

Evaluation of Some Natural Zeolites and Their Relevant Synthetic Types as Sorbents for Removal of Arsenic from Drinking Water

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Abstract

The purpose of this study was to find a relatively inexpensive method for removal of arsenate and arsenite from drinking water. The capability of Iranian natural clinoptilolites, relevant synthetic zeolites A and P and Iron(II) modified of them was investigated for the uptake of arsenic anions from drinking water. Data obtained from ion-exchange using batch (static) technique showed that among the investigated zeolites, modified synthetic zeolite A was the most selective sorbent for removal of arsenic. In this study, the influence of factors including temperature, arsenic concentration, pH and zeolite particle size on removal of arsenic species from water was also determined and studied.

Keywords : Natural zeolites, Clinoptilolite, Zeolites A and P, Arsenate, Drinking water, Water treatment, Iran

Introduction

Arsenic is a naturally occurring element in the environment. Arsenic in the ground water is largely due to minerals dissolving naturally from rocks and soils. It has many industrial applications such as hardening of copper and lead alloys, pigmentation in paint industries, fireworks, glass manufacturing, cloth, and electrical semiconductors. Arsenic is also used extensively in the production of agricultural pesticides, including herbicides, insecticides, desiccants, wood preservatives, and feed additives. Runoff from these industries results in the leaching of arsenic to an increased levels of various forms of soluble arsenic in water(1). Inorganic arsenic is highly toxic to mammals and aquatic species. When ingested, it is readily absorbed from gastrointestinal tract, lungs, and to a lesser extent from the skin, and becomes distributed throughout the body. Recently,

arsenic in water supplies has been linked to arsenical dermatosis and skin cancer(2).

Inorganic arsenic species in contaminated industrial sites exist in the arsenate(As(V)), arsenite(As(III)), arsenic sulfide (HAsS₂), elemental arsenic(As⁰) and arsine gas(AsH₃) forms. Arsenite forms are the reduced inorganic arsenic species and include H₃AsO₃, H₂AsO₃⁻, HAsO₃⁻², and AsO₃⁻³. Arsenate forms include H₃AsO₄, H₂AsO₄⁻, HAsO₄⁻², and AsO₄⁻³. As(V) exists as H₂AsO₄⁻ in aqueous solution especially at pH range of 7-11 and As(III) exists as H₃AsO₃ in aqueous solution especially at pH range of 0-9 (3). The U.S.EPA has classified arsenic as a human carcinogen and is considering lowering the maximum allowable contaminant level for drinking water from the present 50 part per billion to 5 ppb or less.

There are many advantages for the process of using zeolites in arsenic removal, the advantages over other processes are as follows (4):

- provides a method of removing aqueous arsenic species from natural water having a pH range from 3 to 8.
- provides a method of removing arsenic species in the form of both arsenate and arsenite from an aqueous medium without the need to oxidize arsenite to arsenate.
- provides a method of removing aqueous arsenic species from an aqueous medium to a detection level for arsenic species of 5 ppb.
- provides an inexpensive sorbent material to remove aqueous arsenic species from an aqueous medium, which does not need to be reused in order to be economically applicable.
- provides a cost effective means to remove aqueous arsenic species from an aqueous medium, which will not leach aqueous arsenic species and can be readily disposed of as non-hazardous waste.
- the arsenic-laden zeolites have passed the EPA's Toxicity Characteristic Leaching Procedure test and can be safely disposed of in a non-hazardous waste landfill.

Materials and Methods

Three natural Iranian clinoptilolites were selected for the experimental work from Meyaneh (Zm), Firoozkough (Zf) and Semnan (Zs) resources located in the north-west, north, and central areas of Iran respectively. Natural zeolites (NZ) were grind, sieved and washed. The particle size was between 224-500 μ m and 500-800 μ m and prepared using ASTM standard sieve. The particle size of 224-500 μ m was then selected as the main sample for further experiments. The natural and synthetic samples were characterized using x-ray diffraction method: XRD, (Philips PM 9920105, Cu K α , 40kV), x-ray fluorescence: XRF, (Philips PW 1480) and

simultaneous thermal analyzer: STA, (Rheometric Scientific Thermal Analyzer).

