

# Arsenic sorption by modified clinoptilolite–heulandite rich tuffs

M. G. Macedo-Miranda · M. T. Olgún

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**Abstract** Recent works show that modified natural zeolites improve the removal of anionic or non-polar organic pollutants from water. In this work the arsenic sorption from aqueous solutions onto clinoptilolite–heulandite rich tuffs modified with lanthanum, hexadecyltrimethylammonium or iron was investigated considering the arsenic chemical species and the pH of the arsenic solutions. Clinoptilolite–heulandite rich tuffs were characterized by scanning electron microscopy and X-ray diffraction analysis. The elemental composition of the zeolitic samples was also determined. According to the Langmuir isotherm model the arsenic (V) sorption capacity of the zeolites was 75.4  $\mu\text{g As/g}$  at pH 3, 3.9  $\mu\text{g As/g}$  at pH 5 and 53.6  $\mu\text{g As/g}$  at pH 6, for the lanthanum, HDTMA and iron modified clinoptilolite–heulandite rich tuff from Chihuahua (México), respectively. In general, the results suggested that the arsenic retention depends on the precedence of zeolitic material, the nature of arsenic chemical species, pH as well as the characteristics of modified natural zeolites. In this work the arsenic adsorption mechanisms are also discussed.

**Keywords** Arsenic · Clinoptilolite · Natural zeolites · Sorption

M. G. Macedo-Miranda · M. T. Olgún (✉)  
Departamento de Química, Instituto Nacional de Investigaciones Nucleares, A.P. 18-1027, Colonia Escandón, Delegación Miguel Hidalgo, C.P. 11801 Mexico, DF, Mexico  
e-mail: mog@nuclear.inin.mx

M. G. Macedo-Miranda  
División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Toluca, A.P. 890, Av. Tecnológico S/N, Ex-Rancho la Virgen, C.P. 52140 Metepec, Estado de Mexico, Mexico

## Introduction

Arsenic is a semi-metallic element, occurs naturally in rocks and soils and can contaminate water that comes in contact with these natural components. For this reason, well water in certain regions around the world can exceed the Environmental Protection Agency's standards for arsenic in drinking water [1–5]. The WHO established that a low concentration of arsenic levels in drinking water produces negative effects on the health of the people, therefore the arsenic reference value for drinking water is 0.010 mg/L [6, 7].

In aquatic environments, arsenic is found as As(III) or As(V), depending on the oxide-reduction conditions. The arsenic (III) species is the most toxic, although the arsenic (V) species is the most movable. There are reports about treatments that remove arsenic from water; for example, the processes using carbon or alumina as adsorbents [8–10], but this process has some disadvantages such as the generation of large quantities of mud.

In the literature there are reports about treatments, which remove arsenic from water using adsorption properties in different media [8–18].

Several papers reported the use of natural zeolites to remove a variety of environmental pollutants because of their selectivity, ion exchange capacity and low cost [19, 20]. However, these zeolitic materials do not remove anionic or organic pollutants and for this reason it is necessary to treat the zeolitic material to change its surface characteristics and improve the adsorption of this kind of water pollutant [21]. Therefore, the aim of this paper was to modify the adsorption characteristics of natural zeolites using lanthanum, hexadecyltrimethylammonium (HDTMA) and iron compounds to adsorb the arsenic anionic chemical species from water. In this work, the arsenic adsorption mechanisms were discussed

with respect to the components that modify the adsorption properties of the natural zeolites and the Isotherm models explain the As(V) adsorption behavior in the zeolitic materials, which was also considered.

## Materials and methods

### Materials

The clinoptilolite–heulandite rich tuffs from Etna, located 15 km from Oaxaca city, and Arroyo, located 7 km from Parral, Chihuahua (México), were used in this work. The zeolitic materials were ground in an agate mortar and sieved. The diameter of the particles from 0.6 to 1 mm in this work was chosen taking into account future column experimentation. The size of the particles was verified by electron microscopy [22] before the EDS analyses (see Characterization Technique section).

### Natural zeolite treatments

#### *Treatment with NaCl solution*

Natural zeolite samples from Oaxaca and Chihuahua (ZO and ZCh, respectively) were put in contact with 0.3 M NaCl solution (1:6.5 solid–liquid ratio) under reflux for 12 h. This process was repeated one more time changing the NaCl solution. The phases by centrifugation were separated and the solid phases were washed until Cl<sup>−</sup> elimination was achieved using the AgNO<sub>3</sub> test. Then the zeolitic samples were dried at 333 K for 24 h. This sample was called ZONa and ZChNa, respectively.

#### *Treatment with La(NO<sub>3</sub>)<sub>3</sub> solution*

Samples of ZONa and ZChNa were put in contact with 0.1 M La(NO<sub>3</sub>)<sub>3</sub> solution. The mixture was heated in a water bath at 338 K with constant agitation for 4 h until the solution was evaporated. Then, each of the zeolite samples were thermally treated at 773 K for 4.5 h. The samples were stored in a dry atmosphere until they were used. These samples were called ZOLa and ZChLa, respectively.

#### *Treatment with HDTMABr solution*

Samples of ZONa and ZChNa were put in contact with 0.2 M HDTMABr solution for 48 h at 313 K with agitation (80 rpm). The solid phases were separated by centrifugation and were washed exhaustively with distilled water and then dried at room temperature (291 K) for 24 h. In the remaining liquid phases from the washed processes the

presence of HDTMABr was detected using a spectrophotometer UV–Vis at 195 nm. These samples were called ZOHDTMA and ZChHDTMA, respectively.

#### *Treatment with FeCl<sub>3</sub> solution*

Samples of ZONa and ZChNa were treated with 0.1 M FeCl<sub>3</sub> under agitation for 24 h. The solid phases were separated by centrifugation and they were washed with distilled water and dried at 323 K for 17 h. Then, each zeolite sample was thermally treated at 373 K for 24 h. The samples were stored in a dry atmosphere until they were used. These samples were called ZOFe and ZChFe, respectively.

