the arsenite concentration diminution on treated and untreated ZH. Fig. 8 shows the larger removal of As(III) and also the greater As(V) formation on the untreated ZH in an oxygen atmosphere when no ultrasonic activation was applied (Fig. 8A). Surprisingly, we found that after activation and immediate measurement (Fig. 8B), As(III) was totally removed from the solution. When comparing the behavior of mordenite ZME and clinoptilolite ZH (Fig. 7) treated with HCl, it can be seen that the performance of the washed mordenite resembles the behavior of the unwashed clinoptilolite. This can partly be explained by the fact that treatment with diluted HCl leads to the almost complete elimination of sodium ions with the variable dealumination of mordenites [19]. However, the role of decationation and dealumination grade of the zeolites for arsenic removal must be studied in more detail and will be the subject of a future paper. When the natural cations (mostly sodium and calcium) in

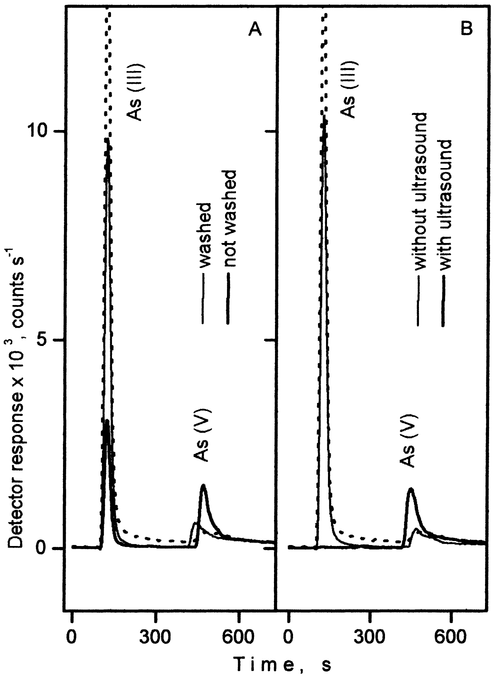

Fig. 8. IC-ICP-MS chromatograms of 170 μg l^{-1} As(III) solution before (dotted line) and after 7 days in contact at 23°C and pH 7 with zeolite ZH (A) and after applying rush ultrasound activation before measurement on the zeolite washed with HCl (B).

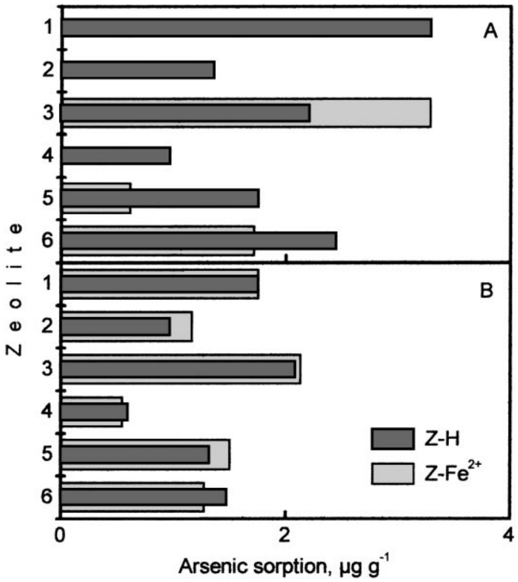

Fig. 9. Sorption of As(III) (A) and DMA (B) from 250 μg l^{-1} solutions (pH 5) after 48 h by hydrogenated and Fe^{2+} modified forms of the zeolites: ZS-M (1), ZME (2), ZMA (3), ZH (4), ZMT (5) and ZMS (6).

a zeolite are partially removed by chemical treatment and substituted by an equivalent amount of hydrogen ions, this process known as decationation can produce a material with different adsorption properties against diverse adsorbates. Among cationated zeolites, the dispersive adsorption energy grows with the cation size in the alkaline group for example. With dealumination understood as the withdrawal of tetrahedral aluminum from the zeolitic framework, higher Si/Al ratios are produced, the thermal stability and the catalytic activity can be varied as a result of this chemical modification. Another factor improving the performance of the washed clinoptilolite ZH could be the secondary porosity formed by the natural material surrounding the crystals, which is of mesoporous and macroporous size. The effect of acid-washing on porosity is not reported for mordenites, while in the case of clinoptilolites it leads to the modification of the pore size distribution curves [19].

