



Adsorption kinetic of arsenates as water pollutant on iron, manganese and iron–manganese–modified clinoptilolite-rich tuffs

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ABSTRACT

Arsenate adsorption from aqueous solutions onto clinoptilolite–heulandite rich tuffs modified with iron or manganese or a mixture of both iron and manganese in this work was investigated. A kinetic model was considered to describe the arsenates adsorption on each zeolitic material. The modified clinoptilolite–heulandite rich tuffs were characterized by scanning electron microscopy and X-ray diffraction analysis. The elemental composition and the specific surface area of the zeolitic material were also determined. The arsenate adsorption by the modified zeolites was carried on in a batch system considering a contact time from 5 min to 24 h for the kinetic experimentation. The arsenic was detected by atomic absorption spectrometer using a hydride generator. The kinetics of the arsenate adsorption processes were described by the pseudo-second-order model and the obtained parameter k varies from 0.15 to 5.66 $\mu\text{g}/\text{gh}$. In general, the results suggested that the kinetic adsorption of arsenates on the modified clinoptilolite-rich tuffs depend of the metallic specie that modified the surface characteristics of the zeolitic material, the chemical nature of the metal as well as the association between different metallic chemical species in the zeolitic surface.

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1. Introduction

Arsenic occurs naturally in groundwater in many parts of the world as arsenites [As(III)] or arsenates [As(V)], and many people worldwide are exposed to them [1]. Ingesting As causes adverse health effects [2,3]. The toxic effect of arsenic in foods is highly dependent on its chemical speciation. Inorganic arsenic compounds are generally thought to be more toxic than organic forms [4]. The United States Environmental Protection Agency's (USEPA) has lowered their regulatory standards for drinking water arsenic from 50 to 10 $\mu\text{g}/\text{L}$ [5] and the World Health Organization's guideline value has been lowered to 10 $\mu\text{g}/\text{L}$ [6,7]. As ingestion continues to be an important public health problem. In the arsenic-affected areas of Bangladesh, for example, groundwater contains up to 2 mg As/L [8]. Similar problems in arsenic water contamination were observed in the Red River Delta (Vietnam) [9], and the western United States [10].

In Mexico, Wyatt et al., Del Razo et al. and Alarcón et al. [11–13], reported the presence of natural arsenic water contamination in

the North and Central areas of the Mexican Republic. Wyatt et al. [11] detected high levels of lead, mercury and arsenic in well water from Hermosillo, Guaymas and Nacozari (Sonora) localities. In drinking water from Coahuila state, a concentration of 0.390 mg As/L has been reported. Alvarado [12] found that drinking water from Durango localities contains more arsenic than the maximum permissible level established by the Mexican Standard NOM-127-SSA1-2000 from 0.045 mg/L in year 2001 to 0.025 mg/L in year 2005 [13].

Considering the high toxicity of arsenic and the nosive effects produced through the contamination of groundwater, the development of alternative arsenic treatment technologies is required.

Several works show that iron and manganese compounds adsorbed arsenates from aqueous solution [14–17] and only in a few of them considered a mixture of iron–manganese compounds for the same purpose [18]. On the other hand, it was found that modified natural zeolites improve the removal of anionic or nonpolar organic pollutants from water [19,20].

Therefore, the aim of this paper was to modify the adsorption characteristics of natural zeolites using iron or manganese or both iron–manganese compounds to adsorb arsenates from water, considering the experimental conditions to obtain the different metallic-modified zeolites.

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2. Materials and methods

2.1. Materials

The clinoptilolite-rich tuff bought to Lunmogral S.A. de C.V. Mexican Company was used in this work. The zeolitic materials were ground in an agata mortar and sieved. A 200-mesh particle size was selected to perform the experimentation. A cation exchange capacity of 1.2 mequiv./g was previously determined by Jiménez [21] for this material.

