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Enhancement effect of phosphate and silicate on water defluoridation by calcined gypsum

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Abstract. Research work on removal of fluoride from water, referred to as water defluoridation, has resulted into the development of a number of technologies over the years but they suffer from either cost or efficiency drawbacks. In this work, enhancement effects of phosphate and silicate on defluoridation of water by low-cost Plaster of Paris (calcined gypsum) were studied. To our knowledge, the influence of silicate on defluoridation was not reported. It was claimed, that the presence of some ions in the treated water samples, was decreasing the fluoride removal since these ions compete the fluoride ions on occupying the available adsorption sites, however, phosphate and silicate ions, from its sodium slats, have enhanced the fluoride % removal, hence, precipitation of calcium-fluoro compounds of these ions can be suggested. Percentage removal of F^- by neat Plaster is 48%, the electrical conductance (EC) curve shows the typical curve of Plaster setting which begins at 20 min and finished at 30 min. The addition of phosphate and silicate ions enhances the removal of fluoride to high extent > 90%. Thermodynamics parameters showed spontaneous fluoride removal by neat Plaster and Plaster-silicate system. The percentage removal with time showed second-order reaction kinetics.

Keywords: water treatment; plaster of Paris; calcined gypsum; adsorption; co-precipitation

1. Introduction

1.1 Defluoridation and literature review

Fluoride in groundwater is mostly of geogenic origin arising from breakdown of rocks containing the fluoride ions. In addition, anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes from industrial entities also contribute to fluoride ions in groundwater. Over the years, fluoride in drinking water above permissible limits has attracted public health interest. At low concentrations fluoride can reduce the risk of dental cavities. Exposure to somewhat higher amounts of fluoride can cause dental fluorosis. When water containing severely higher concentration of fluoride is ingested for a long period of time, changes to bone, a condition known as skeletal fluorosis, may result (Onyango and Matsuda 2006). The

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maximum fluoride level in drinking water set by World Health Organization (WHO) is bellow 1.5 mg/L because excessive intake of fluoride causes dental and skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones, and neurological damage in several cases. The principal source of fluoride in drinking water either in endemic areas with naturally fluoridated drinking water or in non endemic areas where fluoride is added to public drinking water in order to prevent tooth decay (WHO 1993). Research work on removal of fluoride from water, referred to as water defluoridation, has resulted into the development of a number of technologies over the years. Current technologies for defluoridation; such as the use of membrane, ion-exchange, adsorption, coagulation, and electrochemical techniques, suffer from either cost or efficiency drawbacks. Approaches such as ion exchange or membrane-based technologies are not cost effective; other methods such as flocculation and charcoal filtration are less expensive but also less effective. The current best technology involves fluoride adsorption onto activated alumina, however, its adsorption capacity is limited, and its efficiency is affected by the presence of other ions and near neutral pH conditions (Onyango and Matsuda 2006). It is very helpful, to develop a method avoid the drawbacks of the mentioned technologies. It is expected that co-precipitation of F^- by low-cost materials will be a method of choice, especially in the developing countries, because it is relatively cost-effective, easy to use, and can be implemented with less-need of energy.

An extensive list of various adsorbents has been compiled and their adsorption capacities under various conditions (pH, initial fluoride concentration, temperature, contact time, adsorbent surface charge, etc.) for fluoride removal as available in the literature were presented along with highlighting and discussing the key advancement on the preparation of novel fluoride removal adsorbents were presented in a review written by Bhatnagar *et al.* (2011). The various adsorbents have shown good potential for the removal of fluoride. An extensive list of various adsorbents from literature has been compiled and their adsorption capacities under various conditions (pH, initial fluoride concentration, temperature, contact time, adsorbent surface charge, etc.) for fluoride removal as available in the literature have been presented along with highlighting and discussing the key advancement on the preparation of novel adsorbents tested so far for fluoride removal. The review article of Mohapatra *et al.* (2009) was aimed at providing precise information on efforts made by various researchers in the field of water defluoridation. It has been divided into two broad sections; one is dealing with membrane and the other with adsorption techniques.

Positive correlations were observed between concentration of F^- ion retained in the solution with the presence of NO_3^-, Cl^-, CO_3^{2-} and K^+. However, SO_4^{2-}, Ca^{2+}, and PO_4^{3-} correlated negatively with fluoride concentration. Presence of NO_3^-, Cl^-, and K^+ in water reduces capacity of defluoridation with gypsum whereas presence of SO_4^{2-}, Ca^{2+}, and PO_4^{3-} enhances the defluoridation capacity. The negative correlation upon introduction of PO_4^{3-} could be due to the enhanced formation of a precipitate $Ca_5(PO_4)_2(SO_4)F_2$ (Masamba *et al.* 2005). Some researchers (Sundaram *et al.* 2008, Mourabet *et al.* 2011) reported that the presence of HCO_3^- in the water sample lead to significant reduction in defluoridation by adsorption, this is a drawback of the defluoridation on adsorption materials. The results of Gopal and Elango (2007) indicated that addition of Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- on the percentage of fluoride adsorption on Plaster of Paris decreases the amount of fluoride ions removed to a greater extent. This is due to the competition between the anions and fluoride ions for the active sites on the adsorbent.

