Adsorption of fluoride from water by Al³⁺ and Fe³⁺ pretreated natural Iranian zeolites

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ABSTRACT: Besides human dental and skeletal fluorosis, drinking water above permissible levels of fluoride is known to cause a wide range of adverse health effects. In this study, the adsorption of Fluoride from aqueous solution onto pretreated zeolite has been studied by using batch test. The large surface area of natural zeolite (i. e., clinoptilolite from Miyaneh region, Iran) was utilized to create active sites for fluoride sorption by exchanging Na⁺-bound zeolite with Fe³⁺ and Al³⁺ ions. In this study, the effects of variables such as contact time, and Fluoride concentration have been investigated. Since the chemistry quality of groundwater varies from point to point, the effects of pH and electrolytes such as bicarbonate, chloride and sulfate on fluoride uptake are studied too. The performances of the Fluoride adsorption with the natural zeolite (i. e., non modified zeolite) were compared with the pretreated zeolite. Factors from the solution chemistry that affected fluoride removal from water were the solution pH and bicarbonate content. Acidic pH was the better condition for fluoride adsorption and the bicarbonate content cause higher pH values and thus diminished the affinity of the adsorption sites for fluoride. Comparing natural and deionized water with each other it was observed that the existence of onions in natural samples has an intervening effect on absorption rate of fluoride. In overall, among the aforementioned Pretreated Zeolites (i. e., Al³⁺ and Fe³⁺ -modified zeolites), Al³⁺ was particularly found to create adsorption media with high capacity and specificity for fluoride.

Key words: Fluoride; Adsorption; Solution chemistry; Al³⁺ and Fe³⁺; Modified zeolite

INTRODUCTION

Fluorides are released into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes and in marine aerosols (WHO, 2002; Ahmad *et al.,* 2010; Zvinowanda *et al.,* 2009). Fluorides are also released into the environment via coal combustion and process waters and waste from various industrial processes, including steel manufacture, primary aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production and use, glass, brick and ceramic manufacturing and glue and adhesive production (WHO, 2002; Nouri, 2006; Goyal *et al.,* 2008). The presence of fluoride concentration in drinking water in Iran is one of the most problems of water quality (Dobaradaran *et al.,* 2008a; Rahmani Boldaji *et al.,* 2009; Dobaradaran *et al.,* 2009; Dobaradaran *et al.,* 2008b; Mahvi *et al.,* 2006;

Shams, *et al.,* 2010; Vasanthavigar *et al.,* 2009). Dental and bone florosis are major problem of high concentration fluoride in drinking water. Persons suffering from fluorosis manifest discolored teeth and deformed bones. Besides damaging bones and teeth, excessive intake of fluoride cause a wide range of adverse health effects (Shivarajashankara *et al.,* 2001; Rzeusk *et al.,* 1998; Wu *et al.,* 2006). The United States Public Health Service has established the optimum concentration for fluoride in the water with the range of 0.7 mg/L to 1.2 mg/L while World Health Organization recommendation for fluoride permissible limit is 1.5 mgF/L (CDCP, 2001); WHO, 2008). There are several techniques that have been used for treatment of fluoride-contaminated water. These techniques include: coagulation/precipitation, the use of membranes, ion exchange, electrodialysis and adsorption. Among the aforementioned

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technologies for fluoride removal, activated alumina adsorption is the most effective method. Each of the techniques has advantages and disadvantages that limit its use, in overall; it has some disadvantages, such as low sorption capacity, requirement of acidification pretreatment of the influent and high contact of sulfate in treated water (Onyango, 2004). Recently modified zeolite with Trivalent metals (i. e., Al^{3+}, Fe^{3+} and Le^{3+}) and divalent metals (i. e., Ca^{2+} and Mg^{2+}) have been used to adsorb arsenic from polluted water and they show good affinity for fluoride (Shen *et al.,* 2003; Sujana *et al.,* 1998; Onyango *et al.,* 2009). Zeolites are natural minerals characterized by high CEC (Cationic exchange capacity), (Faghihian *et al.,* 1999) and high surface areas (hundreds of m^2/g) and cage-like structures. There are more than 40 different natural zeolites around the world. Clinoptilolite is the most common natural zeolite in the world. Its cage-like structure has the largest cavity dimension measuring 4.4 - 7.2. Angstroms. Zeolites with natural and synthetic origin have high adsorption capability for water pollutants (Faghihian and Kazemian, 2000; Faghihian and Kazemian, 2002**;** Menhaje-Ben, 2004)**.** A lot of work has been done geared toward adsorption of different pollutants from drinking water and wastewater by zeolite (Malherbe *et al.,* 1995; Shahtaheri *et al.,* 2004a; Shahtaheri *et al.,* 2004b; Kazemian *et al.,* 2006a; Kazemian *et al.,* 2006b; Kazemian *et al.,* 2006c; Kazemian *et al.,* 2008). Especially the natural zeolites as molecular sieves with aluminosilicate are more interested because they are very cheap and available. The aim of this study was, therefore, to investigate the fluoride adsorption characteristics of natural zeolite with high active surface area that enhanced its capacity of fluoride removal by exchanging its Na^+-bounds with Al^{3+} and Fe^{3+} ions.

