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Removal of fluoride from water using coagulation–flocculation process: a comparative study

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ABSTRACT

The use of safe and easily available coagulants for removing pollutants from water has been recommended. The aluminum sulfate, polyaluminum chloride and ferric chloride extensively have been used for quantitative elimination of fluoride from water. One factorial method has been used for design of experiments and the main variables such as pH of solution, initial fluoride concentration, coagulants dosage and turbidity were optimized. Results showed that the maximum removal of fluoride was 57%, 50% and 53% using alum (pH 4), PACl (pH 4), and Fe^{3+} (pH 8), respectively. The coagulant dosage showed a significant effect on the process using Al^{3+}. The highest removal efficiency (83%) obtained at 30 mg/L of aluminum sulfate. The effect of turbidity on the process using alum was insignificant. Furthermore, the results showed the insignificant effect of initial concentration of fluoride on the process.

Keywords: Fluoride; Coagulation; Water treatment; Pollutant, Turbidity

1. Introduction

Over the past few decades, increasing population, urbanization, industrialization, and improper consumption of water have reduced water quality and reduced per capita water supply in developing countries. The quality of water resources has declined due to various natural or human factors. Agricultural activities in farms and gardens, disposal of hazardous waste on land, unmanaged disposal of industrial waste such as textiles, pharmaceuticals, petrochemicals [1,2], and domestic wastewater are important factors for polluting surface water and soil. They are important contributors to the entry of contaminants into groundwater resources. The most important hazardous pollutants can be arsenic [3], nitrate [4], fluoride [5], ammonium [6], heavy metals [7,8]. The pollution of groundwater by high concentrations of fluoride is one of the worldwide difficulties that cause significant health problems such as thyroid disorder, Alzheimer's syndrome, brain damage, infertility, cancer, brittle bones, arthritis, and osteoporosis [9,10].

Slight quantities of fluoride in drinking water have a positive effect specifically among children [11]. Therefore, World Health Organization recommended the 1.5 mg/L as suitable concentration of fluoride in drinking water [3]. During last decades, researchers have attempted to adjust the concentration of fluoride in drinking water. The most

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applied materials and methods are liming [12], alum sludge [13], activated alumina [14], aluminum-impregnated carbon [15], poly aluminium chloride [16], adsorption onto low-cost materials using kaolinite, bentonite, charfines, lignite and nirmali seeds [17], electrodialysis [18], nano-filtration membrane [19], electrochemical [20], ion exchange [21], and reverse osmosis [22]. Most of these methods have complex procedure, high maintenance and high operational costs [23], but recently the coagulation process has received a lot of attention for the removal of pollutants such as fluoride from water due to the features such as low energy consumption, relatively simple design and easy operation [24]. Zhang et al. [25] applied a membrane coagulation reactor and aluminum sulfate for the removal of fluoride from water. Result showed that optimum pH value was 6–6.7, and by adding sufficient dosage of aluminum sulfate and sodium hydroxide in reactor, the efficiency of system was 75% when the residual aluminum in treated water was no more than 0.05 mg/L [25]. Hu et al. [26] reported that at the molar ratio of hydroxide and fluoride ions to Al (III) ions close to 3 the efficiency of system for fluoride removal was 100%. Gong et al. [27] investigated the effects of aluminum fluoride complexation on the removal of fluoride by Al salts coagulation. Results showed that the optimal pH for total fluoride removal was 7 and the aluminum fluoride complexes are favored at low pH and high fluoride concentration but this condition had negative effect on the fluoride removal [27].

To the best of our knowledge, no single research work exists on comparing fluoride removal with the three coagulants using different operational conditions. Subsequently, the aims of the current study are to evaluate the effects of pH, coagulant dosage, initial turbidity, and initial fluoride concentration in the removal of fluoride using aluminum sulfate (alum), poly aluminium chloride (PACl), and ferric chloride, and to compare the performance of the coagulants.

2. Materials and methods

2.1. Chemical and reagents

All chemical agents used in this research were analytical reagents that have been supplied by Merck, Germany. Stock solutions of fluoride were prepared using NaF with molecular weight of 41.99 g/mol. The sodium hydroxide 1 N and sulfuric acid 1 N were used to adjust pH using pH meter (WTW, Germany).