Sakhare *et al.* (2012) point out that the overall fluoride uptake is a complex phenomenon, involving more than one type of mechanisms/processes. Fluoride adsorption on calcium aluminate is complex process and involves multiple mechanism at low fluoride concentration physical adsorption is dominating while at high fluoride concentration chemisorption/precipitation dominates. Acid enhanced limestone defluoridation of water has been studied in a crushed limestone column reactor using oxalic acid (Nath and Dutta 2012). The researchers have attributed the good fluoride removal to a combination of two mechanisms of fluoride removal; the first is precipitation of calcium fluoride and the second is adsorption of fluoride ions on limestone surfaces. The Ca^{2+} ions, formed due to dissolution of limestone by the acid, precipitate calcium fluoride along with precipitation of calcium oxalate. While the removal by precipitation remained same on repeated use of the same limestone column, the adsorption was more with the fresh limestone and decreased gradually on repeated use of the same limestone column.

Methods of recovery and recycling of phosphate and fluoride ions as hydroxyapatite (HAp) and fluorite, respectively, have been investigated by seeded reaction crystallization to determine the optimum conditions like supersaturation, temperature, pH, impurities, and kind of solvents (Shimizu and Hirasawa 2012). Growing needs the recovery of resources and the steep increase in the price of resources will promote the ion recovery by crystallization. As seeds of HAp, Jordan phosphate mineral ores were selected because of having a relatively similar component.

1.2 Problem and purpose of the study

Most groundwaters have low or acceptable concentration of fluoride (< 1.5 mgL^{-1}) in the world. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature, the action of other chemical elements, and the depth of wells. The purpose of the study is to effectively remove the excess of fluoride in drinking water. The enhancement effect of the phosphate and silicate addition will be studied and a suitable mechanism will be presented. Because there is less amount of fluoride in the drinking water in Tafila Technical University, south Jordan, we used the local tap water to prepare a certain concentration of fluoride by the addition of sodium fluoride. Low-cost and highly abundant materials will be used in this work to ensure its sustainability and economically-competitiveness.

The proposed method is expected to fulfill the following criteria:

1. Very high capacity of fluoride removal (> 90%).
2. Reduces fluoride content to WHO standard of max. 1.5 ppm.
3. Effectively remove fluoride ions in the presence of other ions in the feed water
4. Effective in the pH range 6.5-8.5 (No pH adjustment).
5. Cost less than US$ 1 per 1 m^3 of treated water (1 ton of Plaster costs < US$ 50)

Because of the use of natural and low-cost chemicals in this proposed method, it is expected that this approach is cost-effective with respect to the materials process, easy to use, sustainable and need less energy.

2. Experimental

In the proposed approach, two low-cost materials were mixed with the feed water; fluoride ions were removed by precipitation by mixing Plaster of Paris or calcined gypsum (Purchased from Rawabi for Gypsum, a local company located in Tafila) with either sodium phosphate or sodium silicate. Calcined gypsum was noted to introduce Ca^{2+} and SO_4^{2-} in the water because of its solubility (Sajidu *et al.* 2008). Calcined gypsum may act as a source of calcium, to induce the precipitation process and offer the suitable environment and surface for the completion of the precipitation.

In the experimental work, normal drinking water from the supply tanks of Tafila Technical University (TTU) was used to prepare the feed water for the fluoride ion removal process. A certain weight of sodium fluoride salt was dissolved in 7 L of the tap water to prepare a stock solution of about 147 ppm F^- concentration, and then used to prepare the desired fluoride concentration for the removal trials. High purity salts were used. Samples of 100 mL were taken for each precipitation trial. The materials were mixed with this partial-synthetic fluoride-containing water, and the mixture was stirred by magnetic stirrer under ambient conditions or the desired temperature (30, 40, 50 and 60°C), for 15, 30, and 60 minutes. The samples were then filtered (125 Blueband paper) and were taken to the analysis of F^- by ion chromatography (Dionex-100 with an AG4A-SC guard column, AS4SC separating column, an SSR1 anion self-regenerating suppressor and a conductivity meter). The water samples were collected in polyethylene bottles. Electrical conductivity (EC) and pH were measured using ORION model 162 conductivity meter and CG 712 (SCHOTT GERAETE) pH meter, respectively. The solid samples were coated with gold under vacuum before being examined with a LEITZ AMR 1000A Scanning Electron Microscope (SEM). The composition of the gypsum samples was analyzed using ARN 9800 X-ray fluorescence. The FTIR spectra were collected using a Unicam (Mattson 5000) spectrophotometer using KBr disks, 32 scans were made at a resolution of 8 cm^{-1}.

3. Results and discussions

3.1 Influence of materials and time

Fig. 1 shows the change in the electrical conductance (EC) of the removal of fluoride ions from synthetic water by Plaster of Paris in the presence of phosphate and silicate additives. Removal of F^- by neat Plaster is 48%, the curve shows the typical setting curve of Plaster which begins at 20 min and finished at 30 min. The setting time of the Plaster in the same tap water in the absence of fluoride, phosphate and silicate was 10-20 min. The addition of phosphate ions enhances the removal of fluoride by 23% to increase the removal up to 71%. The change in the electrical conductance (EC) in the presence of silicate is different than the case of phosphate. The EC begins to decrease directly at the initial mixing time and stop changing after 15 minutes. The percentage removal reaches 76%, i.e., about 28% higher than the case of neat Plaster. It is higher than the percentage removal by phosphate by about 5%. The typical Plaster setting curve is disturbed by the addition of phosphate and silicate because silicate competes the sulfate ions on binding with calcium ions to form what is expected to be calcium fluoro compounds of phosphate and silicate, and disturbed the precipitation of calcium sulfate dihydrate; i.e., serve as a retarder to the setting of the Plaster. The longer the setting time, the more the calcium ions available, and hence the higher defluoridation the process.