2.2. Clinoptilolite-rich tuff treatments

2.2.1. Treatment with NaCl solution

In order to improve the ion exchange characteristics of the zeolitic material [22] to obtain Fe- or/and Mn-modified clinoptilolite-rich tuff with different surface characteristics as well as to follow the mechanism involved as will be discussed later (Section 3.1.1.), 150 g of clinoptilolite-rich tuff (CLI) were treated with 0.1 M NaCl solution under reflux for 3 h. This process was repeated once more, while changing the NaCl solution. The phases were separated by centrifugation and the solid phases were washed until Cl^- was eliminated using the AgNO_3 test. Then, the zeolitic samples were dried at 60 °C for 24 h. This sample was called CLINa.

2.2.2. Treatment with FeCl_3 or MnCl_2 or a mixture of FeCl_3 and MnCl_2 solutions

Fifty grams of CLINa was treated with 500 mL of 0.1 M FeCl_3 solution under reflux for 5 h. This process was repeated once after changing the solution. The solid phase was separated by centrifugation and was washed with distilled water and dried at 80 °C. The sample was stored in a dry atmosphere until the sample was used. This sample was named CLIFeA.

The procedure mentioned before was in a similar manner using 0.01 M FeCl_3 , 0.1 M MnCl_2 and a mixture 0.1 M FeCl_3 and MnCl_2 solutions. The resultant zeolitic materials were named, CLIFeB, CLIMn and CLIFeMn, respectively. It is important to mention that only the sample CLIMn was thermally treated at 100 °C for 5 h before contact with the As(V) solution.

2.3. Characterization techniques

2.3.1. Scanning electron microscopy and elemental analyses

For scanning electron microscopy observation, the samples were mounted directly onto 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 using the EDS system coupled to the electron microscope. A series of 10 analyses were performed for each zeolitic sample.

2.3.2. X-ray diffraction

X-ray diffraction (XRD) analysis was performed on the zeolitic (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 rock.

2.3.3. Specific surface area

The BET specific surface areas were determined by standard multipoint techniques of nitrogen adsorption using a

Micromeritics Gemini 2360 instrument. The untreated and modified clinoptilolite-rich tuffs were heated at 60 °C for 2 h before specific surface areas were measured.

2.4. Kinetics of the arsenates uptake

Hundred milligram of CLIFeA, CLIFeB, CLIMn and CLIFeMn were put in contact with 10 mL of 0.1 mg/L Na_2HAsO_4 solutions at pH 6.5 under agitation from 5 min to 24 h at room temperature (18 °C). The zeolitic materials were separated by centrifugation and HCl was added to the liquid phases to obtain a pH value of 2 to conserve the samples until the As was detected at 193.7 nm using an atomic absorption spectrometer GBC 932 plus with a hydride system. The experimental data was fitted by the first order, Elovich and pseudo-second-order kinetic models [23,24].

3. Results and discussion

3.1. Characterization

3.1.1. Elemental composition

The principal components of CLI are O, Na, Mg, Al, Si, K, Ca and Fe (Table 1). It is reasonable to consider that Na, Mg, K and Ca are the extraframework cations that compensate for the deficiency of negative charge in the zeolite network [25,26]. A Mössbauer study [27] of iron-containing zeolitic rocks from several countries (Mexico, Cuba, Czech Republic, and the Russia) showed that iron is located as high spin Fe^{3+} in framework tetrahedral sites, in extraframework octahedral sites as free $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and as high spin Fe^{2+} in octahedral coordination in extraframework sites or in another aluminosilicate associated with the zeolite. Iron is also located in magnetite contained in the zeolite rocks.

According to the concentration of Na, Mg, K and Ca in the CLI (Table 1), it is considered to be a potassium–calcium zeolite type. A similar result was obtained by Jiménez [21].

