

Adsorption of arsenic (V) from a water solution onto a surfactant-modified zeolite

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Abstract In this study a surfactant-modified zeolite (SMZ) was prepared by adsorbing the cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide on a clinoptilolite. The adsorption of the surfactant modified the surface properties of the clinoptilolite and enhanced the anionic capacity of the SMZ. The adsorption equilibrium data of As(V) from the water solution on the SMZ were obtained in a batch adsorber, and the Langmuir isotherm matched the data reasonably well. The As(V) adsorption capacity of the SMZ was 12.5 times greater than that of the clinoptilolite. The adsorption of As(V) on SMZ was mainly due to the interactions between the anionic sites of the SMZ and the As(V) anions in water solution. The adsorption capacity of the SMZ was dependent on the solution pH. The adsorption capacity was increased and decreased by augmenting the pH from 5 to 7 and from 7 to 12, respectively. This unusual behavior was due to the fact that the affinity of the As(V) for the SMZ was dependent on the As(V) species that were present in solution. The adsorption capacity of the SMZ was slightly favored by decreasing the temperature from 25 to 15 °C. The heat of adsorption was estimated to be $\Delta H_{\text{ads}} = -46.82$ KJ/mol, indicating that the adsorption was exothermic and the As(V) was chemisorbed on the SMZ.

Keywords Adsorption · Arsenic (V) · HDTMA · Surfactant-modified zeolite

Nomenclature

C_0	Initial concentration of As(V) in solution, $\mu\text{g/L}$
C	Concentration of As(V) at equilibrium in solution, $\mu\text{g/L}$
k	Constant of the Freundlich isotherm, $\mu\text{g}^{1-1/n}\text{L}^{1/n}/\text{g}$
K	Constant of the Langmuir isotherm, $\text{L}/\mu\text{g}$
K_0	Frequency factor, $\text{L}/\mu\text{g}$
ΔH_{ads}	Heat of adsorption, KJ/mol
m	Mass of SMZ, g
n	Constant of the Freundlich isotherm
N	Number of experimental data points
q	Uptake of As(V) adsorbed on SMZ, $\mu\text{g/g}$
q_{exp}	Experimental uptake of As(V) adsorbed on the SMZ, $\mu\text{g/g}$
q_m	Maximum uptake of As(V) adsorbed on SMZ, $\mu\text{g/g}$
q_{pred}	Uptake of As(V) predicted with the adsorption isotherm, $\mu\text{g/g}$
q_0	Initial uptake of As(V) adsorbed on the ZMS at the beginning of a desorption step, $\mu\text{g/g}$
R	Ideal gas constant, J/mol K
T	Temperature, K
V	Volume of As(V) solution, L

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1 Introduction

Arsenic is considered as one of the most toxic pollutants because it causes mutagenic as well as carcinogenic effects in human beings. Arsenic ions can be removed from drinking water by several methods such as adsorption and ion exchange.

Adsorption is one of the most efficient separation processes for removing trace concentrations of As(V) from aqueous solution. Activated alumina is commonly used in the removal of As(V) from drinking water (Leyva-Ramos 2007). Several diverse adsorbents have been developed and tested over the last 20 years. Various minerals and industrial wastes such as siderite (iron carbonate) (Guo et al. 2007) and hen eggshells (Oke et al. 2008) have been tested for adsorbing As(V), but the great majority of these materials presented very low adsorption capacities. Activated carbon normally presents a very low As(V) adsorption capacity (Leyva-Ramos 2007) and this capacity has been increased by impregnating or modifying its surface with various metals such as iron (Payne and Abdel-Fattah 2005). Recently, it has been shown that hydrous ferric oxide (β -FeOOH) and granular ferric hydroxide presented very high capacities for adsorbing As(V) from an aqueous solution (Hussan and Munir 2007).

Natural zeolites have a high capacity for exchanging cations but no anions (Leyva-Ramos 2007). Recently, the external surface of the natural zeolite has been modified by adsorbing cationic surfactants (Bowman et al. 2000; Haggerty and Bowman 1994). These adsorbents are called surfactant-modified zeolites (SMZ) and the presence of the amino group in the surfactant forms the active sites of the SMZ, where anions can be adsorbed (Li 1999). Accordingly, SMZ can be an alternative adsorbent for removing arsenate from water solutions.

