



Removal of arsenic from drinking water using modified natural zeolite

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ABSTRACT

Arsenic removal from drinking water by adsorption on natural and iron modified clinoptilolite was investigated. The structure of modified and unmodified clinoptilolite samples from the Gördes–Manisa deposit was studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The elemental composition and specific surface areas of zeolitic samples were also determined. The pretreatment of clinoptilolite using NaCl and FeCl₃ solutions (0.1 and 0.01 M) resulted in 9.2 (92%) and 8.4 (84%) $\mu\text{g g}^{-1}$ of arsenic uptake, whereas only 1.5 $\mu\text{g g}^{-1}$ of arsenic uptake could be detected in the untreated zeolite at equilibrium time. The time required to attain equilibrium for arsenic sorption on all types of clinoptilolite was 60 min. The saturation time was independent of concentration of the initial arsenic solution. The pseudo-second-order rate equation described better the kinetics of arsenic sorption with good correlation coefficients than pseudo-first-order equation. At lower initial arsenate concentration, arsenate exhibited greater removal rates and best removed when the clinoptilolite modified by 0.1 M FeCl₃ was used for adsorbent. This study showed that the amount of arsenic adsorbed on the adsorbents not only depends on the iron concentration in the clinoptilolite, but also depends on the initial arsenate concentrations.

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1. Introduction

Arsenic is a semi-metallic element, occurs naturally in rocks and soils, and contaminates water that comes in contact with these natural components. Therefore varying amounts of soluble arsenic are present in some water sources [1]. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions [2,3] as well as through a range of anthropogenic activities such as gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants and the use of arsenical pesticides and herbicides [2,4,5]. The U.S. Environmental Protection Agency (EPA) decreased the maximum contaminant level (MCL) of arsenic in drinking water from 50 $\mu\text{g L}^{-1}$ to 10 $\mu\text{g L}^{-1}$ due to fatal toxicity of arsenic on human health [6]. The World Health Organization (WHO), the European Union, and several other countries such as Turkey also lowered their recommended or required arsenic limit to 10 $\mu\text{g L}^{-1}$ in drinking water [7]. Natural water sources that contained much higher levels of arsenic (20–3000 $\mu\text{g L}^{-1}$) than MCL were determined in western Turkey. The natural enrichment of arsenic in groundwater is related to the borate deposits, and the arsenic complexes present in soils. Arsenic found in soil either naturally occurring or from anthropogenic releases forms insoluble complexes with iron, aluminum, and magnesium oxides found in soil surfaces, and

in this form, arsenic is relatively immobile. Arsenic can liberate from these complexes under some circumstances. Since arsenic in soils is highly mobile, once it is liberated, it results in possible groundwater contamination [8–12]. According to Human Development Report Beyond Scarcity: Power, Poverty and Global Water Crisis by the United Nations Development Programme, arsenic contaminated water creates risks for millions of people in some countries including Turkey in the world [13].

Occurrence of arsenic in natural water depends on the local geology, hydrology and geochemical characteristics of the aquifer materials [14]. The chemistry of arsenic in aquatic systems is complex, and consists of oxidation–reduction, precipitation, adsorption, and ligand exchange [15]. Arsenic can occur in the environment in several oxidation states but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] [3]. The forms of arsenic present are dependent on the type and amounts of sorbents, pH, redox potential, and microbial activity [16]. Under oxidizing conditions (positive Eh) As(V) is the primary form of arsenic, while under reducing conditions (negative Eh) the primary form is As(III). In the common groundwater pH range of 6 to 9, the predominant As(III) species is neutral (H_3AsO_3), whereas the As(V) species are monovalent (H_2AsO_4^-) and divalent (HAsO_4^{2-}) [17]. Therefore As(III) is less efficiently removed than As(V) from aqueous solutions by almost all of the arsenic removal technologies and preoxidation of As(III) to As(V) and using some oxidizing chemical agents like chlorine and potassium permanganate is necessary for better removal [18].

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The toxicity of an arsenic-containing compound depends on its valence state, its form, and the physical aspects governing its absorption and elimination. In general, inorganic arsenic is more toxic than organic arsenic, and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic [19]. Its toxicity is hard to investigate because of its ability to convert between oxidation states and organometalloidal forms [20]. Two types of toxicity, acute and sub-acute are known for a long time. The major early manifestation due to acute arsenic poisoning includes burning and dryness of the mouth and throat, dysphasia, colicky abdominal pain, projectile vomiting, profuse diarrhea, and hematuria. Sub-acute arsenic toxicity mainly involves the respiratory, gastro-intestinal, cardio-vascular, nervous and hematopoietic systems [14].

