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Efficiency and mechanism of water defluoridation by mixtures of Jordanian Zeolite, Pozzolana, Feldspar, and Tripoli

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ABSTRACT

In this work, removal of fluoride (defluoridation) was investigated using mixtures of Jordanian zeolitic tuff, pozzolana, feldspar, and Tripoli. Triploi was used to increase the silica content of the column material. The flow rate values decrease with decreasing the particle size (from 250+ to 53+). The percentage (%) removal of fluoride ion decreases with increasing the particle size. The size of the powder used in the experiments was <50 µm to ensure the highest removal and to make the comparison acceptable. The correlation between the fluoride removal and the content of SiO_2, Al_2O_3, CaO, MgO, Na_2O, and K_2O were presented and interpreted. The % removal of fluoride ion decreases with increasing the content of silica. Both CaO and MgO have positive influence with correlations of 0.6416 and 0.637, respectively. The relatively high correlation means that there is a significant influence of CaO and MgO contents on the fluoride removal efficiency. While Ca^{2+} and Mg^{2+} ions are converted to insoluble salts, Na^+ and K^+ ions form soluble salts and then can be easily detected in the treated water. Published literature data on fluoride and phosphate ions removal by zeolitic tuff can be re-interpreted in light of our finding. The purpose of this work is to correlate Ca and Mg exchange capability to the removal of fluoride in order to prove that the mechanism of fluoride removal by zeolitic tuff is resulting from Ca and Mg insoluble precipitating salts.

Keywords: Defluoridation; Zeolitic tuff; Adsorption; Ion exchange; Precipitation

1. Introduction

Fluoride ion (or simply fluoride) is a hugely abundant element on Earth which is a naturally occurring compound derived from fluorine [1]. Fluoride is characterized by its small radius and its great tendency to behave as a ligand [2]. Fluoride constitutes a large number of different organic and inorganic compounds in soil, rocks, air, plants and animals. It is found in surface and groundwater as an almost completely dissociated fluoride ion [3], which is usually related to geochemical reactions or anthropogenic activities for example; the disposal of industrial wastewater [4]. The natural amount of fluoride in groundwater depends on the geological, chemical, and physical characteristics of the aquifer, the availability and solubility of fluoride minerals, rate of flowing water, temperature, pH, and concentration of other chemicals like calcium and bicarbonate ions [5]. Many studies reveal that drinking water is the major source of fluoride daily intake [6]. Fluoride is an essential trace element for animals and humans and it makes water hazardous when present in excess. World Health Organization (WHO) has specified the tolerance limit of fluoride content of drinking water at 1.5 mg/L [7]. Excessive fluoride intake

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causes adverse health effects such as crippling skeletal fluorosis that is a significant cause of morbidity in a number of regions of the world. Fluoride is also toxic and its accumulation causes harm of brain/mind development of children [8]. Studies have shown that the exposure to high doses of fluoride leads to Kidney diseases [9].

Defluoridation methods can fall into three categories according to the main removal mechanism; chemical additive, contact precipitation, and adsorption/ion exchange methods [1]. Various methods employed to remove fluoride from water such as coagulation, precipitation, membrane processes, electrolytic treatment, ion-exchange, and adsorption. Adsorption process is commonly used due to its satisfactory results, cost, simplicity of design and operation [4]. In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic and biomass materials such as activated carbons, activated alumina, bauxite, hematite, polymeric resins [1], activated rice husk, brick powder, pumice stone, red soil, charcoal, brick, fly ash, serpentine, seed extracts of *Moringaoleifera*, granular ceramics, chitin, chitosan and alginate, modified ferric oxide/hydroxide, hydroxyapatite (HAP), zirconium and cerium modified materials, titanium-derived adsorbent, schwertmannite, modified cellulose, clays, zeolite and magnesium-modified sorbent [4].

