

## Natural Zeolites Application as Sustainable Adsorbent for Heavy Metals Removal from Drinking Water

Gagik Badalians Gholikandi<sup>1</sup>, Mohammad Mehdi Baneshi<sup>2</sup>, Emad Dehghanifard<sup>3</sup>, Saeed Salehi<sup>4</sup>, Ahmad Reza Yari<sup>5</sup>

### ABSTRACT

**Background:** There are great resources of natural zeolite in Iran. Zeolite, an inorganic ion-exchanger, may be used as a suitable technical-economical solution for water treatment in many regions of Iran. In this study, the characterization of natural zeolite natrolite and the feasibility of removing hardness, cations, and anions were investigated.

**Methods:** First, zeolite composition and type were determined using X-ray Fluorescence (XRF), thermal analysis, and infrared spectrometer. Also, cation exchange capacity (CEC) and its impact on water hardness reduction evaluated. Then, isotherm curves for Fe, Cr, Al, Bi, Cd, Mn, Ca, Mg, Ag, Ni, Zn, Cu, Pb, and their disposition to zeolite phase besides removal rate of the mentioned cations in analyzed water samples identified. Eventually, zeolite structure was rectified using surfactant (HMNDA) for anions removal.

**Results:** Natrolite zeolite was more effective for waters with higher hardness, but it turned out to be moderate for waters with lower hardness. The ability of natrolite zeolite for permanent hardness removal was more than others and was less for temporary hardness. Also, the natrolite zeolite was more effective in removing non-heavy metal cations and by increasing the HMNDA concentration, arsenate anion removed fast from water samples. However, by pH increases in the water sample, the arsenate anion removal arbitrarily changed : less in pH=3. But the removal efficiency got better in alkaline pH. It is obvious that by increasing the pH of water samples, the removal efficiency will decrease. In spite of that, the removal efficiency of chromate ion , in acidity pH, was more than alkaline. The maximum removal of Cr (VI) occurred in acidic media at pH<1.5.

**Conclusion:** The natrolite zeolite could remove different heavy metals from drinking water. Moreover, the removal efficiency of natrolite zeolite was enhanced by surfactant modification.

**Keywords:** Anions, Cations, HMNDA, Natrolite, Natural Zeolite, Water Treatment

### INTRODUCTION

Groundwater contamination by organic or inorganic micro pollutants is a major public concern in many regions across the world (1). About 80% of communicable diseases in the world are waterborne (2). Groundwater

resources play a vital role in supplying drinking water, particularly in urban and suburban areas of Iran, which necessitate providing sufficient safe water for citizen's consumption. Groundwater is the only water supply for domestic, industrial, and agricultural uses in different regions while urbanization has

1- Power and Water University of Technology (PWUT), Water Research Institute (WRI), Tehran, Iran

2- Department of Environmental Health Engineering, School of Public Health, Yasuj University of Medical Sciences, Tehran, Iran

3- Water and Wastewater Research Center, Water Research Institute (WRI)/Environmental Health Engineering Department, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

4- Department of Environmental Health Engineering, School of Public Health, Arak University of Medical Sciences, Arak, Iran

5- Department of Environmental Health Engineering, School of Public Health, Qom University of Medical Sciences, Qom, Iran

6- Corresponding author : Saeed Salehi , Arak University of Medical Sciences , Email : salehi1362@yahoo.com

affected the quality of the groundwater. Water pollution is caused by industrial and municipal wastewater, as well as by agriculture. Concerning municipal wastewater, the bulk of collected sewage is discharged untreated and constitutes a major source of pollution for groundwater and a risk to public health. In this regard, groundwater heavy metal pollution and its technical-economical removal has become a major issue for water supplying systems. Among the wide variety of contaminations affecting water resources, heavy metals receive particular concern considering their strong toxicity even at low concentrations. Some metals, such as calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) are essential and must be present for normal body functions. Also, some metal cations, such as copper ( $\text{Cu}^{2+}$ ), iron ( $\text{Fe}^{2+}$ ) are needed at low levels as catalyst for enzyme activities; however, excessive presence of heavy metals can result in toxicity. Other common ions that humans are exposed to are arsenic, cadmium ( $\text{Cd}^{2+}$ ), lead ( $\text{Pb}^{2+}$ ), mercury ( $\text{Hg}^+$ ), silver ( $\text{Ag}^+$ ), and chromium ( $\text{Cr}^{3+}$ )(2).