Various technologies are available for the removal of arsenic from contaminated water including chemical precipitation or coagulation, adsorption, lime softening, ion exchange, and membrane separation [21–29]. Although precipitation–coprecipitation with ferric and aluminum salts is one of the conventional methods for arsenic removal, handling and disposal of the waste sludge is a significant problem of this process [15]. Adsorption has emerged as an alternative to these traditional methods with advantage of being technically easy, and has the potential for regeneration and sludge free operation [30]. At the same time adsorption will provide an attractive technology if the adsorbent is cheap and ready for use [7]. So far, many kinds of adsorbents such as Zr(IV) loaded orange waste gel [2], iron modified red mud [7], agricultural residue rice polish [30], iron modified calcined bauxite [31], zero valent iron [32], mesoporous alumina [33], and acid modified carbon black [34] have been developed for the removal of arsenic. Arsenic removal efficiency was achieved more than 85% by most of them. However, the necessary time to reach the equilibrium was found as 24 h for Zr(IV) loaded orange waste gel and red mud. For other types of adsorbent, the required time for adsorption was between 1 and 3 h. In the past years, natural zeolite has been explored as effective adsorbent for removal of various heavy metals and other environmental pollutants because of their selectivity, ion exchange capacity, and low cost [35,36]. However, these zeolitic materials do not remove anionic or organic pollutants and for this reason it is necessary to treat the zeolitic material to change its surface characteristics and improve the adsorption of this kind of water pollutant [1]. Few investigations have been reported on arsenate removal using iron modified natural zeolite and arsenic adsorption mechanisms [1,37–40]. In general, very little information is available on the characterization and kinetics of adsorption of arsenic onto natural and iron modified zeolites. In order to gain an understanding of the adsorption process kinetics, a detailed study was conducted in a controlled batch system. Therefore, the major objective of this study is to modify the adsorption characteristics of natural zeolite using ferric chloride for investigation of removal efficiency of arsenate from tap water by adsorption. The present paper reports the synthesis and characterization of natural and iron modified zeolites. Furthermore, the adsorption capacities and adsorption kinetics of clinoptilolite were measured to understand the adsorption process mechanism and kinetics.

2. Materials and methods

2.1. Materials

The chemical composition and some properties of the tap water used in this study are listed in Table 1. Analytical-reagent grade chemicals were used for the preparation of all solutions without further purification. Arsenate stock solution (2 mg L^{-1}) was prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma, USA) in the tap water. In the experimental studies, arsenic working solutions were freshly made by diluting this stock arsenic solution until desired concentration. The natural zeolite (clinoptilolite) of Gördes–Manisa (in Western Anatolia

Table 1

Characterization of the tap water used for the experiments.

Components	Concentration
pH	7.9
Turbidity, NTU	0.1
Chloride, mg L^{-1}	44
Nitrate, mg L^{-1}	4
Iron, mg L^{-1}	0.040
Aluminum, mg L^{-1}	0.012
Manganese, mg L^{-1}	0.00137
Calcium, mg L^{-1}	92
Magnesium, mg L^{-1}	47
Sodium, mg L^{-1}	22.8
Conductivity, $\mu\text{S cm}^{-1}$	462
Sulfate, mg L^{-1}	38

of Turkey) used in this work was supplied from Rota Mining Corporation. The empirical formula of the natural zeolite is $(\text{Ca}, \text{K}_2, \text{Na}_2, \text{Mg})_4\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$. The iron salt solution used for coating clinoptilolite was prepared using ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) with deionized water. Hydrochloric acid (1 M, 0.1 M) and sodium hydroxide (1 M, 0.1 M) solutions were prepared for pH adjustment.

2.2. Preparation of adsorbent

The natural clinoptilolite of Gördes (GC) was first sieved through 1 mm and 0.5 mm sieve and then washed with distilled water. The washed material was heated at $100 \pm 5^\circ\text{C}$ for 24 h. The diameter of the particles from 0.5 to 1 mm was chosen in this study taking into account further processing in the research and column experiments. Prior to use, 30 g of GC was added to 200 mL of 0.1 N NaCl solutions, and the mixture is boiled for 4 h under reflux. The suspension was centrifuged at 3000 rpm for 20 min and the residual solid phase was separated. The NaCl solution was changed and again added to GC and the same procedure was repeated once more. To eliminate chloride ions, the GC was washed with distilled water five or six times until chloride ions were not detected by the AgNO_3 test and dried at 80°C for 24 h. This material was identified as Na-GC. 100 ml of 0.1 M and 0.01 M FeCl_3 solutions were added to 10 g of Na-GC separately and each mixture was heated for 4 h under reflux. The supernatant was separated by use of centrifugation at 3000 rpm for 20 min. The FeCl_3 solutions were changed and again added to Na-GC and the same procedure was repeated once more. The solid phases were washed with distilled water several times and dried at 85°C for 24 h. These materials modified using 0.1 M and 0.01 M FeCl_3 solutions were identified as Fe1-GC and Fe2-GC, respectively. GC, Na-GC, Fe1-GC, and Fe2-GC were stored in a dry atmosphere until further use.

2.3. Characterization of adsorbent

The surface morphologies of clinoptilolite samples were examined by a Scanning Electron Microscope (JEOL-JSM 6060 SEM) with an Energy Dispersive X-ray spectroscopy (IXRF System EDS) system attachment. Firstly, the samples were mounted directly onto the sample holders and covered with gold using SC 7620 Sputter Coater to provide conductivity. Accelerating voltage of 20 kV was used for the SEM imaging and SEM/EDX analyses. Weight percentage distributions and X-ray mapping of elements were determined by EDS.

X-ray diffraction (XRD) analysis was performed to investigate the crystal structure, chemical composition, and physical properties of the natural zeolite. XRD patterns of thin films were determined by means of multipurpose Rigaku D/Max-2200/PC Model diffractometer with a $\text{Cu K}\alpha$ radiation by using multipurpose thin film attachment. Measurements were performed by applying 40 kV voltages and 36 mA current.

The natural and iron-coated clinoptilolite were first heated at 60°C for 12 h previously to BET analysis. The surface areas of natural and iron-coated clinoptilolites were determined according to the Brunauer–

Emmett–Teller method (BET) by nitrogen adsorption using a NOVA 2200e Surface Area & Pore Size Analyzer instrument.

