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ORIGINAL ARTICLE

Anionic sorption onto modified natural zeolites using chemical activation

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Abstract The sorption of arsenate on modified-natural zeolites was investigated at varying chemical pretreatment. Zeolites were used extensively for water softening, however, a few arsenic studies have been conducted with zeolites. Arsenic pollution of the environment has received renewed attention due to toxicological evidence of its potential health hazards to humans. The ability of modified natural zeolites (stilbite and laumontite) to remove inorganic anion was investigated. The zeolites used in this work are stilbite-laumontite from Zeolitic Zone of the Corda Formation. Experiments were conducted to evaluate the relationships of the arsenate in the modified natural zeolites. Laboratory experiments were conducted examining the effect of the sorption of cationic surfactants and coagulant on stilbite-laumontite mixtures and on the subsequent sorption of arsenate by modified zeolites. Removal of arsenate using hexadecyltrimethylammonium (HDTMA)-modified zeolites was satisfactory whereas ethylhexadecyldimethylammonium (EHDDMA) and ALUM-modified zeolites were not removed with the same efficiency.

Keywords Natural zeolites · Coagulant · Cationic surfactants · Removal · Arsenate · Brazil

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Introduction

Different techniques have been tried to increase the reactivity of natural zeolites to remove the inorganic anion. The addition of chemical activators results in the possibility of anion sorption. The effect of the coagulant $Al_2(SO_4)_3$ and cationic surfactants ethylhexadecyldimethylammonium (EHDDMA) and hexadecyltrimethylammonium (HDTMA) on arsenate sorption by modified natural zeolites was examined. Arsenic is a toxic element in the environment and is found in all living tissues, waters, and soils. The bioavailability, toxicity, and mobility of arsenic in soil-water systems are determined largely by its speciation. Metallic arsenic, arsine, and methylated forms of arsenic are thermodynamically stable in reduced systems, whereas $H_2AsO_4^-$ [As(V)] and H_3AsO_3 [As(III)] predominate in oxidized systems, though the most stable species of arsenic in oxidizing environments is arsenate. The oxyanions of As also exhibit various degrees of protonation and valence charge, depending on pH (Meng et al. 2001; Bose and Sharma 2002). Arsenate exists in solution as the pH-dependent deprotonated oxyanions of arsenic acid ($H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}). High levels of arsenic in different chemical species can therefore be introduced into the food of others animals and man, in particular, with important ecological consequences (Bentley and Chasteen 2002; Smedley and Kinniburgh 2002; Abernathy et al. 2003). Traditional agriculture faces environmental contamination by pesticides and synthetic manure. Phosphate fertilizers are potential sources of arsenic. The concentration of arsenic in manure will vary with the source rock for phosphate to produce the fertilizer (Campos 2002). The use of large quantities of arsenic

has resulted in elevated arsenic levels in soil or groundwater.

Clay minerals and zeolites have permanent negative charges on their surfaces, which enable them to be modified by cationic surfactants to enhance contaminant retention and retard contaminant migration. Zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, internal and external surface areas of up to several hundred square meters per gram and cation-exchange capacities of up to several equivalents per kilogram (Pabalan and Bertetti 2001). In contrast to clays, natural zeolites can occur as millimeter or greater sized particles and are free of shrink-swell behavior. As a result, zeolites exhibit superior hydraulic characteristics and are suitable for use in filtration systems. The magnitude of the surfactant-modified zeolite and stability of sorption of the surfactant on the zeolite and anion exchange are influenced by the couterion, for example, Cl^-, Br^- or HSO_4^- of the surfactant (Krishna et al. 2001). Ion exchange with cationic surfactants has been used to alter the surface properties of clays and other natural materials. HDTMA is a tetrasubstituted ammonium cation with permanently charged pentavalent nitrogen and a long straight alkyl chain (C16), which imparts a high degree of hydrophobicity. It is well-established that clays modified with quaternary amines such as HDTMA can substantially enhance the removal of nonionic organic solutes from aqueous solution.

