Water Defluoridation Using Modify Zeolite by Al⁺³ Ions and Nanoscale Zero-Valent Iron (nZVI) in a Fixed Bed Column

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ABSTRACT

Removal of the fluoride ion of drinking water requires an effective technique. In study zeolite clinoptilolite by Al⁺³ ions and nanoscale iron (nZVI) modify was used to remove fluoride from water. Contact was done by a fixed bed absorbent column. In this column, experiments were carried out using aqueous solutions and drinking water with mass. The dynamics of the adsorption process were fitted to Langmuir and Freundlich models. The results showed that highest uptake capacities 1.14 and 2.4mg/g for the modified zeolitic Al and nanoscale iron (nZVI) respectively, were obtained with a 5g mass column, an inlet 10mg/L fluoride solution, and a flow rate of 3mL/min, but the sorption capacities decreased when drinking water used. Experimental data were fitted to both models Langmuir and Freundlich, and the methods indicated that these materials are suitable for the removal of fluoride from water in fix bed systems. In general, it can be concluded that modified zeolite clinoptilolite with fixed bed an effective and economical method to remove fluoride from groundwater.

Keywords: Zeolite Clinoptilolite, Fluoride, Breakthrough Point (BTC), Al⁺³, nZVI, Absorbant

INTRODUCTION

Fluoride can be found in air, food, soil water and is a necessary element to human health, and a moderate amount of fluoride intake is confirmed that it is the effective way of reducing dental caries among children and adult [1, 2].

In the last decades, scientific literature in fluoride research suggests that fluoride has beneficial effects on teeth at low concentrations in drinking water (0.4– 1.0mg/L), especially for young children because it promotes calcification of dental enamel and protects teeth against tooth decay. Several investigations have widely studied drinking water using various adsorption media in a fixed bed column [3]. However, bone char is disapproved in some communities due to sociocultural reasons and also because of the final water quality after the process is low [4]. However, batch equilibrium studies that surface-tailored zeolite has a higher adsorption capacity for fluoride than most commercial adsorbents (for example bone char, Al–zeolite F9, activated alumina (AA) and Fe–Al–Ce oxide, La–CCB, Zn–Al-LHDs, alum sludge, Al₂O3/ CNT and ACNTs) [5-11]. Moreover, it is competitive in cost [8].

This work is a continuation of our earlier studies for removing fluoride from the aqueous solution fixed-bed adsorption an upward flow was applied [10, 12]. The modified zeolite with The metals (i.e. La³⁺ and Mg²⁺) had been used to adsorbent fluoride from water and they show good affinity [13]. Nano-scale particles have a large surface area that is useful for adsorption processes. For nZVI with a diameter of 1-100 nm and surface area in the range of 20-40m²/g, provides 10-1,000 times greater reactivity than granular iron, which has a surface area $< 1m^2/g$ [14]. In recent years, nZVI has been considered due to its high efficiency in the removal of various contaminants such as heavy metals, chlorinated organic, compounds, diphenyl ethers, fluoride, pesticides clindamycin [15-21]. The objective of this study is to remove fluoride using zeolite clinoptilolite by two methods of modified Al⁺³ions and nanoscale iron (nZVI), which are carried out in the presence of different adsorbent masses and in samples of drinking water and aqueous solution.

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MATERIALS AND METHODS

Reagents

Chemicals used in the synthesis of nZVI, zeolite, NaF, acid, sodium hydroxide, ferric sulfate ($Fe_2(So_4)_3$), sodium ($NaBH_4$), ethanol, and starch were prepared from CMC (Germany).

Preparation and Characterization of NZVI Zeolite and Al^{+3} Zeolite

NZVI particles were synthesized by sodium boro hydride ($NaBH_4$) reduction method. . The steps in the chemical reactions that produce iron are described by Eq. (1).

$$Fe\ (H_2O)_6\ ^{2+} + 2BH_4^- \rightarrow Fe^0 + 2B(OH)_3 + 7H_2\uparrow \quad (Eq.1)$$
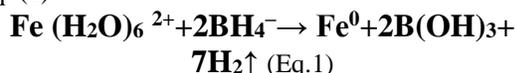
1g of the zeolite with 30mL of $Fe_2(So_4)_3$ solution (1M) in the presence of nitrogen gas was mixed for 3 hours. Then this solution was diluted in 5-fold with ethanol and water solution (1:1). In the next step, 100 mL of NaBH4 was added to this mixture in the $25^{\circ C}$ and placed on the magnetic stirrer for 30 minutes. After this time period, according to the Eq. 2 zeolites was coated. The nZVI was separated and then washed three times with acetone at $65^{\circ C}$ using injecting nitrogen gas stored in a desiccator [12]. In this study, X-ray diffraction (XRD)and scanning electron microscope (SEM) were used for the structure and size of the nanoparticles.