After combining clinoptilolite-rich tuff with a NaCl solution, the Na concentration in the CLINa increased from 0.4 to 1.7% and a similar result was observed by other researchers [21,22]. In the clinoptilolite-rich tuffs treated with FeCl_3 solutions, the sodium concentration diminishes, more importantly in the CLIFeA relative to the CLIFeB (Table 1), in comparison both of them to CLINa and the concentration of iron increase (11.6 and 4.0%, respectively), depending on the initial concentration of FeCl_3 in the solution (0.1–0.01 M). However, it is important to mention that both K and Ca were also diminished (Table 1). This suggests that Na^+ , K^+ and Ca^{2+} play an important role in the conditioned processes of the clinoptilolite-rich tuff with the iron salt, probably due to an ion exchange mechanism. It is important to mention that the initial pH of the FeCl_3 solutions are into the range of 2 and 3, therefore it is also consider that H^+ could compete for the ion exchange sites from the zeolite network [28]. The cation exchange capacity of the zeolitic material is 1.2 mequiv./g, this means that besides being fully iron exchanged the CLIFeA (6.2 mequiv. Fe^{3+} /g) and CLIFeB (2.15 mequiv. Fe^{3+} /g) contains also an additional fraction of iron ions that does not act as charge-balancing species as was mentioned by Doula [29] who also comment that in general, samples which contain more iron (or other metallic cation) than calculated from the theoretical ion exchange capacity, are characterized as overexchanged samples. The additional Fe^{3+} ions most likely form iron oxo or hydroxo cations according to Gervasini [30], amorphous extra framework metallic cations can be deposited on both internal and external surfaces.

When the clinoptilolite-rich tuff is treated with a MnCl_2 solution, the Na concentration decreases in the zeolitic material, but

Table 1
Elemental composition of unmodified and modified clinoptilolite-rich tuffs

Element	Composition (wt.%)					
	CLI	CLINa	CLIFeA	CLIFeB	CLIMn	CLIFeMn
O	51.23 ± 2	51.05 ± 1	48.16 ± 2	52.8 ± 1	51.63 ± 2	50 ± 1
Na	0.44 ± 0.1	1.78 ± 0.5	–	1.14 ± 0.2	0.71 ± 0.2	0.7 ± 0.2
Mg	0.4 ± 0.1	0.52 ± 0.1	0.34 ± 0.1	0.48 ± 0.1	0.53 ± 0.1	0.39 ± 0.2
Al	7.44 ± 0.4	7.74 ± 0.8	5.87 ± 0.6	6.6 ± 0.2	7.34 ± 0.8	5.6 ± 0.2
Si	34.56 ± 1	33.49 ± 0.5	29.91 ± 2	31 ± 0.9	33.8 ± 1.1	28.7 ± 1.7
Cl	–	–	0.72 ± 0.2	0.25 ± 0.03	–	0.7 ± 0.1
K	3.1 ± 0.4	2.68 ± 0.2	1.98 ± 0.2	2.3 ± 0.2	2.11 ± 0.2	1.7 ± 0.2
Ca	2.29 ± 0.3	1.47 ± 0.2	0.97 ± 0.2	1.15 ± 0.1	1.14 ± 0.2	0.9 ± 0.2
Mn	–	–	–	–	2 ± 0.4	0.7 ± 0.1
Fe	0.93 ± 0.5	1.09 ± 0.3	11.66 ± 3	4.24 ± 0.5	0.92 ± 0.2	11 ± 2

variations in K or Ca concentration was not observed, as compared to the concentration of these elements in the CLINa (Table 1). The Mn concentration in the modified clinoptilolite-rich tuff is 2 wt.% corresponding to 0.72 mequiv. Mn²⁺/g, this value is less than the effective cation exchange capacity of the zeolitic material. According to the chemical speciation distribution diagram obtained by MEDUSA program [31], manganese predominant specie under the experimental conditions is Mn²⁺, therefore it is probably that this specie could play a role in an ion exchange processes during the preparation of the manganese-modified clinoptilolite rich-tuff. It is important to note that the initial pH of the MnCl₂ solutions was 4, therefore H⁺ could compete with the Mn²⁺ for the ion exchange sites from the zeolitic network in a similar way than Fe³⁺ mentioned above.

In the clinoptilolite-rich tuff treated with a mixture of FeCl₃ and MnCl₂ solutions, it was found that the concentration of Fe is similar to that obtained for CLIFeA (11% corresponding to 5.94 mequiv. Fe³⁺/g), due to the initial concentration of the iron salt in the solution (0.1 M), however a decreased concentration of manganese (0.7% corresponding to 0.25 mequiv. Mn²⁺/g) was observed in the same zeolitic material (CLIFeMn) relative to the Mn concentration obtained in the CLIMn (2%). In this case, selectivity is an important point to be considered because the CLI is more selective for Fe³⁺ relative to Mn²⁺ ions. The Na, K and Ca concentrations in the zeolitic material notably decrease after treatment (Table 1). Again, this suggests that sodium, potassium and calcium, as a cationic specie, are involved in the conditioned processes of the clinoptilolite-rich tuff by a mixture of iron and manganese salts in aqueous solution.