The advantages of using such materials are their low cost and high contaminant removal (Haggerty and Bowman 1994; Brown and Burris 1996). Historically, the most common technologies for arsenic removal have been coagulation with metal salts. Since the WHO Guideline Value for arsenic in drinking water was lowered from 50 to 10 μg L^{-1} in 1993, several countries have lowered their drinking water standards, in some cases to 10 μg L^{-1}. In 2001, the USEPA lowered the US drinking water standard from 50 to 10 μg L^{-1}. Coagulation processes are sometimes unable to efficiently remove arsenic to these low levels. As a result, various alternate technologies have been developed or adapted that are capable of removing arsenic to trace levels (Magalhães 2002; Dixit and Hering 2003). The most commonly used metal salts are aluminum salts such as alum and ferric salts such as ferric chloride or ferric sulfate. Aluminum sulfate is an effective primary coagulant based on trivalent aluminum. The product is used for the treatment of potable water as well as process water, sewage, and industrial effluents. Laboratory batch and column tests demonstrate that surfactant-modified zeolite can simultaneously remove multiple types of contaminants from water, including inorganic anions such as chromate and hydrophobic organics such as chlorinated solvents and fuel components (Bowman et al. 1995; Li et al. 1998).

The stilbite and laumontite zeolites were used in the investigation. The Brazilian stilbite-laumontite zeolites have suitable mineralogical and technical properties that enable them to be used for ion-exchange process. Stilbite and laumontita commonly occur together, Zeolitic Zone of the Corda Formation also contains smectite and less commonly calcite. Despite their importance and the wide variety of environments in which zeolites occur, the objective of this study was to examine the ability of stilbite-laumontite modified natural zeolites to remove arsenic from solution concentrations of $H_2AsO_4^-$. The reactivity of an effective zeolite could be greatly increased, particularly at early stages, by chemical treatment. Removal of arsenate by alum and cationic surfactants from water was studied separately in the laboratory.

Materials and methods

Natural zeolites were collected from the Zeolitic Zone of the Corda Formation, Brazil. The local geological setting comprises an aeolian and fluvial sedimentary system developed on basaltic lava flows which were important source rocks of the detrital components of the zeolite-bearing sandstones, as well as of the solutions for zeolite formation (Rezende and Angélica 1999). In the zeolite water system, adsorption and exchange reactions govern cation fixation. The main cation in laumontita-stilbite is typically Ca^{2+}, however, Na^+, K^+, and Mg^{2+} are also present in stilbite. Major-element concentrations were determined by inductively coupled, plasma atomic emission spectroscopy (Spectro Flame). The chemical composition and the calculated, idealized chemical formulas are tabulated in Table 1. Laumontite is a widespread zeolite that occurs in many environments, including in vugs of plutonic, volcanic, metamorphic, and sedimentary rocks; as a cement of plagioclase-rich sandstone; as a precipitate from spring waters at atmospheric pressure and temperature; and as an alteration product of vitroclastic sediments. Laumontite coexists with other zeolites, for example, stilbite. Stilbite is the most common among the three zeolites and has been described in vugs of plutonic, volcanic, and metamorphic rocks and as sandstone cement (Armbruster and Gunter 2001). In this study, the stilbite and laumontite may be written as: STI = $Na_{0.13}K_{0.74}Ca_{4.03}$ $Mg_{0.07}(Al_{9.31}Si_{26.65}O_{72})$.22.47-$H_2O$; LAU = $K_{0.09}Ca_{4.08}(Al_{7.76}Si_{16.18}O_{48})$.18.27$H_2O$.

Table 1 Chemical composition samples used in this study

	Stilbite[a]	Laumontite[b]
SiO_2	58.19	49.76
TiO_2	<0.01	<0.01
Al_2O_3	17.26	20.27
Fe_2O_3	<0.02	<0.02
MgO	0.11	<0.01
CaO	8.23	11.72
MnO	<0.01	<0.01
Na_2O	0.16	<0.01
K_2O	1.27	0.09
LOI	14.72	18.11
Total	99.99	99.95
Si	26.65	16.18
Al	9.31	7.76
Mg	0.07	–
Ca	4.03	4.08
Na	0.13	–
K	0.74	0.09
H_2O	22.47	18.27

Note: *STI*[a] Formula proportions based on 72 atoms; *LAU*[b] formula proportions based on 48 atoms; *LOI* loss of ignition (50% relative humidity)

The sample consists of stilbite, laumontita, calcite, and trace amounts of clay minerals. Potassium and calcium are the major exchangeable cations. Natural zeolites have cation exchange capacities—CEC usually between 100 and 400 meq 100 g^{-1} (Dyer 1995). The samples were subjected to grinding and sieving and additionally benefited with coagulant and surfactant.