2.4. Analytical methods

Arsenic in the influent and effluent aqueous solutions was measured by the hydride generation procedure coupled with ICP-atomic emission spectrometry (HG-ICP-AES) (Optima 2100 DV). Hydride generation involves the production of volatile hydrides upon a chemical treatment with a strong reducing agent, typically sodium borohydride (NaBH_4). The sodium borohydride instantaneously converts As^{+3} to arsine gas at room temperature, while the reduction of As^{+5} to arsine occurs relatively slow. Therefore, a total arsenic determination requires a prereductant such as KI to convert all arsenic to the +3 oxidation state prior to the arsine formation step. The use of arsine gas formation provides both a way to separate the analyte from potential chemical interferences in the sample and to preconcentrate to improve analytical sensitivity. The primary advantage of this approach is the ability to simultaneously determine other hydride forming elements such as antimony, selenium, etc. The other advantage of HG techniques is that only gaseous hydrides are introduced to the detector and the remaining sample matrix is discarded. As a result, chemical interferences are eliminated. Unfortunately, the complexity of this technique can be time consuming and thus costly [41]. In this study, the sample water (20 mL) was first mixed with 6 mL HCl (10%) and 2 mL of reducing agent (5% KI and 5% ascorbic acid), and allowed to react for 30 min at a dark place to reduce As(V) to As(III). Then, 10 mL solution was taken for the analysis of As(III) concentrations. In this study, arsenic concentrations were measured at 193.7 nm wavelength and detection level was found as $1 \mu\text{g L}^{-1}$. Each analysis of arsenic concentrations was duplicated. The arithmetic average of the two analyses results was reported in the study.

The characterization of the tap water was determined according to standard methods. Iron, aluminum, manganese, and sodium concentrations were measured by ICP-AES. Determinations of pH, turbidity, and conductivity were made by use of the WTW 340i/SET pH-meter, Velp TB1 turbidimeter, and WTW Cond 3210 SET conductivity meter, respectively. The concentrations of chloride, sulfate, and nitrate were determined by ion chromatography.

2.5. Adsorption studies

The adsorption studies were carried out in 250 mL Erlenmeyer flasks. Specifically, a series of test bottles were shaken in a shaker at room temperature (nearly 20°C) and 150 rpm. In each test, 50 mL of $100 \mu\text{g L}^{-1}$ arsenate solution was loaded in the bottle. 500 mg of GC, Na-GC, Fe1-GC, and Fe2-GC were dispersed in the arsenate solutions. The pH value was adjusted to 7, generally representative of the typical pH of natural waters, with HCl and NaOH solution. The test bottles were taken out from the shaker at pre-determined intervals (from 5 min to 30 h), then the suspension were immediately centrifuged at 3000 rpm for 20 min to separate the solid from the solution. The supernatant liquid was analyzed for the residual concentration of arsenate using ICP-AES. Blank experiments were conducted without the adsorbent.

All the experiments were performed in duplicate to evaluate test reproducibility under identical conditions and the arithmetic average result of the two experiments was reported in this study. The amount of arsenate adsorbed was calculated for each adsorbent (GC, Na-GC, Fe1-GC, Fe2-GC), based on the difference of arsenate concentration in aqueous solutions before and after adsorption experiments, the volume of aqueous solution, and the amount of adsorbent used by weight, from the following equation:

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

where q is the arsenate adsorbed ($\mu\text{g g}^{-1}$), C_0 is the initial concentration of arsenate ($\mu\text{g L}^{-1}$), C_e is the concentration of arsenate in solution at equilibrium time ($\mu\text{g L}^{-1}$), V is the solution volume (L), and m is the adsorbent dosage (g).

The adsorption kinetics of arsenate on the GC, Na-GC, Fe1-GC, and Fe2-GC was also carried out at three initial arsenate concentrations (100, 250, and $500 \mu\text{g L}^{-1}$) as a function of time. The most commonly used pseudo first-order, and pseudo second-order models were applied to experimental data according to the above procedure.

3. Results and discussion

3.1. The zeolite characterization

The chemical composition of the raw zeolite and modified zeolites is shown in Table 2. The major constituents of the raw zeolite are silicate and alumina. According to the concentration of Na, Mg, K and Ca, GC is a K–Ca zeolite type. The iron found in the natural zeolite GC was less than 1.6 wt.%.

The raw zeolite GC was first pretreated with NaCl solution to improve the ion-exchange capacity of zeolite. Pretreatment of natural zeolite containing several multivalent exchangeable cations by only one kind of monovalent cations, like Na^+ cations, should generally enhance the zeolite exchange capacity, which means that more sites are capable of undergoing ion-exchange. Further modification of Na-treated zeolites with iron species leads to a material that can sorb anionic species by forming Lewis acid sites (zeolite–Fe–OH), where arsenate ion acts as a Lewis base [42]. The chemical analyses showed that the raw zeolite partly converted to the sodium form by the NaCl treatment. The amount of sodium increased, while at the same time the amount of the other exchangeable ions decreased as shown in Table 2. When the Na-GC was treated with FeCl_3 solutions, the amount of sodium diminished from 1.24 to 0.03 wt.% for Fe1-GC and from 1.24 to 0.45 wt.% for Fe2-GC. Moreover the amount of iron increased to 54.66 wt.%, 5.25 wt.% for Fe1-GC and Fe2-GC, respectively. The reduction in sodium concentration and the increase in iron concentration were more significant in the Fe1-GC than Fe2-GC depending on the initial concentration of FeCl_3 in the solution (0.1 and 0.01 M). Furthermore, the magnesium, potassium, aluminum, silicon, and calcium concentrations in Na-GC were decreased after FeCl_3 treatment. The obtained results showed that the iron ions are exchanged by not only sodium ions but also other exchangeable ions from the zeolite network and all these elements were contributed in clinoptilolite condition for arsenic removal. Macedo-Miranda and Olguin [1] showed that the treatment of the Mexico-natural zeolite with NaCl solutions increased the amount of sodium 2.34 times. However, when these natural zeolites were treated with FeCl_3 solutions, the amount of sodium diminished from 1.05 to 0.97 wt.%. Jimenez-Cedillo et al. [40] also noted that after combining clinoptilolite-rich tuff with NaCl solution, the Na concentration increased from 0.4 to 1.7%. In the zeolite treated with iron solutions, sodium concentration diminished but iron concentration increased from 1.09 to 11.66 wt.%.