Zeolite A was synthesized by treating a stoichiometric amount of sodium aluminate and 2N sodium hydroxide with clinoptilolite at 80°C for 4h (5). Zeolite P was synthesized by treating of natural clinoptilolite powder with 3N sodium hydroxide solution at 100°C for 48h (6, 7). All of the natural and synthetic samples were modified with treating the zeolite material with an aqueous solution of FeCl₂ for obtaining an iron-laden exchanger in order to increase the zeolites affinity toward the arsenic. Iron (II) modified zeolite, was prepared according to the following procedure:

Zeolite powder (5g) was mixed in a 100ml polyethylene vessel with 50ml of 1M solution of FeCl₂ and shaken for 72 h at 24°C and then finally washed with distilled water.

Preliminary batch experiments were carried out to determine the distribution coefficient (K_d) and choose the best sample(s) for supplementary experiments. The kinetic of sorption reaction for the two selected samples (synthetic zeolite A from Zm (ZAm) and synthetic zeolite P from Zf (ZPf)) showed the highest K_d values.

The sorption of arsenic from aqueous solution with 0.005N arsenic, obtained by dissolution of the appropriate amount of Na₂HAsO₄·7H₂O sodium arsenite solution (Merck), was made, using a batch type technique. For the individual experiments, 200mg of the zeolite powder was shaken with 50ml of the aqueous solutions in a 50ml polypropylene tube for 24 h at 25°C. To adjust pH, NaOH (6N) and concentrated HNO₃ have been used.

Arsenic concentration in the supernatant solution was measured by ICP (Inductive Coupled Plasma) technique (Liberty 150 AX Turbo) after centrifugation at 5000rpm for 30 minutes. According to the kinetic experiments, the reaction reached to equilibrium point after 48 h. The effects of temperature, concentration, pH, particle size, and interferences on the K_d were also investigated at equilibrium time (48h).

Distribution coefficient ($K_d:dm^3.g^{-1}$) was calculated from the concentration of the arsenic in the initial and resulting solution, C_i and C_f : (1)

$$K_d = ((C_i - C_f) / C_f) V / W$$

C_i = initial concentration

C_f = final concentration

V = the volume of the solution (ml)

W = the mass of the zeolite powder (g)

Results

Table 1: Percentage of chemical components in composition of the different zeolite samples (XRF)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
Semnan	64.4	12.80	1.31	0.31	2.37	1.15	1.13	2.64	0.21	13.19	99.55
Firouzkooh	67.24	11.71	0.58	0.42	3.04	1.16	1.19	1.48	no	13.47	100.43
Meyaneh	67.35	11.73	0.88	0.34	2.34	1.21	0.88	1.72	no	12.94	99.43

no: not observed

Table 2: X-Ray diffraction data obtained from XRD patterns of the natural samples

Zm		Zf		Zs	
d(A°)	I/I ₀	d(A°)	I/I ₀	d(A°)	I/I ₀
39.96	100	3.97	100	3.97	100
8.98	52	9.03	48	9.02	64
3.17	44	2.97	41.9	2.397	42.8
2.97	43.5	3.41	35.5	3.42	34.3
2.379	41.6	3.17	32.3	3.17	32.4
3.55	24	2.79	24.5	2.80	25.7
58.11	17.6	7.92	22.4	7.92	20
7.97	16	5.10	19.4	5.12	19.38
5.24	16.1	3.55	16.2	3.55	15.5
6.73	12.8	5.72	14.8	5.23	15.4
2.79	12	6.76	13.5	6.77	14.3
2.72	10.4	2.73	12.9	2.701	12.5

I/I₀ = Intensity (final) / Intensity (initial)

Composition of the chemical components present in the natural zeolites samples has been illustrated in Table 1. These findings are well correlated with the finding of natural clinoptilolite reported by the others. The data obtained from the XRD pattern is shown in Table 2. Scanning electron micrograph of a typical clinoptilolite sample from Meyaneh (Zm) region of Iran can be seen in Figure 1.

