

ORIGINAL RESEARCH PAPER

## Modification of Nano Clinoptilolite Zeolite Using Sulfuric Acid and Its application Toward Removal of Arsenic from Water Sample

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### ABSTRACT

Zeolites are widely used in wastewater and contaminated water refinement due to their great adsorption properties. However, Clinoptilolite (as one type of Zeolites) has a relatively low adsorption capacity at least for arsenic ions. Therefore, in order to increase the adsorption capacity, natural Clinoptilolite was modified with sulfuric acid and various tests were then conducted to determine the best conditions for obtaining the maximum capacity of adsorption. The results showed that parameters such as arsenic initial concentration, adsorbent's particles size, adsorbent dosage and solution pH affect the adsorption capacity. Arsenic maximum adsorption was obtained at pH 8. Furthermore, the maximum adsorption capacity was found to be in an adsorbent modified with 1 M acid. The contact time or the time of balance between the adsorbent and analyte was determined to be 240 min and the optimal amount of Zeolite to obtain was determined to be 480 g/L. The rate of arsenic removal under the optimal conditions is 27.69%. The modified Clinoptilolite capacity for arsenic adsorption increased with reducing the adsorbent particles size to 0.5 mm. Besides, among the three examined isotherms including the Langmuir, Freundlich and Dubinin-Radushkevich isotherms, the Langmuir and Freundlich models well described arsenic adsorption. Considering the more favorable adsorption efficiency of Clinoptilolite modified with sulfuric acid compared to natural Clinoptilolite, the modified one can be proposed as an appropriate and inexpensive adsorbent for arsenic removal in waste water refinement.

**Keywords:** Clinoptilolite, Arsenic, Adsorption, Waste water, Sulfuric acid

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### INTRODUCTION

Studies show that global population will significantly grow by 2020 as a consequence of which the need for more water supplies in different areas will intensify and thus the production of wastewater

will increase. Reuse of wastewater is of particular importance especially in several societies around the world which suffer lack of water supplies or will face such a dramatic problem soon. This issue is so serious that the World Health Organization put the reuse of wastewater for non-drinking purposes among its important guidelines. The production of wastewaters has a significant volume in the industrialized countries.

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There are lots of papers focusing on removing of some ions toward refinement of wastewaters [1-4].

The conventional methods for removing the heavy metals include multiple processes such as precipitation, coagulation, ion exchange, electro-dialysis, reverse osmosis, evaporation and filtration [5, 6]. Although there are several methods for removing the metals, most of the above-mentioned processes have significant disadvantages, such as high energy requirements and consequently high costs with low efficiencies, sludge disposal problems with large amounts of heavy metals which require special chemicals [7]. Therefore, due to the technical and economic constraints of the above-mentioned methods, a search for new methods is highly recommended and in this regard adsorption by a new adsorbent is considered as a new option.

Arsenic is a metalloid, which is an element with both metal and nonmetal properties. It is a potent contaminant in waterways across the world. As is used in agriculture as an insecticide, herbicide, fungicide, and algacide, and also for cleansing the sheep, dyeing, eradicating the tapeworm in the sheep and cows [8,9]. As may be ingested, inhaled or adsorbed through the skin or mucous membranes and seriously damage the digestive system, nervous system, respiratory system and the skin. Inorganic As can have serious cancerous effects including skin cancer and internal cancer as well as non-cancerous effects on the skin, cardiovascular system, digestive system and liver [10]. According to WHO guidelines, the amount of As in the drinking water should not exceed 0.01 mg per liter. The oral lethal dose of As oxide in human beings has been reported to be 50 to 300 mg [11]. Lin and Chen [12] developed a feasible approach to wastewater treatment, including the removal of arsenic ions using mesoporous  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> structures. Sheng et al. [13] prepared magnetic graphene oxide (MGO) composites used it as a versatile adsorbent for As (V) removal from aqueous solutions. Their results showed that the MGO composites had a good adsorption capability for As(V) removal and the adsorption isotherms were described by the Langmuir model better than by the Freundlich model. The adsorption properties of the porous magnesium oxide (MgO) nanowires were investigated for As(V) removal by Jia et al. [14]. They found a high As(V) adsorption capacity of this adsorbent. Mahanta

and his co-worker [15] used Fe ion immobilized poly(vinyl alcohol) (PVA) nanofibers for the removal of arsenic (As) from water. They reported that these modified PVA nanofibers are efficient for removing arsenic from water and may be used for water purification.

One of the adsorbents studied extensively in the recent years are Zeolites [16]. Zeolites are microporous, aluminum-silicate minerals commonly used as commercial adsorbents due to their exceptional adsorption properties. Dimensions of pores and channels of each Zeolite are its main characteristics causing a selective adsorption of specific ions or molecules in the presence of the other species. Zeolites are extensively used before or after the modifications to adsorb the cations and anions from the contaminated environments [17-20].