Adsorption of fluoride onto solid absorbent usually occurs through three phases [10]: (1) diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle; (2) adsorption of fluoride ions on to particle surfaces; (3) the adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials. Natural zeolite is a hydrated aluminosilicate material which has a cage-like structure with internal and external surface areas of up to 1000 m^2/g [5]. Most natural zeolites consist of a framework built up of SiO_4 and AlO_4 tetrahedraas.

Natural zeolite was effectively used as adsorbent material due to its advantages over other adsorbent materials; low cost, local availability, requires little processing, and superior in performance as cation exchange resin. Natural zeolite usually has negative surface charges at all pH values, which causing a high adsorption capacities for cations, but low for anions; because of electrostatic repulsions when anions approach the negatively-charged zeolite surface [11]. Numerous studies have been conducted in order to enhance the zeolite surface adsorption capacity [12]. In 1994 Shrivastava and his team were utilized natural zeolite for the removal of fluoride from drinking water [13]. For zeolite modifications, three methods were proposed including skeleton element modification, non-skeleton element modification and surface modification [14]. Na^+-bound zeolite was exchanged with Al^{3+} or La^{3+} ions by Onyango and his team in order to remove the fluoride ion from contaminated ground water. They are concerned with the effect of pH and bicarbonate content on fluoride removal. It was found that removal of fluoride by aluminum-modified zeolite take place with an ion exchange mechanism, while lanthanum-modified zeolite conducted by electrostatic interaction. It was also found that lanthanum-modified zeolite is more effective than aluminum-modified zeolite [15]. Samatya and Yuksel loaded natural zeolite with Al^{3+}, La^{3+}, and ZrO^{2+} and used for the removal of fluoride from water [11].

In 2010, Lu and his team synthesized the modified zeolite NaP1 by a hydrothermal method from coal fly ash and use it to remove fluoride from drinking water. They found the removal uptake of fluoride was increased by increasing the contact time between water and modified zeolite [16]. Zhang et al. reported that the chemical modification of natural zeolite with $CaCl_2$ results in enhancement in its fluoride removal efficiency and removal efficiency was increased from maximal 9.6% for untreated zeolite to 94.3% for calcium chloride modified zeolite (adsorbent dose of 100 g/L, initial fluoride concentration 70 mg/L, contact time 6 h, initial pH = 6.0, temperature 25°C) [17]. Gómez-Hortigüela and his team used naturally-occurring zeolites in Ethiopia (Tigrae region) for the removal of fluoride from drinking water. They found that about 76% of the fluoride was removed from real samples with 9.7 mg/L fluoride content using 100g/L zeolite at pH 8.5 and contact time of 20 h. [18]. Teutli-Sequeira and his team used zeolite from Oaxaca and modified it electrochemically with aluminum [19]. Experiments were conducted using fluoride solutions with different initial concentrations and drinking water containing naturally 8.29 mg of fluoride ions per liter during different contact times ranging from 50 min to 72 h and adsorbent doses ranging from 0.02 g to 0.2 g. Rahmani and his group investigated and compared adsorption capacities of unmodified and modified zeolite from Miyaneh region, Iran. The zeolite in this study was modified with trivalent metal ions (Al^{3+} and Fe^{3+}). Results showed that the untreated zeolite showed very low adsorption efficiency (less than 20% of fluoride was removed) while aluminum- and ferric-modified zeolite showed nearly 76% and 65% of fluoride uptake from solution with initial fluoride concentration of 5 mg/L, while the equilibrium conditions were reached after 20 h. [20]. In a recent study that carried out by Waghmare and his group, it was found a modified form of calcium aluminum zeolite (CAZ) would be significantly used for the removing of fluoride from drinking water without any hazardous effects. This study also includes the effect of dose, contact time, and initial fluoride concentration [21]. In India, batch adsorption studies were carried out in order to remove fluoride from ground water using different low cost adsorbent materials [22].

The purpose of this work is to correlate Ca and Mg exchange capability to the removal of fluoride in order to prove that the mechanism of fluoride removal by zeolitic tuff is resulting from Ca and Mg insoluble salts precipitating.