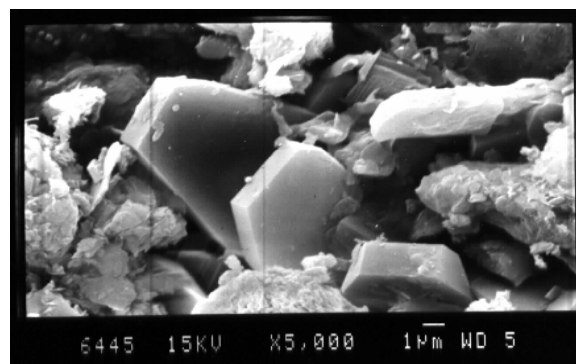


Fig. 1: Scanning electron micrograph of a typical clinoptilolite sample from Meyaneh (Zm) region of Iran.

Absorption behaviors of the natural, synthetic, and modified zeolites (200mg zeolite powder, 50ml of 0.005N arsenate concentration in 25°C at 24 h) are compared in Fig.2. These data shows that the Iron-laden samples have increased the zeolites affinity toward the arsenate.



Fig. 2: Comparison of the natural (Zm, Zf, and Zs), synthetic (ZAm, ZPm, ZAf, ZPf, and ZAs) and modified zeolites (ZAm-Fe, ZPm-Fe, ZAf-Fe, ZPf-Fe, and ZAs-Fe)

The kinetic curves for arsenate and arsenite on the various iron modified zeolites are shown in Figs. 3 and 4. These experiments have been performed with 200mg zeolite powder and

50ml of 0.005N arsenic solution in 25°C at 1, 5, 9, 14, 24, 48 and 72h to obtain equilibrium time.