3.4. Sorption by hydrogenated and modified zeolite forms

When modified forms of the studied zeolites were studied, a higher degree of elimination of arsenite and DMA was achieved in some experiments, as can be seen from Fig. 9. This corresponds with reported data [12] for Californian clinoptilolite and Tucson chabazite. However, it cannot be described here as general behavior since it depends on the degree of modification. Our results present modified zeolites after being in contact with equal amounts of bivalent iron. The iron exchange capacity decreased in the clinoptilolites series: ZMS>ZMT>ZH and in the mordenites series: ZS-M>ZME, which correlates with the removal grade of arsenite: ZMS-Fe>ZMT-Fe>ZH-Fe and ZS-M-Fe>ZME-Fe. More effective for arsenite retention among the unmodified samples were the synthetic mordenite ZS-M and the natural clinoptilolite ZMS, while the mixed phase zeolite ZMA was the most successful of the modified group. Since the exchange of cations is generally determined by the zeolite structural characteristics, this erionite-containing sample ZMA, as well as the reported chabazite [12] as modified iron forms, exhibited considerable retention improvement in relation to the clinoptilolite type, because the exchange capacity of the latter is lower due to a higher SiO_2/Al_2O_3 ratio. It is significant that (as mentioned above) zeolites are able to concentrate arsenite, arsenate and DMA. In order to test the removal of a second arsenorganic species, sorption of PHA was performed. As was shown in the kinetic part of the study, detectable amounts of sorbed DMA and PHA by the natural ZME were registered after 5 days. Nevertheless Fig. 10A shows the sorption of high arsenate, DMA and PHA concentrations after 18 days on unmodified and also on iron- and lead-modified zeolite. Retention of the species by the hydrogenated form decreases in the series As(V)>DMA>PHA and of arsenate by the modified forms Z-H>Z-Fe>Z-Pb.

3.5. Desorption and readsorption capacity

Fig. 10 demonstrates that desorption and the readsorption of As(V) are possible on both unmodified and modified forms of the zeolite ZME. The total desorption of arsenate considered with respect to the sorbed amount is greater from