The structure of zeolite clinoptilolite is made of alumina and silica and has a high value of negative entrust caused by oxygen atoms. The zeolite clinoptilolite is also negatively charged, but the charges are made equal by the various bound cations. For the preparation of surface-tailored zeolite with aluminium sulfate solution, 50g zeolite was added into a 1000mL of 0.075M aluminium sulfate solution. The mixtures were intermittently agitated with a shaker at 200rpm. After 48h the zeolites were washed several times using demineralized water to decrease the electrical conductivity. Finally, the modified zeolite was dried in the ambient air for 4h [22]. After converting the zeolite to its cationic form with NaCl solution and adding the cationic zeolite into the metal salt solution, the Na^+ bound in the structure of the zeolite was exchanged with Al_3^+ from aqueous solution Eq. 2:

$$Al^{3+}(solution) + 3Na^+(zeolite) \rightarrow$$
$$Al^{3+}(zeolite) + 3Na^+(solution)$$
$$(Eq.\ 2)$$
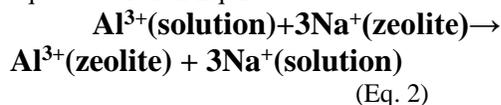
Analytical methods

For the residual fluoride concentration analyses, the standard SPADNS method was used with a Spectrophotometer (HACH Company, USA: limit of detection) 0.02mg/l) correspondingly, DR5000 can detect the potential values for a range of known fluoride concentration, usually 0.02 to 25mg/l. The accumulation of fluoride in a fixed-bed column is dependent on the quantity of adsorbent inside the column. The adsorption process was performed in columns of 2cm internal diameter and 15cm the heights of beds, the columns were loaded with 5, 7and 10g of Al and nZVI modified zeolite clinoptilolite. The solution was introduced at a constant volumetric flow rate of 3mL/min, and fluoride concentrations were 10mg for aqueous solution and drinking water. The Breakthrough point (BTC) was measured when the fluoride concentration reached 2mg/l, according to WHO guidelines [24].

The removal efficiency (R) of BTA was calculated by the following equation:

$$R = \frac{C}{C0} \quad\quad (Eq.\ 3)$$

Where R is the removal efficiency, C0 the initial concentration before absorption (mgl^{-1}), and C is the concentration in after absorption (mgl^{-1}).

The study of Langmuir and Freundlich models of isotherms were used for mathematical modelling of the fluoride absorption process. The relationship between the amount of substance adsorbed and its concentration in the equilibriums solution and constant temperature is called the adsorption isotherm [25]. This model is applicable to homogenous adsorption and can be expressed by the Eq. 4:

$$q_e = q_{max}\ bc_e/1 + bc_e \quad (Eq.4)$$

This model is applicable to heterogeneous adsorption and can be expressed by the Eq. 5:

$$q_e = K_f\ C_e^{1/n} \quad\quad (Eq.5)$$

The equations q_{max} is the maximum adsorption capacity (mg/g), c_e is the equilibrium concentration of adsorbate (mg/l), q_e is the adsorption capacity (mg/g), b is the adsorption reaction constant (l/mg), and K_f and n are empirical constants[26].

RESULTS AND DISCUSSION

The crystal structure of nZVI nanoparticles was determined by the XRD device, with its results demonstrated in Fig. 1. The surface morphology of coating the zeolite was observed with scanning electron microscope (SEM) image (Hitachi S4160, Japan) provides an excellent high-resolution quality picture that is particularly valuable when studying particles in the size range of 1–200μm (Fig. 2a Al-Z, b nZVI-Z). As seen in Fig.2, the coating of nanoparticles and iron are suitable for zeolite. The results Fig.2 indicated that the surface properties of zeolite before and after immobilization of