As an effective, efficient, and economic approach for water purification, adsorbents and adsorption processes have been widely studied and applied to different purposes for long. The development of low-cost adsorbents has led to the rapid growth of research interests in this field. In recent years, a lot of novel adsorption processes have been developed for enhancing the efficiency of removing the organic and inorganic contaminants from water. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as zeolites, which have a high adsorption capacity and are locally available. It is imperative to observe that capacities of the adsorbents may vary depending on the characteristics, chemical modifications, and concentrations of the adsorbent. Removal kinetics is found to be based on the experimental conditions viz. pH, concentration of the adsorbate, quantity of the adsorbent, and temperature (2).

The term zeolite was originally coined in the 18<sup>th</sup> century by a Swedish mineralogist named Cronstedt who observed that upon rapidly heating a natural zeolite, the stones began to move about as the water evaporated.

Using the Greek word which means 'stone that boils', he called this material zeolite (2).

Zeolites are crystallized, hydrated aluminosilicate alkalines and earth alkalines cations which possess endless three-dimensional crystal structures which make them hard in water and insoluble which enables them to exchange their ions with suitable amounts of other ions substance. The process of ions exchange is a heterogeneous process, while the zeolite structure (the changer of ion) practically does not change (2,4).

The zeolites are framework silicates consisting of interlocking tetrahedrons of  $\text{SiO}_4$  and  $\text{AlO}_4$ . In order to be a zeolite, the (Si+Al)/O ratio must equal 1.2. The aluminosilicate structure is negatively charged and attracts the positive cations that reside within. Unlike most other tectosilicates, zeolites have large vacant spaces or cages in their structure that allow space for large cations, such as sodium, potassium, barium, calcium, and even relatively large molecules and cation groups such as water, ammonia, carbonate ions, and nitrate ions. In the more useful zeolites, the spaces are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites are characterized by their ability to lose and absorb water without damage to their crystal structures. The large channels explain the consistent low specific gravity of these minerals (5).

Among such methods as precipitation, oxidation, ultrafiltration, reverse osmosis, and electro dialysis, ion exchange on natural zeolites seems to be the most attractive method. Natural zeolites have been intensively studied recently because of their applicability in removing trace quantities of different ions from aqueous solutions by utilizing the ion exchange phenomenon (6,7). Natural zeolites are low-cost aluminosilicates, with a cage-like structure suitable for ion exchange due to isomorphous replacement of  $\text{Al}^{3+}$  with  $\text{Si}^{4+}$  in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ . These

cations are coordinated with the defined number of water molecules located on specific sites in framework channels (8).

In terms of price and physical, chemical, mechanical, and hydrodynamic properties, natural zeolites are interesting materials to perform these processes. The selectivity of a sorbent depends on the ionic radius, cation charge, zeolite structure, distribution of active centers, and the temperature of the process (9). The efficiency of the sorption process depends on the pure zeolite content in a mineral, preparation processes of the mineral, accessibility of active centers, concentration of removed pollution, precipitation types, hydration degree, and the reaction of this suspension (10,12).

Synthetic zeolites are also a large group of hydrated alumino-silicates with symmetrically stacked alumina and silica tetrahedral which result in an open and stable three-dimensional honeycomb structure with a negative charge. The simplest synthetic zeolite is "zeolite A" with a molecular ration of one silica to one alumina to one sodium cation. Synthesis of pure-form zeolite A (LTA) was studied by Gharebaghi (2008) from Hesarbon Mine natural clinoptilolite in Iran using different concentrations of NaOH solution to dissolve Si source, and with addition of sodium aluminate as Al source to prepare the initial gel. The chemical analysis of the clinoptilolite samples showed a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 6.29. Before the synthesis experiments, the beneficiation methods, like desliming and flotation were applied to the samples to remove impurity, improving the ratio to 5.37. Zeolites are generally synthesized by the hydrothermal reactions of sodium aluminosilicate gels in alkaline medium using conventional heating systems. In the synthesis experiments of Hesarbon sample, the effect of important variables, such as reaction time, NaOH concentration, weight of sodium aluminate, clinoptilolite to sodium aluminate ratio, and temperature were studied. The results of synthesis experiments indicated that NaOH concentrations in initial gel played an important role in the synthesis. It was found that the higher the NaOH concentration, the shorter crystallization time of zeolite A would

be. The nucleation and crystallization rates as well as the yield of zeolite A increased as the NaOH concentrations increased. It was revealed that zeolite A could be synthesized from clinoptilolite under the following conditions: NaOH concentrations of 3 N, synthesis temperature of  $90^\circ\text{C}$ , corresponding crystallization time of 8 hours, and clinoptilolite to sodium aluminate ratio of 3/25. The products of the reactions were characterized using XRD, and chemical analysis to confirm zeolite crystallinity and phase purity. The synthesized product  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was 2.4, which is consistent with the ratio of zeolite A (13).