2.2. Experimental procedure

In order to remove fluoride from water, coagulation and flocculation process were performed in laboratory scale using a jar test (AQUALYTIC, Germany). The jar test was conducted at the three phases; coagulation, flocculation, and sedimentation based on performance program in Table 1. The fresh turbid water at the desired level of pH has been added into all jar beakers and by adding coagulant, rapid mixing was carried out at a speed of 90 rpm for 60s, after that the mixed liquor has been agitated at 30 rpm for 30 min, followed by 30 min settling. Sampling has been carried out after settling at 5 cm under the surface of solution, without any delay the fluoride concentration was measured using spectrophotometer (Jenway 6305, Germany) at a wavelength of 570 nm based on the standard methods for the examination of water and wastewater [28]. All experimental tests were repeated three times, and approved when showed less than 5% difference. The efficiency of the process (R%) was calculated by Eq. (1) [29].

Table 1
Operational conditions for jar test

No.	Parameters		Values
1	Coagulant doses, mg/L		10–50
2	Turbidity, NTU		5–25
3	pH		4–8
4	Fluoride concentration, mg/L		4–20
5	Temperature, °C		25 ± 2
6	Coagulation and	Rapid mixing (90 rpm)	1 min
	flocculation cycle	Slow mixing (30 rpm)	30 min
	time	Settling time (min)	30 min

$$R\% = \frac{A - B}{A} \times 100 \quad (1)$$

where A and B were initial and final F^- concentration.

3. Results and discussion

In this study, aluminum sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$), polyaluminum chloride ($Al_2(OH)_5Cl_{2.6}$), and ferric chloride ($FeC1_3$) were used as the coagulants. The mechanism of fluoride removal is the generation of coagulants–fluoride complexations, which are difficult to dissolve [25]. Based on previous studies, several mechanisms have been reported for the removal of fluoride, precipitation, co-precipitation (occlusion and adsorption) and adsorption. Among them, co-precipitation and adsorption are main mechanisms during coagulation using aluminum salts (Eqs. (2) and (3)) [30,31].

Adsorption on $Al(OH)_3$:

$$Al_n(OH)_{3n(s)} + mF^-_{(aq)} \rightarrow Al_nF_m(OH)_{3n-m(s)} + mOH^-_{(aq)} \quad (2)$$

Co-precipitation:

$$nAl^{3+}_{(aq)} + (3n-m)OH^-_{(aq)} + mF^-_{(aq)} \rightarrow Al_nF_m(OH)_{3n-m(s)} \quad (3)$$

Among different parameters pH, coagulants dosages, initial turbidity, and initial fluoride concentration are important and they have especial effects on the process, which have been discussed at the following sections separately.

3.1. Effect of pH

Fig. 1 plots pH against percentage removal of fluoride in the coagulation process using three types of coagulants. However, the efficiency of process for the removal of fluoride increased at lower and higher pH but the concentration of free fluoride increased at pH ranging 5–7 for PACl. The concentration of fluoride was slightly increased for Al^{3+} and Fe^{3+} in complex with increasing pH. At the pH < 5, the most F^- is in the form of Al F complexes [27]. Fig. 1 confirms the fluoride removal at different pH values. The best pH for drinking water is 7, which at this value as optimum pH, fluoride removal was 50%, 29.5%, and 10% for Fe^{3+}, Al^{3+}, and PACl, respectively. The maximum removal of fluoride by alum obtained at the pH 4 (Fig. 1). Similar results in this case have been reported by Kalantary et al. [32]. They confirmed that the optimum fluoride removal strongly depends on the pH value and the pH 4 was desired when Al^{3+} was used as coagulant [32]. On the contrary, Aoudj et al. [31] indicated that the optimum operating pH was between 6 and 7 for the removal of fluoride when aluminum sulfate was used as coagulant. Dargahi et al. [33] investigated the efficiency of alum as coagulants in the removal of fluoride. In this study, pH varied from 4 to 9, and the results showed that at alum dosage of 300 mg/L and initial fluoride concentration of 3 mg/L, removal efficiency increased with increasing pH from 4 to 6 but from pH 6 to 9 decreased [33]. In the study by Shen et al. [20], the pH was varied from 2 to 9 and the results showed that at the initial concentration of fluoride 15 mg/L, retention time 30 min, NaCl 400 mg/L and charge loading = 4.97 F/m^3 with increasing pH from 2 to 3, the residual F^- concentration decreased from 15 mg/L to approximately 1 mg/L but continued with increasing pH from 3 to 5 and the residual F^- concentration increased to 3 mg/L and then was constant.