### Elemental composition

Samples of 500 mg of each of the natural and modified zeolites were treated with mixtures of sulfuric, nitric and fluorhydric acid. The ratio of these acids depended on the characteristics of the digestion liquor obtained in each case [23]. The digestions were carried out on a hot plate and each sample was analyzed in duplicate. The Na, K, Ca, Mg, Al, Fe were determined using a Perkin Elmer 3110 atomic absorption spectrometer and lanthanum was determined using a Perkin Elmer analyst 700 atomic absorption spectrometer. Si was determined by gravimetric analysis [24].

Carbon in the sodic and HDTMA modified zeolitic rocks were determined using Tekmar Dorman Apollo 9000 total organic carbon analyzer at 1,073 K.

### Cation exchange capacity

Effective cation exchange capacities were determined in the untreated and treated zeolitic samples with sodium chloride solution by using a technique reported by Ming et al. [25]. The materials were treated with 1 M sodium acetate buffered solution of pH 5 to eliminate the carbonate coating on the zeolitic rocks, then they were treated with 1 M potassium chloride solution and finally with 0.2 M cesium chloride solution.

The effective cation exchange capacities were calculated from the quantity of potassium removed per gram of zeolitic rock and it was expressed in meq/g. Potassium was determined in the solutions by atomic absorption spectroscopy (Atomic absorption spectrometer Perkin Elmer 3110).

The external cation exchange capacities of the clinoptilolite-rich tuffs were determined using the Ming and Dixon technique [26], the surfactant HDTMABr was used instead of *ter*-butylammonium chloride.

Samples of sodium zeolitic rock were placed in contact with a buffered 1 M sodium acetate solution with pH 5 for 18 h, at room temperature. The solids were separated and left at room temperature for 24 h. Again, they were mixed with 0.1 M of surfactant (HDTMABr) solution and left for another 48 h at 303 K. The samples were then separated and washed twice with 5 mL of the surfactant solution.

The surfactant retained in the zeolitic rocks was determined as follows: the solids were dried at 298 K for 12 h, then they were milled and carbon was determined in each sample using an elemental analyzer of C-366N, Tekmar Dorman Apollo 9000. The quantities of surfactant retained on the zeolitic materials were calculated from the carbon determined in the samples. The external cation exchange capacity (ECEC) was calculated in meq of surfactant retained in each gram of clinoptilolite–heulandite rich tuff.

### Characterization techniques

#### *Scanning electron microscopy and elemental analyses*

For scanning electron microscopy observation, the samples were mounted directly on the sample holders and covered with gold. Finally the images were observed at 25 KeV by a Phillips XL30 electron microscope. The chemical composition of the zeolitic samples was determined by an EDS system coupled to the electron microscope.

#### *X-ray diffraction*

X-ray diffraction (XRD) analysis was performed on the zeolitic minerals (treated and untreated) to confirm the crystal structure and the identity of the components of the zeolitic material. Powder diffractograms of the sample were obtained with a Siemens D500 diffractometer coupled to a copper-anode X-ray tube. Conventional diffractograms were used to identify the compounds present in the zeolitic mineral.

#### Arsenic uptake

Samples of 100 mg of ZOLa, ZChLa, ZOHDtMA, ZChHDTMA, ZOFe, and ZChFe were treated with 10 mL of 0.1 mg/L NaAsO<sub>2</sub> or Na<sub>2</sub>HAsO<sub>4</sub> solutions (a pH from 3 to 7) for 3 h under agitation at room temperature (291 K). The zeolitic materials were separated by decantation or centrifugation and in the liquid phases HCl was added to obtain a pH value of 2. Then As was detected at 193.7 nm using an atomic absorption spectrometer GBC 932 plus with a hydride system.

As(V) was chosen in order to determine the isotherms. For this purpose samples from 5 to 120 mg of each

conditioned natural zeolite were treated with 0.1 mg/L Na<sub>2</sub>HAsO<sub>4</sub> solution for 3 h at 291 K and pH 3, 5 or 6 depending of the modified zeolite. The measurements of As in each solution were performed as described before. The experimental data was fitted by the Langmuir and Freundlich [27] adsorption models.

## Results and discussion

### Elemental composition

It was found that both natural zeolites (from Oaxaca and Chihuahua) have a similar elemental composition, however, different amounts of Na, Mg, K, Ca, and Fe were observed. The natural zeolite from Oaxaca contains more sodium than the zeolite from Chihuahua but a contrary result in the case of potassium was found (Table 1). The amount of magnesium is similar in both ZO and ZCh. Although the calcium is not observed in the natural zeolite from Oaxaca, this element was only found in the ZCh. According to these results, the ZO is a Na–K natural zeolite and the ZCh is a K–Ca natural zeolite. Iron has been associated with impurities present in zeolitic tuffs such as iron oxides [28]. The iron found in both natural zeolites was less than 1.0 wt.% (Table 1).

The treatment of the natural zeolites with NaCl solutions increased the amount of sodium 2.34 times in the ZCh (Table 1). The amount of sodium was similar before and after the sodic treatment in the case of ZO. When both natural zeolites, ZONa and ZChNa, are put in contact with the La(NO<sub>3</sub>)<sub>3</sub> solution or HDTMABr no significant changes in the amount of sodium before and after the treatments was observed. However, when these natural zeolites were treated with a FeCl<sub>3</sub> solutions, the amount of sodium diminished from 3.20 ± 0.17 (ZONa) to 2.2 ± 0.01 wt.% for ZOFe and from 1.05 ± 0.01 (ZChNa) to 0.97 ± 0.01 wt.% for ZChFe. This result suggests that the iron ions are exchanged by the sodium ions from the zeolite network but not in the case of lanthanum because of the preparation technique (see Materials and methods section). It is important to mention that in the case of HDTMABr zeolite treatments, the HDTMA<sup>+</sup> ions could only be exchanged by the sodium ions on the surface of the crystalline zeolites [29] and for this reason is difficult to note the differences between the sodium amount before and after the surfactant treatment.