Gypsum material may act as a *sacrifier*, to induce the precipitation process and offer the suitable environment and surface for the completion of the precipitation, and consequently increases sulfate ions in the solution. The product should be subjected to a sulfate removal step to decrease the amount of sulfate in the produced water. Some researchers claimed that the removal mechanism is either by the precipitation of CaF_2 or adsorption on gypsum, but the addition of phosphate or silicate proves that the predominant mechanism is not adsorption because the added

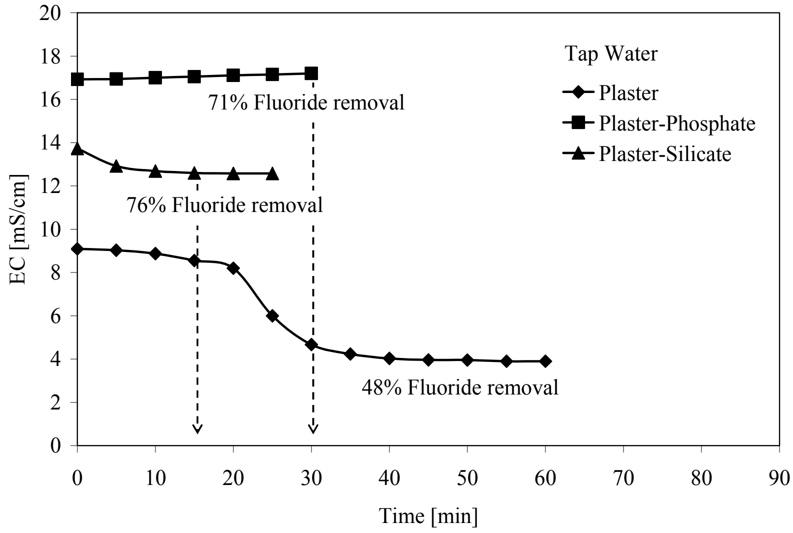

Fig. 1 The change in the electrical conductance (EC) of the removal of fluoride ions from synthetic water by Plaster of Paris in the presence of phosphate and silicate additives

ions should compete the fluoride ions on occupying the adsorption sites on the host material and should, if this is correct, decreases the percentage removal. CaF_2 may precipitate in the case of removal of fluoride by neat Plaster but the maximum efficiency is 48%.

The concentration of fluoride in the effluent of a fluoride removal process, in the presence of Ca^{2+} ions can be expressed according to the following equations (Yang *et al.* 1999)

$$Ca^{2+} + 2F^{-} \rightarrow CaF_2 \tag{1}$$

$$Ksp = [Ca^{2+}] + [F^{-}]^2 = 3.5 \times 10^{-11} \tag{2}$$

Supersaturation of F^- and Ca^{2+} is the necessary condition for precipitation of CaF_2. The supersaturation can be easily achieved at a high initial F^- concentration. So, the performance of a F^- removal process not only depends on the Ca^{2+} doses but also is largely affected by the initial F^- concentration making it difficult to remove fluoride from low initial concentrations.

Mean loading capacities of 3.4 and 0.85 mg F^-/g material were obtained for calcined gypsum and raw gypsum, respectively (Thole 2011, Thole *et al.* 2012). This can be attributed to the differences in solubility of the Plaster and raw gypsum. The available concentration of calcium ions react with fluoride ions to form stable and less soluble precipitate such as calcium fluoride, calcium flurophosphate or calcium fluorosilicate, depending on the available ions in the treated water. This can be evident from the literature data of using calcium-containing materials such as calcium aluminate (Sakhare *et al.* 2012). Total hardness was reduced by defluoridation process from 280 to 120 mg L^{-1} as $CaCO_3$, and calcium ion concentration was reduced from 73.6 to 28.8 mg L^{-1}, respectively. There were no significant changes in chloride, sulfate and nitrate ions concentration which is somehow strange because if the mechanism is adsorption, these ions should be susceptible to be adsorbed on the adsorption sites and compete fluoride ions to a certain extent. Sundaram *et al*. (2008) reported a reduction in hardness from 70 to 0 mg L^{-1} in defluoridation of 2.33 mg L^{-1} fluoride-containing water by hydroxyapatite.

Fig. 2 shows the effect of increasing the amount of Plaster on the percentage removal of fluoride ions in the presence of phosphate and silicate additives. In the Plaster-phosphate system, the removal of fluoride increases with increasing the amount of Plaster. This can be attributed to the fact that calcium ion concentration increases with increasing the amount of Plaster, and hence, increases the available Ca^{2+} to from the precipitate. The percentage removal may reach almost 100% when 15g of Plaster are added to the treated water. The remaining fluoride concentration was 1.47 ppm at 99% removal when an initial concentration of 147 ppm was used. In the Plaster-silicate system, the removal of fluoride increases with increasing the amount of Plaster up to 2:1 ratio (optimum value) and begins to decease thereafter. The percentage removal may reach 80% when 10g of Plaster are added to the treated water. Adding much higher amount (5 g more than the optimum 10 g) of Plaster, increasing the amount of sulfate ions and disturbing the ion balance between sulfate and sodium of the sodium phosphate, which force sulfate ions to withdraw the calcium ions from the fluoride-contain precipitate which leads to *flooding* the fluoride ions again to the water.