To increase the efficiency of the zeolites, the samples were used without pretreatment for aluminum sulfate and surfactants (EHDDMA and HDTMA) sorption and the subsequent arsenic sorption experiments. Coagulation is the most common arsenic removal technology. For comparative purposes, experiments with the same total amount of cationic surfactants and coagulant were equilibrated with zeolites. For zeolites treated with EHDDMA, HDTMA-HSO_4 and ALUM, 1 g of zeolites mixture and 10 mL of HDTMA and EHDDMA solutions were placed into 50 mL centrifuge tubes. Samples were equilibrated on a shaker at 650 rpm at 25°C ± 0.4 for 8 h. The pH values of the equilibrium solutions were on average 5.8 (±0.3) and 5.3 (±0.5) after surface modification with alum and cationic surfactants, respectively. The amount of coagulant and surfactants sorbed (mmol kg^{-1}) on the zeolites is presented in Fig. 1. After the pretreatment, modified-zeolites were tested for arsenate sorption. The simulated drinking water contaminated with As^{5+} was used in the experiments. All experiments were conducted in triplicate. The arsenate stock solution was prepared from sodium salt heptahydrate $Na_2HAsO_4.7H_2O$ dissolved in double distilled

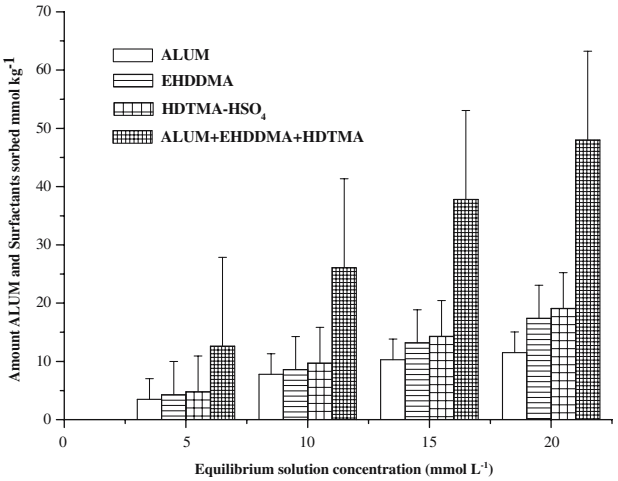

Fig. 1 Treatment of natural zeolites with different chemical activators (mmol L^{-1})

water. The total arsenic content in the water sample was measured spectrophotometrically using the silver-diethyldithiocarbamate method. Sorption studies were carried out by shaking 1 g of the sample with 50 mL of arsenic solutions containing from 0 to 0.4 mmol L^{-1}. After 8 h of shaking (650 rpm), the suspension was centrifuged and the supernatant solutions passed through a 0.45-μm filter. Nonacidified samples were analyzed simultaneously for total arsenic. Figure 2 shows the amounts of arsenate sorbed. A modified form of the Freundlich equation was used to explain the As (V) sorption rate data. Removal efficiency also appeared to increase with increasing settling time as shown in Fig. 3.

Results and discussion

Modified-natural zeolites samples have been tested for pentavalent arsenic removal from water in laboratory experiments. Like many clays, most zeolites possess a net negative structural charge resulting from isomorphic substitution of cations in the crystal lattice. Due to this negative charge, natural zeolites have little or no affinity for anionic species. In this study, the efficiency of surfactant-modified natural zeolites on the removal of arsenic was examined using ion-exchange batch. Removal of arsenic by EHDDMA, HDTMA-HSO_4 (surfactants) and aluminum sulfate (coagulant) on stilbite-laumontite zeolites were studied separately in the laboratory. To increase the efficiency of the zeolites, the samples were treated with HDTMA-HSO_4. Arsenate and sulfate are tetrahedral oxyanions that can compete for adsorption sites on materials surfaces.