3.1.2. Morphology

The SEM images of CLI showed morphologies characteristic of clinoptilolite, which occurred as euhedral plates and laths, crystals displaying 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 CLI after its treatment with NaCl, FeCl₃ or MnCl₂ or a mixture of both FeCl₃ and MnCl₂ solutions. Only for comparison purposes, the SEM images of CLINa, CLIFeA and CLIFeMn were observed. It is important to mention that the CLIFeMn showed the highest *k* kinetic parameter as will be discussed later.

3.1.3. X-ray diffraction

Clinoptilolite (JCPDS 25-1349) and quartz (JCPDS 33-1161) were found in CLI. A sodium-conditioned sample of natural zeolite showed no significant changes in the position of the most intense reflexions corresponding to clinoptilolite ($2\theta=9.85^\circ$, 22.4° and 30.0°). This result suggests that sodium chloride conditioning has no effect on the structure of zeolitic material. The diffractogram

of the sodium natural zeolite was also compared to that of the halite (JCPDS 5-0628) and indicated that it was NaCl free (Fig. 1a). The CLIFeA, CLIFeB, CLIMn, and CLIFeMn, X-ray diffraction patterns (Fig. 1b–e, respectively) showed differences in the intensity of reflexions, but no changes in their position were observed relative to CLINa. These results suggest the presence of Fe, Mn and Fe–Mn in the ion exchange sites (probably M1 and M2) from the zeolitic network. Similar results were found by Concepción-Rosabal [33] in silver-modified natural zeolites. By the other hand in the Fe–Clin system (with 14 wt.% of Fe) no notable changes in the basic zeolite diffraction were found by Doula [29], indicating no detectable damage to the clinoptilolite framework, nor the presence of additional Fe oxidic or oxo-hydroxidic crystalline phases. The author comment that this absence of additional reflexions is in agreement with the results from the determination of the amorphous Fe species content and thus, is expected since no crystalline Fe-phases have been formed at clinoptilolite surface sites. In the case of the X-ray diffraction pattern of CLIMn is not observed the presence of other manganese phases.

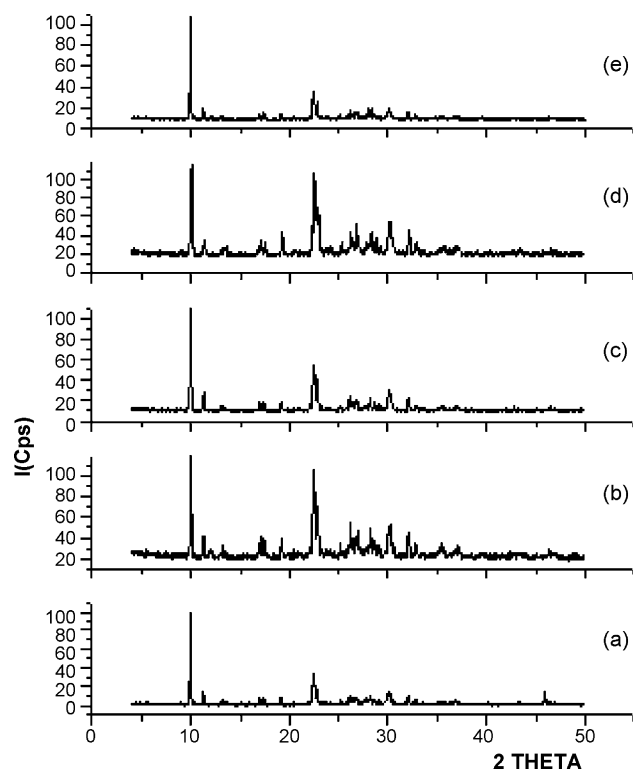


Fig. 1. X-ray diffraction patterns of the different zeolitic materials: (a) CLINa; (b) CLIFeA; (c) CLIFeB; (d) CLIMn; (e) CLIFeMn.

