Arsenic removal from groundwater by MnO$_2$-modified natural clinoptilolite zeolite: Effects of pH and initial feed concentration

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ABSTRACT

Adsorption of arsenic (As^{5+}) on natural and MnO$_2$-modified clinoptilolite-Ca zeolite adsorbents was investigated to explore the feasibility of removing arsenic from groundwater using natural zeolite adsorbents. The natural and MnO$_2$-modified clinoptilolite-Ca zeolite adsorbents were characterized with nitrogen adsorption at 77 K for pore textural properties, scanning electron microscopy with energy dispersive X-ray spectroscopy and X-ray fluorescence for morphology, elemental composition and distribution. Batch adsorption equilibrium experiments were conducted to study the effects of pH and initial feed concentration on arsenic removal efficiency. It was found that the amphoteric properties and arsenic removal efficiency of the natural clinoptilolite-Ca zeolite were significantly improved after modification with MnO$_2$. The MnO$_2$-modified zeolite could effectively remove arsenic from water at a wide pH range, and the arsenic removal efficiency that is basically independent of the pH of feed solutions varies slightly with the initial arsenic concentration in the feed solutions. The removal efficiency obtained on the modified zeolite was doubled as compared to that obtained on the unmodified zeolite. The MnO$_2$-modified clinoptilolite-Ca zeolite appears to be a promising adsorbent for removing trace arsenic amounts from water.

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1. Introduction

Arsenic (As) is considered a contaminant of major concern due to its high toxicity at small concentrations and its ability to go undetected [1]. It is naturally present in the environment due to geological formations, such as lacustre sediments and volcanic rocks [2]. From these As-rich geological sources, soluble forms of the metal leach into shallow groundwater [3] and transform due to oxidation–reduction, ligands exchange, precipitation and biochemical reactions [2]. Industrial processes and products such as wood preservatives, semi-conductors, and agricultural applications may also introduce arsenic into the environment [4,5].

Even though arsenic is found in several forms in food and environmental media, it is predominantly encountered in drinking water as inorganic arsenic. In this form it is both highly toxic and readily bioavailable. Chronic ingestion of inorganic arsenic contaminated drinking water can develop into arsenicosis which causes respiratory, renal, and immunologic effects [6]. Evidence that inorganic Arsenic may be diabetogenic has been also reported [7]. The World Health Organization [8] established a maximum contaminant level (MCL) for arsenic in drinking water of 10 μg/L.

This limit was also adopted in the United States (US) in 2006 [9].

Treatment methods for arsenic contaminated waters include oxidation, lime softening, coagulation/precipitation, anion-exchange, adsorption, membrane process, and phytoremediation [10,11]. In the majority of the treatment cases, Arsenic removal was affected by the initial pH of the water which can be between 7 and 12 [12–14]. One of the disadvantages of working at these pH levels is the sludge generation, which makes the process inefficient from a waste minimization point of view. Adsorption has proven to be an efficient method for treating arsenic contaminated waters [15]. Some of the adsorbents widely used include silica, alumina, granular ferric hydroxides, synthetic resins, and zeolites [16]. Among these materials, natural zeolites, a group of crystalline alumina-silicates, gained increasing attention due to their specific structure and adsorption and ion-exchange capabilities. However, its main disadvantage is the low arsenic removal capacity.

Studies have been conducted using modified natural zeolites for arsenic removal. Some of the reported modifications include iron-modified [17,18], surfactant-modified [19,20] and lanthanum-modified zeolites [21]. Chemical pre-treatment and initial pH adjustment were required in most of the cases and no significant improvement in the arsenic removal efficiency was reported [22,23]. The objective of this work was to investigate the adsorption performance of a MnO$_2$-modified natural clinoptilolite zeolite

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without chemical pre-treatment, and to compare it with the Arsenic adsorption by the unmodified clinoptilolite zeolite at similar conditions. The effect of pH and initial concentration on the arsenic adsorption capacity were given emphasis in this work. The results obtained will enhance the understanding of adsorption equilibrium of arsenic by clinoptilolite zeolite and its modification, and provide valuable insights on adsorption breakthrough process development and implementation.

2. Materials and methods

2.1. Modification of natural clinoptilolite zeolite

The natural clinoptilolite zeolite used in this study is from a zeolite deposit located in Truth or Consequences, New Mexico (St. Cloud Mining Company, USA). Prior to modification, the clinoptilolite zeolite (CZ) was washed with deionized water and dried at room temperature. The modified clinoptilolite zeolite (MCZ) was obtained by pouring a mixture of 50 mL of 2.5 M $MnCl_2$ and 0.5 mL of 10 M NaOH over 50 g of the washed clinoptilolite zeolite in a heat-resistant dish and then heating the mixture in a furnace at 150 °C for approximately 5 h. Afterwards, the modified adsorbent was heated at 500 °C for 3 h, cooled at room temperature and washed several times with distilled water.