Several investigators have studied the adsorption of the hydrogen chromate, sulphate and selenate anions on SMZ (Bowman et al. 2000; Leyva-Ramos et al. 2008; Majdan et al. 2006). Misaelides et al. (1998) have reported the adsorption of As(V) on a SMZ prepared by adsorbing polyhexamethyleneguanidine-chloride on a zeolite sample and found that the As(V) adsorption capacity of SMZ was around 6 mg/g at a concentration of As(V) at equilibrium of 1000 mg/L. Recently, Chutia et al. (2009) studied the adsorption of As(V) onto SMZs and found that the SMZ prepared by adsorbing HDTMA on mordenite exhibited greater adsorption capacity than that prepared by adsorbing HDTMA on clinoptilolite. However, the effect of the temperature and pH on the SMZ capacity for adsorbing As(V) as well as the reversibility of the adsorption of As(V), has not been thoroughly investigated.

Chutia et al. (2009) and Misaelides et al. (1998) determined the adsorption isotherm of As(V) on SMZ at concentrations of As(V) at equilibrium ranging from 1 mg/L to 1000 mg/L. This concentration range is very high for drinking water application since the permissible level of As(V) in drinking water is 10 μ g/L. Besides, an estimated population of 90 million is currently being exposed to high concentrations of arsenic in drinking water, and more than 90% of this population is consuming water with concentrations

ranging from 10 to 300 μ g/L (Nriagu et al. 2007). Thus, the adsorption isotherm of As(V) is required at concentrations of As(V) below 300 μ g/L.

The main objective of this work was to investigate the adsorption of As(V) from an aqueous solution on a SMZ at concentrations of As(V) below 300 μ g/L. The effects of the pH and temperature on the SMZ adsorption capacity were also studied in detail. Moreover, the reversibility of the As(V) adsorption on SMZ was analyzed by desorbing As(V) from SMZ.

2 Materials and methods

2.1 Natural zeolite

A natural zeolite from a deposit located in San Luis Potosi, Mexico was used in this work. The zeolite sample was ground and sieved to an average particle diameter of 0.42 mm ($-20 + 30$ US mesh). The ground zeolite was washed with deionized water several times, dried in an oven at 110 °C during 24 hours and stored in closed plastic containers. The cation exchange capacity (CEC) of the zeolite was determined using the procedure proposed by Ming and Dixon (1987).

2.2 Surfactant-modified zeolite (SMZ)

The external surface of the zeolite was modified by adsorbing the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA). The preparation procedure was proposed by Jacobo-Azuara (2007). A portion of 50 g of zeolite and 1 L of a 40 mmol/L HDTMA solution were added into an Erlenmeyer flask. The flask was placed inside a thermostatic bath at 25 °C and manually stirred 4 to 6 times during the first 8 hours to facilitate reaching equilibrium faster. The HDTMA solution and the zeolite were left in contact for 24 hours, which was enough time to attain equilibrium. The SMZ particles were separated by decanting the solution and washed 4 times with 500 mL of deionized water to eliminate the excess of surfactant. Afterwards, the SMZ was dried with an air stream at room temperature during 24 hours and stored in closed plastic containers.

2.3 Determining the As(V) concentration in an aqueous solution

The concentration of As(V) in an aqueous solution was determined by an Atomic Fluorescence Spectrophotometry method. The emission intensity of a sample was determined in an atomic fluorescence spectrophotometer, Millennium Excalibur, PSA 10.055, and the concentration of As(V) in the sample was estimated with a calibration curve,

concentration of As(V) vs. emission intensity. The calibration curve was prepared with 5 standard solutions of As(V) with concentrations ranging from 4 and 20 µg/L. Further details regarding this method were reported by Jacobo-Azuara (2007).