the nanoparticles had no significant difference due to the presence of nZVI nanoparticles. Furthermore, a major portion of nZVI particles have been loaded onto the surface and have not been rejected in the pores, thereby increasing the possibility of permeation of light onto the nZVI surface.
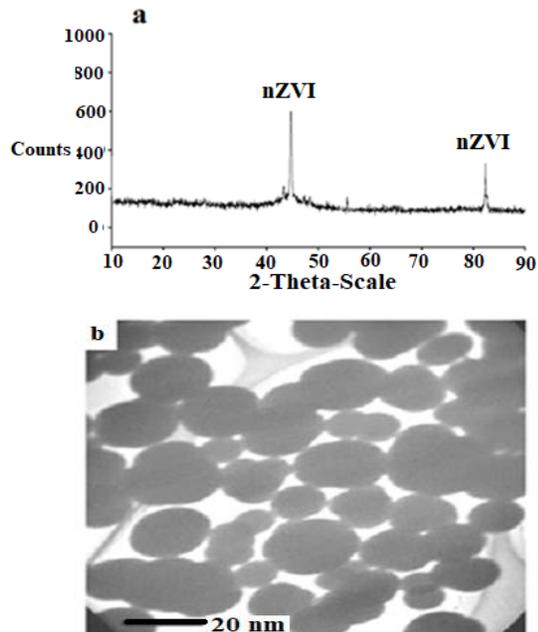
Fig. 1: Characterization of nZVI particles coating **a)** (XRD pattern, **b)** TEM pattern
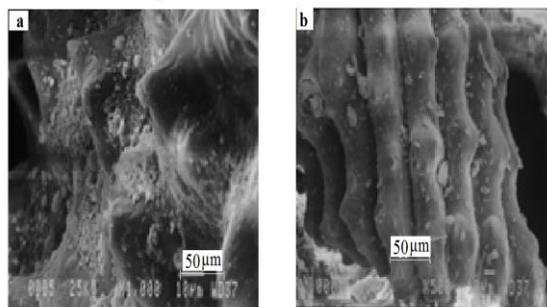
Fig. 2: The surface morphology SEM of coated zeolite (aAl-Z, b nZVI-Z)

Effect of Adsorbent Mass

By fixed, the initial solute concentration and flow velocity, the variation of bed mass determines the number of active sites available for sorption and the contact time of solute with the adsorbent. The Breakthrough point (BTC) is acquired from the examination of fluoride removal in three different bed mass of 5, 7, and 10g. In the examination fixed parameters for initial concentration, flow, and pH are 10mg/l, 3ml/min and 7 respectively. The experiments were conducted to recognize the absorption by both adsorbents. The BTC was measured when the fluoride

concentration reached 2mg/l, according to WHO guidelines [24]. The BTC for synthetic samples corresponds to C/C0= 0.2(2mg/l). As shown in Table 1 were found at 184, 240, and 298min for Al-Z and 410, 570, and 683min for nZVI-Z with bed mass of 5, 7, and 10 g, respectively. The BTC for natural sample water corresponds to C/C0=0.2 (2mg/l), and they were found at 54, 72, and 171 min for Al-Z, and 181, 255, and 385 min for nZVI-Z with bed mass of 5,7, and 10g, respectively. Regarding the results of Table 2, the efficiency of removing fluoride in the nanoparticle-modified zeolite is considerably higher than that of aluminium. Regarding the structure of zeolite clinoptilolite surface modification with nanoparticles produces more active surface than aluminium to absorb fluoride that it increases the removal efficiency [27].

The BTC time increased with increasing mass from 5 to 10g by both absorbents. At low bed mass, the fluoride ions do not have sufficient time for diffuse into the surface of the zeolite and see a reduction in BTC time occurs. Increasing bed mass, the retention time of the sample inside the column increased, allowing the F to diffuse mass into the zeolite (Fig. 3).

In this research, a sample of drinking water with a concentration of fluoride 10 mg/L and TDS= 210 mg/l in both forms of zeolite modification were investigated. The maximum adsorption bed mass capacities (Table 3 and Fig. 4) of the bed to the BTC were 0.51 and 1.14mg/g with Al-Z and nZVI-Z, respectively. As shown in Fig. 1 and Table 1, the time to reach the breaking point and the maximum absorption of fluoride has significantly decreased compared to the synthetic sample. Different anionic and cationic water properties in this experimental investigation are illustrated as well. This study shows that anions within natural water have the intervening state in the adsorbent rate of fluoride by zeolite and it occupies part of Al-Z and nZVI-Z sites on the surface of. For using this matter must be taken into account either [27].

Studies showed that the anions reduced the fluoride adsorption in the order, $Po_4^{3-} > So_4^{2-} > NO^{3-}$ [28].