MATERIALS & METHODS

The zeolite used in this investigation was a natural zeolite that was obtained from Miyaneh region (Azarbayjan province, North West of Iran). Chemical composition of the zeolite determined by an Oxford (ED2000) XRF equipments. For mineral identification and characterization of the zeolite sample a shimadzu X-ray diffractometer (XRD; model: XD-5A) was used. The surface morphology and shape of samples were taken by a scanning electron microscopy (SEM) system (model: XL-30, Philips). Total cation exchange capacity (CEC) and the external CEC (ECEC) of Miyaneh zeolite were measured by the Haggerty and Bowman method (Haggerty and Bowman, 1999). All chemicals used in this research (i. e., sodium fluoride, sodium chloride, aluminum sulfate and ferric sulfate) were purchased from Merck company.

Before modification of zeolites, sample was milled & sieved to ranges of 0.21-0.25 mm (ASTM sieve size no. 70 to 60). Then, the zeolite sample was washed out several times with tap water for removing any mud and dust, and then saturated in deionized water for 24 hr for dissolution of salts. Samples were then dried at 250 ºC oven for 24 h to remove any organic materials (Koh and Dixon, 2001). Then For saturation of zeolite adsorption sites with sodium, zeolite sample were shaked in 2M sodium chloride solution by stirring (i. e., 150 rpm) at room temperature for 72 h to saturate the exchange sites with sodium ions (Prikryl and Pabalan, 1999). Since chloride anions may affect modification of zeolites and change its characteristic after filtration, the zeolite rinsed several times with deionized water for removing any remained chloride ions (Li and Kirk, 1999). And to be sure there was no chloride in the modified samples Argentometric tests were used (Ghiaci , 2004). Then samples were dried in ambient air for 48 h.

For preparation of surface-tailored zeolite with aluminum sulfate ($Al_2(So4)_3$. $14H_2O$) and ferric sulfate ($Fe_2(So_4)_3$), 50 g clinoptilolite zeolite was poured into a 1000ml of 0.075M aluminum sulfate or ferric sulfate solution. The mixtures were intermittently agitated for 48 h at 150rpm shaker and then washed several times using demineralised water to decrease the electrical conductivity. Finally, the modified zeolite was dried in ambient air for 48 h.

After Converting zeoliye to its cationic form with NaCl solution and pouring cationic zeolite into metal salt solution, the Na^+-bound zeolite is exchanging with Al^{3+} or Fe^{3+} from aqueous solution and form trivalent exchanged zeolite. The reaction of exchanging trivalent ions such as Al^{3+} and Fe^{3+} (Ionic radius of Fe^{3+} and Al^{3+} is 0.64 Å and 0.51 Å respectively) with Na^+ ions of clinoptilolite zeolite (pore size 7 Å, silica/alumina ratio 4.72) can theoretically be written (Reddy and Sarma, 1999) as:

Al^{3+} or Fe^{3+} (solution) + $3Na^+$ (zeolite) $\rightarrow$ Al^{3+} or Fe^{3+} (zeolite) + $3Na^+$ (solution)
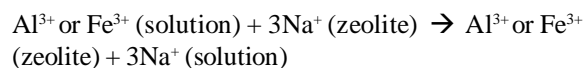
Fluoride concentration were prepared from sodium fluoride in the range of 0.5- 4 mg/L. fluoride ion concentration were measured by standard SPADNS method was used with a DR/5000s Spectrophotometer (HACH Company, USA).