3.2. Effects of coagulants dosage

Fig. 2 illustrated the effects of coagulants dosage on the removal of fluoride using three different coagulants; aluminum sulfate, PACl, and ferric chloride. The effects of coagulant concentration at fixed initial fluoride concentration of 2 mg/L, pH 4, and turbidity 40 NTU showed that aluminum cations are more efficient than iron one. The highest fluoride removal observed (83%) compared with the other coagulants and the fluoride removal as almost consistent with the increase of the alum dosages that mean alum dosage does not impact on the performance of fluoride removal. For PACl and ferric chloride, best efficiency was achieved at lower concentration and the increase of ferric ions concentration showed not significant effect, even at high concentrations. A 10% removal of fluoride was recorded for Fe^{3+} concentration of 50 mg/L. The maximum removal of fluoride occurred

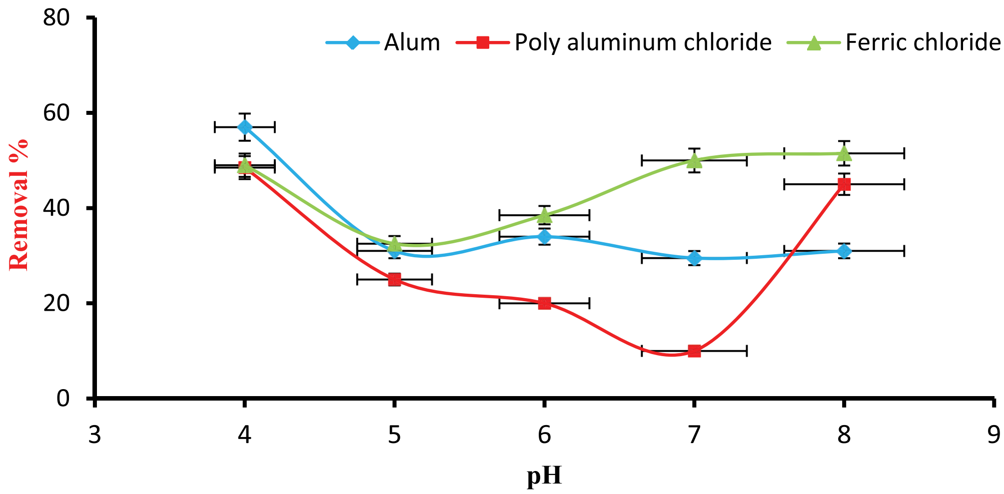

Fig. 1. Fluoride removal at different pH: coagulant dosage (30 mg/L), turbidity (40 NTU), and fluoride concentration (2 mg/L).

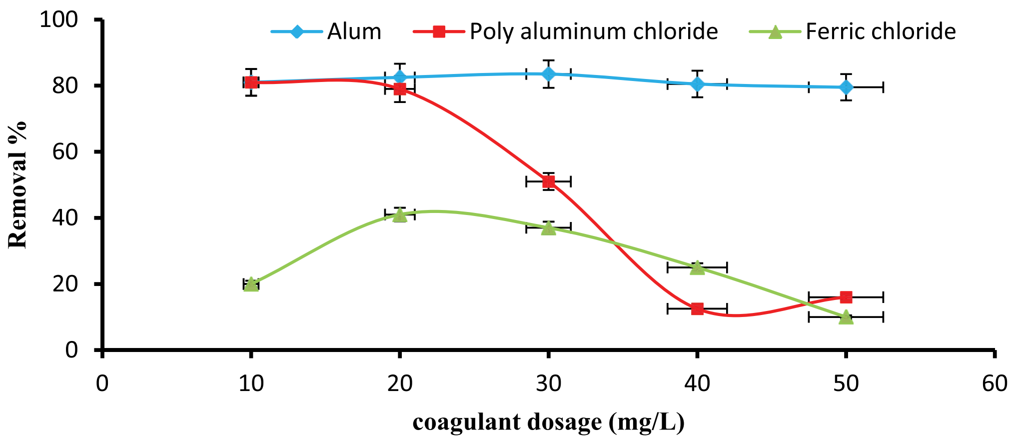

Fig. 2. Fluoride removal at various dosages of coagulants (alum, PACl, and ferric chloride): pH 4, turbidity of 40 NTU and concentration of fluoride equal to 2 mg/L.

when the coagulant dosages were 30, 10, and 20 mg/L and they were 83%, 81%, and 42% for alum, PACl, and ferric chloride, respectively. Tolkou et al. [34] revealed that at initial fluoride concentration 5 mg/L and pH 7.0 ± 0.1, with increasing coagulant dosage (2–50 mg/L), the residual concentration of fluoride decreased. Ghafari et al. [35] investigated the effect of polyaluminum chloride dosage (1–3 g/L) and alum coagulants (8–10 g/L) on the stabilization of leachate. Results showed that with increasing alum dosage, the turbidity removal rate was constant between 90% and 91% but with increasing PACl dosage from 1 to 3 g/L, turbidity removal increased from 40% to 80% [35].