2.2. Adsorbent characterization

Physical and chemical properties of the natural and modified clinoptilolite zeolite were determined by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), and N_2-adsorption analyses. Elemental analysis of the natural CZ was obtained by X-ray fluorescence (XRF) analysis. Prior to SEM analysis the samples were sieved (mesh size 14×30), washed with deionized water, and dried at room temperature for 48 h. The dried samples were coated with a gold film to minimize charging and improve resolution, and then analyzed with SEM/EDS (Hitachi S-3400 N).

The sample for major element analysis was prepared by mixing calcined, natural clinoptilolite zeolite powder (325 mesh, 900 °C) with lithium tetraborate and lithium metaborate, and then heating in a muffle furnace at 1100 °C for 30 min. For trace element analysis, the sample was prepared by mixing zeolite powder (325 mesh) with a binder solution (Ultra bind®) in a steel pellet and pressing the mixture in a press plate at 20 tons for 1 min. The sample was then dried and analyzed. Major and trace element analysis of the clinoptilolite zeolite samples were conducted with a XRF (Rigaku ZSX, 100-e) analyzer.

The BET and Langmuir specific surface area, pore size distribution, and pore volume of both CZ and MCZ samples were determined in an accelerated surface area and porosimetry instrument (Micromeritics ASAP 2020) operated with liquid N_2 at −196 °C. The specific surface area, pore volume, and median pore size were calculated with the built-in software of the Micrometrics ASAP 2020 equipment.

2.3. Variation of pH with adsorption time

Two 10-mL of 20 μg/L arsenic standard solutions were adjusted with 0.10 M NaOH and 0.1 M HCl solution to pH 7.0. The arsenic standard solutions were prepared from an As^{5+} stock standard solution of 100 mg/L, (Sigma Aldrich, reagent grade). Each solution was then mixed with 1.0 g of CZ and MCZ samples in 200-mL, high-density, polyethylene plastic bottles. The bottles were placed on an automatic shaker (Lab-line Orbit, Model No. 359) at 100 rpm for 67 h. A standard pH meter (Accumet Excel XL25, Fisher Scientific) was used to monitor changes in solution pH every 15 min and half
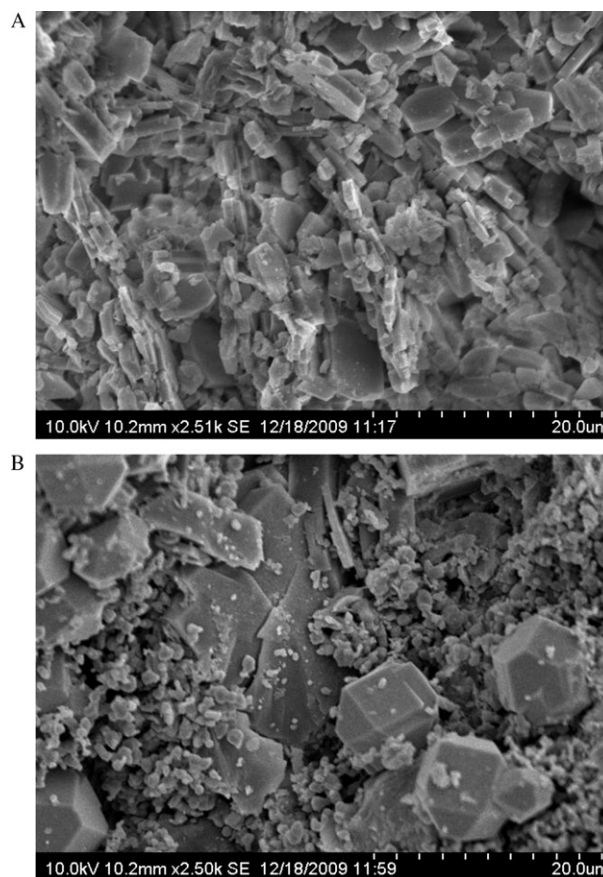
Fig. 1. SEM of natural clinoptilolite zeolite: (A) original; (B) MnO_2-modified (magnification = 2.5 K, scale bar = 20 μm).

an hour for the first 4 h, and then every 2 and 6 h. For every sample a replicate was run to ensure the accuracy of the data. Blanks of CZ and MCZ in deionized water (pH = 6.5) were run for 48 h to observe the effect of manganese on the amphoteric property of the modified zeolite.

2.4. Effect of pH on arsenic adsorption

The effect of pH on arsenic adsorption by CZ and MCZ samples was investigated at acidic, neutral, and basic conditions. The pH of eight 100-mL solutions of 20 μg/L arsenic was adjusted to values ranging from 2.0 to 9.0 (each pH level in duplicate) by adding 0.1 M HCl or 0.1 M NaOH. Initial and final solution pH-values were recorded. The solutions were then mixed with one gram of NZ and MCZ sample in 200-mL, high-density, polyethylene plastic bottles and placed in an automatic shaker at 100 rpm for 48 h to ensure that adsorption equilibrium was obtained. After 48 h, samples were removed from the shaker, filtered (0.45 μm nylon) and analyzed with an inductively coupled plasma-mass spectrometer (ICP-MS) (Elan DRC-II, Perkin Elmer) for arsenic concentration.