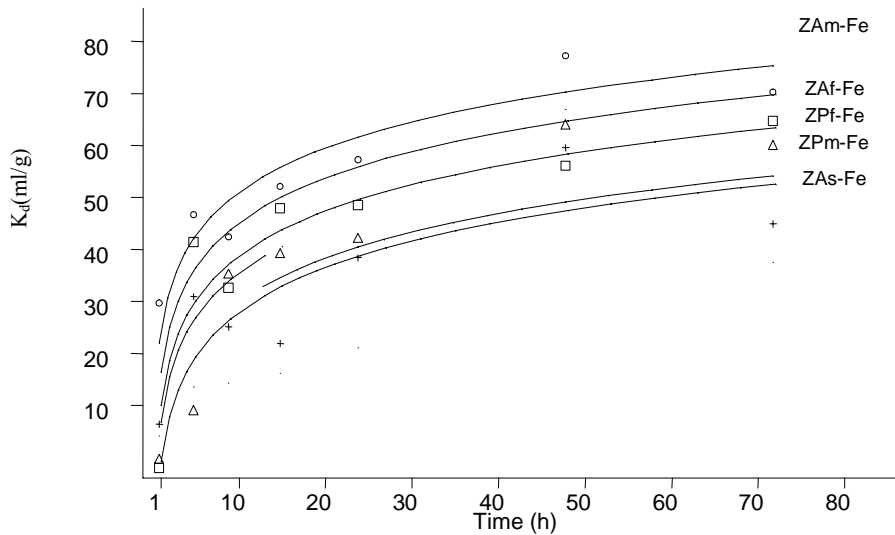


Fig. 3: Variation of K_d Vs time for As (V) on the Iron-laden zeolites

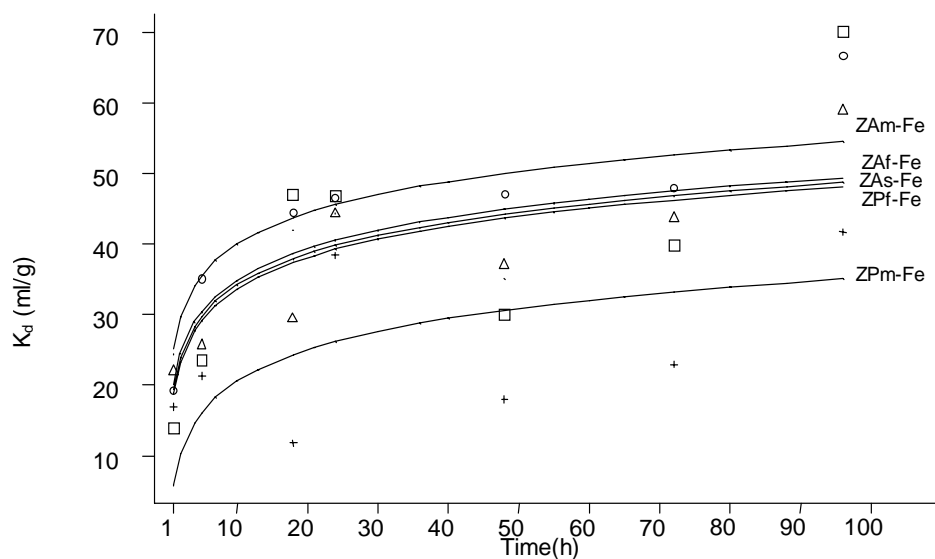


Fig. 4: Variation of K_d Vs time for As (III) on the Iron-laden zeolites

According to the data obtained, a general trend of arsenate absorption over investigated sorbent was: Am>ZAf>ZPf>ZPm>ZAs and for arsenite absorption was ZAm=ZAf=ZPf=ZAs>ZPm. It can be concluded that among all of iron-laden synthetic zeolites, modified zeolites A have shown more selectivity toward the arsenate and arsenite and equilibrated after 48 h.

Statistical comparison has shown that ZAm can adsorb more effectively As(V) as compared to As(III).

Elemental analyses of the synthetic zeolites A and P have been presented in Table 3.

Elemental analyses of the iron modified synthetic zeolites Am and Pf are presented in Table 4.

Table 3: Percentage composition of the chemical components presented in the ZAm and ZPm samples (XRF)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
ZAm	42.3	26.7	1.50	0.21	1.28	0.67	17	1.15	no	7.74	99.83
ZPm	50.25	18.87	3.82	0.36	2.88	2.88	4.92	1.24	0.21	16.50	100.02

no: not observed

Table 4: Percentage composition of the chemical elements present in the ZAm-Fe (<224 μm) and ZPf-Fe (224-500μm) samples (XRF)

Sample	Si	Al	Fe	Ti	Ca	Mg	Na	K	P ₂ O ₅
ZAm-Fe	29.73	8.94	8.67	0.24	1.0	0.72	no	2.16	0.09
ZPf-Fe	28.19	8.52	11.1	0.24	1.42	0.54	0.52	1.66	no

no: not observed

The effects of temperature, concentration, pH, particle size, and interferences on the K_d are also investigated. Effects of temperatures 8, 25, 50, and 60°C with 200mg of zeolite powder of ZAm or ZPf and 50ml of 0.005N solution of arsenate for 48h were also studied (Fig. 4).

Adsorption is increased with the increased temperature and the ion mobility.

The influence of ion concentration on the K_d was also investigated with various ion solutions (Fig. 5).

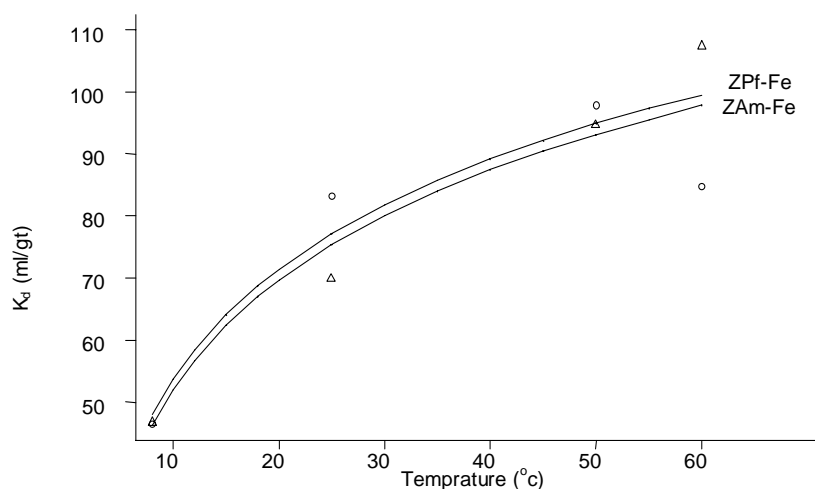


Fig. 4: Effect of temperature on K_d .