The amount of lanthanum was higher in the ZChLa than in the ZOLa (1.88 and 1.27 wt.%) and similar behavior was also found for iron (1.944 ± 0.06 wt.% and 1.364 ± 0.03 wt.%) and HDTMA (1.52 and 0.68 wt.%), respectively.

**Table 1** Elemental composition of ZO and ZCh

Zeolitic sample	Na (wt.%)	Mg (wt.%)	K (wt.%)	Ca (wt.%)	Fe (wt.%)
ZO	3.20 ± 0.17	0.18 ± 0.01	2.18 ± 0.06	ND	0.77 ± 0.02
ZCh	0.45 ± 0.02	0.12 ± 0.01	3.24 ± 0.01	1.03 ± 0.01	0.99 ± 0.05

ND: no detected

### Cation exchange capacity

A similar content of silicium and aluminum was found in ZO and ZCh. The ratio of Si/Al was 4.98 and 5.14, respectively; these values are higher than the value reported by Tsitsishvili et al. [30] for clinoptilolite (Si/Al about 4), which provides evidence of other mineral components present in the zeolitic samples studied. The ion exchange capacity of the zeolites depends on this Si/Al ratio [28] and it is expected that both ZO and ZCh have a similar ion exchange capacity. The effective cation exchange capacity (EfCEC) found for ZONa was  $1.870 \pm 0.002$  and for ZChNa was  $1.350 \pm 0.001$  meq/g. This value is similar with that obtained by Diaz-Nava et al. [31] for Mexican natural zeolites, and the EfCEC is important to consider in the decontaminated water processes because arsenic is not only the pollutant species in natural water, but cationic metallic species could also be present.

It was found that the maximum capacity for La or Fe in the modified zeolites was 0.27 meq/g ZOLa, 0.40 meq/g ZChLa, 0.73 meq/g ZOFe and 1.04 meq/g ZChFe. According to these results, the lanthanum impregnated in both zeolites corresponds to the 14.4 and 29.6% of their EfCEC (ZONa and ZChNa, respectively). However 39.04 and 77.03% of the ZONa or ZChNa effective cation exchange capacity was found for iron. The differences observed between the maximum capacity of both zeolites by La and Fe can be attributed to the nature of the species present in the zeolite network after the modified zeolite preparations (see Materials and Methods section). Under the experimental conditions of this work, it is reasonable to think that lanthanum could be deposited as an oxide on the ZOLa or ZChLa and in the case of Fe (III) an ion exchange with the native cations from the zeolitic rock could be expected.

The arsenic is found as an anion species in water, and this kind of species is not exchanged by the ions from the zeolite. Bowman et al. [29], shows that by treating clinoptilolite-rich tuffs with cationic surfactant (e.g. HDTMABr), their surface chemistry becomes drastically altered and organic and anion species could be adsorbed. Large organic cation exchange is essentially irreversible with native cations such as  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ , located on the material's surface. This is the reason for determining the external ion exchange capacity (ECEC) of these materials [31]. The results show that the ECEC of the natural zeolite

from Chihuahua ( $0.095 \pm 0.001$  meq/g) is higher than the ECEC of the natural zeolite from Oaxaca ( $0.051 \pm 0.001$  meq/g), which means that the ZCh has more surface ions to be exchanged with  $\text{HDTMA}^+$  than ZO. The HDTMA amount found in the natural zeolites after the contact time with the HDTMABr solution was  $0.053 \pm 0.006$  and  $0.024 \pm 0.001$  meq/g for ZCh and ZO, respectively. These results represent the 55% and 47% of the ECEC of the natural zeolites mentioned before.

### Characterization

#### Scanning electron microscopy and elemental analyses

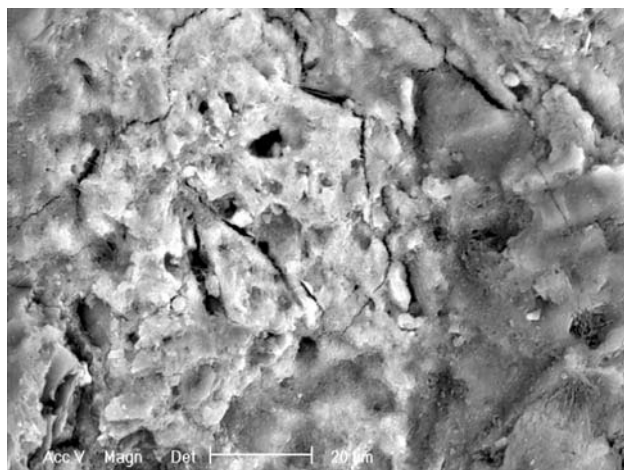
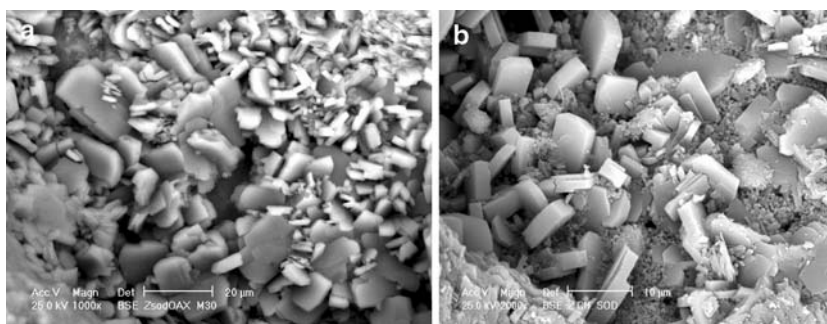
The SEM images of both Mexican zeolites from Oaxaca and Chihuahua showed morphologies characteristic of clinoptilolite, which occurred as euhedral plates and laths, whose crystals display characteristic monoclinic symmetry, and many are coffin-shaped, and cubic-like crystals [32].