2.5. Adsorption equilibrium measurements

Eight arsenic solutions having an arsenic concentration ranging from 0.5 to 50 μg/L were prepared by diluting the corresponding quantity of a 1 mg/L arsenic solution with deionized water to a final volume of 100 mL in 200-mL, high-density, polyethylene plastic bottles. The 1.0 mg/L arsenic standard solution was prepared from the 100 mg/L stock standard solution. The pH of the prepared solution was adjusted to mimic the drinking water purification condition (pH of 6.5–7.0) by adding 0.10 M NaOH or 0.1 M HCl solution,
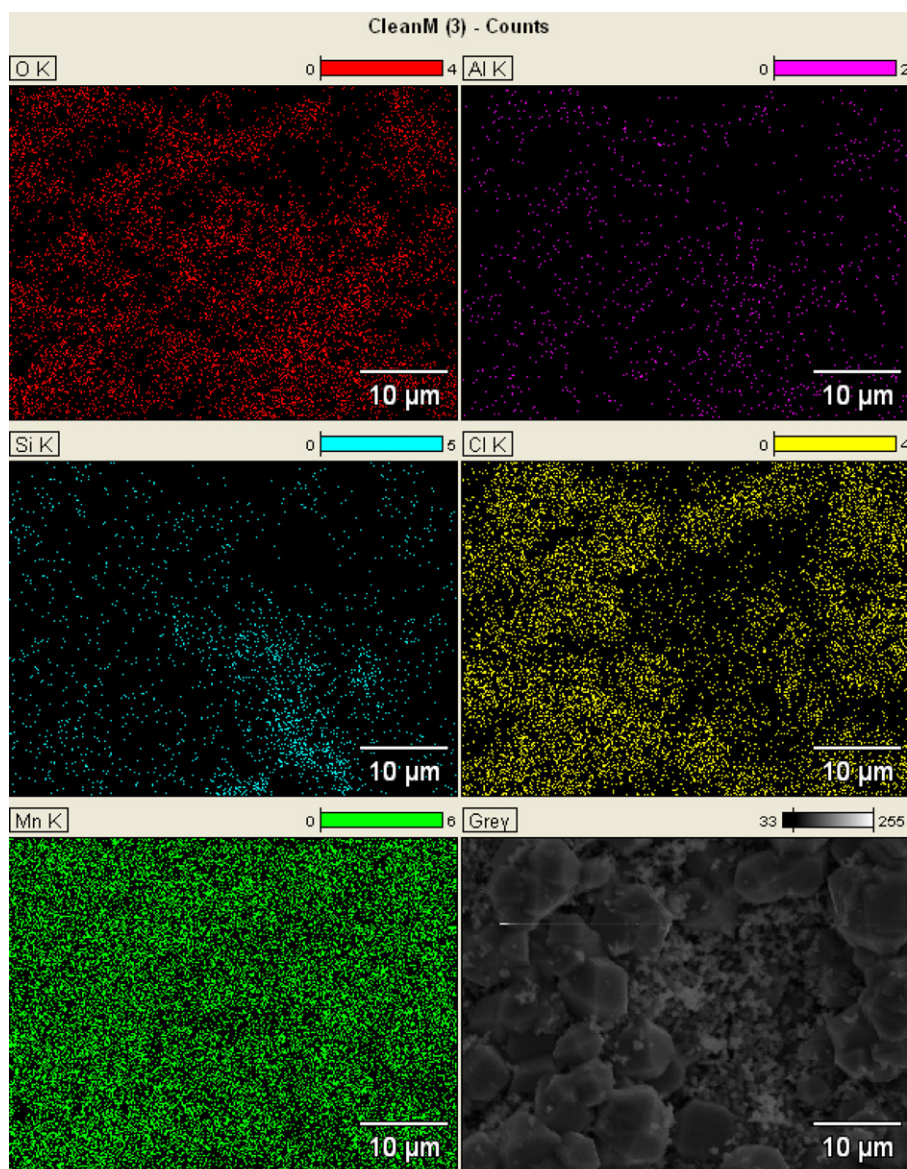
Fig. 2. EDS mapping of MnO_2-modified natural clinoptilolite zeolite.

and measured with the Accumet pH meter. One gram of the NZ or MCZ was added to each solution. The bottles were closed tightly and placed on the automatic shaker at 100 rpm and after 48 h, the samples were removed from the shaker, filtered (0.45 μm nylon), and analyzed by ICP-MS for arsenic concentration. A simple mass balance on the water solution and the adsorbent was carried out for each solution to calculate the amount of arsenic adsorbed by the zeolites. The final amount of arsenic remaining in solution was defined as the equilibrium concentration. The arsenic adsorption amount (μg/g) in equilibrium with the final arsenic concentration was obtained by dividing the adsorbed amount (μg) by the mass of the adsorbent (1.0 g).