As a result, acid modification of Zeolite induces replacing of unstable ions by H<sup>+</sup> ions in Zeolite. This process results formation of porosity structure having high specific area which results higher adsorption. To the best of our knowledge there is no As removal based on acid treatment of Zeolite in the literatures. The aim of the present study is to modify Clinoptilolite as a cheap and available kind of Zeolite with sulfuric acid and compare its adsorption capacity with the natural Zeolite Clinoptilolite and then evaluate different parameters in order to obtain maximum As adsorption as a water contaminator.

## MATERIAL AND METHODS

To prepare As samples with various concentrations, As oxide (Merck, Germany) was used to prepare 1000 ml samples with different concentrations from 25 to 105 milligrams per liter. To measure the amount of As, an atomic adsorption device based on the ICP (inductively coupled plasma) method. Furthermore, the Zeolite used in this study was prepared in Afrazand Company, Iran; its property is presented in Table 1. X-ray fluorescence CORTEX (Corescanner Texel) was used to determine the elemental composition of materials. The other chemicals used in this study were prepared with laboratory purity grades in Iran Chem Company.

Table 1. Clinoptilolite physical properties

pH	Humidity	Density (g/cm <sup>3</sup> )	Special area (m <sup>2</sup> /g)	CEC	Adsorbent Name
7.1	52	2.31	21.005	86.95	Unmodified Clinoptilolite
8	-	-	34.655	-	Modified Clinoptilolite

### Zeolite Physical Properties

Determining Zeolite physical properties is one of the most common laboratory tests on soil samples that include moisture percentage tests, and pH, CEC (cation exchange capacity) and specific surface area determination. The specific surface area was calculated by using the Brunauer Emmett Teller (BET) equation. As can be seen in Table 1, the specific area of modified adsorbent is increased than unmodified adsorbent. Having this information, some other physical properties are also predictable.

### Cation Exchange Capacity

CEC (cation exchange capacity) generally includes the maximum amount of cation that a certain weight of soil (Zeolite) is capable to adsorb or retain. This capacity is shown in terms of mEq per hundred grams of dry soil. To determine this parameter, all the adsorbed cations in the soil with a certain weight are extracted by substituting another cation. (Ammonium acetate solution is usually used for this purpose.)

### Density

Determining the density of a normal non-damaged sample is relatively easy since by dipping a sampling cylinder into the target mass of soil and knowing the weight and volume of the soil that fills the cylinder, the density can be calculated through the following equation [21]:

$$U=(W_2-W_1)/V$$

In which  $W_1$  and  $W_2$  respectively indicate the soil initial weight and the weight of the soil in the cylinder in terms of g, and  $V$  indicates the volume of the soil in the cylinder in terms of  $cm^3$ .

### pH

Soil pH is one of the most important measures showing the type of the adsorbed cations onto the colloidal surfaces. To measure the pH, a pH meter is used. This device is composed of sodium silicate electrodes which report the potential difference if the concentrations of hydrogen in and out of the electrode are not equal.

### Zeolite Preparation and Modification

To prepare the adsorbent, the Zeolites were firstly isolated in three sizes by ASTM (American society for testing materials) standard sieves. To isolate the impurities, the Zeolites must be stirred

for 6 hours in distilled water, then the liquid phase must be separated by the standard sieve and after being rinsed several times with distilled water, the Zeolites must be dried at a temperature of  $65^\circ C$  and kept in the desiccator.

To modify the Zeolites, they stirred with sulfuric acid with a molar ratio of one to ten for 24 hours. Then, they must be filtered and rinsed with distilled water. Rinsing will continue until the water pH reaches 7. Then, the Zeolites must be dried at a temperature of  $70^\circ C$  and kept in the desiccator. Maximum care is required to prevent loss of samples in all the stages.

The adsorption tests were conducted to determine the optimal pH, the effect of As initial concentration, the appropriate concentration of acid for Zeolite modification, the size of the adsorbent particles for obtaining the maximum adsorption and to determine the isotherm constants. In each case, the adsorption capacity is calculated through the following equation [22]:

$$Q_e=V(C_i-C_t)/m$$

In which  $Q_e$  indicates the amount of the adsorbed As per unit mass of adsorbent,  $C_i$  indicates the initial concentration of dissolved As,  $C_t$  indicates the secondary concentration of As in time  $t$ ,  $V$  indicates the solution volume and  $m$  indicates the adsorbent mass.

In order to determine the effect of various parameters, tests were conducted with a constant concentration of dissolved As ( $100mg/l$ ). In order to mix the adsorption and contaminator, a mixer was used. After completing the process, the solution was filtered by a filter paper and the remained solution was put in the atomic adsorption device to determine the adsorption percentage.