2.4 Adsorption equilibrium data

A 50 mL centrifugal plastic vial was used as the batch adsorber for obtaining the experimental adsorption equilibrium data of As(V) on SMZ. A portion of 0.2 g of SMZ and 40 mL of an aqueous solution with an initial known concentration of As(V) were added to the adsorber. The initial concentrations of the As(V) solutions were varied from 20 to 400 µg/L. All the As(V) solutions were prepared by adding a given aliquot of a 1000 µg/L As(V) standard solution into a 50 mL volumetric flask, and dissolving with a solution whose pH was adjusted to a certain value by mixing predetermined volumes of 0.01 M HNO₃ and NaOH solutions. The adsorber was placed in a thermostatic bath and manually mixed for 5 minutes 3 or 4 times daily. The solution pH was measured periodically with a pH-meter and kept constant by adding 0.01 or 0.1 N HNO₃ or NaOH solutions, as required. The total added volume was insignificant compared to the initial volume of 40 mL. The solution was sampled at certain times and the As(V) concentration was determined in each sample. The solution and the SMZ were left in contact until reaching equilibrium. In previous studies, it was found that 5 to 7 days were enough to attain equilibrium. The mass of As(V) adsorbed at equilibrium was estimated by performing a mass balance of As(V), which is represented by the following equation:

$$q = \frac{V(C_0 - C)}{m} \quad (1)$$

2.5 Desorption equilibrium data

The experimental desorption equilibrium data of As(V) from SMZ was obtained by a two-step procedure. In the first one, As(V) was adsorbed on SMZ at pH = 7 and $T = 25^\circ\text{C}$ and was performed by the adsorption procedure described previously. In the second one, As(V) was desorbed from the SMZ surface at pH of 7, 9 and 12 and $T = 25^\circ\text{C}$. The desorption step was carried out by the following procedure. The SMZ saturated with As(V) was decanted from the solution and washed with deionized water to eliminate the excess solution of As(V) retained within the SMZ particles. Afterwards, 40 mL of a solution without As(V) and at pH of 7, 9 or 12 was poured into the adsorber containing the SMZ saturated with As(V). The solution pH was measured periodically with a pH-meter and kept constant as described earlier. The solution and SMZ particles were left in contact during

5 days until equilibrium was reached again. The concentration of As(V) present in the solution was determined, and the mass of As(V) that remained adsorbed was estimated by performing a mass balance of As(V):

$$q = \frac{mq_0 - VC}{m} \quad (2)$$

3 Results and discussion

3.1 Characterization of natural zeolite and SMZ

The natural zeolite was characterized in previous works (Berber-Mendoza et al. 2006; Leyva-Ramos et al. 2008). The XRD pattern of the natural zeolite revealed that the zeolite was chiefly composed of clinoptilolite, and it contained impurities such as quartz, calcite and feldspar (Leyva-Ramos et al. 2008). The chemical composition of the natural zeolite is given in Table 1 (Berber-Mendoza et al. 2006). The natural zeolite had a Si/Al molar ratio of 6.89. The CEC of this zeolite was determined to be 130 meq/100 g.

The XRD analysis of the SMZ showed that the zeolite structure was not affected by the adsorption of HDTMA since the HDTMA was adsorbed on the external surface of the zeolite. The molecular size of HDTMA was greater than the diameter of the channels of the clinoptilolite and the HDTMA did not penetrate the pores of the zeolite. The Si/Al molar ratio of the zeolite was not influenced by the adsorption of HDTMA.

The thermogravimetric analysis of the SMZ showed that the amount of HDTMA adsorbed on the surface of the SMZ was 17.8 mmol/100 g, which represented a weight percentage of 6.6% (Leyva-Ramos et al. 2008). The amount of HDTMA adsorbed on the zeolite can be used to estimate the external cationic exchange capacity (ECEC) (Haggerty and Bowman 1994). At the preparation conditions of the SMZ, the HDTMA was adsorbed on the surface of the zeolite forming a double layer of HDTMA molecules. Thus, the ECEC was 8.9 mmol/100 g. The ECEC represented only

Table 1 Chemical composition of natural zeolite (Berber-Mendoza et al. 2006)

Oxide	Weight percentage (%w)
SiO ₂	77.9
Al ₂ O ₃	9.58
K ₂ O	5.93
CaO	2.00
Na ₂ O	0.30
Fe ₂ O ₃	0.93
MgO	0.39

6.8% of the total cationic sites available in the zeolite. Haggerty and Bowman (1994) reported a value of 15 meq/100 g for a SMZ prepared by adsorbing HDTMA on a clinoptilolite.