No changes were observed in the morphology of the clinoptilolite crystals of the ZO and ZCh after their treatment with NaCl solution (Fig. 1 a, b); however the ZOLa have a cover in the surface probably due to the experimental conditions to obtain the lanthanum natural zeolite from Oaxaca (Fig. 2). This effect was not observed in the ZChLa. After the zeolites were treated with a HDTMABr solution, a thin cover was found in some regions of the surface of the natural zeolite from Chihuahua (Fig. 3). This thin cover was not observed in the natural zeolite from Oaxaca. No changes were observed after the treatment of the ZChNa or ZONa with the  $\text{FeCl}_3$  solution. These results suggest that the iron ionic species could be exchanged by the sodium ions from these sodic zeolitic materials.

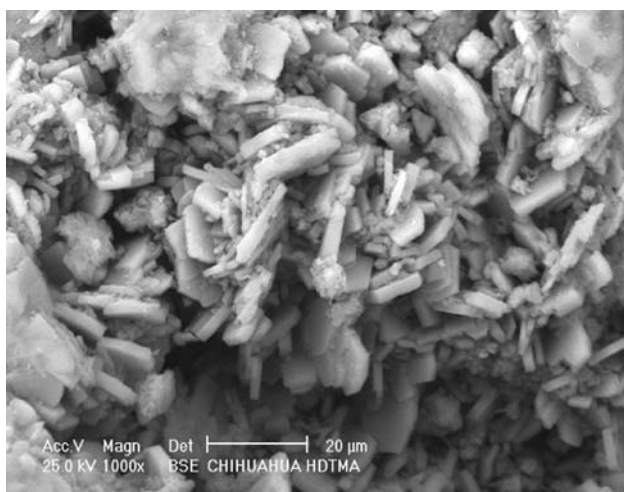
The elemental composition (EDS analyses) of both Mexican natural zeolites have slight differences. The O, Si, Al, Na, K, Ca, and Fe are the principal components of these materials. Magnesium was not detected by this technique in the natural zeolite from Oaxaca. According to the wt.%, the natural zeolite from Oaxaca contains  $\text{Na} > \text{K} > \text{Ca}$ , and  $\text{K} > \text{Ca} > \text{Mg} > \text{Na}$  is the composition of the natural zeolite from Chihuahua. These results confirm that ZO is a Na–K natural zeolite and ZCh is a K–Ca natural zeolite, as was discussed in the elemental composition section. The iron content in both zeolites is around 1 wt.%. It is clear that when the natural zeolites are conditioned with NaCl



**Fig. 1** SEM images of zeolitic tuffs from (a) Oaxaca and (b) Chihuahua, after the treatment with a NaCl solution



**Fig. 2** SEM images of zeolitic tuff from Oaxaca, after the treatment with a  $\text{La}(\text{NO}_3)_3$  solution



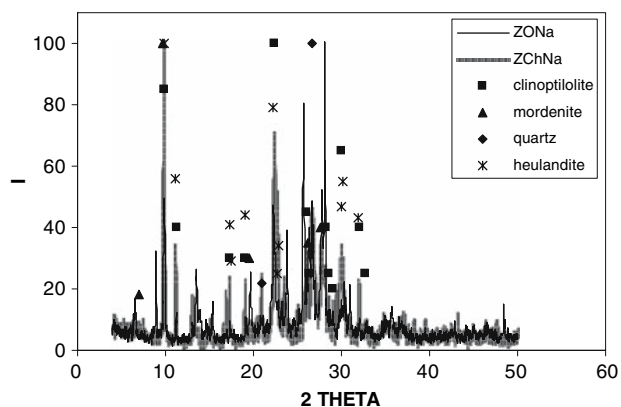
**Fig. 3** SEM images of zeolitic tuff from Chihuahua, after the treatment with a HDTMABr solution

solution, the sodium content does not vary in the natural zeolite from Oaxaca, however, in the natural zeolite from Chihuahua there is a notable increase. The sodium amount decreased after the ZChNa or ZONa were put in contact with the  $\text{FeCl}_3$  solution and the amount of iron increased in

comparison with the ZONa and ZChNa materials, indicating an ion exchange process. This behavior was not observed when the natural zeolites were put in contact with the  $\text{La}(\text{NO}_3)_3$  or HDTMABr solutions. The results obtained by the EDS technique are complementary to those obtained by atomic absorption spectroscopy (see Elemental composition section).

#### *X-ray diffraction*

Figure 4 shows the powder diffraction patterns of the natural zeolites from Oaxaca and Chihuahua (Mexico). In both zeolitic materials the principal mineral components clinoptilolite (JCPDS 25-1349), heulandite (25-144) and quartz (JCPDS 33-1161) were found. However, the presence of mordenite (29-1257) in the ZO was also observed. It is important to mention that both clinoptilolite and heulandite mineral species have a similar XRD pattern and it is difficult to differentiate one from another. For this reason, we mention it as clinoptilolite–heulandite rich tuffs in this paper. Sodium conditioned samples of these natural zeolites showed no significant changes in the position of the most intense diffraction peaks. These results suggest that sodium chloride conditioning has no effects on the structure of the zeolitic material. The diffractograms of the



**Fig. 4** Powder diffraction patterns of clinoptilolite–heulandite rich tuffs from Oaxaca and Chihuahua

sodium natural zeolites were also compared with that of the halite (JCPDS 5-0628) and it indicated that it was NaCl free. The ZOLa, ZOHDtMA, ZOFe, ZChLa, ZChHDTMA, and ZChFe patterns showed differences in the intensity of the diffraction peaks, but no changes in their position were observed in comparison with ZONa and ZChNa. These results suggest the presence of La, HDTMA, and Fe in the zeolitic networks.