The obtained amounts were analyzed through the Langmuir, Freundlich, and Dubinin- Radushkevich isotherms equations and the reaction rate constants and the various isotherms constants were extracted to interpret the adsorption process and capacity. All the experiments were repeated twice to reduce the error rate. To avoid any error, all the used utensils were washed with acid and eventually distilled water.

## RESULTS AND DISCUSSION

### Zeolite Phases and Elements

Samples were examined by X-ray diffraction (XRD) and transmission electron microscopy

(TEM) to determine the type of constituting phases of inorganic parts. The shapes and dimensions of the particles can be seen in Figure 1. The TEM techniques proved the XRD patterns in which nano sized zeolite were indicated by distinctive peaks.

Furthermore, the compositions of the elements (in weight percentage) in the structure of the unmodified and modified Zeolite samples obtained

through the X-ray fluorescence (XRF) method are shown in Table 2. The numerical value of RL factor which obtained from dividing the amount of Ci into the sum of the amounts of Ci in the sample was, respectively 0.86 and 0.93 for the unmodified and modified Zeolites indicating that it belongs to the acidic Zeolites. In the acidic Zeolites, the numerical value of R factor is higher than 0.75 [23, 24].

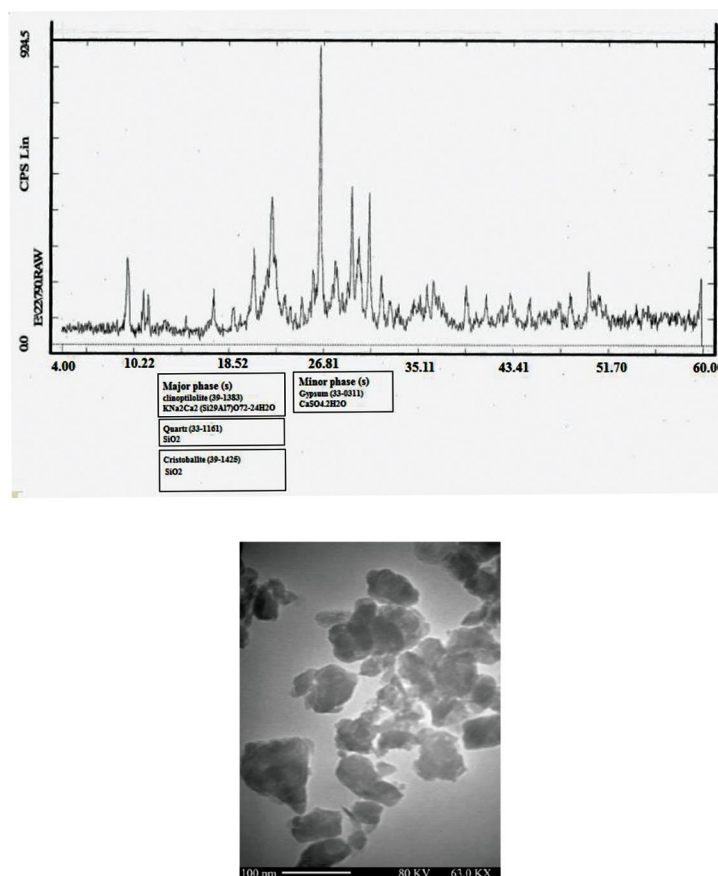


Fig. 1. XRD spectrum (top) and TEM (down) of clinoptilolite.

Table 2. Chemical composition of the unmodified and modified Zeolite (weight percentage)

Modified Zeolite	Unmodified Zeolite	chemical formula	chemical composition
87.07	67.44	Si O <sub>2</sub>	Silicon oxide
5.92	10.9	Al <sub>2</sub> O <sub>3</sub>	Aluminum oxide
0.83	0.84	Fe <sub>2</sub> O <sub>3</sub>	iron oxide
0.28	0.19	Ti O <sub>2</sub>	Titanium oxide
0.91	1.24	Ca O	Calcium oxide
0.55	0.33	Mg O	Magnesium oxide
2.93	4.39	K <sub>2</sub> O	Potassium oxide

### The Effect Of Sulfuric Acid Concentration On Zeolite Surface Modification

The results obtained from the XRF test (Table 2) showed that the As adsorption capacity of Zeolite will increase upon acid treatment. As it is clear in Figure 2, the Zeolites modified with 1M acid had a higher efficiency compared to the other concentrations. In general, the modified Zeolite compared to the unmodified Zeolite had a higher efficiency in As adsorption. The substantial increase of As adsorption capacity of the modified Zeolites with acid compared to the natural Zeolites is due to the dominant role of the hydrogen ions as an interchangeable ion in the Zeolites. Therefore, when most of the interchangeable sites are occupied by the small hydrogen ions, the access of the As ions to the deeper parts of the adsorbent is easier [25].