Natrolite is a tectosilicate mineral species belonging to the zeolite group. It is a hydrated sodium and aluminium silicate with  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$  formula. It was named natrolite by Martin Heinrich Klaproth in 1803. Needle stone and needle-zeolite are other names, alluding to the common acicular habit of the crystals which are often very slender and are aggregated in divergent tufts. Crystal habits include sprays of needle thin acicular crystals with a pyramidal termination and nodules, fibrous, and massive crusts.

Anion removal, especially chromium (VI) and arsenic adsorption on hexadecylpyridinium bromide (HDPB), bolaform  $\text{N}_3\text{N}'_3\text{N}'_3$ -hexamethyl-1,9-nonanediammonium dibromide modified natural zeolites (HMNDA), and cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide was investigated by Zeng et al (2010) and Noroozifar et al (2008) (5,14). Modified clinoptilolite zeolite as a new green sorbent for simultaneous separation and pre-concentration trace amounts of  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  was investigated by Afzali et al (2008). In another study, they investigated the potential of modified natural natrolite zeolite for simultaneous separation and preconcentration of trace amounts of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions (2006). Natural zeolite was collected from Rafsanjan area, Kerman, central Iran (15,16). Experiments were set up by Faghihian (2005) to estimate the effectiveness of clinoptilolite from deposits of Absard in Damavand area in northern Iran for the removal of arsenate from aqueous solutions. The removal of arsenate by

the exchanged forms (Fe, Pb, and Ag-exchanged forms of clinoptilolite) was analyzed in the light of the Langmuir model of adsorption. A kinetic study of adsorption was carried out at different time intervals, and the  $K_{ad}$  values were calculated using Lagergren's equation. Adsorption of arsenate proceeded through the formation of arsenate precipitates (17). Sorption processes and XRD analysis of clinoptilolite zeolite exchanged with  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Zn^{2+}$  cations were investigated by Castaldi (2008)(18).

Larger zeolite deposits of potential economic interest exist in different regions of Iran. Iran has a great potential for zeolite formation (19). The zeolites of zeolitic horizons of Tehran are located in the east part. Several zeolitic zones are determined. The geographical view all of these zones is in the same direction and stratigraphic point of view; they are in the last part of Karaj formation (20). Field studies, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thin section data of some outcrops in Guilan, North of Iran, show vein and amygdale zeolite occurrences in volcanic host rocks. The rocks belong to Cretaceous and Eocene ages and they are of basalt, andesitic basalt, andesite, and basaltic pillow lava types. The zeolites found in these regions are natrolite, tetranatrolite, analcime, and stilbite in amygdales and veins. In the studied areas, the zeolite facies, based on the mineral assemblages is hydrothermal metamorphism (21). Based on field studies and thin section, XRD, SEM, and microprobe analysis data indicate occurrences of natrolite, tetranatrolite, epistilbite, and analcime in amygdales of altered andesite and andesitic-basaltic rocks in north Parandak, central Iran. Minerals associated with these zeolites are calcite, pyrolusite, hematite, opal, chalcedony, and quartz. The sequence of mineral formation in the amygdales and veins are primary calcite, analcime, natrolite, mesolite, stilbite-Ca, stilbite, secondary calcite, and pyrolusite. In the studied areas, the zeolites are formed hydrothermally (22). The zeolitic-bentonitic sequences of the eastern Semnan province, northern part of central Iran, have been formed in a nearly closed chemical system in a near surface condition in marine environments; the

solution is resident in rocks. Clinoptilolite, mordenite, smectite, trace amounts of illite, quartz, opal-CT, plagioclase, dolomite, calcite, together with rocks fragments were determined in these sequences. XRD data have showed that zeolite minerals, smectite, illite, quartz, and dolomite are major components. SEM images indicated that zeolite and smectite, namely modernite and clinoptilolite are mainly formed from volcanic glasses (shards). The data obtained indicate the zeolitic-bentonitic sequences formed by the alteration of volcanic ash of rhyodacite/dacite composition (23). Other larger deposits of potential economic interest are situated in central Iran, central Alborz region, and western Iran. Zeolites are used for a variety of applications with a global market of several thousand tons per annum in Iran. Major uses are in petrochemical cracking, detergent industries, and other applications are in agriculture and aquaculture. They are often also referred to as molecular sieves (24).