#### Arsenic uptake

##### *Mexican sodium modified natural zeolites conditioned with La(NO<sub>3</sub>)<sub>3</sub> solution*

No significant differences were observed in the adsorption of arsenic (III) chemical species by the ZOLa at a pH from 3 to 7 (around 22%), however, ZChLa adsorbed 1.5 times more than ZOLa at pH 3 (Table 2). Notable differences in the As(V) chemical species adsorption by ZOLa and ZChLa were observed. In both cases, the best condition to remove As(V) from aqueous solutions is at pH 3 but ZChLa presents more efficiency at adsorbing As(V) than ZOLa at the same pH (90% and 60%, respectively). According to the results, ZChLa is the zeolitic material that most efficiently removes As(V) from aqueous solution at pH 3.

It is important to mention that less than 1.5% of the lanthanum deposited on the ZChLa or ZOLa is desorbed at pH 3 and only 0.02% at pH > 4 [33]. The pH influence on the As(V) adsorption behavior by the Mexican sodium modified natural zeolites previously conditioned with a La(NO<sub>3</sub>)<sub>3</sub> solution. This effect by the As(III) was not observed because the chemical species present in water at a pH from 3 to 7 is H<sub>3</sub>AsO<sub>3</sub>.

**Table 2** As(III) and As(V) remotion from water by lanthanum conditioned Mexican natural zeolites

Zeolitic sample	pH	Remotion (%)	
		As(III)	As(V)
ZOLa	3	21.3 ± 0.9	60.0 ± 0.4
ZChLa		33.9 ± 0.8	90.5 ± 0.7
ZOLa	4	12.1 ± 1.2	20.0 ± 2.5
ZChLa		26.6 ± 0.1	30.0 ± 3.0
ZOLa	5	24.9 ± 4.8	15.0 ± 7.0
ZChLa		28.5 ± 1.3	30.0 ± 3.0
ZOLa	6	28.5 ± 2.0	10.0 ± 1.5
ZChLa		28.7 ± 0.8	25.0 ± 7.0
ZOLa	7	23.8 ± 4.6	10.0 ± 0.5
ZChLa		15.9 ± 2.6	30.0 ± 0.8

##### *Mexican sodium modified natural zeolites conditioned with HDTMABr solution*

The ZOHDtMA and ZChHDTMA adsorbed a small amount of As(III) from the aqueous solution at a pH from 3 to 7 (around 10%). In the case of the adsorption of As(V) by both zeolites this behavior was not observed and about 40% was removed from the aqueous solution at a pH between 4 and 5 (Table 3). In this case both ZOHDtMA and ZChHDTMA natural zeolites present similar adsorption behavior for As(III) or As(V), respectively.

##### *Mexican sodium modified natural zeolites conditioned with FeCl<sub>3</sub> solution*

About 60% As(III) is removed from the aqueous solution by the ZChFe at a pH from 3 to 7 and 30% by the ZOFe at a pH between 3 and 4. When the natural zeolites previously conditioned with a FeCl<sub>3</sub> solution are put in contact with the As(V) chemical species, both ZOFe and ZChFe remove about 95% of the arsenic from aqueous solution. According to these results, ZChFe is the natural zeolite that most efficiently removes As(III) and As(V) from aqueous solution at a pH from 3 to 7 (Table 4).

The pH values do not influence the sorption behavior of As(III) or As(V) by the ZChFe, but this is not the case in As(III) adsorption by the ZOFe. The efficiency of arsenic adsorption by the Mexican sodium modified natural zeolites conditioned with a FeCl<sub>3</sub> solution depends on the arsenic chemical species present in the aqueous solution, the composition of the natural zeolite as well as the amount of iron distributed in the zeolitic network, only in the case of As(III) as it can be observed in Table 4.

**Table 3** As(III) and As(V) remotion from water by hexadecyltrimethylammonium conditioned Mexican natural zeolites

Zeolitic sample	pH	Remotion (%)	
		As(III)	As(V)
ZOHDtMA	3	1.6 ± 0.7	34.9 ± 3.3
ZChHDTMA		7.4 ± 1.1	29.0 ± 3.2
ZOHDtMA	4	2.1 ± 0.3	41.5 ± 2.4
ZChHDTMA		9.0 ± 0.7	29.5 ± 4.8
ZOHDtMA	5	5.5 ± 1.6	42.3 ± 5.4
ZChHDTMA		11.2 ± 1.4	43.8 ± 0.6
ZOHDtMA	6	3.8 ± 0.8	29.1 ± 2.3
ZChHDTMA		7.8 ± 0.7	32.4 ± 2.3
ZOHDtMA	7	3.7 ± 0.7	34.8 ± 3.0
ZChHDTMA		5.6 ± 0.7	27.7 ± 3.8

**Table 4** As(III) and As(V) remotion from water by iron conditioned Mexican natural zeolites

Zeolitic simple	pH	Remotion (%)	
		As(III)	As(V)
ZOFe	3	33.9 ± 1.5	95.2 ± 2.1
ZChFe		57.5 ± 3.5	97.4 ± 1.7
ZOFe	4	34.7 ± 3.2	94.8 ± 2.6
ZChFe		67.5 ± 3.5	98.7 ± 1.8
ZOFe	5	0	93.9 ± 1.4
ZChFe		67.5 ± 3.5	98.7 ± 1.9
ZOFe	6	11.0 ± 1.0	95.7 ± 1.4
ZChFe		69.4 ± 3.9	98.7 ± 1.8
ZOFe	7	11.0 ± 1.1	93.6 ± 1.9
ZChFe		72.2 ± 1.5	98.7 ± 1.8

It was found in this work that both ZChFe and ZOFe selectively sorb As(V) species in the presence of F<sup>-</sup> ions, however, the selectivity of these zeolitic materials changes in the presence of SO<sub>4</sub><sup>2-</sup> or PO<sub>4</sub><sup>3-</sup> ions according to their concentration in the aqueous media [34].