The textural properties (surface area, pore volume and average pore diameter) of clinoptilolite and SMZ were obtained using the N_2 -BET method. The modification of the zeolite caused that the surface area and pore volume of clinoptilolite decreased from 21.8 to 6.9 m²/g and from 0.05 to 0.030 cm³/g, respectively. This behavior was explained considering that the adsorbed surfactant blocked a significant part of the clinoptilolite pores. Besides, the average pore diameter of the SMZ increased from 9.3 to 17.6 nm due to blocking of the smaller pores by the surfactant.

3.2 Adsorption isotherm of As(V) on SMZ

The Langmuir and Freundlich isotherms were fitted to the adsorption equilibrium data of As(V) on SMZ. These isotherm models can be mathematically represented by the following equations:

$$q = \frac{q_m K C}{1 + K C} \quad (3)$$

$$q = k C^{1/n} \quad (4)$$

The constants of these isotherms were computed with a least-squares method based on an optimization algorithm. Additionally, the average absolute percentage deviation was evaluated with the following equation:

$$\%D = \left(\frac{1}{N} \sum_{i=1}^N \left| \frac{q_{\text{exp}} - q_{\text{pred}}}{q_{\text{exp}}} \right| \right) \times 100\% \quad (5)$$

The Langmuir and Freundlich isotherm constants as well as the values of the percentage deviation are shown in Table 2.

It was assumed that the isotherm that better fitted the adsorption equilibrium data of As(V) was the one that presented the lower percentage deviation. Based upon this criterion, the Langmuir isotherm interpreted the experimental

data better since the percentage deviations of the Langmuir isotherm were lower than those of the Freundlich isotherm, except for the data at a pH = 12, $T = 25^\circ\text{C}$ and pH = 7, $T = 35^\circ\text{C}$ (Table 2). In some cases, the percentage deviation for both isotherm models was slightly higher than usual, but satisfactory.

3.3 Effect of modification on the capacity of SMZ for adsorbing As(V)

The adsorption equilibrium data of As(V) on SMZ and clinoptilolite at pH = 7 and $T = 25^\circ\text{C}$ are plotted in Fig. 1. It can be clearly observed that the As(V) was practically not adsorbed on the clinoptilolite; this result was expected since the As(V) was present as anions (HAsO_4^{2-} , H_2AsO_4^-) in aqueous solution and the clinoptilolite mostly had sites for exchanging cations.

It is well documented in literature that clinoptilolite is an excellent cation exchanger but not so for anions (Gotardi and Galli 1985). However, it was observed that the anionic exchange capacity of the clinoptilolite increased considerably while modifying the clinoptilolite surface with the surfactant (Fig. 1). This revealed that the SMZ possessed anionic sites, originated by the presence of the surfactant amino groups on its surface. At an equilibrium concentration of 200 µg/L, the mass of As(V) adsorbed on SMZ and clinoptilolite was near 25 µg/g and 2 µg/g, respectively (see Fig. 1). This revealed that the adsorption capacity of the SMZ was approximately 12.5 times greater than that of the clinoptilolite.

The adsorption of As(V) on SMZ was favored by the electrostatic attractions between the surfactant amino group and the As(V), these interactions are illustrated in Fig. 2.