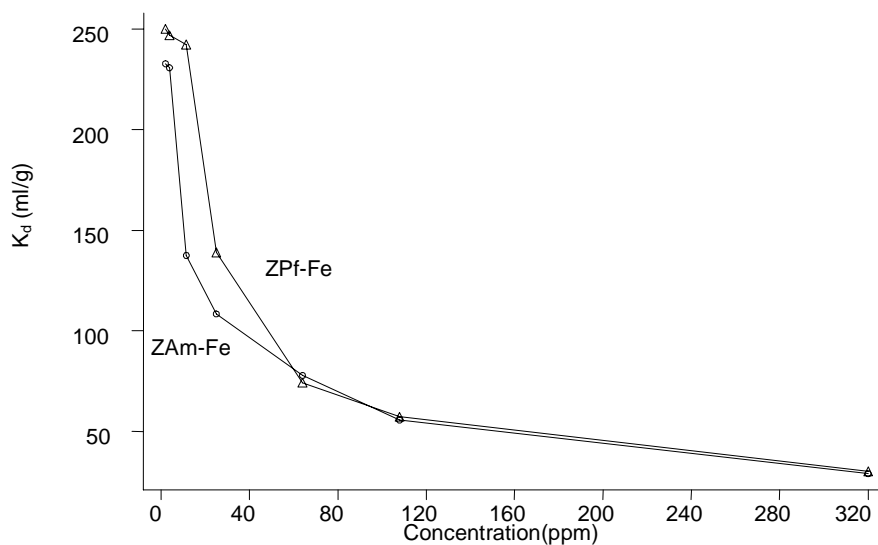


Fig. 5: Effect of concentration on K_d

The results have shown that there is a reverse correlation between the concentration and K_d . As the concentration is decreased, K_d is increased.

The standard range of pH for drinking water is 6.5-8.5. Since the stability and dominance of

the arsenic species directly depend on the pH of the solution, the pH changes over a reaction period were also studied. A 0.2g of zeolite samples was left for 48h in contact with 50ml aqueous solution of 0.005N As(V) at different pH values at 25°C. After 48 h, all of the

solution with pH less than 7 showed an increase in its pH whereas solution with pH higher than 7 did not show any significant changes (Fig. 6).

The influence of particle size was investigated

at the three different temperatures of 25, 50, and 60°C (Fig. 7). The results obtained showed that, ZPf sample (500-800µm) is better than ZPf one (224-500µm) at the three temperatures (Table 5).

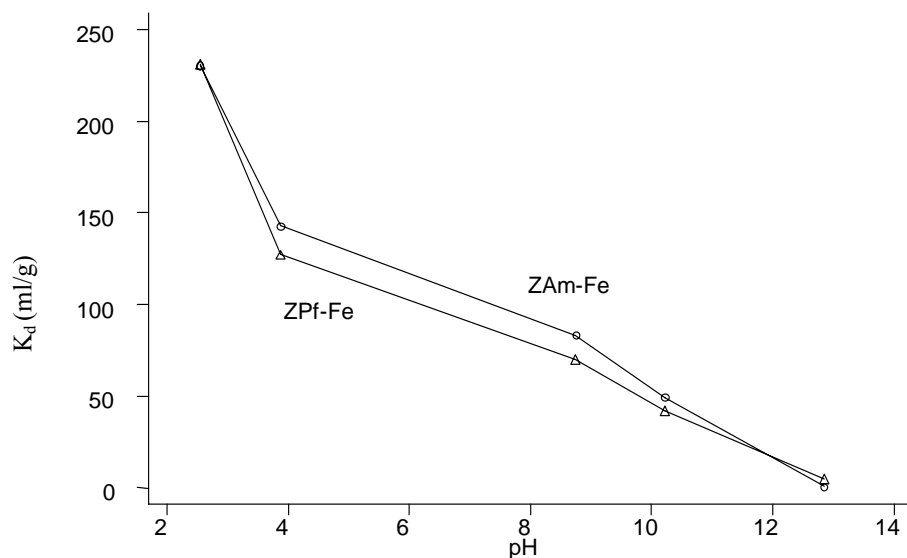


Fig. 6: Effect of pH on K_d .