Batch method studies were performed using an initial fluoride concentration of 5 mg/L and 2 g/l of adsorbants (i. e., Al^{3+} and Fe^{3+}-modified and raw zeolite) in 50 ml plastic bottles. The bottles were agitated on a reciprocating shaker at 150 rpm for period of 24 h.

For determining the contact time effect on adsorption, 5 mg/L of Initial fluoride concentration was mixed with 2 g/L of adsorbents (i. e., Al^{3+} and Fe^{3+} - modified and raw zeolite) for periods of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 h at 150 rpm.

Since the chemistry quality of groundwater varies from point to point, drinking waters obtained from groundwater resource have a different pH and ions concentration which in turn can influence the fluoride adsorption process. In order to determination the effects of solution pH on adsorption efficiency; fluoride adsorption was examined by adding different amounts of 0.1 M hydrochloric acid and 0.1M sodium hydroxide to obtain different pH (i. e., 4, 5, 6, 7, 8, 9 and 10). In the study of the effect of pH and ions, 2 g/l of exchanged zeolites were poured in a 50ml solution of 5 mg /l fluoride, and then bottles were agitated on a reciprocating shaker at 150 rpm for periods of 24 h. Operation and performance of flouride adsorption is generally reported in terms of removal efficiency:

Removal Efficiency $= RE = (C_{in} - C_{out}) / C_{in} \times 100\%$

RESULTS & DISCUSSION

In order to characterize the Miyaneh zeolite, X-ray fluorescence method (XRF) was used. The obtained result from chemical analysis of the sample are shown in Table 1 The results of the structural characterization tests showed that this mineral sample was mostly composed of clinoptilolite (over 70%) and some impurities such as clays (smectite), feldspar and quartz (Stankovic and Kazemian, 2000; Orabian et al., 2010). For zeolite used in this study (Miyaneh clinoptilolite), CEC and ECEC values were 3.58 Meq/g, and 0.8462 Meq/g respectively. The X-ray diffraction pattern was also obtained and its results (d-spacing and I/I0 values) are presented in Table 2 Results show the fact that main lines have appeared in relatively high intensity and similar d-spaces. The lines in 8.98, 3.96, and 2.79 with relative intensity of higher than 40% have been observed in test samples and reference clinoptilolites, which can be concluded that clinoptilolite is the major component of zeolite used in this study. The SEM image of the Miyaneh zeolite sample is illustrated in Fig. 1.

Primary Fluorides Adsorption Tests that examined in a 50 ml plastic bottles with adsorbents (i. e., Al^{3+} and Fe^{3+}-modified and raw zeolite) concentration of 2 g/l and 5 mg /l fluoride with contact time of 24 h are summerized in Fig.2. Acording to the results, it was obvious that raw zeolite (I. e., non modified zeolite) with weakly adsorption, was the worst adsorbent. But in comparison, Al^{3+} modified zeolite with nearly 76%

Table 1. Semi quantitative XRF analysis results

SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO	TiO_2	P_2O_5	SrO	LOI*	Total
63.1	12.6	4.03	2.63	1.68	1.67	1.12	0.23	0.19	0.13	12.3	99.68

Table 2. XRD results of Meyaneh zeolites

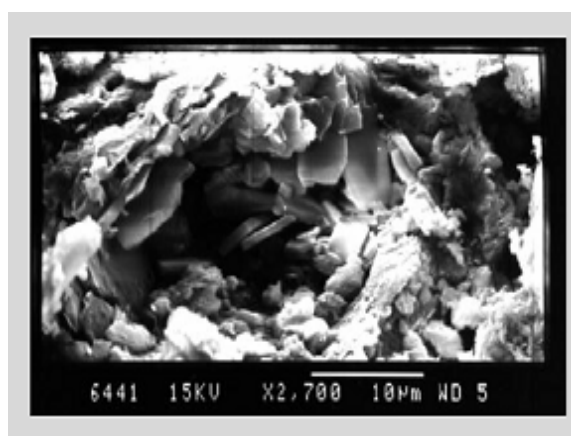| d(A°)	3.96	8.98	3.17	2.97	2.79	3.55	5.11	7.95	5.24	6.73	2.79	2.72
I/I_0	100	52	44	43.5	41.6	24	17.6	16	16.1	12.8	12	10.4

Fig. 1. SEM images of Miyaneh zeolite

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perform the highest adsorption of fluoride and Fe^{3+} modified zeolite whit 65% adsorption was the next highest adsorbent.