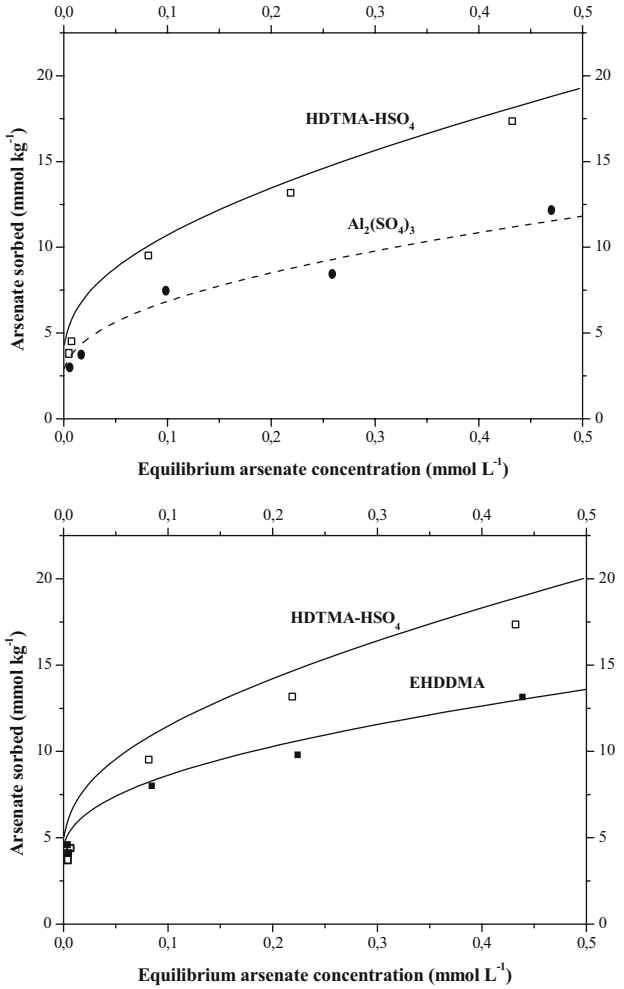

Fig. 2 Arsenate adsorption envelopes on coagulant and surfactants (mmol L^{-1})

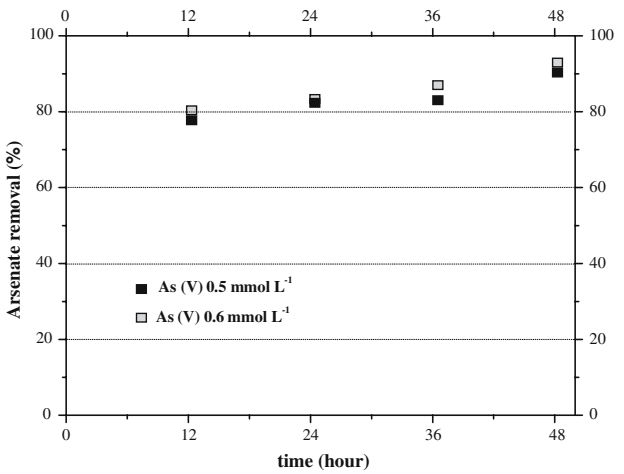

Fig. 3 Removal arsenate (%), present at different initial concentrations, by surfactant-modified zeolites as a function of time (h)

Most commonly, zeolites are pretreated with HDTMA, to establish counterions at the surface which are easily displaced by arsenic. The cationic surfactant HDTMA on zeolites was tested and the subsequent sorption of arsenate on the HDTMA-hydrogen sulfate zeolite was also determined. The stilbite-laumontite zeolites have a good efficiency to remove arsenic from water. The sorption of cationic surfactants on clay minerals and the potential applications of such modified clays as environmental remediation materials have been studied recently. According to Bowman et al. (1995), sorption of inorganic anions on cationic surfactant-modified zeolite has been attributed to the formation of a surface-anion complex. To sorb anions and form a complex, the modified surface must possess positively charged exchange sites. These sites are formed when positively charged exchange sites. These sites are formed when positively charged surfactant head groups are presented to the surrounding solution in the form of a bilayer or patchy bilayer. The positively charged head groups are balanced by counterions, and the sorption or exchange of the other anionic constituents involves the replacement of weakly held counterions by more strongly held counterions. The effects of counterions on stabilizing surfactant micelle formation in solution follow the lyotropic series (Kalló 2001). Li et al. (1998) studied counterion effects on the sorption of cationic surfactant on natural zeolite and found that the HDTMA-Br and HDTMA-Cl formed complete bilayers on the zeolite, whereas HDTMA-HSO_4 showed less than full bilayer formation.