2. Experimental

Jordan zeolitic stuff (Z), pozzolana (P), feldspar (F) and Tripoli (T) samples were collected from south Jordan (near Tafila except F from near Aqaba). The XRF analysis, from previous studies of our group [23], of the used samples is shown in Table 1.

A column (15-cm height and 3-cm diamater) containing 7-g of the pre-cleaned zeolitic tuff with deionized distilled water (DDW) was used in the defluoridation experiments

Table 1
The chemical analysis of Jordanian zeolite, pozzolana, feldspar and Tripoli [23]

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	TiO_2
Zeolite	48.00	10.80	10.10	8.10	7.70	0.50	1.50	–	–
Pozzolana	40.52	12.62	10.99	13.42	8.38	0.65	2.41	0.06	–
Feldspar	75.52	13.00	0.50	0.24	0.20	5.83	2.44	–	0.03
Tripoli	98.70	–	0.185	0.15	0.18	0.07	0.44	–	–

of previously fluorinated tap water. The water samples were then filtered (125 Blueband paper) and collected in polyethylene bottles and then analyzed for F^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+. The analysis of F^- was performed by ion chromatography (Dionex-100 with an AG4A-SC guard column, AS4SC separating column, an SSR1 anion self-regenerating suppressor and a conductivity meter), and Ca^{2+}+ Mg^{2+} and Na^+ +K^+ were analyzed by EDTA titration and flame photometry method (Jenway PFP7 Flame photometer), respectively. The composition of the column materials was analyzed using ARN 9800 X-ray fluorescence. The XRD was studied using Shimadzu X-Ray Powder Diffraction instrument model XRD-6000. The FTIR spectra were collected using a Unicam (Mattson 5000) spectrophotometer.

3. Results and discussions

Table 2 shows the average flow rate of columns of different sizes of materials used in this study. The flow rate values decrease with decreasing the particle size due to the well-known result; the smaller the size, the higher the compaction and the lower the permeability.

The influence of the particle size, and consequently the influence of flow rate or permeability, on fluoride removal by Jordanian zeolitic tuff is shown in Fig. 1. The % removal of fluoride ion decreases with increasing the particle size. The smaller the particle size the higher the % removal due to the longer time of contact with the particles and hence more enhancement of ion exchange. According to Krishna and Swamy [24], the increase in the uptake of Cr (VI), by smaller particles of calcined bricks, was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. The size of the powder used in the experiments was < 50 µm to ensure the highest removal and to make the comparison acceptable.

Mixtures of Jordanian Tripoli and zeolitic tuff (0 to 100% T/Z) were used in the removal experiments to investigate the influence of exchanging site on the removal efficiency of zeolitic tuff. The % removal of fluoride ion decreases with increasing the content of Tripoli as shown in Fig. 2.

Different mixtures (i.e. from 0 to 100%) of Jordanian Z, P, F and T were used to get different content of SiO_2, Al_2O_3, CaO, MgO, Na_2O, and K_2O. The influence of the different metal oxides contents on the percentage removal of fluoride are drawn in Figs. 3–5. The influences of $SiO_2$and Al_2O_3 on the fluoride removal efficiency are shown in Fig. 3. The SiO_2 content has negative influence while the Al_2O_3 content has positive influence with very small gradient closest to constant removal values. This means that there is negligible influence of SiO_2 and Al_2O_3 contents on the fluoride removal efficiency.

Table 2
The average flow rate of the columns of the different sizes of materials used in this study

Size [µm]	Flow rate [ml/min]
250+	54.8
125	17.6
90	1.2
53+	0.4

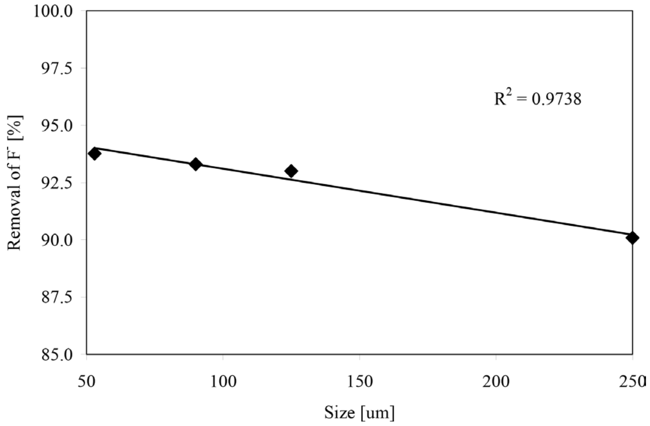

Fig. 1. The influence of particle size distribution on fluoride removal by Jordanian zeolite.