The amount of surfactant adsorbed on the zeolite was 0.178 mmol/g. The HDTMA adsorbed on the external surface of the zeolite formed a double layer so that the amount of available sites for anion exchange would be 0.089 mmol/g. The maximum mass of As(V) adsorbed was

Table 2 Isotherm constants for adsorption of As(V) onto SMZ

Adsorbent	pH	T (°C)	Langmuir			Freundlich		
			q_m (µg/g)	K (L/µg)	D %	k (µg ^{1-1/n} L ^{1/n} /g)	n	D %
Clinoptilolite	7	25	2.21	1.11×10^{-2}	30.5	9.31×10^{-3}	1.87	35.7
SMZ	5	25	74.5	1.36×10^{-3}	5.94	2.36×10^{-3}	1.26	12.5
	7	25	74.3	2.62×10^{-3}	27.3	3.78×10^{-3}	1.25	33.1
	9	25	56.3	2.70×10^{-3}	41.0	3.28×10^{-3}	1.30	54.4
	12	25	377	1.42×10^{-4}	41.3	3.08×10^{-3}	0.65	10.7
	7	15	55.1	5.05×10^{-3}	28.4	6.73×10^{-3}	1.42	38.7
	7	35	65.9	3.29×10^{-3}	43.6	4.73×10^{-3}	1.32	10.1

32.7 $\mu\text{g/g}$ (0.436×10^{-3} mmol/g) at an equilibrium concentration of As(V) close to 300 $\mu\text{g/L}$ (4.0×10^{-3} mmol/L). If this amount is compared to the concentration of anionic sites in the SMZ, it can be pointed out that only 0.5% of the total anionic sites were occupied by the As(V) anions. This result implied that the As(V) anions had very low affinity toward the anionic sites of the SMZ. Hence, the anionic sites of SMZ were not efficiently used for adsorbing As(V) anions from an aqueous solution.

Chutia et al. (2009) reported that the As(V) maximum adsorption capacity of a clinoptilolite modified with HDTMA was 45.0×10^{-3} mmol/g. On the average this capacity was 100 times greater than that of the SMZ prepared in this work. This difference was due to that Chutia et al. (2009) varied the concentrations of As(V) from 0.01 to 3.0 mmol/L, whereas the concentration of As(V) in this work ranged from 0.1×10^{-3} to 4.0×10^{-3} mmol/g. This means that the SMZ cannot be applied for the removal of As(V) from drinking water.

3.4 Effect of pH solution on the adsorption capacity

The adsorption of As(V) on SMZ was considerably influenced by the solution pH since the As(V) species present in solution and the surface charge of the SMZ depended on the

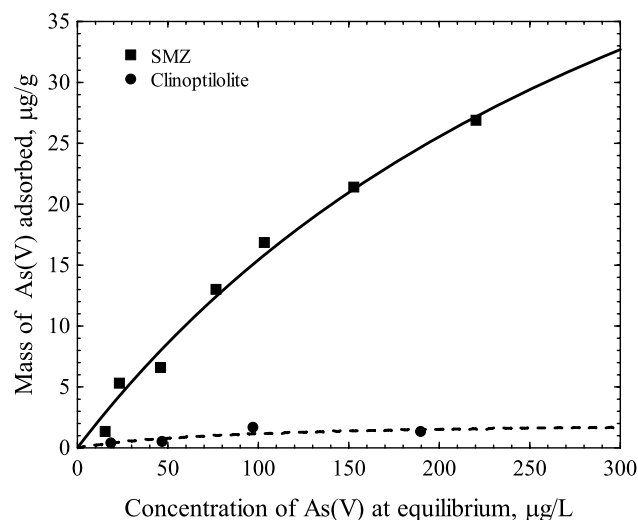


Fig. 1 Adsorption isotherm of As(V) on clinoptilolite and SMZ at pH = 7 and $T = 25^\circ\text{C}$

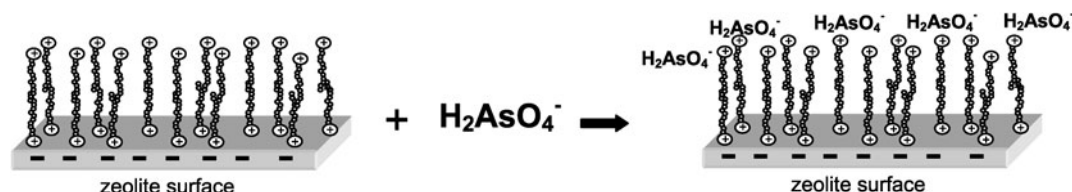


Fig. 2 Schematic illustration of the adsorption of As(V) on the anionic sites of SMZ

solution pH. The point of zero charge (PZC) of the SMZ was determined in a previous work (Leyva-Ramos et al. 2008) and was $\text{PZC} = 8$. Thus, the surface of the SMZ was positively charged at $\text{pH} < \text{PZC}$, and the surface was charged negatively at $\text{pH} > \text{PZC}$. Besides, the positive charge of the SMZ was increased while reducing the pH below the PZC.