In this research, natrolite and clinoptilolite zeolites applications are investigated for heavy metals removal from groundwater resources. The cation exchange capacity (CEC) and its impact on water hardness reduction, and ions exchange efficiency of considered zeolites are also investigated.

## MATERIALS AND METHODS

### Hardness removal

Two grams of agitated sodium zeolite were mixed with 100 ml of water sample and was stirred for 24 hours by a shaker, and the total, temporary, and permanent hardness values were determined via EDTA titration method.

### Cation exchange capacity

Zeolite samples, mesh 80, were used after mixing with 4M sodium chloride for 24 hours and the decantation of supernatant liquid. After washing the zeolite with distilled water (2 times distillation), removing the remaining salt, and drying, the process was performed. Considering the adsorption coefficient significance of each adsorbent phase, the adsorption isotherms were determined based on

the Freundlich isotherm. For this purpose, 1 gr of zeolite was mixed with 50 ml of liquid of different analytes with different concentrations for 48 hours. The remaining concentration of the analyte was determined via an Atomic Adsorption Spectrometer.

### Cations removal

10 gr zeolite was added to 100 ml synthetic water sample with different cations (concentration of each cation was 100 ppm). After 24 hours of mixing and thereafter filtrating, the remaining concentration of each cation was determined via an atomic adsorption spectrometer. The considered cations of this study were Fe, Cr, Al, Bi, Cd, Mn, Ca, Mg, Ag, Ni, Zn, Cu, and Pb. The Atomic Adsorption Spectrometry method (AAS) was used for measuring the cations in water samples.

### Anions removal

For determining anions removal from water samples by natrolite zeolite, a synthetic HMNDA compound (-N,N,N,N',N',N'-hexamethyl-1/9-nonanediam ammonium bromide,  $2/72.10^{-4}$  molar) was used. This compound could modify the zeolite surface and changed to positive charge that could remove anions from water.

In each phase, 10 gr of zeolite was mixed with 40 mL HMNDA compound in 65% ethanol liquid. After the 48 hour detention time in mixer, the zeolite color changed from white to gray. The remediate material had to be removed via washing by water, distilled twice, and ethanol liquid (65%) for several times. Then, this zeolite was dried (24 hours in open air). In this section, removal of arsenate and chromate anions in groundwater samples by modified natrolite zeolite was investigated in different pH and zeolite quantities. All analyzing methods were in accordance with the standard methods for examination of water and wastewater (25).

## RESULTS

Figure 3 shows the hardness removal efficiencies of 7 different water samples by natrolite zeolite. The natrolite zeolite was more effective for waters with higher hardness and

had a moderate efficiency for waters with lower hardness. The ability of the natrolite zeolite was more for permanent hardness removal than others and was the least for temporary hardness. It seems that carbonate (major part of temporary hardness) could less be removed by this zeolite. Figure 4 demonstrates metallic cations removal from synthetic water samples by natrolite zeolite. As can be seen, natrolite zeolite was more efficient for  $Fe^{2+}$  and less efficient for  $Cu^{2+}$ . It could be concluded that natrolite zeolite was more effective in removing non-heavy metal cations. Moreover, analyses showed that by increasing the HMNDA concentration for zeolite surface modification and zeolite quantity, more arsenate anion could be removed from water samples. However, by increasing the pH of water sample, arsenate anion removal was arbitrarily changed to lower degrees in  $pH=3$ . But the removal efficiency got better in alkaline pH. Thus the best removal efficiency was in  $pH<1$  (Figure 5). Moreover, as it is demonstrated in Figure 6, the more the zeolite weight is modified in samples, the greater the removal efficiency that can be achieved for arsenate anion. Therefore, it can be concluded that for better removal efficiency of arsenate anion, zeolite quantity needs to be increased. The removal efficiency of chromate ion Cr (VI) in different pH level is shown in Figure 7 from which it can be understood that by increasing the pH of water samples, the removal efficiency decreases. However, it can be argued that the removal efficiency of chromate ion was more in acidity pH than alkaline. The maximum removal of Cr (VI) occurred in acidic media at  $pH<1.5$ . Figure 8 shows the removal efficiency of chromate ion in different concentrations of HMNDA surfactant. As can be seen, the removal efficiency was getting more by increasing the HMNDA concentration, especially in concentrations of less than  $5*10^{-3}$  M of HMNDA. However, the removal efficiency slightly increased in concentrations of more than  $5*10^{-3}$  molar of HMNDA. Therefore, increasing the HMNDA concentration has strong effects on chromate ion removal in concentrations of less than  $5*10^{-3}$  Molar. Figure 9 illustrates the UV-visible spectrum absorbance of chromate ions