The removal of fluoride increases with increasing the amount of phosphate which increases the amount of fluoroapatite precipitate. The removal of fluoride in the Plaster-silicate system shows a maximum percentage removal of 90% at a 1:3 ratio.

The effect of time on the percentage removal of fluoride ions by 5 g of Plaster in the presence of phosphate and silicate is shown in Fig. 3. In the presence of phosphate, the % removal increases with the time up to reaching the end time of the Plaster setting. The results demonstrate that the 5% removal is directly proportional to the contact time, particularly in the first 30 min. The % removal reaches a maximum at 30 min (optimum time) and begins to decrease thereafter.

This implies that equilibrium is established within 30 min. The treated water should be filtered

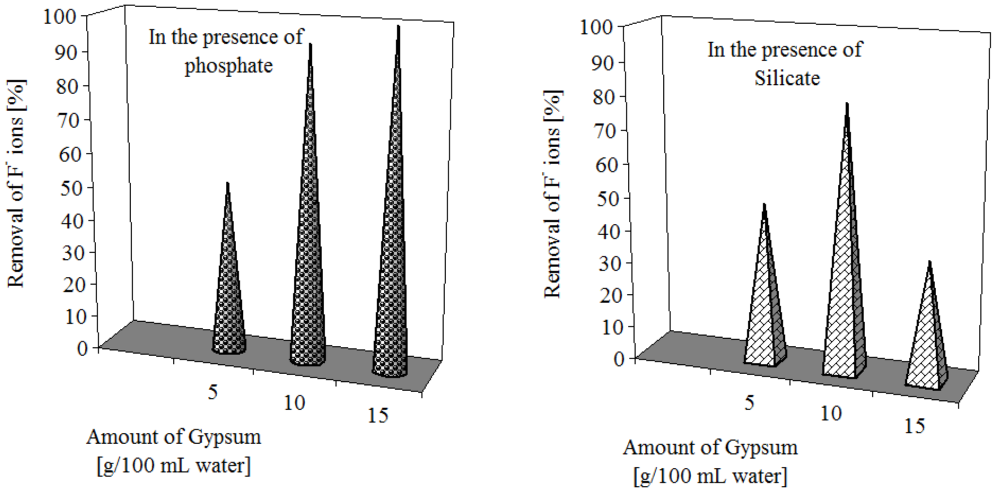

Fig. 2 The effect of the amount of plaster on the percentage removal of fluoride ions in the presence of phosphate and silicate

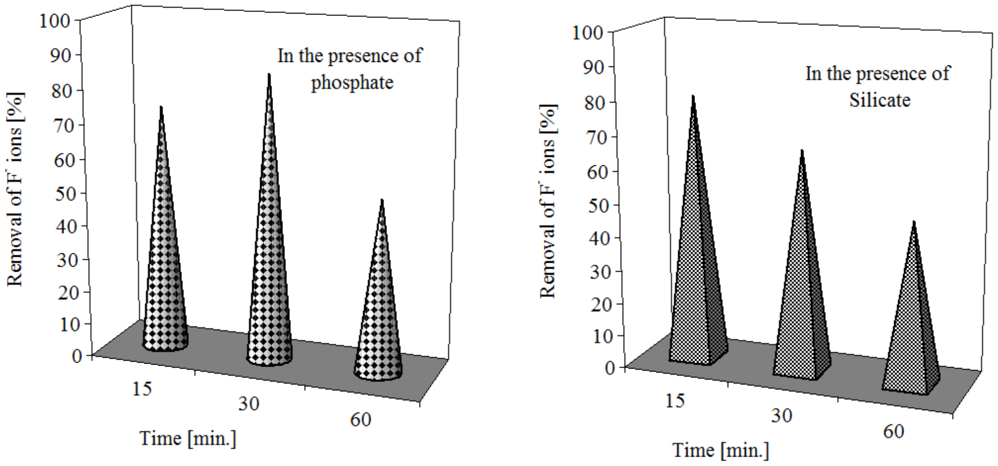

Fig. 3 The effect of time on the percentage removal of fluoride ions by plaster in the presence of phosphate

or sludge should be removed within the time needed to the maximum removal. In the presence of silicate, the removal decreases with the time. The maximum removal is at < 15 min. This implies that equilibrium is established within 15 min. In both cases, the treated water should be filtered or sludge should be removed at maximum 15 min to ensure that the precipitate will not dissociate and give back the fluoride ions to the solution.

The dissociation of the precipitate in both cases, may be exploited in a reverse application to add the fluoride ions to the F-deficient waters and enables the “regeneration” or, in other words, to clean the dihydrate in a preparation step for its “re-calcination”.