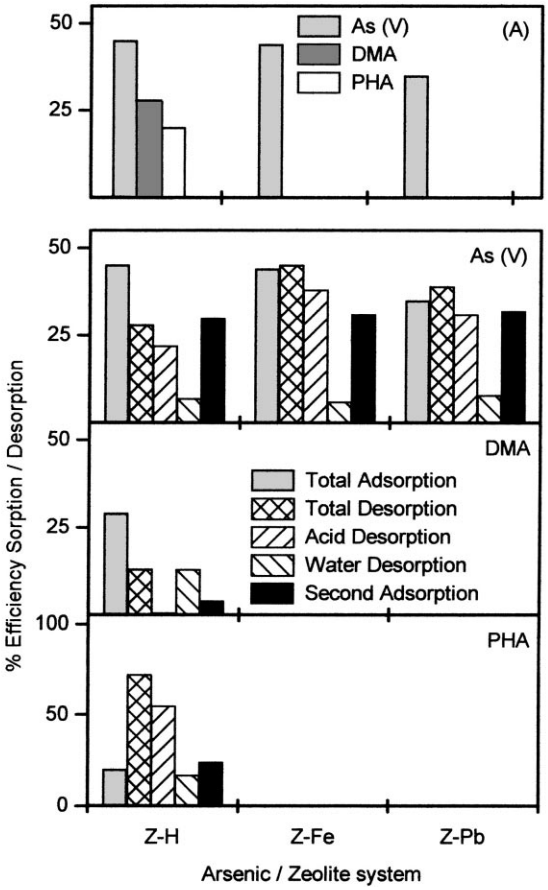

Fig. 10. Sorption efficiency (A) after 18 days from 5 mg l^{-1} solutions (pH 5) of As(V), DMA and PHA by hydrogenated and modified forms (Fe^{2+}, Pb^{2+}) of the zeolite ZME. Solid–solution relation: 1:80. Desorption capacity against sorbed As(V), DMA and PHA.

the two modified forms and also greater with HCl than with water. A smaller amount of the species PHA is sorbed by the hydrogenated form in comparison with the species DMA, while desorption occurs vice versa. An equivalent amount of arsenate can be resorbed in a second procedure by the unmodified and modified forms, although it does not reach the amounts retained in the first contact — probably due to a residual sorption level.

3.6. Comparative sorption by natural solids

It is well known that arsenic is mostly adsorbed by hydroxides in the environment [8,16,17]. Comparison between sorption on iron hydroxides and the studied zeolites demonstrated that the elimination of arsenite by two iron-modified forms, synthetic mordenite ZS-M-Fe and natural ZMA-Fe reaches 89 and 75%, respectively, of the amount removed by the hydroxide (Fig. 11). The most effective hydrogenated forms, synthetic mordenite ZS-M and natural clinoptilolite ZMS, achieve removal rates of 75 and 56%, respectively, in relation to the hydroxides. Arsenate is similarly sorbed on the iron hydroxides and on the volcanic stone and cactaceous powder, while DMA is removed to a greater extent by zeolites in comparison with iron hydroxides.

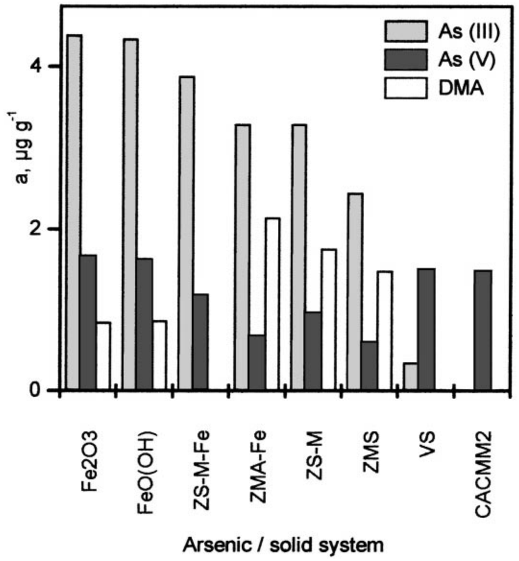

Fig. 11. Sorbed amounts of As(III), As(V) and DMA after 24 h from 250 μg l^{-1} solutions (pH 5) by hydrogenated and Fe^{2+} modified zeolites, iron hydroxides, volcanic stone (VS) and cactaceous powder CACMM2.

4. Conclusions

Arsenite, arsenate DMA and PHA were removed to different extents by the solids studied. Mordenite and clinoptilolite type zeolites showed additional As(V) formation. The sorption of arsenic takes place more slowly on zeolites in comparison to ferrihydrite. Both arsenite and arsenate were very efficiently removed in the pH interval 4–11 after contact with zeolite ZH and ZMA. Oxygen favored As(V) formation and the effect on arsenite concentration was 80% diminution when ultrasonic activation was applied, contrasting sharply with 20% without activation. More effective for arsenite retention among the unmodified zeolite samples was the natural clinoptilolite ZMS, while the mixed phase zeolite ZMA showed the highest efficiency in the iron-modified group. It was demonstrated in the case of zeolite ZME that desorption followed by re-adsorption of As(V) are achievable. Removal of arsenite by some of the iron-modified zeolites is comparable with the amount removed by iron hydroxide. Arsenate is sorbed on volcanic stone and cactaceous powder, while DMA is retained to a greater extent by zeolites.