with concentrations of 0.001 and 0.0001 molar (before zeolite application) and also after application of modified zeolite in optimum operating conditions. As shown, the concentration of chromate ion after modified zeolite application significantly decreased and it can be concluded that modified natrolite zeolite is a proper absorber for chromate ion removal from water.

The experimental results of cations removal by Castaldi et al (2008) showed that the zeolite adsorption capacity for the three cations was Zn>Pb>Cd. A sequential extraction procedure [H<sub>2</sub>O, 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> and 0.02 M EDTA] was applied to zeolite samples used in the adsorption experiments to determine the chemical form of the cations bound to the sorbent. Using this approach, it was shown that low concentrations of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Zn<sup>2+</sup> were present as water-soluble and

exchangeable fractions (<25% of the Me adsorbed), while EDTA extracted most of the adsorbed cations from zeolite (>27% of the Me adsorbed). The XRD pattern of zeolite, analyzed according to the Rietveld method, showed that the main mineralogical phase involved in the adsorption process was clinoptilolite. Besides, structure information showed that the incorporation of the three cations into the zeolite frameworks changed slightly but the lattice parameters changed remarkably. XRD analysis also showed the occurrence of some isomorphic substitution phenomena in which the Al<sup>3+</sup> ions of the clinoptilolite framework were replaced by exchanged Pb<sup>2+</sup> cations in the course of ion exchange reaction. This mechanism was, however, less evident in the patterns of the samples doped with Cd<sup>2+</sup> and Zn<sup>2+</sup> cations (18).

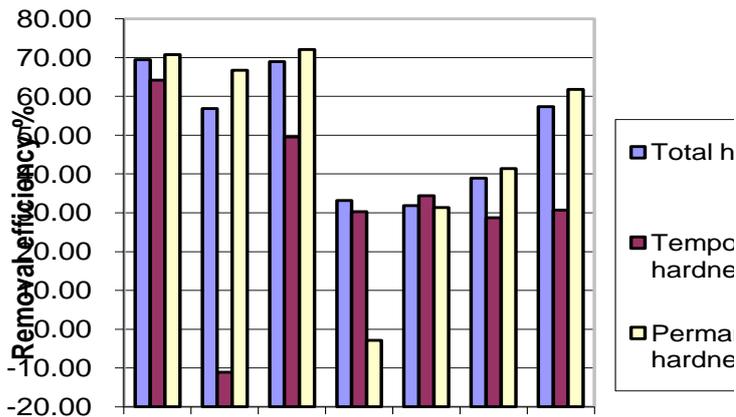


Figure 3 Hardness removal efficiencies of 7 different water samples by natrolite zeolite