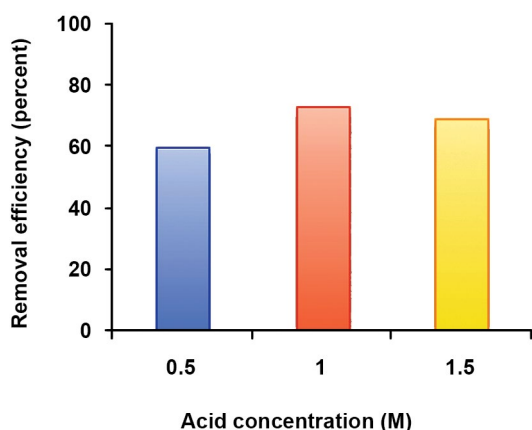


Fig. 2. The effect of sulfuric acid concentration on Zeolite modification process.

### The Effect Of Zeolite Particles Diameter

The Zeolites separated by the sieves were exposed to As solution and it was concluded that as shown in Figure 3, the Zeolites with a diameter of 50 nm have more adsorption than those with larger diameters. The reason for this difference is that as the adsorbent particles get smaller, the ratio of the surface to the volume increases and eventually due to the increase of the specific surface area, the number of the ion exchange sites and the total efficiency of As adsorption increases.

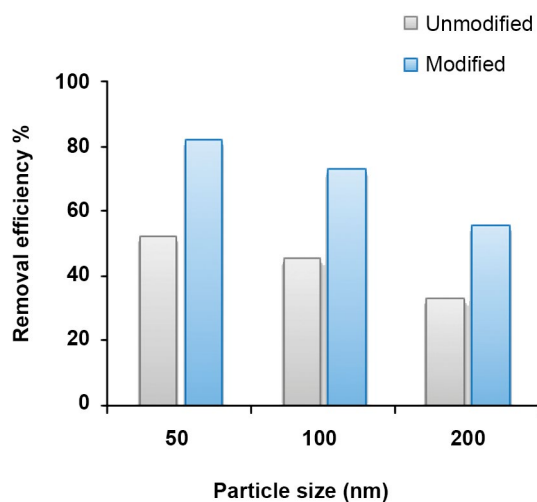


Fig. 3. The effect of Zeolite particles diameter on As adsorption (Time: 60 min, pH=7).

### The Effect Of pH

The pH influences the electric charge of adsorbent, so different pH result different electric charge. The effect of  $H^+$  ion concentration on As adsorption by Zeolite is shown in Figure 4. Regardless of the type of Zeolite (modified or unmodified), the adsorption efficiency is lower at an acidic pH and with increasing the pH, the efficiency increases so that the change of pH from 2 to 10 would increase the efficiency of the unmodified adsorbent from 7.38 to 38.12 and the modified one from 29.73 to 75.1. However, the maximum As adsorption was obtained at pH 8 in which As adsorption was respectively 48.83 and 78.22. Clearly, pH changes affect As adsorption efficiency since the solution pH affects both the adsorbent surface charge and the As ions charge. At low pH, there is a competition between  $H^+$  and As III ions in adsorption sites. In particular, the Zeolite preferably adsorbs the hydrogen ions better compared to the As ions. In addition, due to the small size and high mobility of the hydrogen ions, these ions enter the Zeolite pores and easily substitute the interchangeable ions in the Zeolites. Therefore, in the acidic conditions with lower pH, this property increases. However, with increasing the pH, the concentrations of the hydrogen ions decreases while the adsorption of As increases [26-27]. In other hand as can be seen in Figure 4, at very high pH values, the adsorption of As is increased. This is because of the  $OH^-$  tends to complex with As ion, so decreases its adsorption.

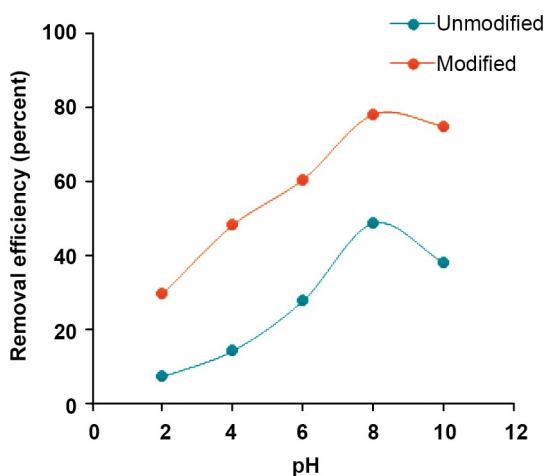


Fig. 4. The effect of solution pH on As adsorption efficiency (time: 60 min, adsorbent dosage: 3gr).

#### The Effect Of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption process indicates that with increasing the adsorbent amount, the adsorption rate will increase so that according to Figure 5, with increasing the adsorption dosage from 20 grams per liter to 480 grams per liter, As adsorption rate increased from 10.1 to 66.33% for the unmodified Zeolite and from 36.18 to 77.66% for the modified Zeolite. While increasing the Zeolite dosage from 480 grams per liter to 600 grams per liter, the adsorption efficiency increased for the unmodified and modified Zeolites, respectively from 67 to 78.1%. As expected, with increasing the Zeolite adsorbent, the adsorption rate also increased. The cause of this increase is that with increasing the adsorbent dosage, the number of the active adsorption sites on the adsorbent surface adsorbing As will increase [28].