For assessment of contact time effect on fluoride adsorbtion, periods of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 h were investigated. as illustrated in Fig. 3 it was obvious that approximately 20h is enough to reach equilibrium conditions for fluoride adsorbtion.

For determining the effect of fluoride concentration on its adsorption, mixture of fluoride solution and adsorbrnts (i. e., $Al^{3+}$and Fe^{3+}-modified and raw zeolite) were shaked for 24 h at 150 rpm with the fluoride initial concentrations from 2 to 20 mg/L. The results are presented at Fig. 4. As expected, with increasing of fluoride concentration, the adsorption potential will decrease. Again the Al^{3+} modified zeolite was the best adsorbant for fluoride adsorbtion.
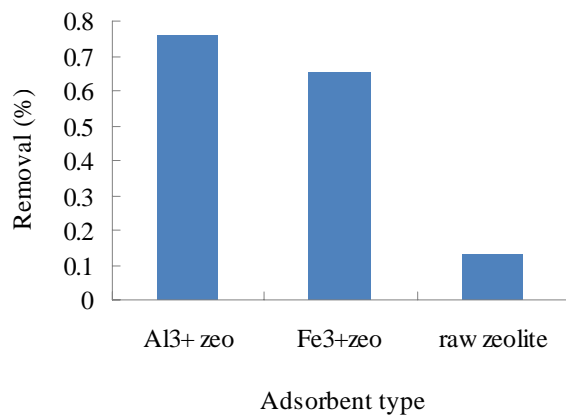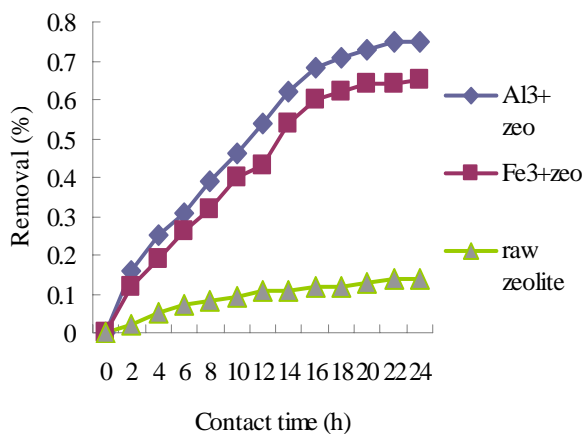
Effect of solution pH value and electrolytes such as bicarbonate, chloride and sulfate on fluoride uptake was studied. Experiments were carried out by taking 50 ml of fluoride-ions-spiked aqueous solution of initial concentration 5 mg/L fluoride and adsorbents (i. e., $Al^{3+}$and Fe^{3+}-modified and raw zeolite) dose of 2 g/l. In this study, the pH values were varied from 4 to 10 while the effects of ions were studied with neutral pH. The investigation was limited to allowable ranges of the concentration of electrolytes in drinking water. The impact of pH is illustrated in Fig. 5 and the impact of bicarbonate, chloride and sulfate concentrations on fluoride adsorption are presented in Fig. 6.

Natural samples used in this study obtained of supply groundwater in the Dashtestan area of the Bushehr Province in Iran. The method of sampling was clusture. Anionic and cationic Characters of these samples showed in Table 3.
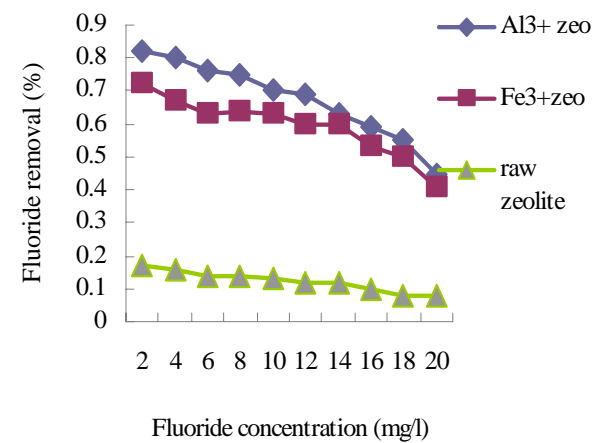