In an aqueous solution, As(V) may form several oxyanions according to the following reactions (Kartinen and Martin 1995):



The speciation diagram of As(V) in an aqueous solution was prepared using these equilibrium constants and it is displayed in Fig. 3. At $\text{pH} = 7$, the species distribution percentage of As(V) in solution was 50% HAsO_4^{2-} and 50% H_2AsO_4^- ; while at $\text{pH} = 5$ almost all the As(V) was found as the H_2AsO_4^- species and the HAsO_4^{2-} was the predominant species of As(V), close to 100%, in the pH range between 9 and 12.

The effect of the solution pH on the SMZ capacity for adsorbing As(V) was studied determining the adsorption equilibrium data at pH of 5, 7, 9 and 12 and $T = 25^\circ\text{C}$. The adsorption equilibrium data of As(V) on SMZ at different pH values is shown in Fig. 4 and it can be discerned that the maximum adsorption capacity occurred at $\text{pH} = 7$, while the lowest capacity was observed at $\text{pH} = 12$. A similar behavior was found for the adsorption of As(V) on SMZs prepared from mordenite and clinoptilolite (Chutia et al. 2009). At an equilibrium concentration of As(V) of 200 $\mu\text{g/L}$, the mass of As(V) adsorbed was near to 27, 21, 16 and 10 $\mu\text{g/g}$ at a pH of 7, 9, 5 and 12, respectively. Accordingly, the adsorption capacity was reduced 1.3 and 2.7 times while increasing the pH from 7 to 9 and from 7 to 12, respectively, and 1.7 times while decreasing the pH from 7 to 5.

The adsorption capacity was greater at $\text{pH} = 7$ than at $\text{pH} = 5$. This result seemed to be unreasonable since the surface was more positively charged at $\text{pH} = 5$ than at $\text{pH} = 7$. Consequently, the electrostatic attraction was greater at $\text{pH} = 5$ than at $\text{pH} = 7$. According to the speciation diagram, at $\text{pH} = 5$ there was hardly any HAsO_4^{2-} , whereas at $\text{pH} = 7$ the HAsO_4^{2-} represented only 50%. This

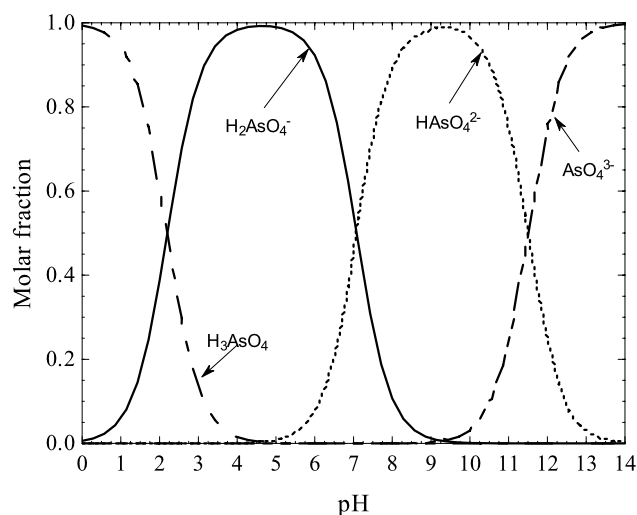


Fig. 3 Speciation diagram of As(V)