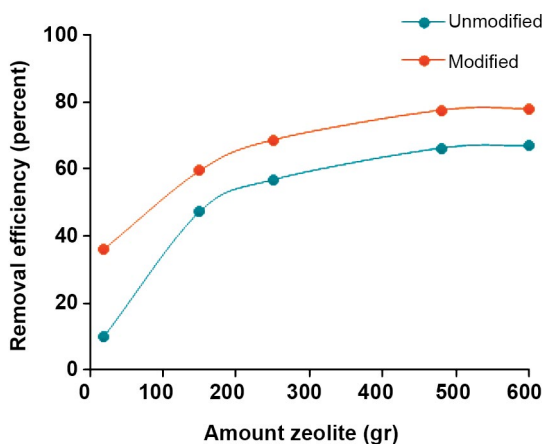


Fig. 5. The effect of adsorbent dosage on As adsorption efficiency (time: 60 min, pH=8).

#### The Effect Of Process Time

The effect of process time on As adsorption is shown in Figure 6. The process time increases As adsorption rate. The highest rate of As adsorption happened quickly in the first 50 minutes and after that, the contact time reduced the amount of adsorption. The percentages of As adsorption by the unmodified and modified Zeolites are respectively 67.68 and 97.02 in 300 min and 66.33 and 96.72 in 240 min. These results indicate that the equilibrium time of the process is 240 min.

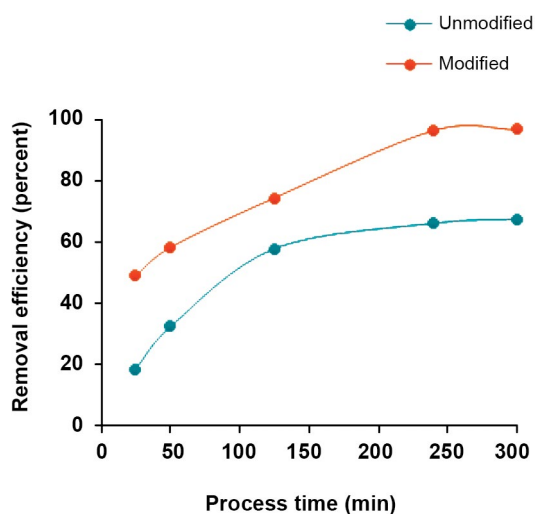


Fig. 6. The effect of process time on As adsorption efficiency (adsorbent dosage: 480 g, pH=8).

#### The Effect Of Dissolved As Initial Concentration

Figure 7 shows the effect of dissolved As initial concentration on the removal and adsorption efficiencies. Obviously, the adsorption equilibrium capacity increases with increasing As initial concentration while the removal efficiency has a reverse process which decreases with increasing the initial concentration.

In an adsorption process, the initial concentration of the adsorbing ions in the solution plays a key role as the driving force to overcome the resistance against the mass transfer between the liquid and solid phases. It is expected therefore that with increasing the concentration, the amount of the adsorbed ions increases [28]. It can be seen that the more concentrated on a solution is in terms of the number of the ions, the better the adsorption will

be. Secondly, the adsorption speed was high at the beginning of the process due to the presence of a prepared adsorbent surface, or the presence of the active adsorbent sites that quickly adsorb the As. However, the number of these active sites decreases gradually with increasing the process time and the number of the ions adsorbed onto the adsorbent surface. The high efficiency at a low initial concentration is due to the fact that the adsorption sites are easily accessible and occupied. But at higher concentrations, fewer sites are available compared to the number of the As moles. Therefore, the removal percentage depends on the initial concentration. We can say, the reduction of the removal rate with the increase of the initial concentration is due to the increase of the number of the ions competing for the available adsorption sites on the adsorbent surface and finally, due to the lack of the above-mentioned sites at high concentrations. Moreover, the reduction of the average distance between the adsorbed components affects the distribution of the adjacent electric charge on higher concentrations. Therefore, it influences the ability of the adsorbing particles to migrate to the adsorbent surface and thereby reduces the consolidated ions on the adsorbent [29].

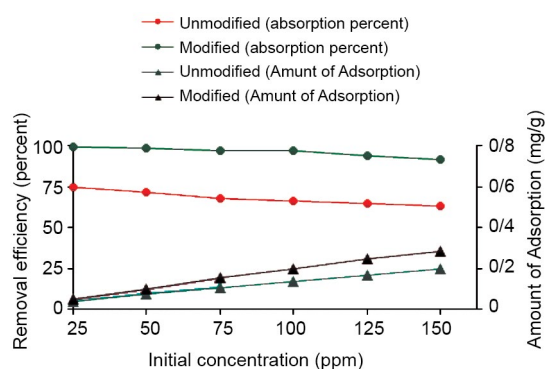


Fig. 7. The effect of initial concentration on As adsorption efficiency (adsorbent dosage: 4.5 g, pH=8, time: 945 min).