3.2 Defluoridation reactions

Gypsum has high content of sulfite species (SO_3). In Thole’s *et al.* (2012) study, gypsum samples were containing 34.96% SO_3, 2.26% Al_2O_3, 28.09% CaO, and 1.02% MgO. SO_3 may react as follows

$$SO_{3(aq)} + H_2O_{(l)} \rightarrow [O_2S(OH)_2]_{(aq)} \tag{3}$$

$$[O_2S(OH)_2]_{(aq)} + H_2O_{(l)} \rightarrow [O_2S(OH)]^-{}_{(aq)} + H_3O^+{}_{(aq)} \tag{4}$$

Such reactions should lower the pH of treated water, but Thole *et al.* (2012) reported the reverse. On contrast, oxides are basic in aqueous medium

$$CaO_{(S)} + H_2O_{(l)} \rightarrow Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \tag{5}$$

$$CaO_{(S)} + H_2O_{(l)} + F^-{}_{(aq)} \rightarrow Ca(OH)F_{(aq)} + OH^-{}_{(aq)} \tag{6}$$

Formation of $Ca(OH)F_{(aq)}$ should not mean the reduction of the F^- content in the treated water, it can be proposed that the formation of Ca(OH)F is a first step that should be followed by taking another F^- to form a precipitate and appropriately explains the reduction of F^-

$$Ca(OH)F_{(aq)} + F^-{}_{(aq)} \rightarrow CaF_{2(S)} + OH^-{}_{(aq)} \tag{7}$$

It is expected that the phosphate and/or silicate may react to occupy the place of OH^- in the Ca(OH)F species to form a less soluble form containing Ca-PO_4-F and/or Ca-SiO_3-F in a mixture with CaF_2 which explains the significant increase in the percentage fluoride removal.

In a study of defluoridation of water using nanostructured hydroxyapatite (HAp), Poinern et al (2011) reported the formation of a mixture containing HAp, fluorapatite [$Ca_5(PO_4)_3F$] and calcium fluoride (CaF_2). The XRD patterns that indicates the formation of distinctive calcium fluoride peaks are at 28.13° (1 1 1), 46.87° (2 2 0) and 55.59° (3 1 1). The presence of fluorapatite is indicated by peaks that are similar to nano-HAp occurring at 28.92° (2 1 0), 31.85° (2 1 1), 39.97° (3 1 0), 43.81° (1 1 3), 56.02° (3 2 2) and 60.11° (4 2 0). These peaks are the result of an ion-exchange mechanism (Sundaram *et al.* 2008) according to the following equation

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^- \tag{8}$$

The uptake of Ca from the Plaster causes solubility of the raw material. This can be inferred from the increase in sulfate ion concentration beyond the standard limits (WHO standard limit of sulfate is 400 mg L^{-1}). The extra sulfate ions could be attributed to dissolution of $CaSO_4$ due to the larger solubility constant of $CaSO_4$ ($6.5\cdot10^{-5}$) than that of CaF_2 ($3.5\cdot10^{-11}$). Sodium ions normally substitute the reduction in the ion balance resulted from the increase of sulfate ions concentration. Sulfate ions should be treated in a next step because its high concentration in potable water is known to cause diarrhea and dehydration (Lenntech). Normally, setting of the Plaster decreases the amount of water and this leads to increase concentration for the non-removed ions. If about half of the treated water is absorbed by the Plaster setting, the concentration of the ions will be doubled.

Calcination of gypsum (production of Plaster) was found to increase the defluoridation efficiency from 0.85 to 3.4 mg F^-/g material (Thole 2011, Thole *et al.* 2012) and this can be explained by the increase in Plaster solubility which offers more calcium ions for the precipitation reaction. In contrast to bauxite (5.18% SO_3, 30.33% Al_2O_3, 0.76% CaO, and 0.56% MgO), calcination of bauxite could mitigate in the treated water through the reduction of disintegration of the media during defluoridation because the removal mechanism is different; it is adsorption on the alumina content of the bauxite. In a different study, Gopal and Elango (2007) noticed interestingly that, in the same range of dosage non-calcined gypsum exhibited in comparison to Plaster, very low fluoride removal capacity. On a 30 g/L dosage, the non-calcined gypsum showed a percentage defluoridation of only about 15% in comparison to about 95% removal by Plaster. The presence of SO_4^{2-}, $PO4^{3-}$ and Ca^{2+} further increased the defluoridation processes; however, due to associated water quality implications of these parameters, they cannot be deliberately introduced in the drinking water unless their concentrations are within the acceptable drinking water standard limits. In their study on defluoridation capacity of hydrotalcite/chitosan composite, Viswanathan and Meenakshi (2010) reported a decrease in fluoride concentration in a filed study from 2.48 to 1.32 mgL^{-1} when the total hardness decreased from 420 to 370 mgL^{-1}. In the seeded reaction crystallization study of fluoride recovery as CaF_2 (Shimizu and Hirasawa 2012), the effect of phosphate and sulfate ions, as impurities exist in the wastewater samples, on the fluoride recovery rate was detected by changing the suitable pH value of recovery; 3.7-5.3 and 7.7-9.6, respectively.

Precipitation reaction should lead to changes in molecular and crystalline structure of the used materials. Hence, the FT-IR spectra of the Plaster before and after removal should be recorded. If the mechanism is adsorption, there should be no significant changes after the adsorption of fluoride ions and suggests that the uptake of fluoride ions by the adsorbent occurs especially by physisorption (Mohan 2001).