3. Results and discussion

3.1. Physical and chemical properties of natural and modified zeolites

Major and trace element compositions of the CZ sample showed that aside from the main Si and Al components, Ca is the next high-est component at 3.18 wt.% followed by K at 2.44 wt.% (Table 1). Silica to alumina ratio (Si/Al) of 5.16 was obtained for the natural clinoptilolite zeolites. The Si/Al ratio provides the negatively charged structure of the zeolite due to the difference between

Table 1
Elemental analysis of a natural clinoptilolite zeolite from New Mexico, USA.

Major elements	Concentration (wt.%)	Trace elements	Concentration (mg/L)
SiO_2	66.61	Rb	110.0
TiO_2	0.25	Th	28.17
Al_2O_3	12.91	Nb	27.0
Fe_2O_3	1.7	Sr	1030.0
MnO	0.04	Zr	156.0
MgO	1.54	Y	24.2
CaO	3.18	Pb	18.0
Na_2O	0.39	U	3.34
K_2O	2.44	V	14.0
P_2O_5	0.06	Cr	18.0
Loss on ignition	10.72	Ni	20.0
		Cu	14.0
		Zn	65.0
		Ga	17.8

Table 2
Summary of pore textural properties for natural and modified clinoptilolite zeolite.

Property	Natural clinoptilolite	MnO$_2$-modified clinoptilolite
BET surface area (m^2/g)	11.62	7.74
BJH pore volume (cm^3/g)	0.024	0.017
BJH median pore size (Å)	96.09	120.01

the $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedral [24]. Positive sites may be available from the alkaline and alkaline-earth cations contained in the zeolite that are available for ion exchange [24]. The XRF elemental analysis data shown in Table 1 identified the CZ used as Ca-clinoptilolite ($KNa_2Ca_2(Si_{29}Al_7)O_{72}\cdot24H_2O$), which is consistent with findings of Boles [25].

Three dimensional clinoptilolite crystal clusters with open channel networks were seen in the SEM image of the CZ (Fig. 1A). Small lamellar particles and larger crystalline structures, different from the clinoptilolite crystals, surrounded and covered most of the MCZ (Fig. 1B). Energy dispersive X-ray spectroscopy mapping of the MCZ shown in Fig. 2 identified the lamellar particles as manganese and the newly formed crystalline structures as chloride. Large quantities of oxygen were observed along the structure, corroborating the formation of MnO$_2$. Silica and alumina, in a five to one ratio, filled the spaces underneath the new formation. The EDS spectrum (not shown) demonstrated the peaks corresponding to manganese. Chloride, which was not discharged from the new structure after several washing with distilled water, was also observed in the EDS spectrum.

Table 2 summarizes the pore textural properties for CZ and MCZ. The BET surface areas for CZ and MCZ are 11.62 m^2/g and 7.74 m^2/g, respectively. This reduction in surface area after the modification is not surprising because the manganese oxides introduced to the CZ occupy the pores otherwise available for ion exchange [26]. Jiménez-Cedillo et al. [22] reported a BET surface area of 5.37 m^2/g and 4.61 m^2/g for modified and unmodified clinoptilolite–heulandite rich tuffs, respectively. He suggested that the preparation conditions of the modification procedure will determine the final surface characteristics of the modified zeolite. Reduction in the surface area of modified natural clinoptilolite has also been reported by Qiu and Zheng [27]. The average pore size of CZ and MCZ is 96.09 Å and 120.01 Å, respectively; the corresponding pore volumes are 0.024 cm^3/g and 0.017 cm^3/g. The pore volume of MCZ is consistent with the pore volume of 0.037 cm^3/g for Na-modified clinoptilolite reported by Ackley and Yang [28].

N$_2$ adsorption and desorption isotherms for CZ and MCZ (not shown) are of Type-III [29], indicating the heterogeneity of the pore size within the adsorbent material. The observed slope of the hysteresis is characteristic of the presence of mesopores in the materials [30].