### The Adsorption Isotherms

Adsorption isotherm is an important factor in the design of the adsorption systems. The adsorption isotherm explains the interplay between the adsorbent and the adsorbing material. Thus, it has always been a key factor in determining the adsorbent capacity and optimizing the use of the target adsorbents. The equilibrium

adsorption isotherms are explained by plotting As concentration in the solid phase against the solution phase.

### Langmuir Isotherm

Langmuir isotherm for As adsorption by the unmodified and modified Zeolites are shown in Fig. 8 and Fig.9, respectively. The adsorption capacity coefficient ( $Q_{Max}$ ) and Langmuir constant (K) in Langmuir adsorption isotherm are shown in Table 3. The basic characteristic of Langmuir isotherm is a dimensionless constant called the balance parameter ( $R_L$ ) which can be calculated through the following equation [30]:

$$RL=1/1+KC_i$$

In which  $C_i$  indicates As initial concentration, K indicates the Langmuir constant, and RL indicates the type of the isotherm.  $0 < R_L < 1$  for optimal adsorption,  $R_L > 1$  for undesirable adsorption,  $R_L = 1$  for linear adsorption and  $R_L = 0$  for irreversible adsorption.

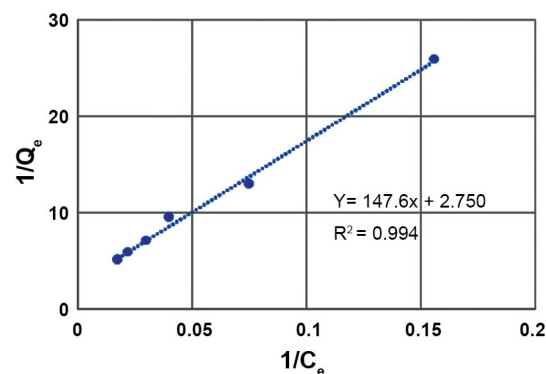


Fig. 8. Langmuir isotherm for As adsorption by the unmodified Zeolite.

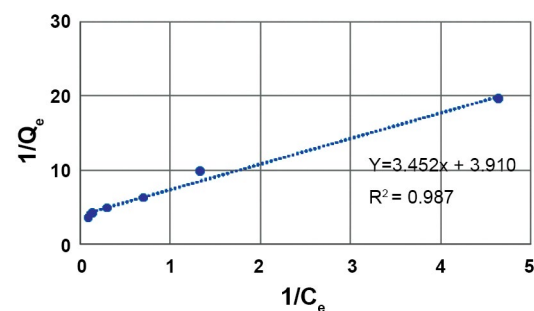


Fig. 9. Langmuir isotherm for As adsorption by the modified Zeolite.

Table 3. The parameters of the Langmuir, Freundlich and D-R isotherms for As adsorption

Type adsorbent	Langmuir isotherm			Freundlich isotherm			isothermD-R		
	R <sup>2</sup>	K	Q <sub>max</sub>	R <sup>2</sup>	n	K	R <sup>2</sup>	β	E
Unmodified Zeolite	0.9949	0.0186	0.363	0.9981	1.33	0.01	0.8279	-1E-05	223.6
Modified Zeolite	0.987	1.13	0.256	0.9929	2.27	0.113	0.8588	-8E-08	2500

**Freundlich Isotherm**

Figs 10 and 11 show Freundlich isotherm for As adsorption by the unmodified and modified Zeolites, respectively. The amounts of n and K for As adsorption onto the unmodified and modified Zeolitesurfaces are obtained by plotting the Figure of log C<sub>e</sub> against log Q<sub>e</sub>. Freundlich coefficient (n) must be a value in the range of 1 to 15 in order to be considered as optimal adsorption [31].

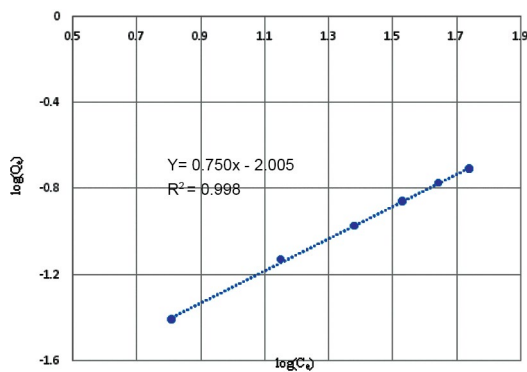


Fig. 10. Freundlich isotherm for As adsorption by the unmodified Zeolite.