Table 2
Elemental composition of unmodified and modified clinoptilolites.

Element	Composition (wt.%)			
	GC	Na-GC	Fe1-GC	Fe2-GC
O	30.489	28.307	14.280	26.002
Na	0.490	1.240	0.033	0.453
Mg	1.062	0.892	0.240	0.590
Al	9.431	9.174	3.126	8.527
Si	51.259	52.673	20.891	53.466
Cl	–	–	5.296	–
K	2.948	3.163	0.824	2.850
Ca	2.783	2.602	0.649	2.862
Fe	1.537	1.949	54.66	5.251

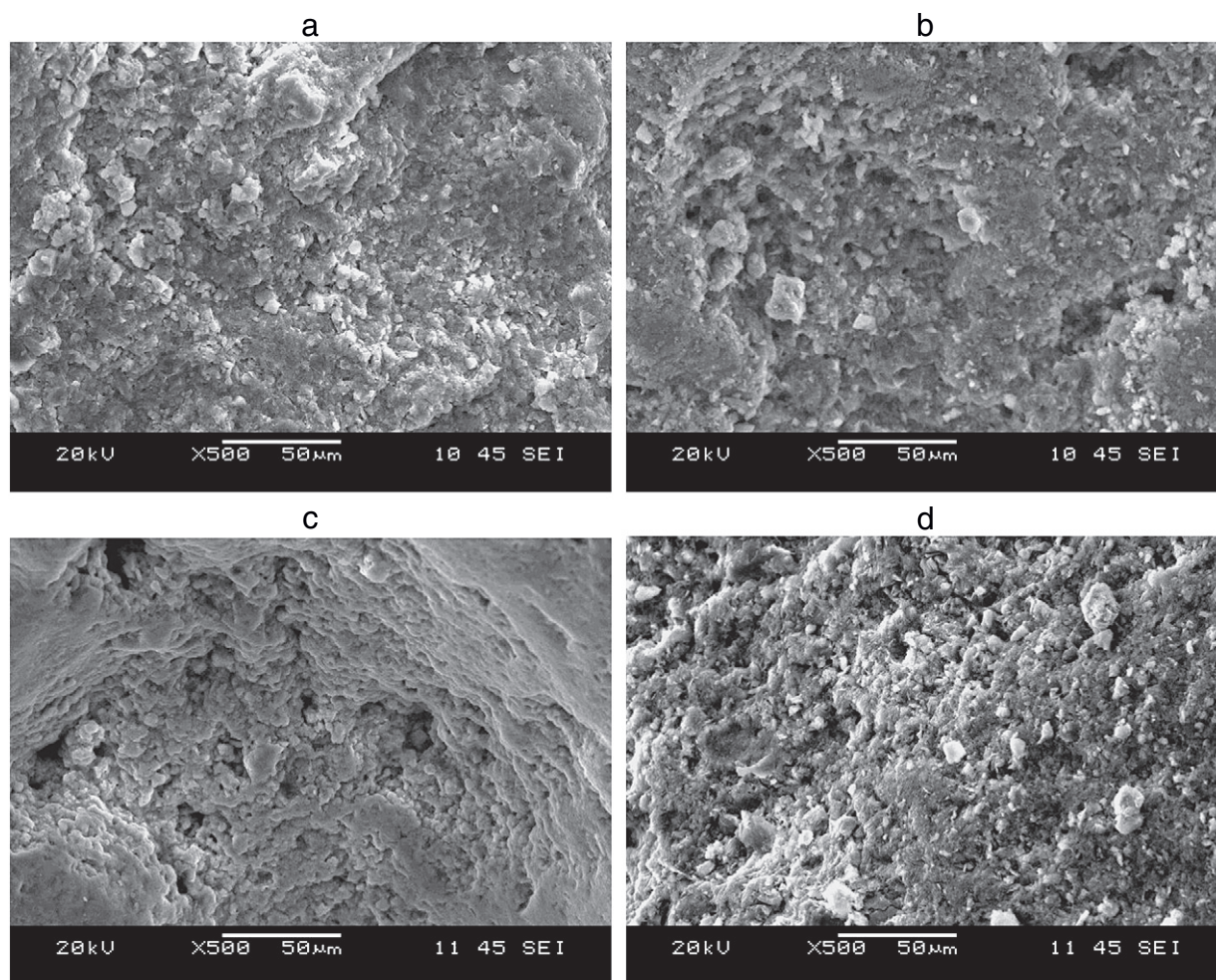


Fig. 1. SEM images of a) unmodified clinoptilolite (GC), b) after the treatment with NaCl solution (Na-GC), c) after treatment with 0.1 M FeCl_3 solution (Fe1-GC), and d) after treatment with 0.01 M FeCl_3 solution (Fe2-GC).

This decrease and increase in the amount of sodium and iron concentration in the clinoptilolite was also observed by other researchers using clinoptilolite for arsenic removal [38,42].