3.2. Variation of pH with adsorption time

Analysis of pH as a function of time was conducted to determine the minimum time required to obtain arsenic adsorption equilibrium. Fig. 3 displays the pH data for the 20 μg/L arsenic solutions placed in contact with CZ and MCZ on the shaker for 67 h at pH of 7.0. The overall trend in pH change with adsorption time for CZ and MCZ samples was slightly different. For the CZ-containing solution, a sharp pH decrease from the initial pH of 7.0 to a pH of 4.4 was observed during the first 5 min. The decrease in pH was followed by a slow increase and after 24 h a pH value of 6.5 was reached. After approximately 43 h, the pH of this solution stabilized. A sharp decrease from the initial pH of 7.0–5.6 was observed in the MCZ-containing solution during the first 5 min. Slight variations in the
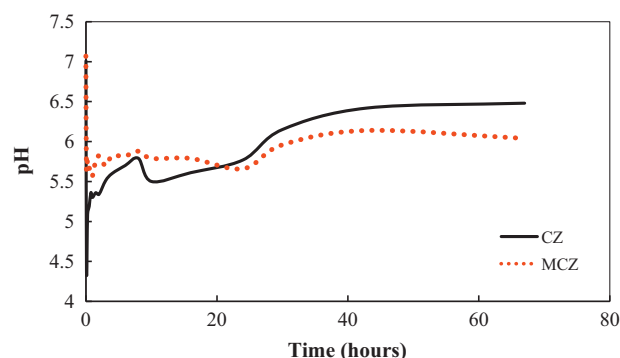

Fig. 3. Variation of Solution pH with adsorption time for natural CZ and MCZ.

pH followed and after 24 h a pH of 6.14 was obtained. This solution reached equilibrium after approximately 43 h.

The observed pH behavior of both CZ and MCZ suggests that more than one process may occur between the adsorbent materials and arsenic, and they are controlled by the specific pH properties of each material. The first process occurs at the very beginning of adsorption and may be the result of neutralization reactions and the ability of the zeolite to act as an amphoteric material, as recently reported by Camacho et al. [31]. Filippidis and Kantiranis [32] also observed a similar phenomenon when adding Ca-rich clinoptilolite zeolite into acidic-stream and basic lake water.

The second process occurs within the next 24 h. While pH dependent reactions may still occur in the arsenic solution containing CZ, ion exchange reactions between As^{5+}, in the form of HAsO$_4^{2-}$, which is readily available for sorption at pH 6.0 (Fig. 4), and available anions within the MCZ, specifically chloride ions, may compete with the adsorption process. The availability of chloride ions in MCZ is evident from the EDS mapping (Fig. 2). The observed pH variations during the adsorption process by MCZ are similar to the pH variations reported by Ouvrard et al. [33] when feeding a column filled with natural MnO$_2$ with a sodium arsenate and chloride solution. They suggested that the pH variations during the first period of time were due to ion exchange reactions between arsenate and the chloride present on surface sites of the adsorbent material. The actual adsorption process for MCZ may start only after the first 24 h, once there are no more chloride ions available for ion exchange. Surface complexation mechanisms have also been suggested as responsible for arsenic retention on natural manganese sand [34].

Blank solutions of CZ and MCZ samples in deionized water (pH = 6.5) were run for 48 h to observe the effect of manganese on
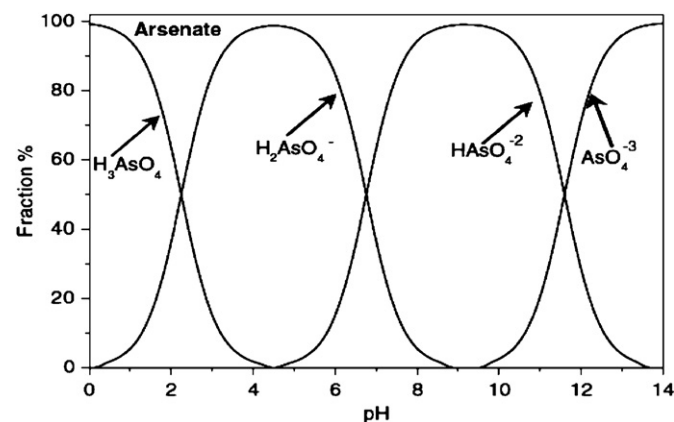
Fig. 4. Arsenic speciation as a function of pH for total As(V) (concentration 50 mg/L) [5].

the amphoteric property of the zeolites. After 24 h the pH of the CZ solution was 8.0 and the pH of the MCZ 6.1. After 48 h the pH of CZ was 7.5 and the pH of MCZ 6.3. It is evident that MCZ is not affected by pH. Observed pH behavior of MCZ with water and with arsenic solutions suggests that its properties improve after it is modified with MnO_2.

3.3. Effect of pH on arsenic adsorption

Fig. 5A and B shows the effect of initial pH on arsenic equilibrium concentration and adsorbent amount by CZ, respectively. The effect of initial pH on the shift in equilibrium pH is also presented in Fig. 5B. Under high acidic conditions (pH of 2.0–3.0), arsenic adsorption by CZ was minimal and it reaches a maximum at pH 6.0 (Fig. 5B). At this pH the arsenic concentration decreased from 20 µg/L to 15 µg/L (Fig. 5A). This change corresponds to 20% arsenic removal, indicating that 0.38 µg As/g adsorbent were adsorbed (Fig. 5B). Arsenic adsorption decreased as pH increased from 6.0 to 9.0. At pH 9.0, only 0.18 µg As/g adsorbent were adsorbed and the equilibrium solution concentration of Arsenic reached 16.6 µg/L, which corresponds to only 9.5% arsenic removal.