#### Arsenic adsorption mechanisms

##### Lanthanum modified zeolites

Removal of arsenic is one of the most interesting areas of wastewater treatment and for this reason is important to know the mechanics involved. In this section, the interactions between arsenic species and each of the modified zeolites according to the literature will be discussed.

Removal of As(III) from aqueous solutions is usually poor compared to that of As(V) by almost all of the technologies. This is because the predominant As(III) compound is neutral in charge and can undergo only Lewis acid-base interactions, while the As(V) species are negatively charged in the pH range of 4–10 and can undergo Coulombic (ion exchange) as well as Lewis acid–base interactions [35].

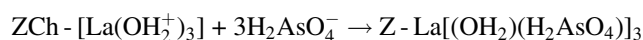
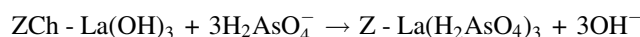
The predominant species of As(III) at a pH from 3 to 7 is the neutral species HAsO<sub>2</sub> (or H<sub>3</sub>AsO<sub>3</sub>) with a pK<sub>a</sub> value of 9.2. In the case of As(V), the predominant species are H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> at a pH from 3 to 6 and a mixture of both H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> at a pH 7. The pK<sub>a</sub> values from H<sub>3</sub>AsO<sub>4</sub> are: pK<sub>a1</sub> = 2.2, pK<sub>a2</sub> = 6.98, and pK<sub>a3</sub> = 11.6 [10, 35]. Considering the experimental conditions of the present work, the arsenic chemical species mentioned before are responsible for the arsenic removal by La, HDTMA or Fe modified natural zeolites from water.

Lanthanum compounds are used to remove arsenic from aqueous solutions. Tokunaga et al. [36] showed that La-hydroxide (LH) removed As(V) from water at a pH

from 3 to 8. These authors proposed that the mechanism of the As removal consists of (a) precipitation at initial pH < 4 and (b) adsorption at initial pH > 4.

For the aluminum-loaded Shirasu-zeolite (Al SZP<sub>1</sub>), Xu et al. [37] found that the adsorption of As(V) proceeds from formation of aluminum hydroxide on the surface of the SZP<sub>1</sub>, followed by the replacement of the hydroxide anion by the As(V) ion in aqueous media. This study mentions that similar mechanisms have been reported in the adsorption of As(V) by lanthanum-loaded silica gel and that of phosphate by an aluminum-loaded alumina.

It is important to considered that in the present work the La modified natural zeolites were obtained in two steps, (a) La(NO<sub>3</sub>)<sub>3</sub> was impregnated in the zeolitic materials and (b) the zeolites were heated at 773 K. As a result of this procedure, it is probable that lanthanum was deposited on the natural zeolites as La<sub>2</sub>O<sub>3</sub>. When the ZChLa was put in contact with the As(V) solutions at pH 3, the following interactions are proposed:



and a similar reaction was expected for ZOLa.

##### Hexadecyltrimethylammonium modified zeolites

Ion exchange with cationic surfactants has been used to alter the surface properties of zeolites and other natural materials. A general model of sorption of ionic surfactants on a solid surface is the formation of a monolayer or hemimicelle at the solid–aqueous interface via strong Coulombic (ionic) bonds at surfactant concentration at or below its critical micelle concentration (cmc). If the surfactant concentration in solution exceeds the cmc, then the hydrophobic tails of the surfactant molecules associate to form a bilayer or admicelle.

Hexadecyltrimethylammonium is a tetra-substituted ammonium cation with a permanently charged pentavalent nitrogen and a long straight alkyl chain which imparts a high degree of hydrophobicity [38].

It was found that the zeolite treated with HDTMA at amounts equal to 100% of the external CEC resulted in the highest sorption capacity for chromate and selenate anions [39–41].

Haggerty and Bowman [39], in order to explain the sorption of the oxyanions by HDTMA–zeolite, proposed the following mechanisms: (1) Sorption due to admicelle formation, (2) Chemical reduction of anions to less soluble forms, and (3) Surface precipitation of oxyanions with HDTMA.

Anion exchange sites for chromate sorption have been demonstrated, occurring on surfactant bilayers on HDTMA-modified zeolite. Alternately, hexavalent chromate may act as a Lewis base by donating an electron pair to acid sites present on the zeolite surface. The presence of Lewis acid sites on zeolite has been demonstrated. These sites on adsorbates are known to affect the polarizability and dipole moment of the conjugate acid or base and, thus, the Raman and IR band frequencies. Lewis acid sites occur when the zeolites have been completely alkali-exchanged and dried under vacuum.

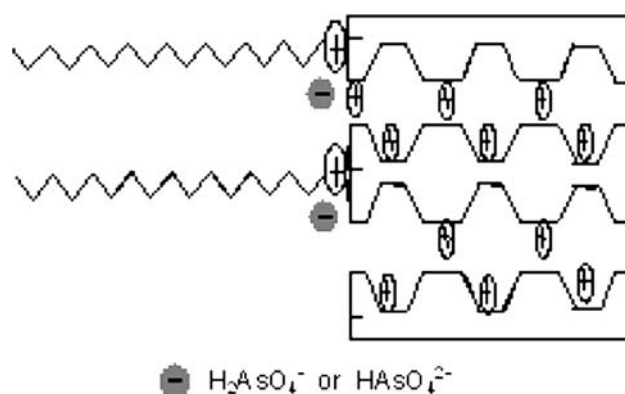
The presence of the surfactant may substantially reduce the amount of near-surface water in an aqueous system, enhancing the relative acidity of such sites and subsequently promoting chromate sorption [42].

Vujaković et al. [21] found that the organo-zeolite obtained by oleylamine modification of the  $H^+$  form of zeolite is an effective adsorbent of  $SO_4^{2-}$ ,  $Cr_2O_7^{2-}$ , and  $H_2PO_4^-$  anions present in water. The protonated amine molecules at the external surface of the  $H^+$  clinoptilolite act as much stronger anion adsorption sites than the quaternary ammonium salt cations on natural clinoptilolite.