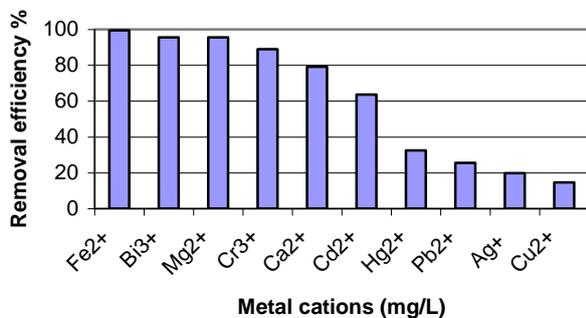


Figure 4 Metal ions removal from synthetic water samples by natrolite zeolite

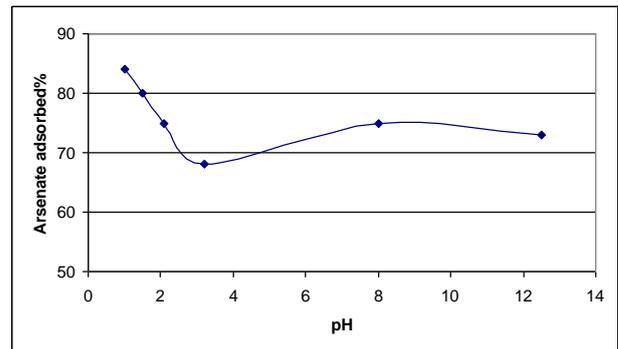


Figure 5 Arsenate anion removal by modified natrolite zeolite in different pHs

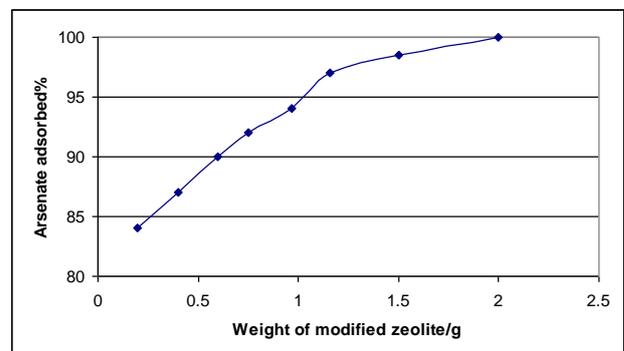
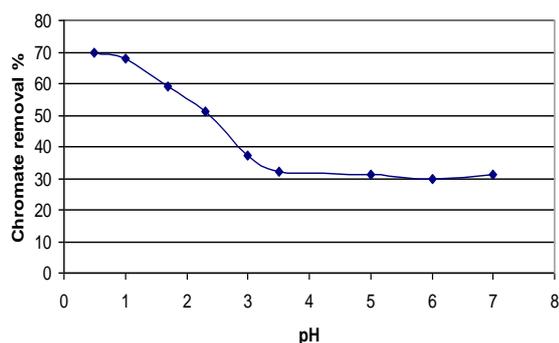
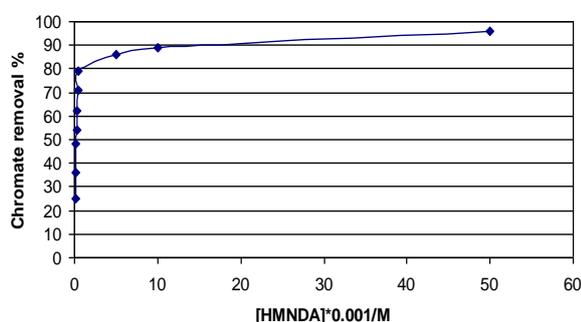


Figure 6 Arsenate anion removal by modified natrolite zeolite in different quantities



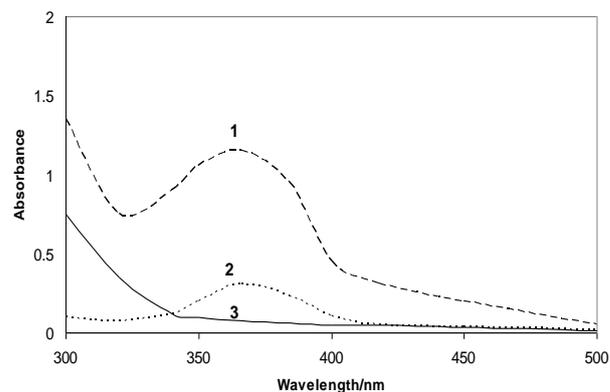
**Figure 7** The removal efficiency of chromate ion in different pHs



**Figure 8** The removal efficiency of chromate ion in different HMNDA concentrations

Laboratory results of arsenic removal with six zeolite types by Elizalde-Gonzalez et al (2001) showed that As (III) was simultaneously oxidized and removed. The resultant As (V) was subsequently sorbed by the zeolite. Both As (III) and As (V) were removed efficiently in the pH interval 4-11 after contact with zeolite ZH and ZMA for a few days. Residual arsenic and arsenate were 0-5  $\mu\text{g/L}$  and 30-40  $\mu\text{g/L}$ , respectively. Erionite-bearing ZMA showed the highest removal efficiency in the iron-modified group, and natural clinoptilolite ZMS showed the highest removal efficiency in the unmodified group. Compared with conventional treatment using iron hydroxide, iron-modified mordenite ZM-M and ZMA remove As (III) up to 89% and 75%, respectively, in comparison to the amount removed by conventional iron treatments (26,27).