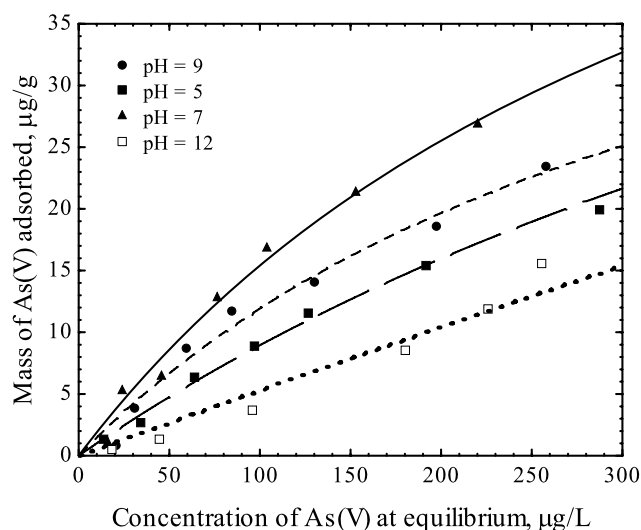


Fig. 4 Effect of solution pH on the adsorption isotherm of As(V) on SMZ at $T = 25^{\circ}\text{C}$

behavior may be explained by assuming that the affinity of the HAsO_4^{2-} anion toward the SMZ was greater than that of the H_2AsO_4^- anion. At $\text{pH} = 5$, the As(V) was mostly as the H_2AsO_4^- anion and the surface of the SMZ was charged positively. At a $\text{pH} = 9$, the predominant As(V) species was the HAsO_4^{2-} anion and the surface charge was negative. The electrostatic attraction favored adsorption at a $\text{pH} = 5$ but not at a $\text{pH} = 9$. However, the SMZ capacity for adsorbing As(V) was greater at a $\text{pH} = 9$ than at a $\text{pH} = 5$. Again, this result indicated that the SMZ presented a greater affinity toward the HAsO_4^{2-} than toward the H_2AsO_4^- . At $\text{pH} = 12$, the surface charge of the SMZ was negative and the predominant species is HAsO_4^{2-} . Although, the SMZ presented an affinity for this type of species as observed at a $\text{pH} = 9$, there exists less adsorption brought on by an increase in the

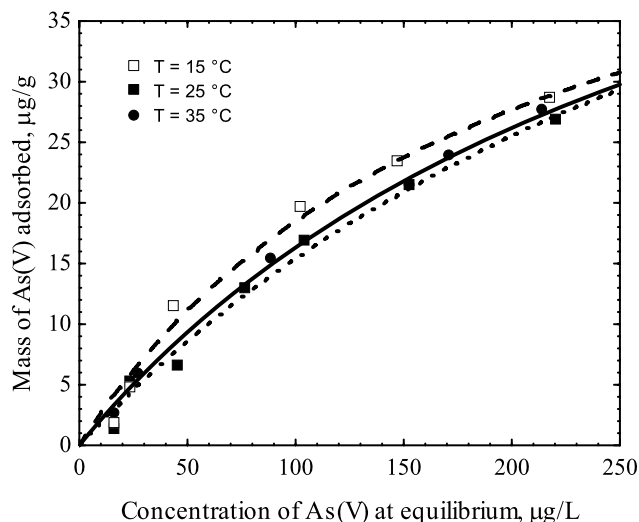


Fig. 5 Effect of temperature on the adsorption of As(V) on SMZ at $\text{pH} = 7$

forces of repulsion between the surface charge of the SMZ and the HAsO_4^{2-} anion.

3.5 Effect of the temperature upon the adsorption capacity

The effect of the temperature on the adsorption of the As(V) on SMZ was studied by determining the adsorption equilibrium data at temperatures of 15, 25 and 35°C and $\text{pH} = 7$. The adsorption equilibrium data and the Langmuir isotherms are displayed in Fig. 5, and the adsorption capacity increased slightly when the temperature was diminished from 25 to 15°C . However, the adsorption capacity varied slightly while increasing the temperature from 25 to 35°C . In this case the effect of temperature on adsorption capacity cannot be argued since the magnitude of this effect may be masked by the dispersion of the data due to experimental error.