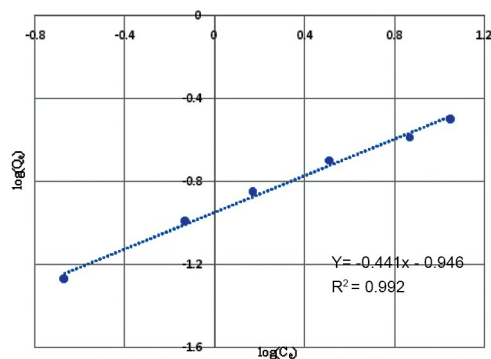


Fig. 11. Freundlich isotherm for As adsorption by the modified Zeolite.

**D-R Isotherm**

After plotting the LN Q<sub>e</sub> Figure against ε<sup>2</sup>, the value of β and E are calculable [32]. As shown in Figures 12 and 13, the coefficient of this isotherm is lower than the Langmuir and Freundlich isotherms. These amounts represent the less compliance of the D-R isotherm with the experimental data.

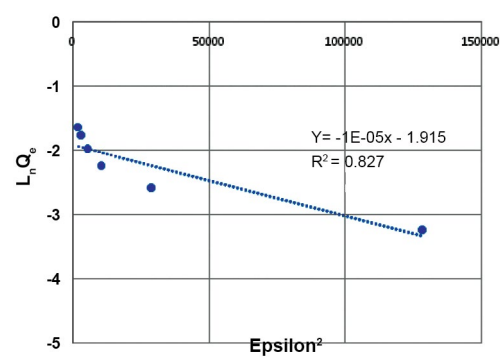


Fig. 12. D-R isotherm for As adsorption by the unmodified Zeolite.

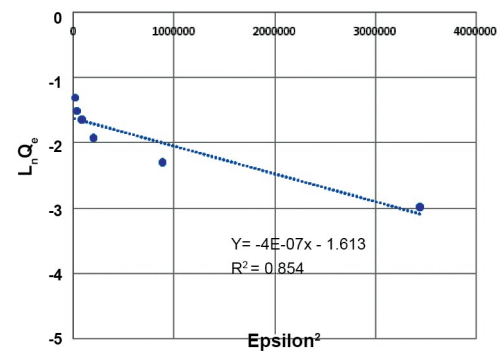


Fig. 13. D-R isotherm for As adsorption by the modified Zeolite.



### The Appropriate Isotherm

In the Langmuir isotherm, the determination coefficient ( $R^2$ ) for As adsorption on the raw and modified Zeolites is 0.99 which shows the high coordination of the Langmuir monolayer model and As adsorption by the modified Zeolite. This coordination may be due to the homogenous distribution of the adsorption sites on the adsorbent surface since the Langmuir isotherm assumes the adsorbent surface as homogeneous [30].

Although the Langmuir monolayer adsorption model was appropriate to describe the experimental data obtained from the adsorption tests, the process of adsorption was also evaluated by the Freundlich model and it was determined that the Freundlich model describes As adsorption as well as the Langmuir model. The Dubinin-Radushkevich model was also examined. According to this model, the determination coefficient for As adsorption by the modified adsorbent is low. Therefore, this model does not capture the adsorption process as well as the previous models. In general, the determination coefficient in the Freundlich model is better than the Langmuir model. Thus, the Freundlich isotherm model is chosen and proposed as the appropriate model to predict the As adsorption from the solution onto the modified Zeolite adsorbent with sulfuric acid.

### Adsorption thermodynamics

By using the Langmuir isotherm and application of following equation, the Gibbs function can be calculated:

$$\Delta G = RT \ln KL$$

where  $KL$ ,  $R$ , and  $T$  correspond to Langmuir equilibrium constant, the universal gas constant, and temperature in Kelvin, respectively.

As can be seen from Table 4, the more negative value of Gibbs function for modified zeolite points to the feasibility of the process and the spontaneous nature of adsorption with a high preference for As on modified zeolite

Table 4. Thermodynamic parameters for the adsorption of As onto modified and unmodified zeolites

Type adsorbent	$\Delta G$ (KJ/mol)
Unmodified Zeolite	-0.07
Modified Zeolite	-0.3

### Kinetic models

The prophecy of kinetics is essential for the plan of adsorption systems. The kinetic parameter, which is useful for the forecast of adsorption rate, gives significant data for scheming and modeling the processes. Two kinetic models, that is, the Elovich and the intra-particle diffusion equations were used to understand the time-dependent data of experimental.