Experimental results for arsenate removal by Faghihian (2005) showed the theoretical cation exchange capacity (CEC) of the zeolite to be 2.21 meq/g. The maximum exchange level



**Figure 9** UV-visible spectrum absorbance of chromate ions with different 0.001 and 0.0001 molar concentrations (before zeolite application) and also, after application of modified zeolite in optimum operating conditions

was 1.31, 0.47, and 0.41 meq/g for Ag, Pb, and Fe forms, respectively, and less than 100% of the theoretical exchange capacity. The failure to attain a 100% exchange appears to be the most striking feature of this set of experiments since these cations react with arsenate to form entrapped arsenate precipitates. Initial measurements showed that the uptake of arsenate by untreated clinoptilolite was negligible. It is believed that the presence of Pb, Fe, and Ag promotes anions precipitation on the surface and in the cavity of zeolite. The driving force to overcome the charge repulsions between arsenate and the framework is probably the small solubility products of arsenate precipitates. Adsorption of arsenate showed to be concentration dependent. The amount of zeolite was held constant, while the initial concentration of the anion varied from 1.0 to 60 mmol/L. The  $K_{ad}$  values were measured using Lagergren's equation and were 0.2533, 0.1865 and 0.1543 for Pb, Ag, and Fe-exchanged forms, respectively. As expected, the highest adsorption rate was observed for

Pb-exchanged forms due to the lower  $K_{sp}$  of lead arsenate (17).

The experimental results obtained by Zeng et al (2010) showed that Cr (VI) adsorption on HDPB-zeolites has a quick initial speed and adsorption kinetics follow pseudo-second order kinetic model within the initial adsorption stage. HDPB-zeolites have higher affinities toward chromate than that to natural zeolites, and particularly, HDPB-HZ exhibits the highest adsorption capacity in all the studied samples. Additionally, the adsorption of Cr (VI) on HDBP-PZ is almost constant in a wide pH range 3.0-11.0 of solution. In contrast, the Cr (VI)-uptake for HDPB-HZ strongly depends on the solution pH. The highest Cr (VI) adsorption on HDPB-HZ occurs in acidic solutions (pH 3.0-5.0) and the amount of adsorbed Cr (VI) decreases rapidly with increasing pH. High solution ionic strength has a significant effect on chromate adsorption. The chromate adsorptions by HDPB-zeolites are not affected by co-existing chloride, nitrate, sulfate, and calcium as well as magnesium ions but are reduced drastically in the presence of bicarbonate and phosphate ions. Moreover, HDPB-zeolites can achieve high regeneration efficiency after using sodium carbonate extraction and hydrochloric acid. The analysis of XRD, FTIR and SEM reveal that HDPB cations are incorporated into the zeolite's structure via ion-exchange and Van der Waals forces. It also suggests that the anion exchange and electrostatic interaction are probably the main mechanisms that govern the Cr (VI) adsorption (5).

The experimental results of atomic absorption spectrometric determination of trace amounts of  $Ag^+$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  after simultaneous separation and pre-concentration onto modified natural natrolite and clinoptilolite zeolite by Afzali (2006) and Mostafavi et al (2008) showed the proposed method to be of good accuracy (recovery > 97%)(15,16).

## CONCLUSION

Heavy metals removal by natural zeolites has been considered in recent years. This study showed that the natrolite zeolite could remove

different heavy metals from drinking water. Moreover, the removal efficiency of natrolite zeolite was enhanced by surfactant modification.

## REFERENCES

1. Katsoyiannisa, I.A., A. Zikoudib, and S.J. Huga, Arsenic removal from groundwaters containing iron, ammonium, manganese and phosphate: A case study from a treatment unit in northern Greece. *Desalination*, 2008. **224**: p. 330-339.
2. Joshi, A. and M. Chaudhuri, Removal of arsenic from ground water by iron oxide-coated sand. *ASCE Journal of Environmental Engineering* 1996. **122**(8): p. 769-771.
3. Vaughan, D.E.W., *Zeolites Natural*. 1988, New York: Pergamon Press.
4. Obradovic, S., et al., The application effects of natural zeolite in feed and water on production results of *Oncorhynchus Mykiss* (Walbaum). *Romanian Biotechnological Letters* 2006. **11**: p. 3005-3013.
5. Zeng, Y., et al., Adsorption of Cr (VI) on hexadecylpyridium bromide (HDPB) modified natural zeolites. *Journal of Microporous and Mesoporous Materials*, 2010. **130**(1-3): p. 83-91.
6. Misaelides, P., et al., Heavy metal uptake by zeoliferous rocks from Metaxades, Thrace, Greece: an exploratory study. *Journal of Radioanalytical and Nuclear Chemistry* 1994. **183**: p. 159-166.
7. Shanableh, A. and A. Kharabsheh, Stabilization of Cd, Ni and Pb in soil using natural zeolite. *Journal of Hazardous Materials*, 1996. **45**: p. 207-217.
8. Peric, J., M. Trgo, and N.V. Medvidovic, Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms. *Water Research*, 2004. **38**: p. 1893-1899.
9. Sprynskyy, M., et al., Influence of clinoptilolite rock on chemical speciation of selected heavy metals in sewage sludge. *Journal of Hazardous Materials*, 2007. **149**: p. 310-316.
10. Kosobucki, P., M. Kruk, and B. Buszewski, Immobilization of selected heavy metals in