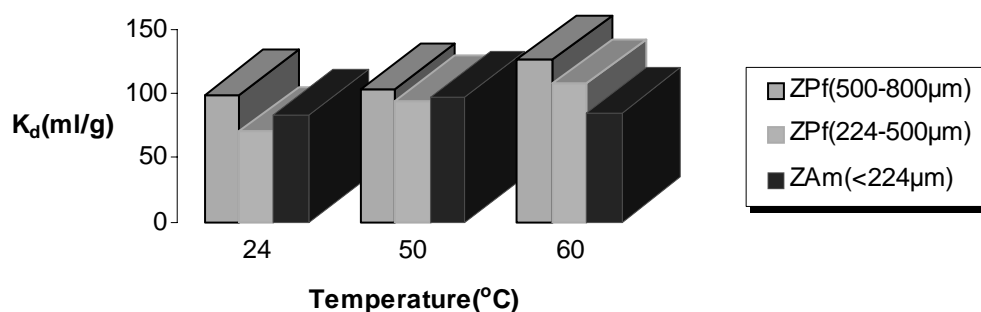


Fig. 7: Effect of particle sizes on the K_d .

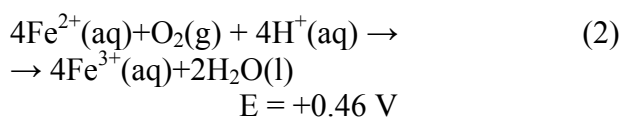
Table 5: Percent composition of the chemical elements present in the ZPf (224-500µm) and ZPf (500-800 µm) samples (XRF)

Sample	Si	Al	Fe	Ti	Ca	Mg	Na	K	P ₂ O ₅
ZPf-Fe (224-500µm)	28.19	8.52	11.1	0.24	1.42	0.54	0.52	1.66	no
ZPf-Fe (500-800 µm)	28.51	8.57	11.33	0.24	1.42	0.42	0.67	1.58	no

no= not observed

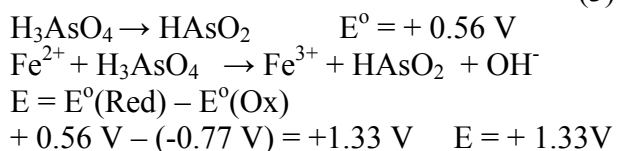
Discussion

The XRD and TG data give the necessary evidence for the structure and thermal behavior of the samples. The structural framework of heulandite and clinoptilolite is similar, whereas, their thermal stabilities are different. The XRD patterns of the heated natural samples proved that the samples were stable up to 700°C. Therefore they must be remarked clinoptilolite since heulandite structure will be collapse at about 400°C (8). All of the natural and synthetic samples were modified with treating the zeolite material with an aqueous solution of FeCl₂ (FeCl₂ in concentrated HCl was used to make Fe²⁺ solutions). Fe²⁺ was oxidized to form Fe³⁺ according to the following equation: (9)



This is a spontaneous reaction. However, +0.46 V is not large enough for a rapid reaction and atmospheric oxidation of Fe (II) in aqueous solutions is relatively slow in the absence of catalysts. As a result, it is possible to use Fe²⁺ aqueous solutions in laboratory procedures with slight precautions. It is suggested that, the absorption of arsenate on the iron-modified zeolite can be through two mechanisms, a redox reaction and formation of a chemical bond between zeolite and arsenate. At pH ranges of 0–2, 3–6, 7–11, and 12–14, the predominant forms of arsenic in aqueous solutions are H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻ respectively.

In solutions with pH of 2–7 the As⁵⁺ can be reduced to As³⁺ and Fe²⁺ can be oxidized to Fe³⁺. The redox potential of this reaction is; (9)

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \quad E^{\circ} = -0.77 \text{ V} \quad (3)$$


The synthesis technique used for producing zeolites A caused finer particle size than zeolites P. The average particle size of zeolite A was less than 100µm compared to zeolite P that were 224–500µm and 500–800µm. Larger particle size will have the minimum pressure drop in column operation subsequently ZPf sample (500–800µm) can be best in continuous condition.

The results obtained from this study showed that, the iron (II) modified synthetic zeolite obtained from Iranian natural clinoptilolite is suitable for removal of arsenic from drinking water. Synthesized zeolite P from Firouzkooh Clinoptilolite (ZPf) with 500–800µm could be a suitable candidate for applying a continuous sorption technique.

This method can be considered to be the most cost effective, simple, rapid, and safe technique for the removal of arsenic. Further researches with aqua medium are needed to obtain the optimal condition for their future application.

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