Under acidic conditions arsenic adsorption by MCZ was significantly higher. Furthermore, at pH 4.0 the amount of arsenic adsorbed was 1.0 µg/g adsorbent (Fig. 6B), six times more than the arsenic adsorbed at the same pH by CZ. The same arsenic amount was adsorbed throughout the pH range of 4.0–9.0. Within this pH range the equilibrium concentration of arsenic reached an average value of 10 µg/L corresponding to almost 50% of arsenic removal (Fig. 6A).

The differences observed in the amount of arsenic adsorbed by CZ and MCZ can be well explained by the shift in equilibrium pH during the adsorption process (Figs. 5B and 6B, respectively). The shift in equilibrium pH of the equilibrated solutions for both CZ and MCZ was more notorious under initial acidic pH conditions than under initial neutral and initial basic pH conditions. Under initial acidic pH conditions, the equilibrium pH of the CZ solution went from 2.0 to 6.5 and the equilibrium pH of the MCZ from 2.0 to 5.2.
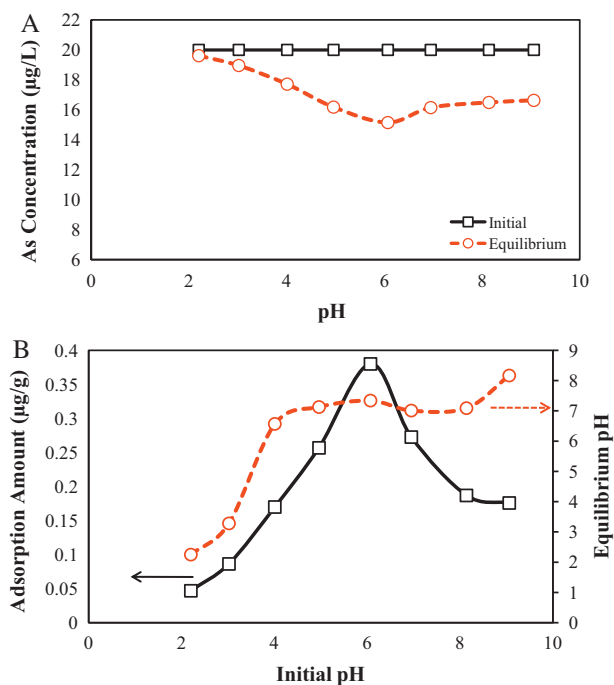

Fig. 5. (A) Effect of solution pH on arsenic adsorption equilibrium concentration at 20 °C. (B) Arsenic adsorption amount at 25 °C for natural CZ.
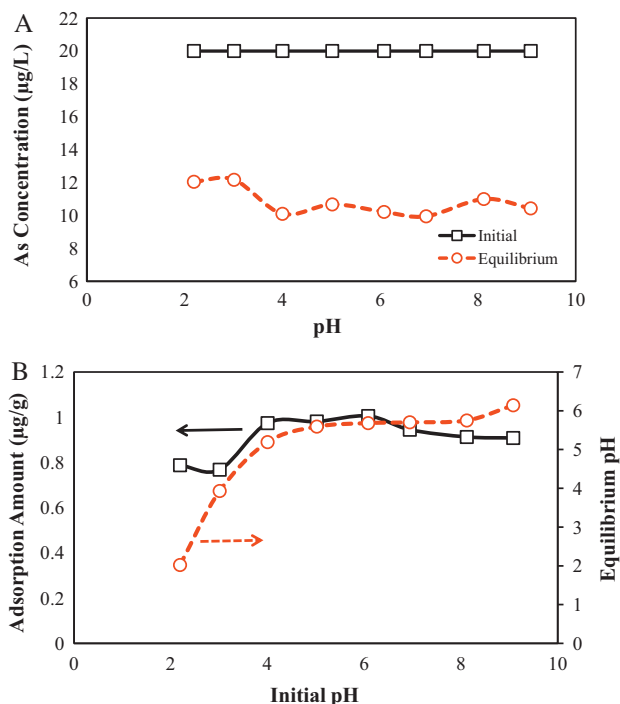

Fig. 6. (A) Effect of solution pH on arsenic adsorption equilibrium concentration at 20 °C. (B) Arsenic adsorption amount at 25 °C for MCZ.

The equilibrium pH for CZ and MCZ remained constant for those solutions with an initial pH ranging between 4.0 and 8.0 (average equilibrium pH of 7.0 and 5.6 for CZ and MCZ, respectively). Arsenic adsorption was more favorable with equilibrium pH 5.6 than with equilibrium pH 7.0, because at the equilibrium pH of 5.5–6.5, an anionic As(V) species is present and is ready to be adsorbed (Fig. 4).