Table 2
Specific surface areas of unmodified and modified clinoptilolite-rich tuffs

Materials	Specific surface area (m ² /g)
CLI	5.37
CLINa	6.18
CLIFeA	45.92
CLIFeB	7.82
CLIMn	4.61
CLIFeMn	46.71

3.1.4. Specific surface area

The specific surface area of the CLINa slightly increases with respect to CLI. However, when the CLINa was treated with 0.1 M FeCl₃ or a mixture of both 0.1 M FeCl₃ and 0.1 M MnCl₂ solutions, the resultant-modified clinoptilolite-rich tuffs (CLIFeA and CLIFeMn, respectively) increased 7.5 times their specific surface areas (Table 2). These changes could be attributed to the iron concentration in both zeolites (11 wt.%, see Table 1) and the speciation of the iron in the zeolite network considering and overexchange zeolites [29]. When the concentration of FeCl₃ in solution was diminished 10-fold, the obtained zeolitic material had a slightly specific surface area compared to CLINa, and was notably low in comparison with the values for CLIFeA and CLIFeMn. Finally, when the clinoptilolite-rich tuff was treated with a 0.1 M MnCl₂ solution and treated at 100 °C, the obtained zeolitic material (CLIMn) had a specific surface area less than that for CLINa. Therefore, from the experimental conditions of the treatment will depend the final surface characteristics of the modified clinoptilolite-rich tuff to consider in the As(V) adsorption processes.

3.2. Kinetics of the arsenates uptake

It was found that the CLIFeA adsorb 6 μg As(V)/g in the first 5 min, reaching equilibrium after 180 min of contact time with a maximum As(V) adsorption of 8 μg/g (Fig. 2).

When the clinoptilolite-rich tuff contains a decreased concentration of iron in its structure (CLIFeB), the time in which equilibrium is reached is 5.6 times greater than in CLIFeA (Fig. 2). The As(V) adsorption at equilibrium is 5 μg/g and this value is 37.5% low than for CLIFeA.

No As(V) adsorption was observed on thermally untreated manganese-modified zeolite, however when the zeolitic material was thermally treated to 100 °C, this ZCLIMn adsorbed 2 μg As/g in the equilibrium which was reached at 900 min (Fig. 2). Therefore, the thermal treatment of the clinoptilolite-rich tuff after it

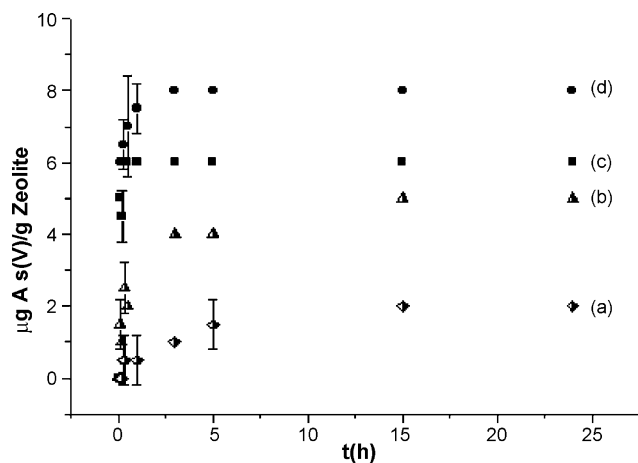


Fig. 2. As(V) sorption uptake by (a) CLIMn; (b) CLIFeB; (c) CLIFeMn; (d) CLIFeA as a function of time.

Table 3
First-order-kinetic parameters obtained for the arsenates adsorption on modified clinoptilolite-rich tuffs

Material	q_e (μg/g)	K_L (h ⁻¹)	R
CLIFeA	7.39	14.82	0.95
CLIFeB	4.49	1.77	0.95
CLIMn	2.00	0.28	0.98
CLIFeMn	5.79	16.53	0.95

was conditioned with the MnCl₂ solution improved As(V) adsorption, however the efficiency is 75 and 60% lower than for CLIFeA and CLIFeB, respectively.