In the present work, the HDTMA modified natural zeolites were obtained by ion exchange considering the surface exchangeable ions of the Mexican zeolitic materials (see Experimental section) and according to the results only 55% and 47% of the sodium ions from the surface of the ZCh and ZO were exchanged by the HDTMA ions, respectively. This means that a hemicelle surfactant arrangement is expected, but it is important to mention that approximately a surfactant semi-layer was obtained in both ZCh and ZO. Due to this fact, it is proposed that the oxyanions may associate with the cationic head of the HDTMA on the zeolite surface to form an organic salt (Fig. 5) as was discussed elsewhere.

#### Iron modified zeolites

The iron (III) oxide surface has a high affinity for As(V) and is capable of forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes. The As(III) species also has a high affinity for the iron (III) oxide surface with evidence from FTIR spectroscopy for an inner-sphere adsorption mechanism similar to As(V). The data obtained by Manning et al. [43] suggests that As(III) would be more strongly bound to iron oxide surfaces than As(V) at neutral to alkaline pH. The difference in macroscopic adsorption behavior between As(III) and As(V) may be partly related to differences in the structure of the As(III) and As(V) surface complexes. Apparently, As(III) forms a single bidentate binuclear As(III) surface structure, whereas As(V) forms at least two complexes. Similar mechanisms



**Fig. 5** Representation of the arsenic adsorption on the HDTMA modified natural zeolites from Oaxaca and Chihuahua (México)

were proposed by Su and Puls [44], with their spectroscopic evidence suggesting that As(V) predominantly forms inner-sphere bidentate surface complexes with goethite.

Both protonated and electrically neutral iron oxides selectively sorb As(V) and As(III) species through Lewis Acid–base interactions, i.e., formation of inner sphere complexes. However, competing  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$  ions form only outer sphere complexes with only weak affinity toward hydrated iron oxide (HFO) [35], using a polymeric/inorganic hybrid sorbent.

It is important to mention that Inner-sphere complexes are defined previously as covalent linkages between the adsorbed ion and the reactive surface with no water of hydration between the adsorbed ion and the surface functional group [43].

With iron hydroxide, As(III) is adsorbed in much larger amounts than As(V) at  $pH > 7.5$  or at high As concentrations in solution. Maximum As(III) adsorption on hematite and amorphous iron hydroxide occurs at pH 7. The pH effect is generally explained by the zero point of charge (ZPC) of the adsorbent. A ZPC of 7.1 has been reported for hematite. When the pH is above 9, the negatively charged  $H_2AsO_3^-$  becomes predominant, whereas the oxide surface also becomes negatively charged; thus, electrostatic repulsion results in decreased adsorption [44].

Numerous studies have quantified and modeled As(V) and As(III) sorption onto amorphous iron oxide (HFO), goethite, lepidocrocite, and hematite. Both As(V) and As(III) sorb strongly to iron oxide; however, the sorption behavior of arsenic is dependent on its oxidation states and the mineralogy of the iron oxides [45].

It was found that in water samples treated with either ferric chloride or ferric sulfate, arsenic adsorption by iron complexes occurs by ligand exchange of the As species for  $OH_2$  and  $OH^-$  in the coordination spheres of surface



structural Fe atoms. The predominant oxidation state of arsenic depends on the pH and the potential redox. Both forms As(III) or As(V) have strong affinities for iron complexes [46].

It can be presumed that the processes involved in arsenic adsorption by natural solids like mordenite-type zeolite is through the basic and acidic Brönsted sites [47].

Vaishya and Gupta [48] proposed that the reaction of As(V) with the iron oxide surface can also be explained with the help of the surface complexation theory. In this case, the site S–Fe–OH acts as a Lewis acid and arsenate ions act as a Lewis base and cause exchange of OH<sup>−</sup>, known as a ligand exchange mechanism. Shevade and Ford [49] also reported that the different arsenic removal capacity of the modified zeolite ‘‘Y’’ indicates that the structure, including Si/Al ratio, plays an important role in the arsenic removal process which also follows a ligand exchange mechanism.

In the present work, the Fe modified natural zeolites were obtained by ion exchange (see Experimental section) and according to the results, 50% of the EfCEC of both ZO and ZCh was occupied by the iron ions but not all of them could play a role in the arsenic adsorption processes because of the arsenic chemical speciation. It is proposed then that only iron found on the surface of the natural zeolites take part in these processes. When the ZChFe and ZOFe was put in contact with the As(III) or As(V) solutions at a pH from 3 to 7, the following interactions are considered:

As(III)

Monodentate inner sphere complex:

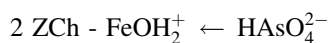
Only Lewis acid–base interaction



As(V)

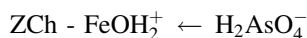
Bidentate Inner sphere complex:

Coulombic and Lewis acid–base interactions

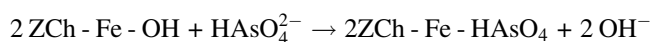
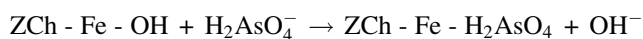


Monodentate Inner sphere complex:

Coulombic and Lewis acid–base interactions



Ligand exchange



Similar arsenic adsorption mechanisms are proposed for ZOFe.

All the mechanisms discussed in this section could explain the differences between the maximum capacities of the modified zeolites (ZCh and ZO) to adsorb As(III) or As(V) from the aqueous solutions.

### Adsorption isotherms

The experimental data obtained for the arsenic (V) adsorption by the natural Mexican zeolites (ZOLa, ZChLa, ZOHDtMA, ZChHDTMA, ZOFe, and ZChFe) were fitted to the well known Langmuir and Freundlich isotherm models, however, the experimental data could not be adjusted to the Freundlich model taking their *r*<sup>2</sup> parameter into account.