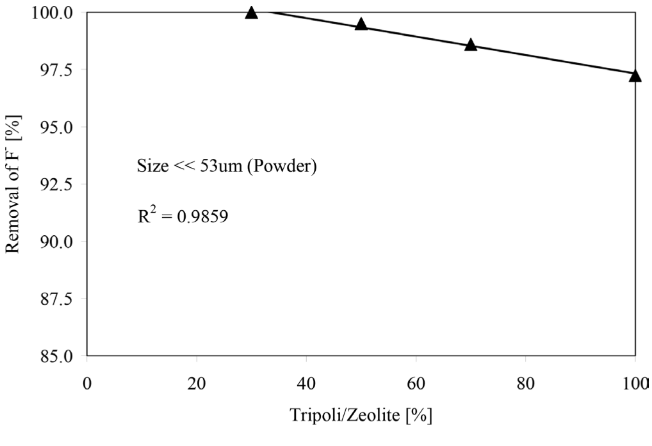

Fig. 2. The influence of the content of Tripoli in T/Z column on the % removal of fluoride ion.

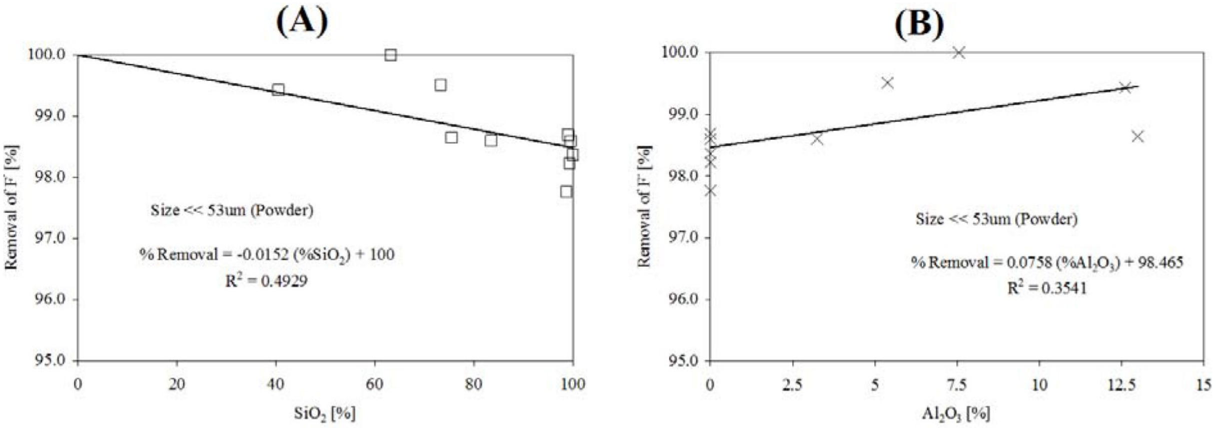

Fig. 3. The influence of SiO_2 and Al_2O_3 contents on the fluoride removal efficiency.