The equilibrium of the As(V) adsorption on the CLIFeMn is reached at 20 min and it is nine times lower than CLIFeA. This suggests that the association between iron and manganese in the zeolite network influence the velocity of As(V) adsorption by CLIFeMn, although the amount of As(V) adsorbed by this material diminishes around 11% in comparison to that obtained by CLIFeA (Fig. 2).

The experimental results presented in Fig. 2 were fitted to First order (Lagergren), Elovich y Pseudo-second-order kinetic models [23,24,34–41], applying a non-linear regression analysis using the STATISTICA 6.0 program for Windows.

3.2.1. Lagergren first-order model

The model is represented by the equation in [42]:

$$q_t = q_e(1 - \exp(-K_L t))$$

where q_t (μg/g) is the amount of As(V) adsorbed at time t , q_e (μg/g) the amount of As(V) adsorbed at equilibrium and K_L (h⁻¹) is the Lagergren rate constant.

It was found that, this equation provided a good description of the current data. Table 3 shows the first order kinetics parameters corresponding to arsenates [As(V)] adsorption on the modified clinoptilolite-rich tuffs. Although, the correlation coefficients showed that this model was not the best fitted to the experimental data, the amounts of As(V) adsorbed at equilibrium (q_e) were the highest for CLIFeA and lowest for CLIMn. This means q_e depends on the iron concentration in the clinoptilolite rich tuff, but also depends on the chemical nature of the metallic species that was modified by the surface properties of the zeolitic material. The Lagergren rate constant K_L was highest for CLIFeMn followed by CLIFeA. This fact shows that manganese increased the adsorption velocity of the As(V) to reach the equilibrium in association with iron because this effect was not observed using CLIMn.

3.2.2. Elovich model

The Elovich rate equation has been used in the kinetics of chemisorption of gases on solids. However, some researchers have applied this model to solid-liquid sorption systems. This model is represented by the following equation [43]:

$$q_t = \left(\frac{1}{t}\right) \ln(1 + abt)$$

where q_t (μg g⁻¹) is the amount of As(V) adsorbed at time t , a (μg g⁻¹ h⁻¹) the adsorption constant for As(V), and b (g μg⁻¹) is the desorption constant for As(V).

Table 4 shows the adsorption initial velocity (a), desorption (b) constants and r obtained applying the Elovich model to the experimental data. The adsorption velocity constant (a) is approximately 6 orders of magnitude greater for CLIFeMn and CLIFeA than for CLIFeB and CLIMn. It is important to mention that the a parameter for CLIFeMn is 10 times greater than that for CLIFeA and this model also shows the influence of manganese associated with iron

Table 4

Elovich kinetic parameters obtained for the arsenates adsorption on modified clinoptilolite-rich tuffs

Material	Adsorption velocity constant, a ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Desorption constant, b ($\text{g } \mu\text{g}^{-1}$)	R
CLIFeA	6.41×10^6	2.34	0.99
CLIFeB	33.23	1.34	0.98
CLIMn	1.42	2.00	0.98
CLIFeMn	65.4×10^6	3.47	0.96

on the adsorption velocity of As(V) on CLIFeMn. On the contrary, the desorption constant (b) shows higher values for CLIFeMn and CLIFeA. This model has proven to be suitable for highly heterogeneous systems. The adsorption of arsenates [As(V)] on modified clinoptilolite-rich tuffs is an example of such a case, since they are composed of different minerals and, therefore, exhibit different activation energies for chemisorption.

3.2.3. Pseudo-second-order model

The pseudo-second kinetic model developed by Ho and McKay [34], is based on experimental information of solid phase sorption, generally it has been applied to heterogeneous systems, where the sorption mechanism is attributed to chemical sorption.

The model can be represented by the following equation:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt$$

Rearranging this equation to a linear form:

$$\frac{t}{q_t} = \left(\frac{1}{kq_e^2} \right) + \frac{t}{q_e}$$

where k ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$) constant of pseudo-second order, q_t ($\mu\text{g g}^{-1}$) the amount of As(V) adsorbed at time t , and q_e ($\mu\text{g g}^{-1}$) is the amount of adsorbed at equilibrium.