The shift in equilibrium pH of the MCZ is in agreement with the observations on pH changes with time from the previous section and confirms the pH independence of this material. It is reported that pH is a controlling factor for the removal of uranium and fluoride by modified clinoptilolite zeolite and MnO_2-coated alumina, respectively [35,36]. Results from the present study showed that solution pH is indeed a controlling factor for effective Arsenic removal by CZ; however, MCZ acts completely independent of pH in a wide range of solution pH and can effectively remove trace arsenic amounts present in water.

3.4. Effect of initial concentration on arsenic removal efficiency

Results on the adsorption of As^{+5} by CZ and MCZ at different initial concentrations and pH 6.5 are presented as percentage of arsenic removal in Fig. 7A. The sharp increase in removal efficiency at low initial concentrations observed on both materials, especially on the MCZ, followed by a gradual decrease and further increase at arsenic concentrations higher than 20 µg/L support the assumption of competing reactions stated in previous sections. At initial concentrations lower than 10 mg/L the CZ reached removal efficiencies of 22% and the MCZ removed twice as much. At initial concentrations higher than 20 µg/L the removal efficiency of MCZ is still high compared to the removal efficiency of CZ. The highest equilibrium adsorption capacity of MCZ was 2.5 µg/g. This value was obtained at the initial concentration of 50 µg/L. The adsorbed amount by MCZ is low compared to the values reported by Pattanayak et al. [37] and Lorenzen et al. [38], but as most of the authors [39], they worked with initial concentrations higher than 500 µg/L. It is difficult to compare our results with results reported in the literature using traditional adsorbents for arsenic removal because
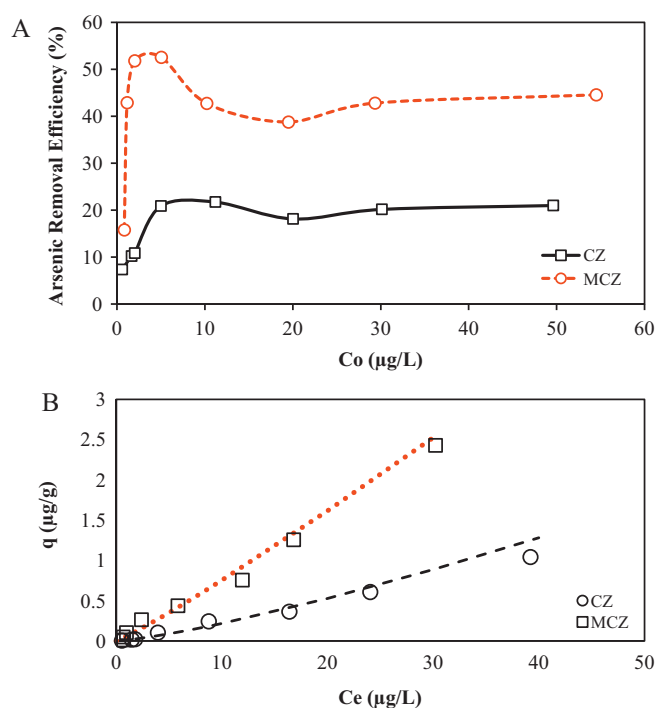
Fig. 7. (A) Removal efficiency of arsenic on natural CZ and MCZ at pH 7.0 and 25 °C. (B) Model correlations of experimental isotherm data for arsenic adsorption on natural CZ and MCZ at pH 7.0 and 25 °C. The lines are Freundlich fit to the observed data.

most of those results deal with much higher initial concentrations. Our results compare well with those reported by Fierro et al. [40] for relative low initial concentrations. Fierro et al. [40] used activated carbon doped with different iron contents and reported adsorption capacities ranging from 1.08 μg/g to 28 μg/g for initial arsenic concentrations of 300 μg/L. Nevertheless, our results indicate that MCZ can remove trace arsenic amounts from contaminated water at a wide range of pH. In fact, the modified adsorbent material works independently of pH in the range of 4.0–9.0 while most of the adsorbent materials for arsenic removal work either at low pH [41,42] or within a small pH range, mostly between 6.0 and 7.5 [14,40]. Another advantage of the MCZ produced in our laboratory over traditional adsorbent materials is that it does not require chemical pretreatment. Studies conducted by Jiménez-Cedillo et al. [22] reported no arsenic removal by manganese-modified clinoptilolite rich tuffs. In their study, the rich tuff was pretreated with 0.1 M NaCl. It has been suggested that pretreatment of the adsorbent material with NaCl forms a negative surface charge that is high enough to prevent anion exchange [33]. Our results demonstrated that in fact no pretreatment is needed to achieve good arsenic removal by MCZ.

The maximum concentration shown in Fig. 7A may be attributed to the presence of the monovalent oxyanionic form $H_2AsO_4^-$ of As(V). This species is presented in the As(V) speciation diagram at pH 5.5–7.0 (Fig. 4) [5].