The heat of adsorption, ΔH_{ads} , can be estimated from the temperature dependence of the Langmuir isotherm constant K . The following relationship was used in this calculation:

$$K = K_0 e^{-\Delta H_{\text{ads}}/RT} \quad (6)$$

The ΔH_{ads} estimated from the values of K at 15 and 25°C (Table 1) was -46.82 kJ/mol . Therefore, the adsorption of As(V) on SMZ was exothermic and this explained why the adsorption of As(V) was favored when the temperature was reduced from 25 to 15°C . Moreover, the order of magnitude of ΔH_{ads} indicated that the As(V) was chemisorbed on the surface of SMZ. In previous works about the adsorption of bichromate anions on bentonite and clinoptilolite modified with HDTMA, the ΔH_{ads} ranged from -35 to -38 kJ/mol

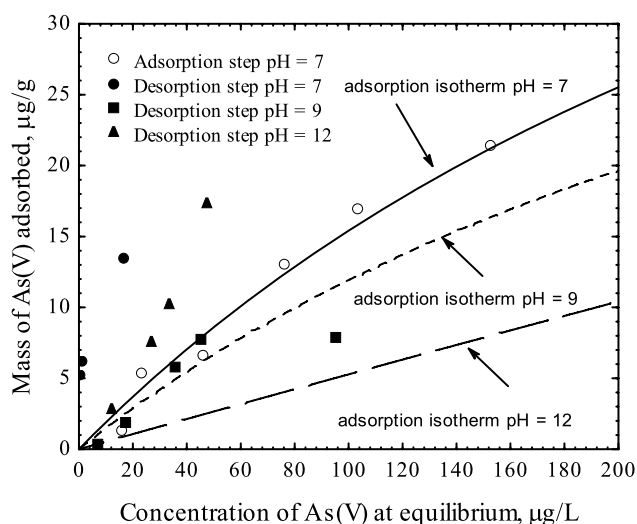


Fig. 6 Reversibility of the adsorption of As(V) on the SMZ at $T = 25\text{ }^{\circ}\text{C}$

(Leyva-Ramos et al. 2008; Majdan et al. 2005). The magnitudes of both values were 1.3 and 1.2 times smaller than the value estimated in this work.

3.6 Reversibility of the adsorption

The reversibility of As(V) adsorption on SMZ at $T = 25\text{ }^{\circ}\text{C}$ was studied by first adsorbing the As(V) at pH = 7 and then desorbing the As(V) at pH of 7, 9 and 12. The results from the adsorption and desorption equilibrium of As(V) on SMZ are displayed in Fig. 6. According to these results, it was observed that the equilibrium attained in the desorption stage at a pH of 7, 9 and 12 did not correspond to the adsorption isotherms at a pH of 7, 9 and 12, respectively. This indicated that the adsorption of the As(V) on SMZ was not reversible at any of these pH values. This result corroborated that the As(V) was chemisorbed on the SMZ.

The mass of As(V) desorbed from the SMZ increased raising the pH of the desorption solution from 7 to 12. This increment was probably due to competing of the OH^- anions for the anionic sites. The As(V) anions adsorbed on the surface of SMZ were displaced by the OH^- anions in the solution since the concentration of OH^- was augmented 100,000 times when the pH was increased from 7 to 12.

4 Conclusions

The adsorption of the cationic surfactant HDTMA on the external surface of clinoptilolite modified its chemical and surface charge characteristics, and considerably enhanced the capacity of the clinoptilolite for adsorbing the As(V) anions from an aqueous solution.

The Langmuir isotherm satisfactorily matched the adsorption equilibrium data of As(V) from an aqueous solution on SMZ. The electrostatic attraction between the positively charged surface of SMZ and the H_2AsO_4^- and HAsO_4^{2-} anions favored the adsorption of As(V) on SMZ.

The effect of the pH on the SMZ capacity for adsorbing As(V) was attributed to the SMZ affinity toward the As(V) species in an aqueous solution and the surface charge of the SMZ.

The adsorption of As(V) on SMZ was irreversible and was slightly favored by decreasing the temperature from 25 to $15\text{ }^{\circ}\text{C}$. The value of ΔH_{ads} (-46.82 KJ/mol) indicated that the adsorption was exothermic. It was concluded that the As(V) was chemisorbed on the SMZ since the adsorption was both exothermic and irreversible.

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