3.3 Morphology and FT-IR spectra of the precipitates

The morphology of the dihydrate crystals is the result of the conditions of Plaster hydration (Correia and Souza 2009). Fig. 4 clearly shows the changes of the appearance of dihydrate gypsum crystals. Images of the Plaster exhibited significant variations in crystal size, although they maintained their original needle shape and arrangement. Dihydrate crystals are predominantly needle-shaped with big length–radius ratio interweaves together vertically and horizontally. Studying the formation of bonds between crystals in a solvent, Shchukin *et al*. (1992) found that the probability of forming strong bridges between any two crystals increased as a function of the time of contact, the contact force (pressure), the degree of supersaturation of the surrounding aqueous solution, and the relative orientations (e.g., the edges of contact) of the crystals. Two types of attractive (or “cohesive”) interactions between gypsum in water can be distinguished: (i) very low-energy Van der Waals forces form “coagulation contacts” that cause flocculation of suspensions but agitation can easily break them, and (ii) much stronger “phase contacts”, i.e., irreversible bridges, between the particles, involve intimate contact between the atoms or molecules of the solid phase over an interfacial area consisting of many atoms—equivalent to a “grain boundary” inside a solid. In Fig. 7, it was clearly seen that the shape appearances of dihydrate gypsum crystal changed with the type of the additive (silicate case is shown here). As the type and amount increased, the crystal shape gradually changed from slender needle to flat.

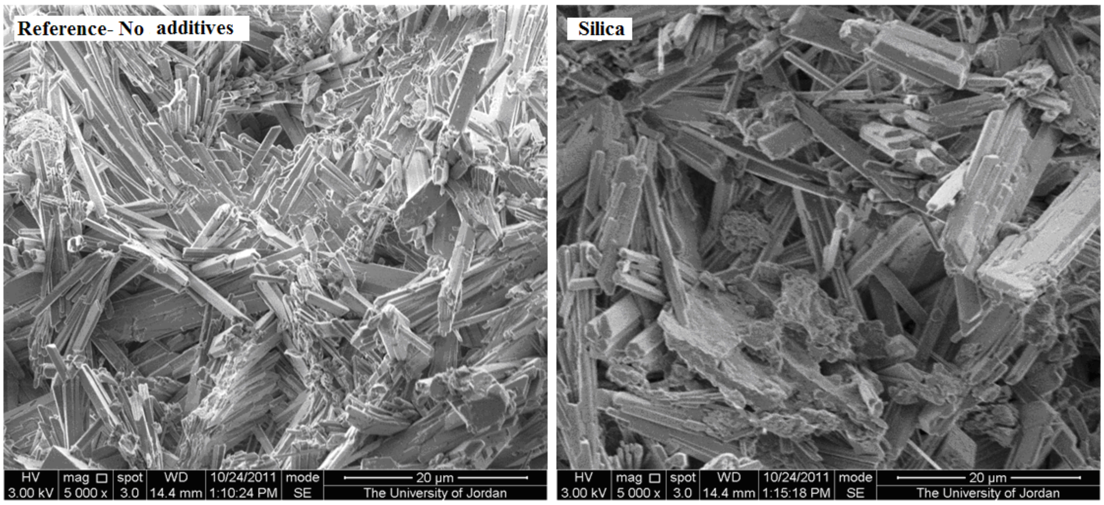

Fig. 4 Influence of silicate on the microstructure (morphology) of dihydrate crystals on the gypsum fractured surface

In a previous study (Al-Rawajfeh 2013), the presence of silica increased the bending breaking from 1.6 MPa of Plaster reference sample to 2.5 MPa. This may be attributed to the growth of small-size fluoro-silicate compound crystals in vicinity of gypsum crystals and consequently closing the pores between the crystals, and hence enforced the structure.

Fig. 5 shows the FT-IR spectra of the precipitates obtained from the defluoridation of water by calcined gypsum. The influences of phosphate and silicate are shown in comparison with a sample of precipitate in the absence of fluoride, phosphate and silicate. The typical gypsum spectrum is shown in the bottom of the figure with bands typical to dihydrate at 1620, 1685 and 3495 to 3542 cm^{-1}. The water of gypsum can be detected by the 1685 cm^{-1} absorption band. The influence of phosphate and silicate is very clear from the changes occurring on the typical bands of

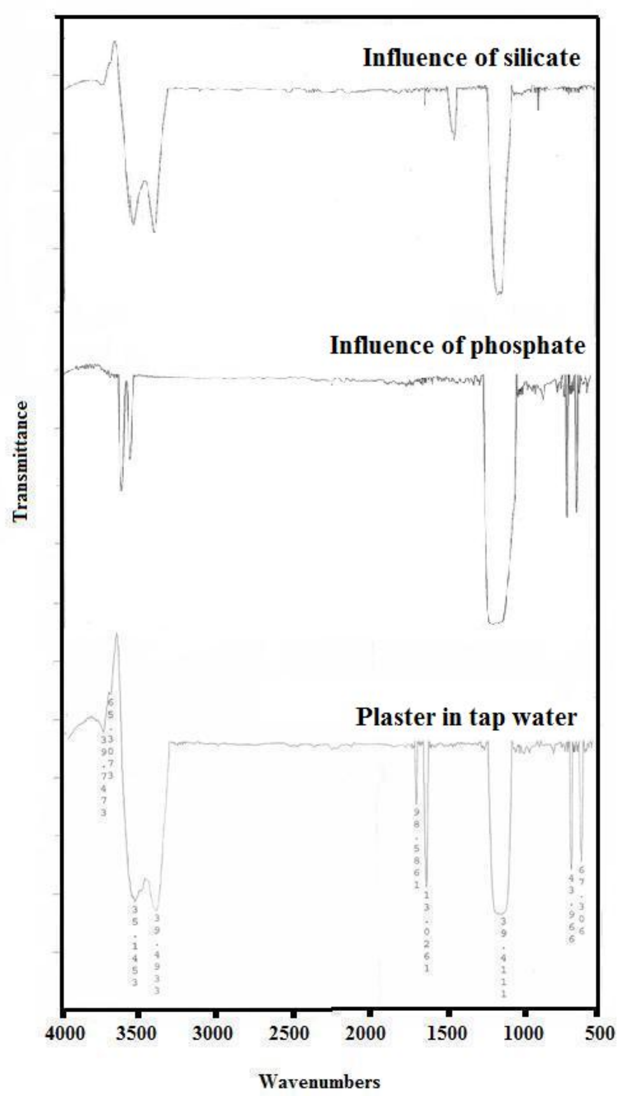

Fig. 5 Influence of phosphate and silicate on the solids precipitated during defluoridation by Plaster