The Langmuir model is represented by the following equation [50]:

$$q_e = Q_0 b C_e / (1 + b C_e)$$

Where *q<sub>e</sub>* is the amount of arsenic (V) per unit weight of zeolite (mg g<sup>−1</sup>), *C<sub>e</sub>* is the equilibrium concentration of arsenic in solution (mg L<sup>−1</sup>), *Q<sub>0</sub>* is the amount of solute retained per unit weight of adsorbent in forming a complete monolayer on the surface, and *b* is the constant related to the energy or net enthalpy of adsorption. One of the typical Langmuir Isotherms obtained in this work is presented in Fig. 6.

Data in Table 5 show that the Langmuir maximum adsorption capacities (*Q<sup>0</sup>*) of Mexican natural zeolites for As(V) is dependent on the type of conditioned zeolite as well as the composition of the zeolitic material. The arsenic adsorption capacities follow the order: ZChLa > ZChFe > ZOFe > ZOLa > ZChDTMA > ZOHDtMA. It is important to mention that according to the results presented elsewhere, the arsenic isotherms were obtained at pH 3 for ZOLa and ChLa, at pH 5 for ZOHDtMA, and

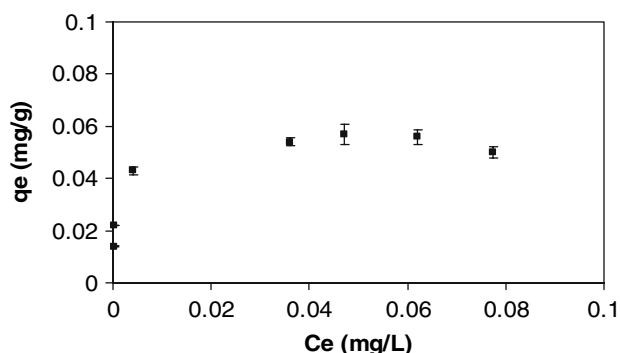


Fig. 6 Langmuir isotherm which describe the arsenic adsorption by ZChFe zeolitic tuff

**Table 5** Langmuir parameters for the As(V) adsorption by Mexican natural zeolites previously conditioned with La(NO<sub>3</sub>)<sub>3</sub>, HDTMABr and FeCl<sub>3</sub> solutions

Zeolitic sample	Equation $1/q_e = 1/Q^o + (1/bQ^o)(1/C_e)$	$Q^o$ mg/g	$b$ (mg/L)	$r^2$
ZOLa	$1/q_e = 4.545 (1/C_e) + 62.859$	0.01590	13.83	0.8327
ZChLa	$1/q_e = 3.5784 (1/C_e) + 13.26$	0.07541	0.02107	0.8808
ZOHDTMA	$1/q_e = 2.0014 (1/C_e) + 299.81$	0.00333	149.799	0.8972
ZChHDTMA	$1/q_e = 1.0501 (1/C_e) + 255.92$	0.003907	243.7	0.9953
ZOFe	$1/q_e = 0.1704 (1/C_e) + 44.86$	0.02229	263.26	0.8214
ZChFe	$1/q_e = 0.0076 (1/C_e) + 18.627$	0.05368	2450	0.9886

ZChHDTMA and at pH 6 for ZOFe and ZChFe. The affinities ( $b$ ) vary remarkably as a result of modification and reflect the ability of the conditioned natural zeolites to adsorb the As(V) chemical species from aqueous solution. The ZChFe presents the highest affinity for the As(V) in comparison to the rest of the zeolitic material (Table 6).

The effect of the isotherm shape can be used to predict whether a sorption system is favorable or unfavorable [51]. For these reasons, a dimensionless constant separation factor or equilibrium parameter  $K_R$  was defined according to the following equation:

$$K_R = 1/(1 + bC_0)$$

Where  $b$  is the constant related to the energy or net enthalpy of adsorption, as was mentioned elsewhere, and  $C_0$  is the initial As(V) concentration in the aqueous solution. According to the  $K_R$  value the isotherm could be:

$K_R > 1$ , unfavorable;  $K_R = 1$ , lineal;  $0 < K_R < 1$ , favorable and  $K_R = 0$ , irreversible.

The  $K_R$  values obtained for the As(V) adsorption by the modified natural zeolites show that the adsorption process is favorable in all cases, and independently if the zeolite contains La, HDTMA or Fe as a result of their conditioning or for their geographic localization (Table 6).

**Table 6**  $K_R$  values for the As(V) adsorption by the conditioned Mexican natural zeolites

Zeolitic sample	$b$ (mg/L)	$C_0$ (mg/L)	$K_R$	Langmuir isotherm
ZOLa	13.83	0.1	0.41966	Favorable
ZChLa	0.02107	0.1	0.9978	Favorable
ZOHDTMA	149.799	0.097	0.0643	Favorable
ZChHDTMA	243.7	0.097	0.0405	Favorable
ZOFe	263.26	0.09	0.0404	Favorable
ZChFe	2450	0.09	0.0045	Favorable

## Conclusions

Clinoptilolite and heulandite are the principal mineral component of both Mexican natural zeolites. Na and K are the predominant native cations of the natural zeolite from Oaxaca and K and Ca of the natural zeolite from Chihuahua.

The content of La, HDTMA or Fe is the highest in the natural zeolite from Chihuahua after the modification processes of the Mexican natural zeolites and morphological changes are observed in the modified natural zeolites.

The presence of La, HDTMA and Fe in the zeolitic network of the Mexican natural zeolites from Oaxaca and Chihuahua improve their arsenic adsorption capacities.

The interaction between the arsenic and the Mexican natural zeolites depend on both the characteristics of the modified surface of each zeolitic material and the nature of the arsenic species present in the aqueous solution at a pH from 3 to 7.

The Langmuir isotherm equation was able to describe the partitioning behavior for the systems.

The natural Mexican iron modified zeolite from Chihuahua (ZChFe) has good characteristics for potential treatment of As(III) or As(V) pollutant waters.

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