The morphology changes of GC, Na-GC, Fe1-GC, and Fe2-GC are showed in Fig. 1(a–d). The scanning electron microscopy images of the raw and modified clinoptilolites revealed the presence of the tabular shaped crystals with excellent crystal edges, different sizes and morphologies. Fig. 1(a) and (b) indicated that there was no significant change in the morphology of the zeolite crystals after its treatment with NaCl. Similarly, after the Na-GC was treated with 0.01 M FeCl_3 solutions, the morphological characteristics of the Fe2-GC did not change but some changes in the morphology of the Fe1-GC was observed as shown in Fig. 1(c) and (d).

Clinoptilolite was the major crystalline phase detected on the X-ray diffraction pattern as shown in Fig. 2(a). XRD peaks of clinoptilolite sample were found to be in good agreement with the data of clinoptilolite. In addition to zeolitic phase, quartz and sanidine in minor quantities were also detectable in X-ray diffraction patterns. X-ray diffraction data of a sodium-conditioned sample of natural zeolite showed no significant changes in the positions and intensities of the diffraction maxima for the two major phases in the natural zeolite (Fig. 2(a–b)). This clearly indicates that the natural zeolite was not distorted during the sodium treatments. Fig. 2(c–d) shows the effect of increasing iron ion content. As the ferric chloride concentration increased, no new diffraction peaks appeared but the intensity of reflections showed differences when the results were compared to the

results of Na-GC. These results suggest the presence of Fe in the zeolitic network. Similar results were found by Jimenez-Cedillo et al. [40].

The BET specific surface area values of the GC, Na-GC, Fe1-GC, and Fe2-GC are presented in Table 3. The data of the unmodified and sodium conditioning clinoptilolite before iron modification indicate that the specific surface area of the samples was low and almost the same. Specific surface area of Fe1-GC substantially increased (about $80 \text{ m}^2 \text{ g}^{-1}$), while the specific surface area of Fe2-GC was slightly increased. These results are consistent with Fe concentration of unmodified and modified clinoptilolites as shown in Table 2.

3.2. Adsorption kinetics of arsenate

Fig. 3 shows the effect of contact time on the adsorption of arsenate by the use of modified and unmodified adsorbents. Fe1-GC and Fe2-GC are very effective for removal of arsenate. Fe1-GC adsorb $7.4 \mu\text{g As(V)} \text{ g}^{-1}$ (74%) in the first 5 min, reaching equilibrium after 60 min of contact time with a maximum arsenate adsorption of $9.2 \mu\text{g g}^{-1}$ (92%). The arsenate adsorption at equilibrium is $8.4 \mu\text{g g}^{-1}$ (84%) for Fe2-GC. It is clear from the figure that adsorption of arsenate on GC, Na-GC, Fe1-GC, and Fe2-GC increases significantly with time and achieves saturation in 60 min for all cases. However, GC and Na-GC are not effective for the purpose and they only adsorb 1.5 and $1.7 \mu\text{g As(V)} \text{ g}^{-1}$ at equilibrium, respectively. The present findings are compared with previous work related to As(V) sorption by iron-modified natural zeolites, where equilibrium time and removal

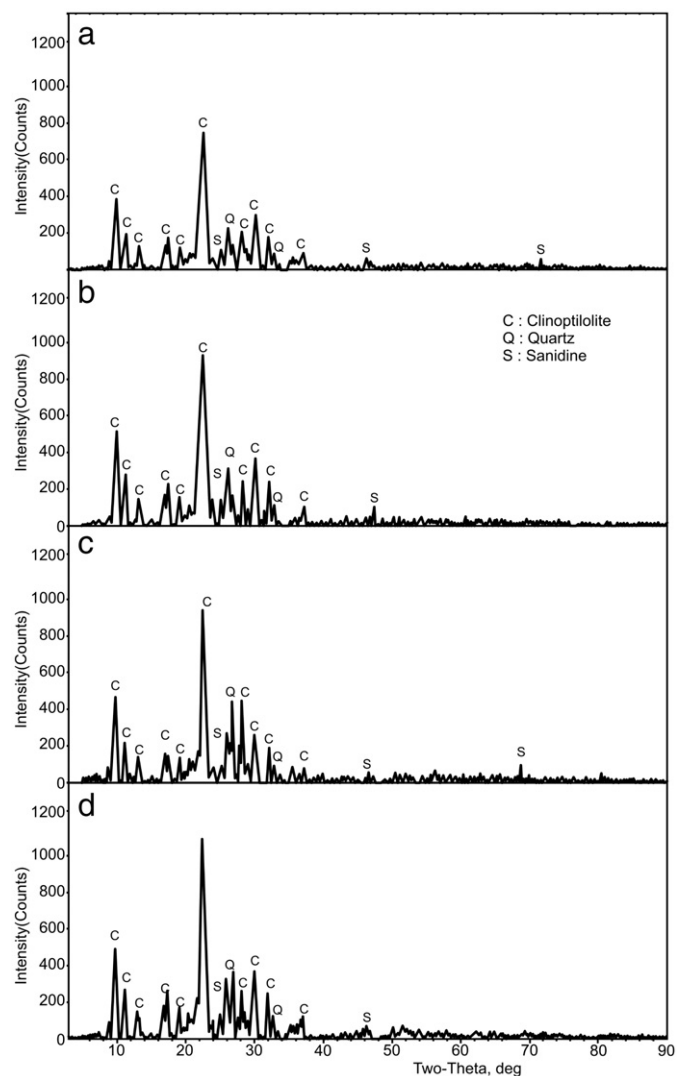


Fig. 2. X-ray powder diffraction pattern of a) GC, b) Na-GC, c) Fe1-GC, d) Fe2-GC.

efficiency was reported to be 180 min contact time with a maximum adsorption of $8 \mu\text{g g}^{-1}$ [40]. Higher removal efficiency was achieved at lower equilibrium time in this study.