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References

[1] L.V. Rajaković, The sorption of arsenic onto activated carbon impregnated with metallic silver and copper, Sep. Sci. Technol. 27 (1992) 1423.

[2] Yu.V. Pokonova, Carbon adsorbents for the sorption of arsenic, Carbon 36 (1998) 457.

[3] R. Jordan, Zur Adsorption von Arsen an Tonminerale, natürliche Eisenverbindungen, Sande und Tone, Ph.D. Thesis, University of Munich, Germany, 1994.

[4] J. Lindberg, J. Sterneland, P.-O. Johansson, J.P. Gustafsson, Spodic material for in situ treatment of arsenic in ground water, Ground Water Monit. Remediation 17 (1997) 125.

[5] A. Carrillo, J.I. Drever, Adsorption of arsenic by natural aquifer material in the San Antonio-El Triunfo mining area, Baja California, Mexico, Environ. Geol. 35 (1998) 251.

[6] J.M. Galer, R. Delmas, C. Loos-Neskovic, Decontamination of arsenic-containing aqueous solutions using inorganic sorbents. Investigation of the arsenic species in solution by means of capillary electrophoresis, in: A. Dyer, M.J. Hudson, P.A. Williams (Eds.), Progress in Ion Exchange: Advances and Applications, The Royal Society of Chemistry, 1997, p. 187.

[7] S. Tokunaga, S.A. Wasay, S.-W. Park, Removal of arsenic(V) ion from aqueous solutions by lanthanum compounds, Water Sci. Technol. 35 (1997) 71.

[8] W. Driehaus, M. Jekel, U. Hildebrandt, Granular ferric hydroxide — a new adsorbent for the removal of arsenic from natural water, J. Water SRT-Aqua 47 (1998) 30.

[9] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, Environ. Sci. Technol. 32 (1998) 344.

[10] J.G. Huang, J.C. Liu, Enhanced removal of As(V) from water with iron-coated spent catalyst, Sep. Sci. Technol. 32 (1997) 1557.

[11] F.G.A. Vagliasindi, M.M. Benjamin, Arsenic removal in fresh and non-preloaded ion exchange packed bed adsorption reactors, Water Sci. Technol. 38 (1998) 337.

[12] D. Bonnín, Arsenic removal from water utilizing natural zeolites, Proc. Ann. Conf. Am. Water Works Assoc. (1997) 421.

[13] M.M. Dávila, M.P. Elizalde, Adsorbente natural para la remoción de contaminantes de aguas industriales, Mexico Patent 041412 (1997).

[14] M.M. Dávila Jiménez, M.P. Elizalde González, A.A. Peláez Cid, A. Juárez Rosas, Dye and water adsorption properties of cactaceous material, J. Mater. Sci. Lett. 16 (1997) 1145–1147.

[15] M.P. Elizalde-González, R. Ruíz-Palma, Gas-chromatographic characterization of the adsorption properties of the natural adsorbent CACMM2, J. Chromatogr. 845 (1999) 373–379.

[16] R.J. Bowell, Sorption of arsenic by iron oxides and oxyhydroxides in soils, Appl. Geochem. 9 (1994) 279–286.

[17] M.J. Haron, W.M.Z. Wan Yunus, N.L. Yong, S. Tokunaga, Sorption of arsenate and arsenite anions by iron(III)-poly(hydroxamic) complex, Chemosphere 39 (1999) 2459–2466.

[18] S. Londesborough, J. Mattusch, R. Wennrich, Separation of organic and inorganic arsenic species by HPLC-ICP-MS, Fresenius J. Anal. Chem. 363 (1999) 577.

[19] G.V. Tsitsishvili, Natural Zeolites, Horwood, New York, 1992, p. 295.