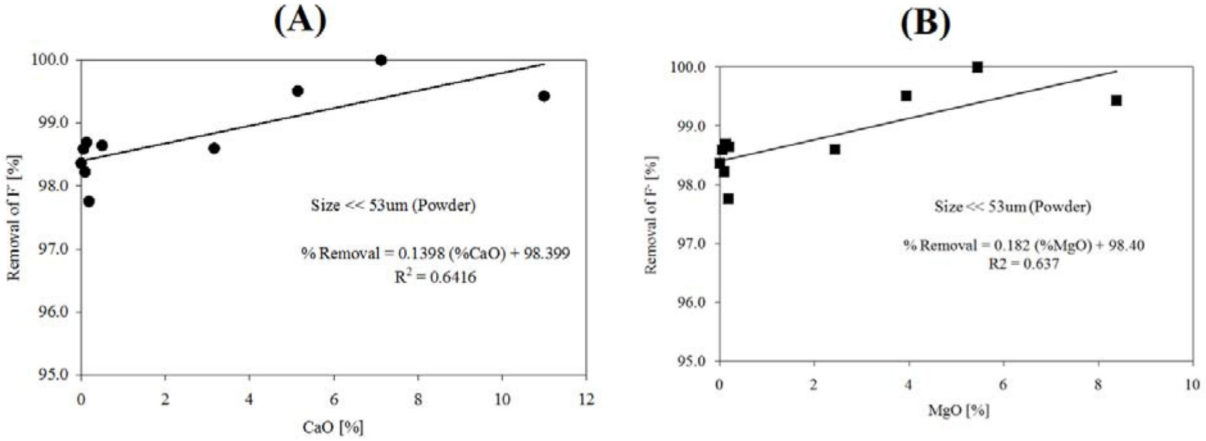

Fig. 4. The influence of (A) CaO and (B) MgO contents on the fluoride removal efficiency.

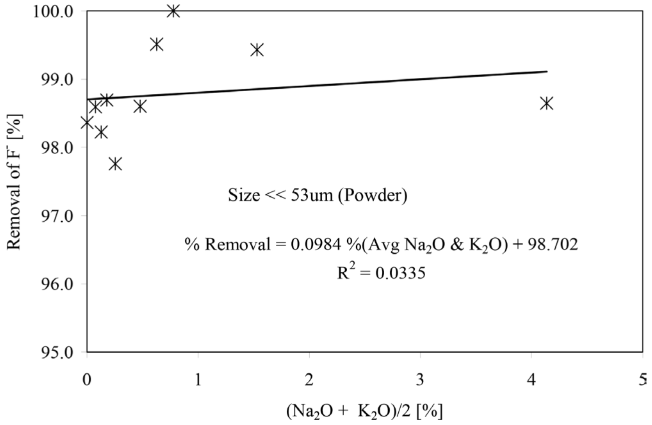

Fig. 5. The influence of Na_2O and K_2O contents on the fluoride removal efficiency.

Table 3
Solubility of the fluoride salts (Mn+F-n) in water

Cation of F- compound	Solubility [g/100mL water]	KSP
Ag^+	179.1 @25°C	–
Na^+	40.4 @20°C	–
Ca^{2+}	0.0016 @20°C	$3.90\cdot10^{-11}$
Mg^{2+}	0.013 @20°C	$5.16\cdot10^{-11}$
Zn^{2+}	1.52 @20°C	–
Al^{3+}	0.67 @20°C	–
Fe^{3+}	49.5 @20°C	–

The influences of CaO and MgO on the fluoride removal efficiency are shown in Fig. 4. Both CaO and MgO have positive influence with higher correlations of 0.6416 and 0.637, respectively. This means that there is a significant influence of CaO and MgO contents on the fluoride removal efficiency. It can be concluded that the removal of the fluoride ion depends on the amount of Ca^{2+} and Mg^{2+} exchanged ions which are then converted to insoluble salts of them (Table **3**). Zeolitic tuff, pozzolana and feldspar contain mixtures of exchangeable Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions.

The influences of Na_2O and K_2O on the fluoride removal efficiency are shown in Fig. 5. The Na_2O and K_2O contents have positive influence with very small slope closest to constant removal values. This means that there is no influence of them on the fluoride removal efficiency. While Ca^{2+} and Mg^{2+} ions are converted to insoluble salts, Na^+ and K^+ ions form soluble salts and then can be easily detected in the treated water.