- sewage sludge by natural zeolites. *Bioresource Technology*, 2008. **99**: p. 5972-5976.
11. Lebedynets, M., et al., Adsorption of ammonium ions on natural zeolite, Transcarpathian clinoptilolite. *Adsorption Science & Technology*, 2004. **9**: p. 731-741.
  12. Zorpas, A.A., et al., Heavy metal uptake by natural zeolite and metals partitioning in sewage sludge compost. *Bioresource Technology*, 2000. **72**: p. 113-119.
  13. Gharebaghi, M., M. Irannejad, and H. Ghased. Synthesis of zeolite A from Iranian Hesarbon natural zeolite. in *International Zeolite Conference*. 2008. Tehran.
  14. Noroozifar, M., et al., Adsorption behavior of Cr(VI) on modified natural zeolite by a new bolaform N,N,N,N',N',N'-hexamethyl-1,9-nonanediammonium dibromide reagent. *Journal of Hazardous Materials*, 2008. **155**(3): p. 566-571.
  15. Afzali, D., A. Mostafavi, and M.A. Taher, Modified clinoptilolite zeolite as a new and green sorbent for simultaneous separation and preconcentration trace amounts of Ag<sup>+</sup> and Cd<sup>2+</sup>, in *International Zeolite Conference*. 2008: Iran.
  16. Mostafavi, A., D. Afzali, and M.A. Taher, Atomic Absorption Spectrometric Determination of Trace Amounts of Copper and Zink after Simultaneous Solid-Phase Extraction and Preconcentration onto Modified Natrolite Zeolite. *Journal of Analytical Sciences*, 2006. **22**: p. 849-853.
  17. Faghihian, H., Adsorption of arsenate ion by Fe, Pb, and Ag-exchanged forms of clinoptilolite. *Iranian Journal of Science & Technology, Transaction A*, 2005. **29**(1): p. 189-193.
  18. Castaldi, P., et al., Sorption processes and XRD analysis of a natural zeolite exchanged with Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> cations. *Journal of Hazardous Materials*, 2008. **156**(1-3): p. 428-434.
  19. Badalians Gholikandi, G., H.R. Orumieh, and H.R. Tashauoei. Characterization of natural zeolite and the feasibility of cations and anions removal from water. in *International Conference on Computational Methods and Experiments in Materials Characterization*. 2009. New Forest, UK.
  20. Vellayati, S., E. Khatibi, and M. Zandi. The Genesis and Formation Source of Zeolites and Determination of Zeolitic Horizons of Tehran Province, Iran. in *International Zeolite Conference*. 2008. Tehran.
  21. Bazargani-Guilani, K., M.S. Rabbani, and M. Faramarzi. Study of few Zeolitic Occurences in Guilan Province, Iran. in *International Zeolite Conference*. 2008. Tehran.
  22. Bazargani-Guilani, K., M.S. Rabbani, and S. Fathi. Natrolite, Epistilbite and Analcime in Amygdales of Altered Andesite from Parandak, Central Iran. in *International Zeolite Conference*. 2008. Tehran.
  23. Bazargani-Guilani, K. and P. Yiusefey. Mineralogy of the zeolitic-bentonitic sequences of the Kuh-e-Arshe, north Central Iran. in *International Zeolite Conference*. 2008. Tehran.
  24. Shojaefard, M., M. Sardari, and H. Kazemian. Zeolite Market Survey in Iran. in *International Zeolite Conference*. 2008. Tehran.
  25. APHA, Standard Methods for the Examination of Waters and Wastewaters. 21 ed. 2005, Washington, DC.: American Public Health Association (APHA)
  26. Elizalde-Gonzalez, M.P., et al., Sorption on natural solids for arsenic removal. *Chemical Engineering Journal*, 2001. **81**: p. 187-195.
  27. Vu, K.B., M.D. Kaminski, and L. Nunez, Review of arsenic removal technologies for contaminated groundwater, in *Argonne National Laboratory*. 2003, University of Chicago: Argonne, Illinois.