In order to establish the equilibration time for maximum uptake of arsenate and to know the kinetics, adsorptions of arsenate on Fe1-GC and Fe2-GC were studied as a function of contact time and initial arsenate concentration and results are shown in Fig. 4(a–b). The rate of uptake of arsenate on used adsorbents is rapid in the beginning and 74% adsorption is completed in 5 min and becomes constant after 60 min for Fe1-GC, which indicates that equilibrium has been achieved. For Fe2-GC, 71% adsorption is completed in 5 min and becomes constant after 60 min. These results indicated that a rapid initial uptake rate of arsenate, followed by a slower removal that gradually approaches an equilibrium condition. For example, about 85–92% removal of arsenate was achieved within the first 60 min of contact, while only 1–4% of additional removal occurred in the following 24 h. The high initial

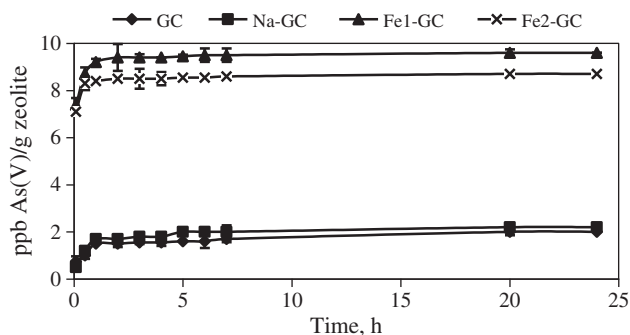


Fig. 3. Arsenate sorption uptake by modified and unmodified clinoptilolite as a function of time.

uptake rate is due to the availability of a large number of sorption sites at the beginning of the process. Further, the sorbent is exclusively mesoporous and therefore, the diffusion of solute into the pores appears to be easier. Faster solute removal as well as low equilibration time attributes highly favorable sorptive interactions. The obtained curves are single, smooth and continuous leading to equilibrium and suggest the probability of monolayer coverage of the sorbate on the surface of the sorbent [30]. It is further noted from the results that in all the systems, the saturation time is independent of concentration of the adsorbate solution. During the adsorption of arsenate by iron modified zeolite, although a similar trend was observed by Jimenez-Cedillo [40], the shortest equilibration time was achieved in this study. Equilibration time is considerably important in the application of an adsorption system because the construction, operating, and maintenance cost considerations are a key factor in process selection for drinking water treatment.

It was also found that adsorption capacity at equilibrium increases from $8.56 \mu\text{g g}^{-1}$ to $9.2 \mu\text{g g}^{-1}$ with a decrease in the initial arsenate concentration from 500 to $100 \mu\text{g L}^{-1}$ for Fe1-GC, and adsorption capacity at equilibrium increases from $8.22 \mu\text{g g}^{-1}$ to $8.4 \mu\text{g g}^{-1}$ with a decrease in the initial arsenate concentration from 500 to $100 \mu\text{g L}^{-1}$ for Fe2-GC. This indicates that with the increase of the concentration of arsenate in solution, the availability of arsenate ions slightly decreases at the solid–solution interface resulting in the

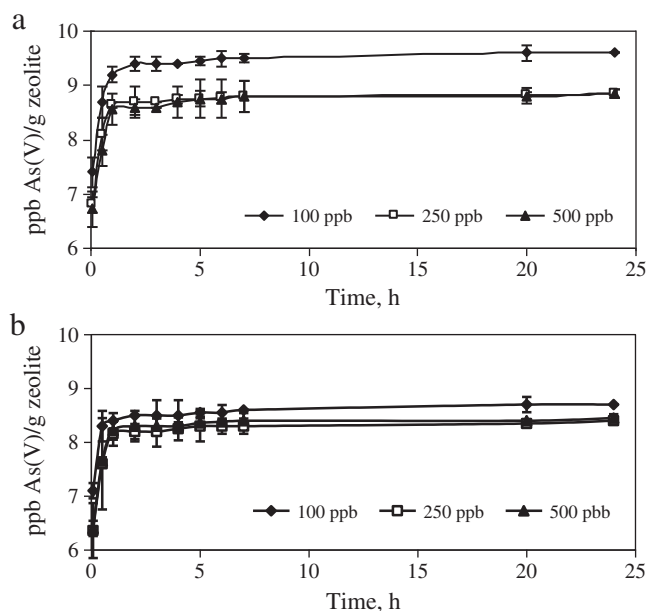


Fig. 4. Effect of contact time and initial metal ion concentration on the removal of As(V) for a) Fe1-GC and b) Fe2-GC (pH 7.0, adsorbent 50 g L^{-1} and temperature 20°C).

Table 3
BET specific surface areas of unmodified and modified clinoptilolite.

Adsorbent	Specific surface area, $\text{m}^2 \text{g}^{-1}$
GC	34.118
Na-GC	33.159
Fe1-GC	79.277
Fe2-GC	36.924

decrease of sorption performance. However, the sorption is reached to saturated point when the limited active surface sites on the sorbents are covered fully by the sorbate. Further the heterogeneous nature of the sorbents with regard to the distribution of the binding sites predicts that all the active sites are not equally effective. At higher concentrations, some energetically less favorable sites become involved. Therefore arsenic uptake decreases with increasing arsenic concentration in the aqueous solution. At lower concentrations, most of the arsenic ions present in solution would interact with the binding sites facilitating higher adsorption [43].