As well as, Liu et al. have also conducted fluoride removal using synthetic siderite which has been found that the presence of Cl- and NO^{3-} had less effect on F-adsorption while PO^{4-} significantly affected F-removal from aqueous solution [29]. In the results examination, it is suggested that bed mass with a large quantity of adsorbent are more worthy of being fawoured in order to produce optmal results during the adsorption process.

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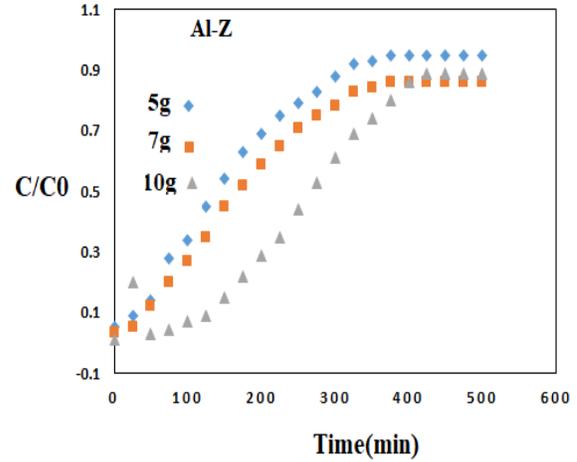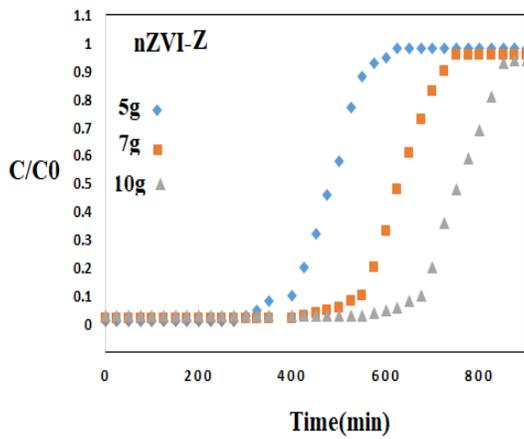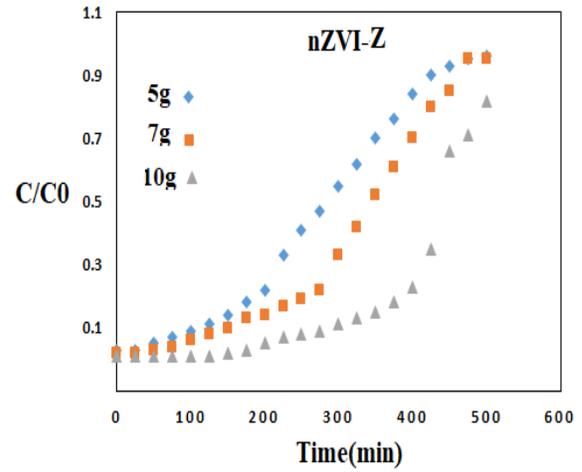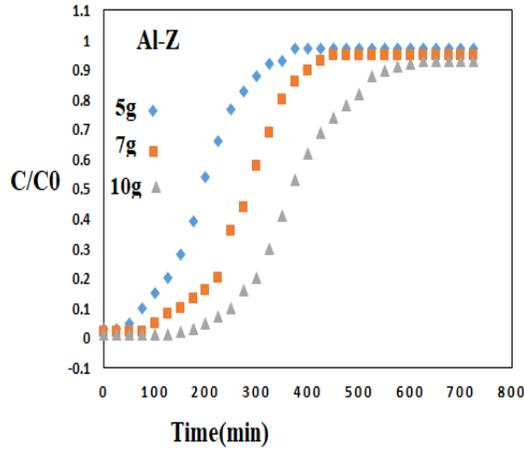
Fig. 3: Breakthrough curves with Al-Z and nZVI-Z synthetic samples at different mass

Fig. 4: Breakthrough curves with nZVI-Z and Al-Z natural samples at different mass

Table 1: The BTC curves and adsorption capacity for Z-nZVI and Z-Al^{+3}

		synthetic sample				*natural sample (Drinking water)*			
	M(g)	BTC(min)	Qb (mg/g)	TDS	R^2	BTC (min)	qb (mg/g)	TDS	R^2
Z-Al^{3+}	5	١٨٤	1.14	12	0.9891	54	0.35	211	0.9878
	7	٢٤0	1.01	12	0.9821	72	0.33	211	0.9972
	10	٢98	0.9	12	09592	171	0.51	211	0.9898
Z-nZVI	5	410	2.46	13	0.9797	181	1.08	211	0.9764
	7	57١	2.34	13	0.9876	265	1.12	211	0.9865
	10	68٣	2.04	13	0.9654	382	1.14	211	0.9976