Fig. 2. Fluoride adsorption with different adsorbents

Fig. 4. Effect of fluoride concentration on its adsorption

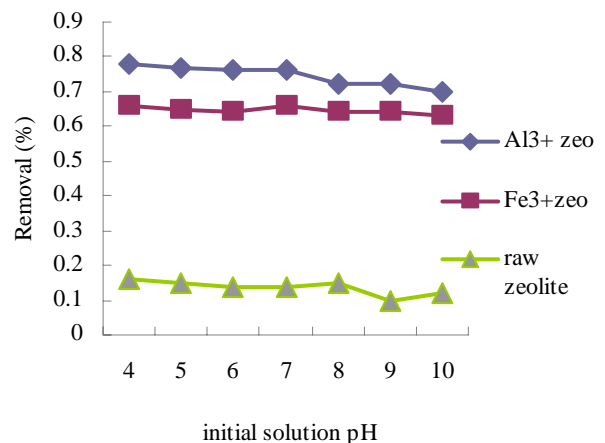**Fig. 3. Effect of contact time on fluoride adsorption**

Fig. 5. Effect of pH on fluoride uptake by raw and modified clinoptilolites

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Fig. 7, 8 depicts three different natural samples water and the deionized water which has been used in this study. Different anionic and cationic water properties in this experimental investigation, is illustrated as well. This study shows that anions within natural water have intervening state in the adsorbent rate of fluoride by zeolite and it occupies part of Al^{+3} and Fe^{+3} sites on the surface of zeolit. For using zeolit this matter must be taken into account either.

CONCLUSION

The XRD and XRF analysis show that Meyane zeolite is mainly composed of clinoptilolite (over 70%) and the CEC and ECEC values of the Meyane zeolite
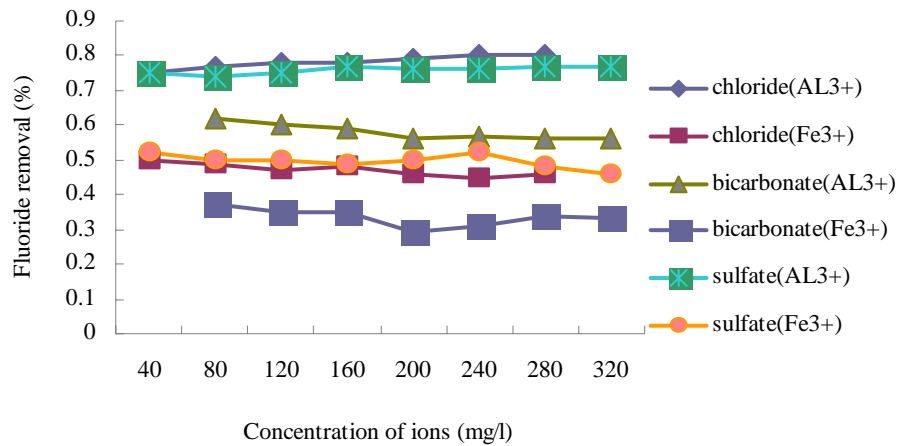

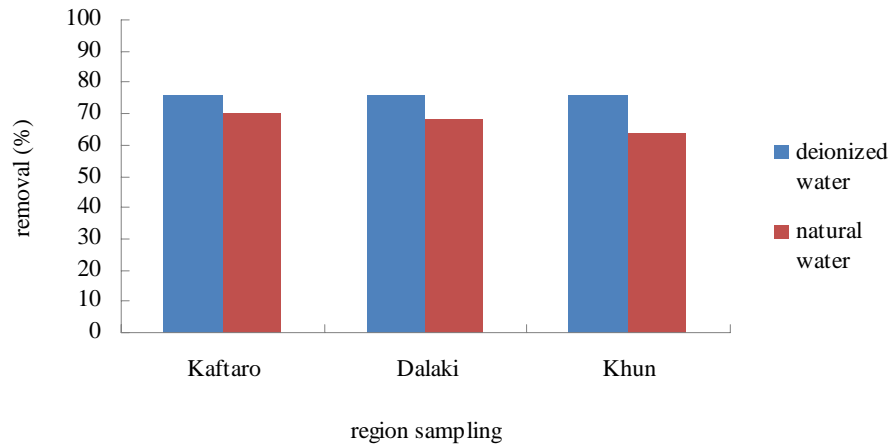**Fig. 6. Effect of ions concentration on fluoride uptake by modified clinoptilolites**

Fig. 7. Fluoride adsorption with different natural water samples by Al³⁺-modified