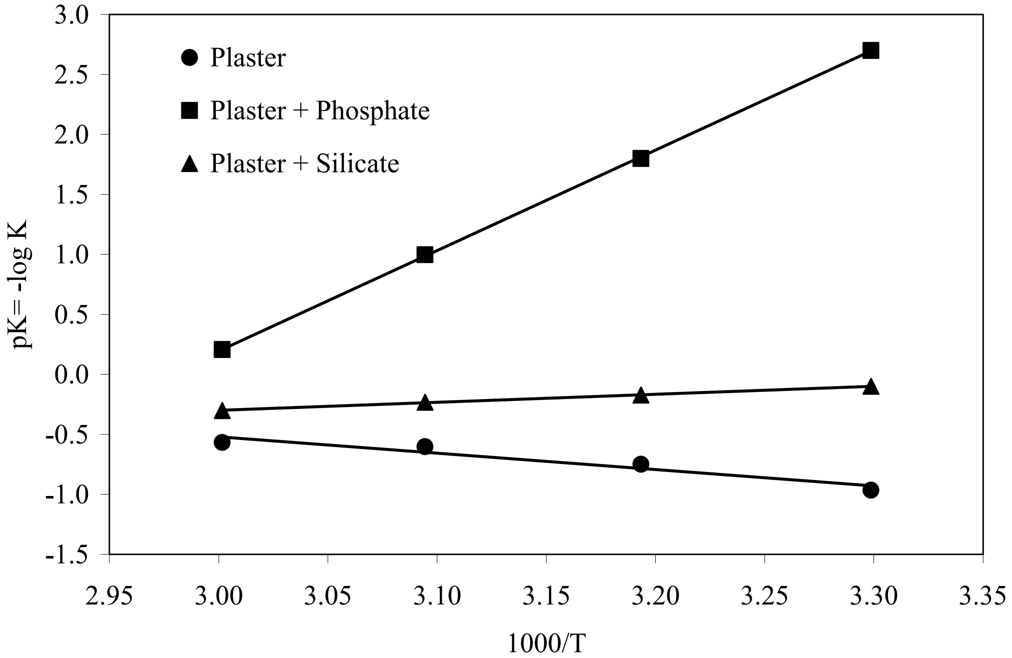

Fig. 6 The linear relation between pK = –log *K* versus 1000/T of the fluoride removal by the neat Plaster, Plaster-phosphate and Plaster-silicate systems

dihydrate. In the phosphate case, the gypsum characteristic bands at 1620 and 1685 cm^{-1} disappeared completely and the 3495-3542 cm^{-1} bands became sharper and shifted to higher frequencies (3555-3610 cm^{-1}), which is the typical region of hemi-hydrate. In the silicate case, new band appeared at 1425cm^{-1} while the 1620 cm^{-1} band became shorter and 1685 cm^{-1} band disappeared. The 3495-3542 cm^{-1} bands became sharper and shifted to lower frequencies (3408-3543 cm^{-1}) and the two bands at 603 and 670 cm^{-1} disappeared. The bands observed at 1685 and 1620 cm^{-1} (bending vibrations) are evidence for the presence of two types of water molecules in the gypsum structure. Vibrations of $v3$ (H_2O) and $v1$ (H_2O) are expected at 3555 and 3408 cm^{-1} (Tomić *et al.* 2010). These changes can be attributed to the retardation of hemi-hydrate setting and to the formation of new compounds other than gypsum.

3.4 Thermodynamics of defluoridation by plaster

The thermodynamic parameters; standard free energy, enthalpy and entropy changes were calculated from the temperature dependence of equilibrium constant, *K*. The standard free energy change (ΔG^0) can be calculated according to

$$\Delta G^o = -RT \ln K \tag{9}$$

where *R* is the universal gas constant and *T* is the temperature in Kelvin.

Table 1 Thermodynamics parameters of the fluoride removal by neat Plaster, Plaster-phosphate and Plaster-silicate systems

Material	Temp. [°C]	K [mol dm^{-3}]	ΔG^0 [kJ mol^{-1}]	ΔH^0 [kJ mol^{-1}]	ΔS^0 [Jmol^{-1} K^{-1}]
Plaster	30	9.2	-5.605	-2.618	-68.579
	40	5.6	-4.494	-	
	50	4.0	-3.725	-	
	60	3.7	-3.617	-	
Plaster + Phosphate	30	0.002	15.672	160.188	476.821
	40	0.016	10.793		
	50	0.100	6.172		
	60	0.621	1.320		
Plaster + Silicate	30	1.2	-0.573	1.286	44.320
	40	1.5	-1.032		
	50	1.7	-1.426		
	60	2.0	-1.920		

Enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using the following equation

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{10}$$

The values of the equilibrium constant (pK = –log K) were plotted versus the reciprocal of the temperature in Kelvin (1/T). Linear plots were obtained for the neat Plaster, Plaster-phosphate and Plaster-silicate systems as shown in Fig. 6.