Table 2: The Langmuir and Freundlich coefficients for Z-nZVI and Z-Al^{+3}

		Langmuir model			*Freundlich model*		
		b	q_{mox}	R^2	K_f	n	R^2
synthetic sample	**Z-Al**	0.33	5.2	0.9892	2.45	4.22	0.9783
	Z-nZVI	1.65	16.9	0.9776	7.63	2.33	0.98873
natural sample	**Z-Al**	0.13	1.9	0.9551	0.88	6.9	0.9776
	Z-nZVI	0.63	8.7	0.9431	2.8	8.9	0.9878

Table 3: Fix bed column of various Adsorption Capacities of Selected

Adsorbent	Q(mL/min)	C_o (mg/L)	q_b(mg/g)	Reference
Al-Z	3	10	1.14	This study
nZVI-Z	3	10	2.46	This study
Kanuma mud	7	20	0.57	Chen *et al.* [36]
Al-Iron oxides	1	4	0.509	García-Sánchez [37]
Red mud	2	4.7	1.274	Tor [38]
Hydrous ferric oxide	0.042	10	1.01	Nur[39]
H3A2h	1	10	1.39	Teutli-Sequeira [40]
Z3A3h	1	10	2.44	Teutli-Sequeira [40]

Absorption Equations

The results of the determination of the Langmuir and Freundlich coefficients and equations models were shown in Table 2.

The maximum absorption capacity for synthetic samples of the nZVI-Z was in 15.1mg/g and for natural samples of the Al-Z was in 8.7mg/g, while maximum absorption capacity of the Al-Z was in 1.9mg/g and the correlation coefficient (R^2), the Freundlich model is much better in description of adsorption isotherm data with a higher R^2 than Langmuir model. In previous research, the capacity found in a batch system and Langmuir isotherm was 1.15 for Z_3A3h, this action is reasonable since the adsorption in columns is not at equilibrium [30].

Comparing the coefficients of linear equations adsorption isotherm, Langmuir isotherm for both absorbent forms provides a better correlation to the data. Other research has reached similar conclusions for the removal of fluoride. For example, studies that use hydroxyapatite, brushite, zirconium-iron oxide and high alumina content bauxite as absorbent, fined similar results [31-33]. The successful design of a bed column fluoride sorption process requires a description of the dynamic actions of fluoride in a fixed bed. Many simple mathematical models had been developed to define and possibly predict the dynamic actions of the solute in column performance [34]. Batch adsorption research provides data on sorption equilibrium characteristics and adsorption kinetics. Nevertheless, batch processes were not economical in practical, and data on fixed bed column operations were essential for industrial absorber design [35]. Column tests were conducted to understand the sorption actions in fixed bed columns. The BTC point was considered when the F concentration in the drinking water reached 1.5 mg/l, according to the World Health Organization (WHO 2011) guidelines [24].

In Table 3, the comparison of the fluoride removal rate with fixed column methods has been presented by various researchers. nZVI-Z and Al-Z show the highest adsorption capacities for fluoride ions in comparison to many other adsorbents reported in the study; it displays its potential as adsorbents for fluoride removal from aqueous solution under continuous operation.

CONCLUSIONS

In this study with using fixed-bed adsorption method modified zeolite clinoptilolite fluoride of water was removal effectively. Parameters investigated in this study showed that with increasing accordingly. Used in this study are found in most region of and also can be obtained easily and is beneficial economically. The other advantage of this method is that it is modified easily as it is shown in this study and in general it can be said that using this sorbent in fixed-bed filter is an appropriate and economical method for removing fluoride from groundwater, whoever there are some in using because of intervening effects of anions in natural water and more is need to be done for study it.

ETHICAL ISSUES

Ethical issues have been observed by authors.

CONLICT OF INTERESTS

The author(s) declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

Authors Contribute to this study as following items: ayat rahmani: study of design and execute the study, Kurosh rahmani: study Supervisor and reviewing the manuscript. Hasan rahmani: Study Advisor, Khalilolla Moeinian: Study Advisor, and Mansour Sarafraz: statistical analysis.

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