The iron(III) oxide surface has a high affinity for arsenate and is capable of forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes. It was found that in water samples treated with either ferric chloride or ferric sulfate, arsenic adsorption by iron complexes occurs by ligand exchange of the As species for OH_2 and OH^- in the coordination spheres of surface structural Fe atoms [1]. Jeon et al. proposed that the adsorption of arsenate onto iron modified zeolite occurred by ligand exchange reactions, and most of the hydroxide groups are involved in ligand exchange reactions [37]. In this study, adsorption of arsenate species, such as H_2AsO_4^- and HAsO_4^{2-} , onto Fe1-GC and Fe2-GC is proposed to take place via Coulombic as well as Lewis acid–base interactions (ligand exchange reactions) and to form monodentate and bidentate inner sphere complexes.

Residual iron concentration after the adsorption experiments using iron modified zeolites was also measured and maximum residual iron values were found as 0.195 mg L^{-1} . Because the amount of iron present in drinking water has been recommended to be below $200 \mu\text{g L}^{-1}$ by the World Health Organization [44], iron modified zeolite was found effective and reliable considering residual iron.

Sorption kinetics shows large dependence on the physical and/or chemical characteristics of the sorbent material, which also influenced the sorption mechanism [30]. Although many models such as the homogeneous diffusion model and the pore diffusion model have been proposed to interpret the transport of solutes inside adsorbents, the mathematical complexity of these models makes them inconvenient for practical use. From a viewpoint of system design, lumped analysis of the adsorption rates is thus considered to be sufficient for practical operation [2].

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process [45]. In the present work, in order to predict the rate and kinetics of sorption of arsenate on Fe1-GC and Fe2-GC, pseudo-first-order and pseudo-second-order kinetic models were applied to the data. The pseudo-first-order rate expression of Lagergren is generally described by the following equation [46]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \quad (2)$$

where q_e and q_t are the amounts of As(V) adsorbed on the adsorbents at equilibrium and at time, t (min), respectively and K_1 is the rate constant (min^{-1}). Integrating and applying the boundary conditions, $t = t$ and $q_t = q_e$ takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

For the studied initial concentrations, the rate constant (K_1) and theoretical equilibrium sorption capacities, q_e (calculated), were obtained from the slope and intercept of the linear plots of the $\log(q_e - q_t)$ against t as shown in Fig. 5(a–b) for Fe1-GC and Fe2-GC, respectively.

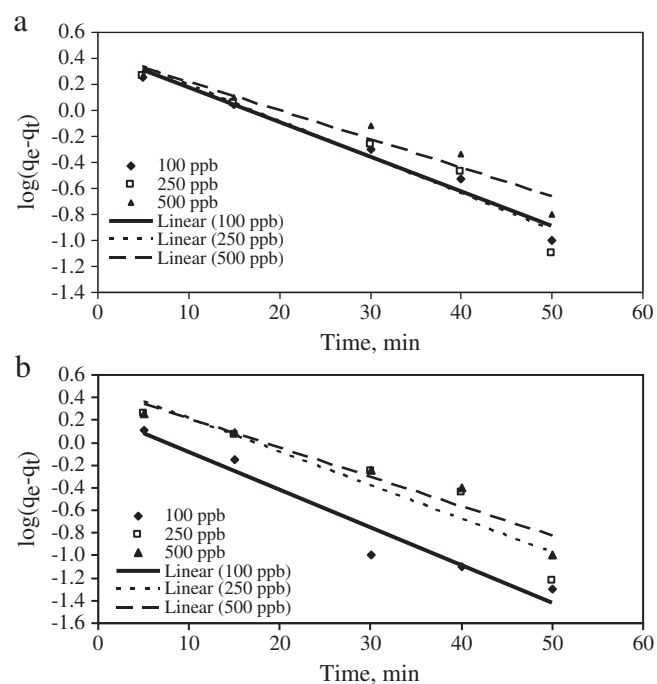


Fig. 5. The pseudo first order model for arsenate adsorption on a) Fe1-GC, b) Fe2-GC.

The kinetics was also described as pseudo-second-order process by the following equation [47]:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \quad (4)$$

Rearranging this equation to a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where, q_e and q_t have the same meaning as mentioned previously, and K_2 is the rate constant for the pseudo second-order kinetics. The plots of t/q_t versus t are shown in Fig. 6(a–b) for Fe1-GC and Fe2-GC.

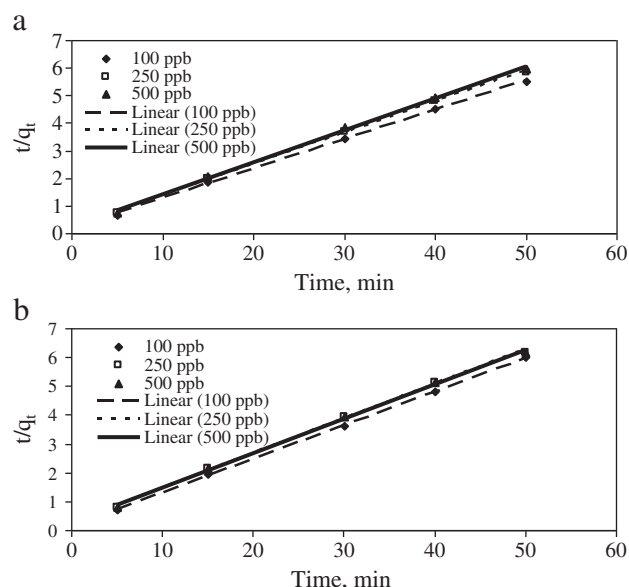


Fig. 6. The pseudo second order model for arsenate adsorption on a) Fe1-GC and b) Fe2-GC.