The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. Although, the experimental points could be fitted to the first and pseudo-second-order kinetic equations, the best adjustments were observed with the pseudo-second-order kinetics equation in general.

The data for all zeolitic materials in straight-line plots of t/q_t against t were fitted to the pseudo-second-order kinetic model to obtain rate parameters (Fig. 3, Table 5).

According to the q_e value, CLIFeA adsorbs the highest amount of As(V) from an aqueous solution and this value (Table 5) is 1.3, 1.6 and 3.4 times higher than that of CLIFeMn, CLIFeB and CLIMn, respectively. This behaviour was similar for that obtained with the first order kinetic model.

The parameter k , which corresponds to the velocity constant of pseudo-second order, is the highest for CLIFeMn. This means that Mn, in association with Fe, increases the As(V) sorption velocity for CLIFeMn. The specific surface characteristics of the iron-modified natural zeolites are also important due to the k value diminishes 1.6 times for CLIFeB in comparison with the CLIFeA (Table 2).

Table 5

Pseudo-second-order kinetic parameters obtained for the arsenates adsorption on modified clinoptilolite-rich tuffs

Materials	q_e ($\mu\text{g/g}$)	k ($\mu\text{g/gh}$)	R
CLIFeA	7.81	3.11	0.98
CLIFeB	4.84	0.44	0.97
CLIMn	2.29	0.15	0.98
CLIFeMn	6.02	5.65	0.97

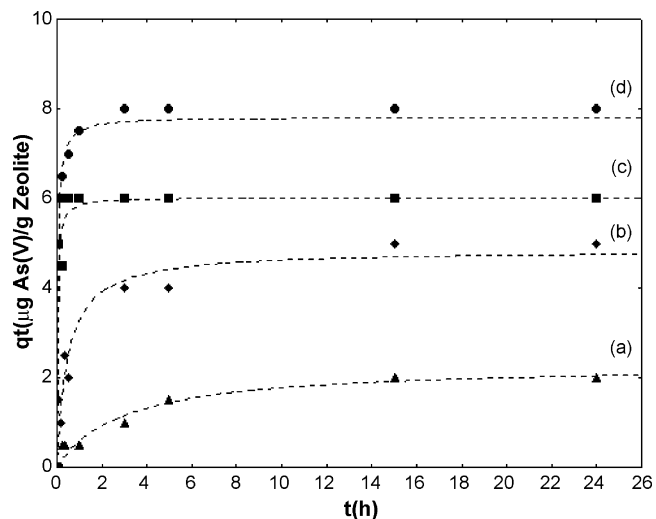


Fig. 3. Pseudo-second-order kinetic model applied to the As(V) sorption by (a) CLIMn; (b) CLIFeB; (c) CLIFeMn; (d) CLIFeA; (-) theoretical data.

Therefore the k value is correlated with the specific surface area of each zeolitic material, due to increases in specific surface area of the zeolitic material. As a consequence of the metallic species, which are modified by zeolite surface characteristics, the pseudo-second-order kinetic parameter increases as well (Fig. 4). Therefore, the k parameter follows the equation:

$$k = (0.094)(\text{specific surface area, } \text{m}^2/\text{g})$$

and the k value follows the order:

$$k_{\text{CLIFeMn}} > k_{\text{CLIFeA}} > k_{\text{CLIFeB}} > k_{\text{CLIMn}}$$

For other materials it was found that the pseudo-second-order kinetic is the best model of describing kinetic data for As(V) removal from water by *Penicillium chrysogenum*, in which k values was 0.028 g/mmol min, respectively [41]. Similar results were obtained to remove As(V) from water by Pokhrel and Viraraghavan [44] using iron-modified *Aspergillum niger* and Maity et al. [24] using a marine nodule.