The negative values (Table 1) of ΔG^0 (-5.6 to -3.6 kJ mol^{-1}) of the neat Plaster system indicate the spontaneity of the removal process, and the spontaneity decreases with temperature while the spontaneity of the Plaster-silicate system increases with temperature from -0.57 to -1.9 kJ mol^{-1}. The positive ΔG^0 (1.3-15.7 kJ mol^{-1}) values of the Plaster-phosphate system indicate that the removal process was non spontaneous. The values of ΔH^0 were -2.168, 160.188, and 1.286 kJ mol^{-1}, for neat Plaster, Plaster-phosphate and Plaster-silicate, respectively. The negative values of enthalpy indicating the exothermic nature of the process while the positive value indicating the change to an endothermic behavior. Further, the magnitude of the enthalpy changes suggested that the possible partial adsorption, if occurs, is a physical process. The ΔS^0 values showed similar trend to the ΔH^0 values. The signs and values of the thermodynamics parameters of defluoridation by neat Plaster were consistent with the study of Gopal and Elango (2007).

3.5 Kinetics of defluoridation by plaster

Kinetics of the fluoride removal by neat Plaster, Plaster-phosphate and Plaster-silicate systems were studied from the analysis of the percentage removal and electrical conductance data. The three systems were found to obey the second-order reaction rate as shown in Fig. 7. The rate equation is of the form

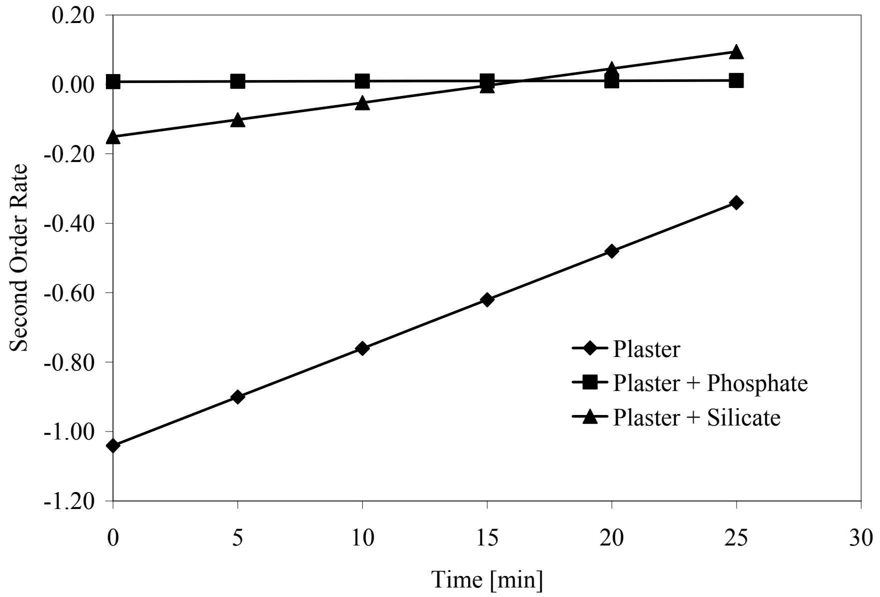

Fig. 7 The linear relation of the second-order reaction rate versus time of the fluoride removal by the neat Plaster, Plaster-phosphate and Plaster-silicate systems

Table 2 Second-order reaction rate constant of the neat Plaster, Plaster-phosphate and Plaster-silicate systems

	k_2 [g mg^{-1} s^{-1}]	R^2
Plaster	0.467	0.999
Plaster + Phosphate	0.00167	0.998
Plaster + Silicate	0.163	0.998

$$\frac{dF}{dt} = -k[F]^2 \tag{11}$$

The reaction rate constants were found to be 0.467, 0.00167, and 0.163 g mg^{-1} s^{-1}, for neat Plaster, Plaster-phosphate and Plaster-silicate systems, respectively. The results are shown in Table 2. The result of the neat Plaster is consistent with the literature as a second-order reaction rate but the value was different (0.0187 g mg^{-1} min^{-1}) as reported by Thole (2011) and Thole *et al.* (2012) for calcined gypsum at 200°C. The difference between the result of this work and Thole's results may be attributed to the difference in the composition and calcination temperature of the Plaster.

4. Conclusions

Percentage removal of F$^-$ by Plaster (calcined gypsum) was increased from about 48%, in neat

Plaster, to 71% and 76% by the addition of 1:1 ratios of Plaster to either phosphate or silicate, respectively. The electrical conductance (EC) curve shows the typical curve of Plaster setting. The addition of phosphate and silicate ions enhances the removal of fluoride to high extent > 90%. The values resulted from the addition of phosphate or silicate proves that the mechanism is not adsorption because the added ions should compete the fluoride ions on occupying the adsorption sites on the host material and should, consequently, decreases the percentage removal. The available concentration of calcium ions react with fluoride ions to form stable and lower soluble precipitate, such as calcium fluoride, calcium flurophosphate or calcium fluorosilicate, depending on the available ions in the treated water. Thermodynamics parameters showed spontaneous fluoride removal by neat Plaster and Plaster-silicate system. The percentage removal with time showed second-order reaction kinetics. It is recommended to continue the research by studying the influence of different organic and inorganic retarders which will be the topic of the coming paper. Natural Jordan phosphate and silicate sources will be used, too.

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