According to Edwards (1994), during coagulation and filtration, arsenic is removed through three main mechanisms: (a) precipitation with formation of the insoluble compounds $Al(AsO_4)$; (b) co-precipitation with the incorporation of soluble arsenic species into a growing metal hydroxide phase; and (c) adsorption where the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide. All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, co-precipitation and adsorption are both active arsenic removal mechanisms.

Alum-modified-zeolites were equilibrated for 2 days at 25°C with dilute HCL and NaOH. Dilute solutions of HCl and NaOH were prepared with final pH values 3.0, 4.0, 5.0, 6.0, and 7.0. One-gram samples and 25 mL of each of these solutions were equilibrated for 2 days at 25°C in a constant temperature water bath shaker. The solution arsenate was equilibrated with the solution in a constant temperature water bath shaker at

Table 2 Ion products for alum-modified zeolites treated with acid-base solutions

Initial pH	3.0	4.0	5.0	6.0	7.0
pH	3.40	4.33	5.29	6.12	7.09
Eh (mV)	714	735	749	758	763
Al (μg mL^{-1})	4.4	1.8	3.2	2.8	2.9
As (μg mL^{-1})	1161	702	447	551	758

25°C for 7 days with constant shaking. After equilibration, Eh, pH, As, and Al were determined on the solution phase (Table 2). When the samples were equilibrated with acid-base solutions there was a greater quantity of arsenic in solution than aluminum. It is probable that a solid phase of $Al(OH)_3$ formed during the equilibration as illustrated in Eq. 1:

$$AlAsO_{4(aq)} + 3H_2O_{(1)} \rightleftharpoons Al(OH)_{3(c)} + H_2AsO^-_{4(aq)} + H^+_{(aq)} \quad (1)$$

Greater Ca content in the solution at pH 3.4 can be explained by release of $CaHAsO_4$ or $CaSO_4$ in solution. This result was due to the tendency for Ca^{2+} to form pairs with sulfate and other anions, for example, arsenate. The SO_4^{2-} level of the solution is elevated; the stability of the soluble Al-SO_4 complexes is not very high in acid waters where: $Al^{3+} + SO_4^2 = AlSO_4^+$ with log $K = 3.2$ and $Al^{3+} + 2SO_4^2 = Al(SO_4)_2^-$ with log $K = 5.1$. Under the acid conditions (pH 4), approximately equal concentrations of SO_4^{2-} and HSO_4^- are present in solution (Pourbaix 1974). Hence, the partial incorporation of arsenate ion in the alum-modified zeolites structure to occur, due to similarities in the ionic sizes of sulfate and arsenate. The larger arsenate ions seem to be accommodated in the tetrahedral sites by the expansion of the unit cell. Despite the similarities in the ionic sizes (the ionic radius of As^{5+} 0.33 Å is greater than that of sulfate) would result in a smaller expansion of the unit-cell parameters. The single or double protonation of the AsO_4^{3-} ion to give $HAsO_4^{2-}$ or $H_2AsO_4^-$ maintains the required balance of charges in the structure. The charge imbalance caused by the substitution of arsenate is compensated by the partial protonation of the AsO_4 and SO_4.

Conclusions

Comparison of different chemical activations to increase the potential anion sorption on natural zeolites was evaluated in the laboratory to determine their suitability for development of a modified-zeolite. While the natural zeolite had no affinity for the oxyanions, the HDTMA-modified zeolite showed significant removal of arsenate from aqueous solution. The results of the present experimental study showed that the counterions content is an important factor. The cationic surfactant is either exchanged or adsorbed by the zeolites. After the neutralization of the zeolites due to the exchange of the positively charged organic agent with cations in the zeolites, charge reversal of the zeolites may occur. The result is a net positive charge on its surface which results in the possibility of anion adsorption. Arsenate sorption was strongly influenced by the HDTMA-zeolite, with arsenate sorption maxima decreasing in the order HDTMA-HSO_4 > EHDDMA > ALUM. Removal system based on alum-modified zeolites and EHDDMA was not found to be suitable due to its lower removal efficiency compared to HDTMA-HSO_4 surfactant. Arsenic removal from water at alum-modified zeolites was observed as a function of pH and coagulant dose. The experimental results, expressed as the percentage removal of arsenate, showed the arsenic adsorption on HDTMA-modified zeolites exceeds the adsorption on EHDDMA-modified zeolites and ALUM-modified zeolites.

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