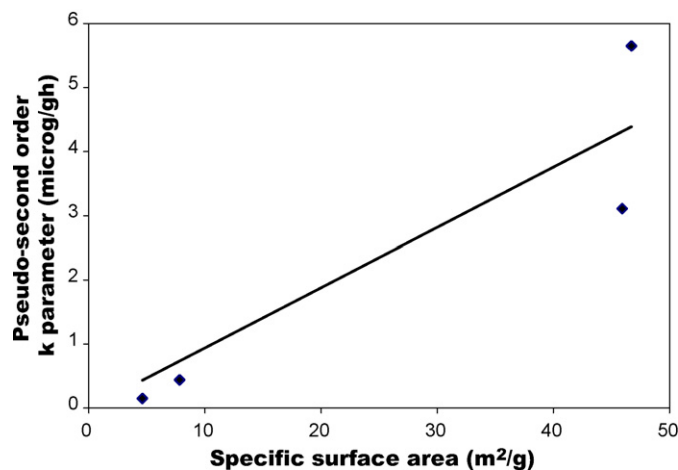


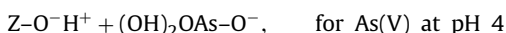
Fig. 4. Pseudo-second-order k parameters vs. specific surface areas from the metallic-modified zeolitic materials.

3.3. Arsenic adsorption mechanisms

The iron(III) oxide surface has a high affinity for As(V) capable of forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes [45]. Similar mechanisms were proposed by Su and Puls [46], with their spectroscopic evidence suggesting that As(V) predominantly forms inner-sphere bidentate surface complexes with goethite.

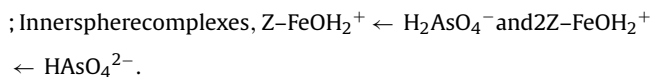
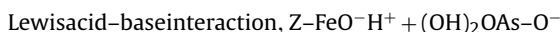
In water samples treated with either ferric chloride or ferric sulphate, arsenic adsorption by iron complexes occurs via ligand exchange of the As species for OH₂ and OH[−] in the coordination spheres of surface structural Fe atoms. The predominant oxidation state of arsenic depends on the pH and the potential redox.

It can be presumed that the following processes are involved in arsenic adsorption by natural solids like mordenite-type zeolite at the basic and acid Brönsted sites [47]:



Vaishya and Gupta [48] proposed that the reaction of As(V) with iron oxide surfaces can also be explained using 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. Due to exchanges of OH[−], this mechanism has been termed, ligand exchange mechanism.

It is proposed by Macedo-Miranda and Olguín [49] that only iron found that the surface of natural zeolites play a role in As(V) adsorption processes via the zeolitic material and the following interactions were considered:



A similar As(V) adsorption mechanism could be proposed by CLiFeA, CLiFeB, CLiMn and CLiFeMn.

4. Conclusions

The zeolitic material is a potassium–calcium clinoptilolite. Na⁺ is partially exchanged with K⁺ and Ca²⁺ extranetwork zeolitic ions, after treating the zeolitic material with a NaCl solution.

The Na⁺ from the sodic zeolitic material plays an important role on Fe³⁺ and/or Mn²⁺-conditioned processes to obtain CLiFeA, CLiFeB, CLiMn and CLiFeMn and the zeolitic material is selective for Fe³⁺ than for Mn²⁺.

The morphology of the zeolitic crystals are characteristic of clinoptilolite. Both clinoptilolite and quartz are the major components of CLI.

The specific surface area of the iron and/or manganese-modified clinoptilolite-rich tuff changes according to the experimental conditions to obtain these zeolitic materials.

The equilibrium time to reach the maximum As(V) adsorption by the modified clinoptilolite-rich tuffs depends on the surface characteristics of iron or/and manganese-modified clinoptilolite-rich tuffs.

No As(V) adsorption is obtained by manganese-modified clinoptilolite rich tuff, however the thermal treatment of the zeolitic material improves the adsorption of this metalloid.

The pseudo-second-order kinetic model is the best to describe As(V) adsorption by the CLiFeA, CLiFeB, CLiMn and CLiFeMn.

The velocity constant *k* of the pseudo-second-order model is greatest when both iron and manganese are in the surface of the zeolitic material.

The *k* value directly depends on the specific surface area of the iron and/or manganese-modified clinoptilolite-rich tuffs.

Therefore, the experimental conditions of the treatment depends on the final surface characteristics of the modified clinoptilolite-rich tuff necessary to consider the As(V) adsorption kinetic processes.

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