Table 3. Anionic and cationic characters of these natural water samples

Region	F (mg/L)	SO₄ (mg/L)	Cl (mg/L)	HCO₃ (mg/L)	Ca (mg/L)	Mg (mg/L)	TDS (mg/L)	Alkality (mg/LCa)	pH
Khun	3	101.7	99.8	246.4	101.4	27.4	542	202	8
Kaftaro	2.8	26	19	219.6	52	21.6	269	180	7.7
Dalaki	2.6	25	16	263.5	59.9	29.8	306	216	7.9
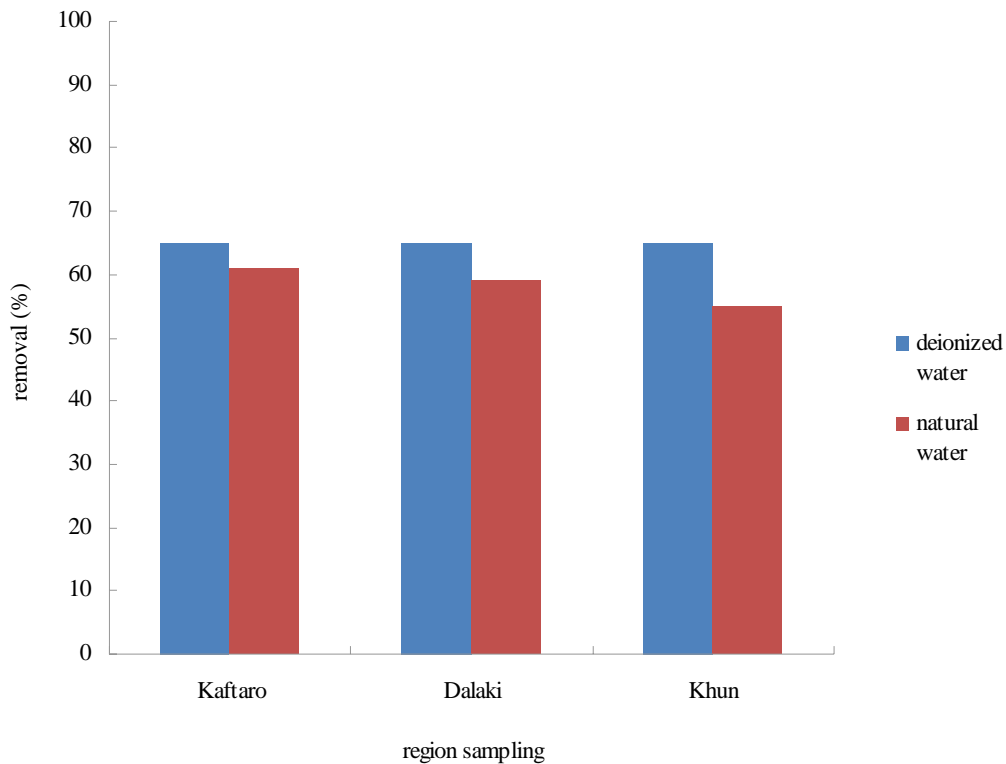
Fig. 8. Fluoride adsorption with different natural water samples by Fe³⁺-modified

exchanged zeolites showed a higher adsorption capacity for fluoride than Fe^{3+}-exchanged zeolites ones and that can be attributed to the chemical characteristic of the two metals. Increasing the contact time and decreasing the initial fluoride concentration resulted in an increase in fluoride adsorption. It can be inferred from Fig.5 that, the pH of the water has no obvious effect on the adsorption of fluoride, although acidic condition was better than other pHs.

The presence of sulfate and chloride in solution generally enhanced fluoride uptake by Al^{3+}-exchanged zeolites, but a decrease in uptake was observed with Fe^{3+}-exchanged zeolite. In contrast, bicarbonate present had large effects when both Al^{3+}-exchanged zeolite and Fe^{3+}-exchanged zeolite were used. Since Bicarbonate is a pH buffering agent, its presence in solution raised pH above neutral values and this led to reduced uptake of fluoride by metal adsorption sites because adsorption capacity is expected to be lower at above acidic pH (deduced from Fig.5). The 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 is an appropriate and economical method for removing fluoride from groundwater, whoever there are some limition in using these absorbant because of intervening effects of anions in natural water and more worke is need to be done for study it.

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