The Elovich equation is given as follows [33].

$$dq_t/dt = \alpha \exp(-\beta qt)$$

where  $\alpha$  is the first sorption rate (mol/g min) and  $\beta$  is the desorption constant (g/mol). To simplify the Elovich equation, it is assumed that  $\alpha \beta t \ll 1$  and by using the boundary conditions  $q_t=0$  at  $t=0$ , this equation turns into:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t$$

Where  $q_t$  is the amounts of As adsorbed on the modified zeolite at different times (mg g<sup>-1</sup>),  $\alpha$  is the initial adsorption rate (mg g<sup>-1</sup> min<sup>-1</sup>) and  $\beta$  is the desorption constant (g mg<sup>-1</sup>) consequently, the constants could be attained using the slope as well as intercept of a straight line plot of  $q_t$  against  $\ln t$ . The intra-particle diffusion equation [34] could be written by the subsequent equation:

$$q_t = K_a t^{1/2} + I$$

where  $I$  is the intercept and  $k_d$  is the intra-particle diffusion rate constant (mg g<sup>-1</sup> min<sup>-1/2</sup>).

We modeled the adsorption kinetics by the Elovich and intra-particle diffusion equations. Linear plots of both considered kinetic models and also the adsorption kinetic rate constants are shown in Figs 14 and 15, and Table 5, correspondingly. All kinetic models demonstrate a fine correlation values.

The Elovich equation, which is well-known to be suitable in describing chemisorption on highly heterogeneous adsorbents, provides a low regression coefficient ( $R^2$ ) value of 0.978 for the plot of  $qt$  versus  $\ln t$  suggesting it may not appropriate to describe this process. The plot for intra-particle diffusion ( $qt$  versus  $t_{1/2}$ ) provides a good account of adsorption of As with  $R^2$  value of 0.986 indicating that this model fits the adsorption process.

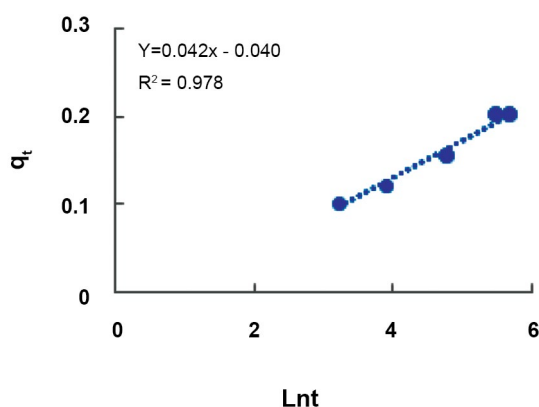


Fig. 14. Plot of Elovich equation for adsorption of As onto modified Zeolite.

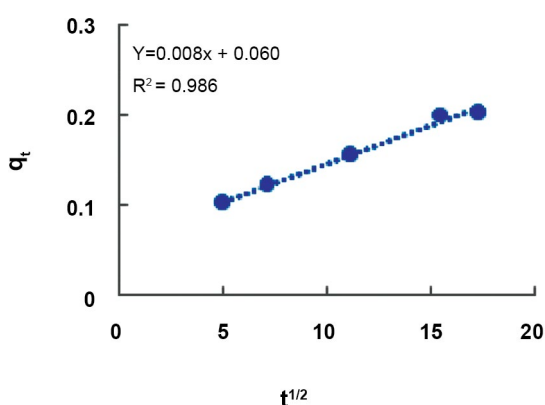


Fig. 15. Intra-particle diffusion kinetics for adsorption of As onto modified Zeolite.

Table 5. Kinetic parameters for the adsorption of As onto modified zeolite

Models	Coefficients	R <sup>2</sup>
Elovich equation	$\alpha=9.08 \text{ mg g}^{-1} \text{ min}^{-1}$ $\beta=0.0426 \text{ g mg}^{-1}$	0.9785
Intra-particle diffusion	$K_d=0.0085 \text{ mg gr}^{-1} \text{ min}^{-1}$ $I=0.0605 \text{ mg g}^{-1}$	0.9865

## CONCLUSION

In this study, the efficiency of the natural Zeolite (Clinoptilolite) and the modified Zeolite with sulfuric acid as an affordable and available adsorbent are studied for the removal of As from the aqueous solutions. The results of the present study showed that the modified Zeolite tends to adsorb more As compared to the unmodified Zeolite. In addition, parameters such as As initial concentration, the

adsorbent particles size, the adsorbent dosage and the solution pH on the affective adsorption rate. The maximum As adsorption was obtained at pH=8. Furthermore, the maximum adsorption capacity was observed in the adsorbent modified with 1 M acid. The contact time of 240 min was the time of balance between the adsorbent and adsorbing material and the appropriate adsorbent dosage for obtaining the optimal amount of Zeolite for maximum adsorption efficiency was determined to be 480 g/L. The rate of As removal under the optimal conditions is 96.72%. Therefore, this adsorbent has a high potential to be used in refining the industrial wastewaters. Furthermore, among the three examined isotherm models including the Langmuir, Freundlich and Dubinin-Radushkevich models, the Langmuir and Freundlich models described fully the process of As adsorption on the adsorbent surfaces.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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