3.5. Adsorption isotherms

The selection of appropriate correlation models for the experimental equilibrium data is important in order to optimize the design of an adsorption system for the removal of arsenic. Freundlich and Langmuir isotherm models have been demonstrated to fit the equilibrium behavior of heavy metals well [14,43]. These two models were used to correlate the observed behavior in the present study. The arsenic adsorption equilibrium data obtained at pH 6.5 for solutions with initial arsenic concentrations varying from 0.5 to 50 μg/L are plotted in Fig. 7B.

The Freundlich model indicates the heterogeneity of the adsorbent material and is given by the equation

$$q = K C_e^{1/n} \tag{1}$$

where q (μg/g) is the amount of arsenic adsorbed at equilibrium, C_e (μg/L) is the equilibrium concentration of arsenic in solution, and K and n are the Freundlich constants related to the zeolite adsorption capacity and adsorption intensity, respectively.

The Langmuir isotherm model assumes the formation of a monolayer onto the adsorbent surface with a finite number of identical sites, and is given by the equation

$$q = \frac{a \times b \times C_e}{1 + b \times C_e} \tag{2}$$

where C_e (μg/L) is the arsenic equilibrium concentration, and a (μg/g) and b (L/mg) are the Langmuir constants related to the capacity and energy of the adsorption, respectively.

Although the Langmuir isotherm model has been reported as a good model to represent the adsorption of arsenic with a variety of adsorbent materials [14,20,43], it failed to correlate the data for arsenic adsorption by the MCZ ($R^2 = 0.528$). This may be attributed to the changes in the surface area of the original material occurred during the modification with MnO_2. The small lamellar manganese particles and larger chloride crystalline structures added to the relative homogeneous crystal structure of the clinoptilolite (Fig. 1A) made this material more heterogeneous (Fig. 1B).

The Freundlich isotherm fits well both the CZ and MCZ, with correlation coefficients of 0.98 and 0.91, respectively. Fig. 7B shows the linear plots of the Freundlich model for the range of concentrations tested. This is in agreement with Payne and Abdel-Fattah [14] who reported that adsorption of arsenate and arsenite by iron-treated activated carbon and zeolite best fit the Freundlich model. The parameters for the Freundlich and Langmuir models are presented in Table 3. The Freundlich constant K is bigger for the MCZ, which indicates that the modification provides a higher adsorption capacity. The n value was greater than one for both materials suggesting binding interactions at adsorbing sites [14]. The correlation coefficient value (R^2) of the Freundlich isotherm for MCZ is less than the R^2 value for CZ. We will expect to have a bigger R^2 for MCZ based on the assumption that supports the Freundlich adsorption model, i.e. an adsorbent material with heterogeneous surface area, which is clearly the case of CMZ as shown in Fig. 1B. However, we have to take into consideration that, as explained in Section 3.2, in addition to the adsorption reactions on the surface of MCZ also anion exchange reactions between the arsenate and chloride ions occur inside of the adsorbent material. The correlation coefficient accounts only for the linearity of the adsorption process.

Table 3
Summary of adsorption isotherm model parameters.

Material	Freundlich isotherm			Langmuir isotherm		
	K	n	R^2	a (μg/g)	b (L/μg)	R^2
CZ	0.01125	1.2836	0.984	0.0079	10.464	0.9813
MCZ	0.05993	1.0997	0.905	0.0338	0.1092	0.5282

The applied models take conventional adsorption into consideration. However, given the complexity of the reactions taking place in arsenic solutions, a model needs to be developed to account for both arsenic ion-exchange and adsorption.

4. Conclusions

A natural clinoptilolite zeolite from Truth or Consequences, New Mexico was modified with MnO_2, without any other chemical pre-treatment and applied for arsenic removal. Both the natural and MnO_2-modified clinoptilolite zeolites were characterized and evaluated to explore the feasibility of using this inexpensive adsorbent for arsenic removal from drinking water. Modification of the natural zeolite produced the decrease of the BET surface area due to the introduction of manganese and chloride ions to the pores otherwise available for ion exchange. The arsenic removal of both CZ and MCZ was found to depend on the initial arsenic concentration. While CZ depends on pH to produce high arsenic removal, MCZ is completely independent from pH and can work in a wide range of pH values.

Modification of natural clinoptilolite zeolite with MnO_2 doubles its removal efficiency for trace amounts of arsenic. The Freundlich isotherm fits well the arsenic adsorption equilibrium data for MCZ. The small lamellar manganese particles and larger chloride crystalline structures added to crystal structure of the clinoptilolite made this material more heterogeneous. Ion exchange as well as adsorption reactions may be involved during the arsenic removal process; both are probably controlled by the unique pH properties of the MCZ. Given the complexity of the reactions occurring during the arsenic removal process, a combined isotherm model should be developed to account for both arsenic ion-exchange and adsorption. The availability of this natural material, simple modification, with no pretreatment requirement, pH independency, and relative good adsorption capacity at trace arsenic levels makes this material suitable for potential practical applications. We demonstrated that MCZ can remove trace amounts of arsenic, which is one of the most persistent contaminants present in drinking water, even at low concentrations.

Acknowledgements

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