Because raw zeolitic tuff, pozzolana and feldspar have unknown amounts exchangeable and non-exchangeable ions and to prove the idea of precipitated salts of the exchangeable ions, the materials of the column were exchanged deliberately by eluting a solution of the targeted ion such as: Ag^+, Na^+, Ca^{2+}, Mg^{2+}, and Zn^{2+}, using its soluble salt, to cover different solubility from very soluble (AgF), to moderate (NaF), to slightly soluble (MgF_2 and CaF_2) salts. The percentage removal of fluoride by Ag^+, Na^+, Ca^{2+}, Mg^{2+}, and Zn^{2+} exchanged zeolite, pozzolana and feldspar are shown in Table 4. The fluoride ion removal efficiency is highest with Ca^{2+} and Mg^{2+} exchanged materials while it is the lowest with Ag^+ and Na^+, which followed exactly the solubility trends of the fluoride salts.

The performances of the fluoride removal with Iranian natural zeolite (i. e., non modified zeolite) were compared with the pretreated zeolite by Al^{3+} and Fe^{3+}. The Na^+-zeolite was exchanged with Al^{3+} or Fe^{3+} from aqueous solution. Raw zeolite was the worst efficiency of fluoride removal (~15%), while Al^{3+} modified zeolite, with nearly 76% removal, performs the highest removal and Fe^{3+} modified zeolite, with 65% removal, was the next. The solubility of AlF_3 and FeF_3 are 0.67 and 49.5 g/100 mL of water at 20°C, respectively. The pH value had no obvious effect on the removal of fluoride by zeolite [20]. The efficiency of fluoride removal by Chinese zeolite was 10% of raw Zeolite, 94% of Ca-modified Zeolite and >90 % of Fe-modified Stilbite [25,26].

Similarly, the adsorption capacities of phosphate increased up to 75 times by Fe (III)-modified zeolite more than that of natural zeolite. Chemical reaction between Fe and P to form new products like cacoxenite or complex $KFeH_{14}(PO_4)_8{\cdot}4H_2O$ is the main reason for the increased capacity. Metal ions such as Fe^{3+}, Al^{3+}, Ca^{2+}, and Mg^{2+} are usually chosen to modify the adsorbers – removing phosphate since metallic phosphate salts can be easily precipitated, which changes the adsorption process into an absorption process [27]. The solubility of Fe(III) phosphate is 0.642 g/100 mL at 100°C. The phosphate removal efficiencies by modified zeolite from coal fly ash (CFA) were >90% for low Ca content zeolite, and >98% for moderate and high Ca content, respectively [28]. These results can be re-interpreted in a similar way of fluoride removal; i.e. by forming Ca- and Mg-insoluble phosphates.

Fig. 6 shows two suggested mechanisms for defluoridation by zeolite and similar exchange materials as proposed by Adem et al. [29]. Most probably in some zeolites containing calcium, or any other divalent cation, on a first step some fluoride is adsorbed in the vicinity of the calcium atoms and, then, the remaining fluoride, in a second step, or simultaneously, is exchanged with the OH radicals of the detrital material.

The XRD and FT-IR of the raw and F-loaded zeolite are shown in Figs. 7 and **8**, respectively. It is evident that the removal of fluoride on zeolite has no influence of the XRD and FT-IR of the column materials as it is approved that it is mainly resulted from the prescipitaetion of the insoluble fluoride salts and the exchanged ion. According to [30], X-Ray Diffraction showed that Jordanian zeolitic tuff sample is rich in Phillipsite and Chabazite together with calcite and forsterite. FT-IR spectroscopy shows H-bonded O-H stretching at 3400 cm^{-1}, H_2O bending at 1600 cm^{-1}, 1400 cm^{-1} asymmetric stretching vibrations of the carbonate in the sample, 1000 cm^{-1} strong band due to phillipsite symmet-

Table 4
The percentage removal of fluoride by Ag^+, Na^+, Ca^{2+}, Mg^{2+}, and Zn^{2+} exchanged zeolite, pozzolana and feldspar