Table 4
Kinetic parameters for sorption of arsenate on Fe1-GC and Fe2-GC.

C ($\mu\text{g L}^{-1}$)	q_e (exp) ($\mu\text{g g}^{-1}$)	Pseudo first-order kinetic model			Pseudo second-order kinetic model		
		K_1 (min^{-1})	q_e (cal) ($\mu\text{g g}^{-1}$)	R^2	K_2 ($\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$)	q_e (cal) ($\mu\text{g g}^{-1}$)	R^2
<i>Fe1-GC</i>							
100	9.20	0.081	2.738	0.9707	0.057	9.363	0.9993
250	8.64	0.082	3.014	0.9326	0.053	8.818	0.9989
500	8.56	0.070	2.726	0.9358	0.051	8.628	0.9979
<i>Fe2-GC</i>							
100	8.40	0.103	1.765	0.9452	0.093	8.576	0.9998
250	8.16	0.084	3.238	0.8904	0.051	8.347	0.9984
500	8.22	0.077	2.913	0.9277	0.051	8.375	0.9984

For various initial arsenate concentrations, pseudo first-order and pseudo second-order rate constants (K_1 and K_2) and the amount of arsenate sorbed at equilibrium (q_e (cal)) were calculated and are listed in Table 4 along with the corresponding correlation coefficients.

The correlation coefficients (R^2) for the first-order kinetic model obtained at all the studied concentrations were low. The theoretical q_e (cal) values calculated for the pseudo first-order model did not give reasonable values with regard to the experimental uptake values, q_e (exp) (Table 4). This indicates that pseudo first-order equation might not be sufficient to describe the mechanism of arsenate adsorption system. The correlation coefficients (R^2) for the pseudo second-order kinetic model are in the range of 0.9979–0.9998 and the theoretical q_e (cal) values were closer to the experimental q_e (exp) values. The observed good correlation coefficients for pseudo-second-order kinetic model in comparison to pseudo-first-order model indicating that arsenate uptake process can be approximated with the pseudo-second-order kinetic model. The amounts of arsenate adsorbed at equilibrium (q_e (cal)) were the highest for Fe1-GC and Fe2-GC in the initial arsenate concentration of $100 \mu\text{g L}^{-1}$. According to the q_e (cal) values, Fe1-GC adsorbs the highest amount of arsenate from an aqueous solution. This means q_e (cal) not only depends on the iron concentration in the clinoptilolite, but also depends on the initial arsenate concentrations. As listed in Table 4, there is no big variation for the overall rate constant values with the change of initial arsenate concentration. The parameter K_2 , which corresponds to the velocity constant of pseudo-second order, is the highest for Fe2-GC at the initial arsenate concentration of $100 \mu\text{g L}^{-1}$. For the initial arsenate concentrations of 250 and $500 \mu\text{g L}^{-1}$, rate constant values for Fe1-GC are the same or a bit higher than Fe2-GC.

For other materials it was found that the pseudo second order kinetics is the best model of describing kinetic data for arsenate removal from aqueous solution by acid modified carbon black [34], agricultural residue rice polish [30], mesoporous alumina [33], Zr(IV) loaded orange waste gel [2], the iron modified red mud [7]. Although the obtained arsenic removal efficiencies for these types of adsorbent were considerably high, the required time to reach the equilibrium was higher than 1 h.

Compared with different methods of arsenic removal from drinking water, which include ion exchange, membrane separation, and conventional coagulation–flocculation processes, the adsorptive removal of arsenic by natural zeolite are the most promising since it is easy to operate and require low investments. Furthermore the arsenic-laden zeolites have passed EPA's Toxicity Characteristic Leaching Procedure test and can be safely disposed of as non-hazardous waste [43].

4. Conclusions

The sorption performance of natural clinoptilolite, sodium conditioning clinoptilolite and iron modified clinoptilolite types for the arsenate removal was evaluated. The surface morphologies, chemical composition, physical properties, and specific surface areas of

unmodified and modified zeolites were determined for adsorbent characterization. After FeCl_3 treatment, the reduction in sodium concentration and the increasing in iron concentration were more significant in the Fe1-GC than Fe2-GC depending on the initial FeCl_3 concentration. The SEM images of the raw and modified clinoptilolites indicated that there was no significant change in the morphology of the zeolite crystals after its treatment with NaCl and FeCl_3 . In addition to zeolitic phase, quartz in minor quantities was detectable in X-ray diffraction patterns. Specific surface area of Fe1-GC and Fe2-GC increased according to the iron concentrations.

In order to predict the sorption kinetic models of arsenate, pseudo-first-order and pseudo-second-order kinetic models were applied to the data. The rate of uptake of arsenate on used adsorbents is rapid in the beginning and 74% and 71% adsorption is completed in 5 min and become constant after 60 min for Fe1-GC and Fe2-GC, respectively. For the $100 \mu\text{g L}^{-1}$ of initial arsenic concentration, the adsorption capacities obtained were 9.2 and $8.4 \mu\text{g g}^{-1}$ for Fe1-GC and Fe2-GC, respectively. Adsorption rate data are best described by a pseudo second-order kinetic model. Iron concentrations in the solution to modify clinoptilolite play important role in the arsenate adsorption. However arsenate adsorption kinetics was slightly affected by them. At lower initial arsenate concentration, arsenate exhibited greater removal rates and best removed when the Fe1-GC was used for adsorbent. Thus, iron modified zeolite can be used as an efficient and economic adsorbent for arsenate removal.

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