% Removal				
Loaded ion	Loading salt	Zeolite	Pozzolana	Feldspar
Ag^+	$AgNO_3$	37	29	45
Na^+	NaCl	58	58	75
Ca^{2+}	CaCl2	95	96	70
Mg^{2+}	$Mg(NO_3)_2$	100	74	80
Zn^{2+}	$(CH_3COO)_2Zn$	84	90	75

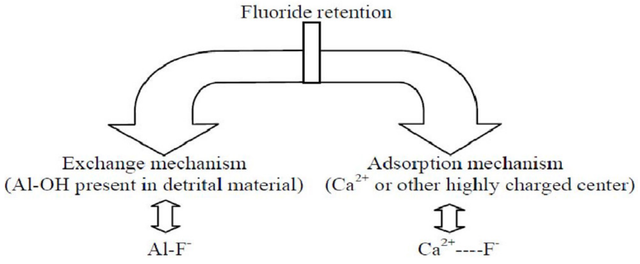

Fig. 6. Suggested mechanisms for fluoride retention in natural zeolites [29].

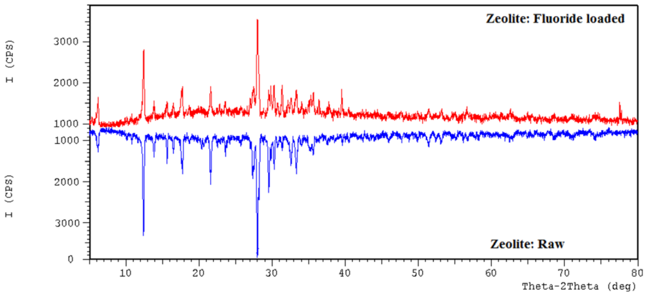

Fig. 7. The XRD of the raw and F-loaded zeolite.

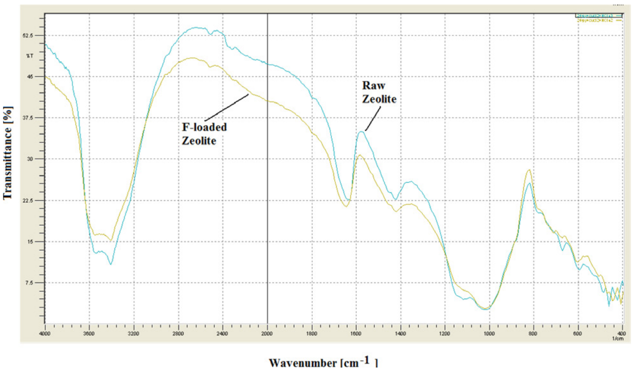

Fig. 8. The FT-IR spectra of the raw and F-loaded zeolite.

ric stretching vibration of silicate group, 600 cm^{-1} symmetric stretching vibration of silicate group for forsterite and 400 cm^{-1} bending vibrations for phillipsite.

4. Conclusion

In sights of the investigation of removal of fluoride using Jordanian zeolitic tuff, it can be concluded that; the percentage removal of fluoride ion decreases with increasing the particle size. The size of <50 µm was the highest. The correlation between the fluoride removal and the content of SiO_2, Al_2O_3, CaO, MgO, Na_2O, and K_2O was as follows: decreases with increasing the content of silica, and both CaO and MgO have high removal efficiency with higher correlations of 0.6416 and 0.637, respectively. It was suggested by some researchers [29] that in some zeolites containing calcium, or any other divalent cation, on a first step some fluoride is adsorbed in the vicinity of the calcium atoms and, then, the remaining fluoride, in a second step, or simultaneously, is exchanged with the OH radicals of the detrital material. Our results suggested that fluoride ions are expected to be converted to insoluble salts in a second step after being adsorbed in the vicinity of the Ca^{2+} and Mg^{2+}, which explains the high removal efficiency by CaF_2 and MgF_2 precipitates. Published literature data on ions removal by zeolite were higher when the zeolitic tuff samples were exchanged by Al^{3+} and Fe^{3+} ions for fluoride removal and Ca^{2+} ions for phosphate removal.

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