3.3. Effect of turbidity

The effect of turbidity (5–25 NTU) on the fluoride removal using the three coagulants alum, PACl, and ferric chloride is shown in Fig. 3. The results showed that the fluoride removal efficiency increased with increasing turbidity from 5 to 15 NTU for ferric chloride and 5 to 20 NTU for PACl and then decreased. However, the results of simultaneous alum and turbidity showed that with increasing turbidity from 5 to 15 NTU, the removal of fluoride was almost constant at approximately 92% but slightly decreased from turbidity of 15 to 20 NTU. In general Fig. 3 indicated that alum coagulant has highest efficiency than PACl and ferric chloride. The highest fluoride removal occurred when the turbidities were 10, 20, and 15 NTU and it was 90%, 80%, and 30% for alum, PACl, and ferric chloride, respectively. It is clear that alum can handle the variation in turbidity when used as coagulant for fluoride removal. The results of study by Al-Husseini et al. [36] showed that at the pH 6 and alum dosage of 20 mg/L, with increasing initial turbidity the efficiency of turbidity removal decreased. Kumar et al. [37] investigated the effect of turbidity removal from washing machine discharge using *Strychnos potatorum* seeds when initial turbidity was varied from 50 to 145 NTU, results revealed that at 0.6 g/L coagulant dosage and pH 7 with increasing initial turbidity, turbidity removal efficiency increased. Ramavandi [38] indicated that with increasing varied initial turbidity (50–300 NTU), turbidity removal decreased from 99% to 95.6%.

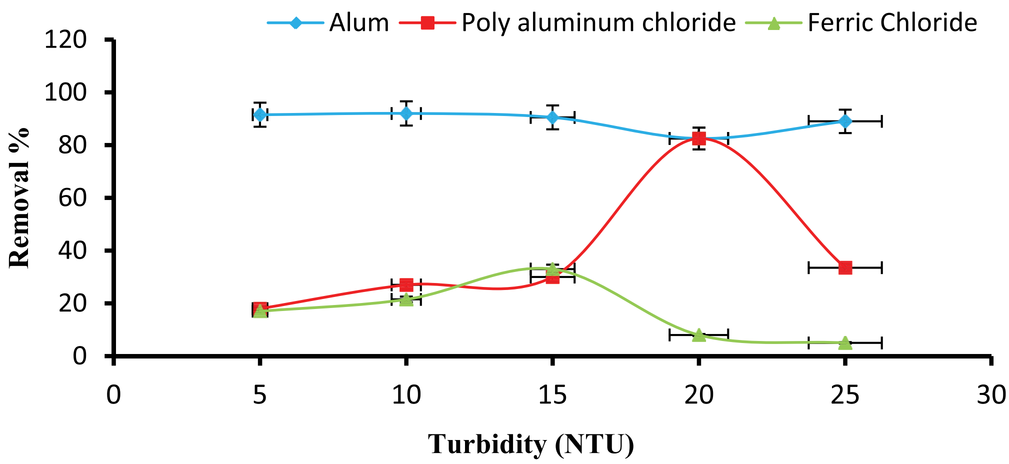

Fig. 3. Fluoride removal at various turbidities: (30 mg/L alum, 10 mg/L PACL at pH 4, 20 mg/L of ferric chloride at pH 8, and 2 mg/L fluoride).

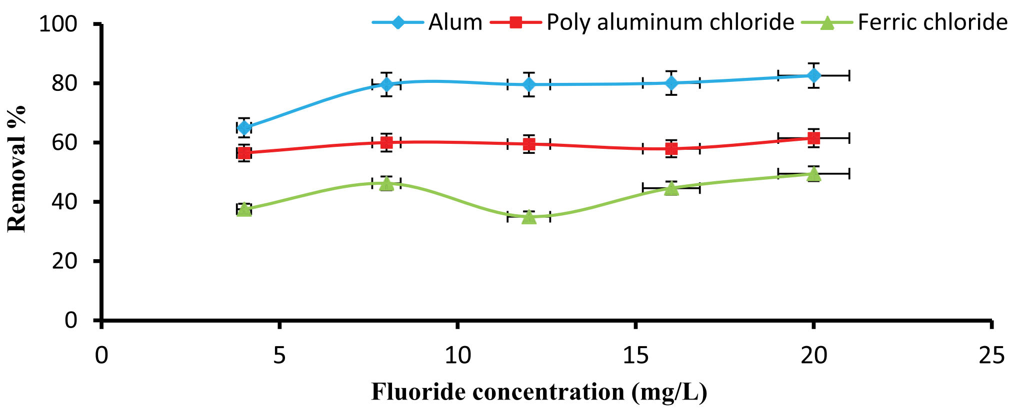

Fig. 4. Fluoride removal at various fluoride concentration: (30 mg/L alum at pH 4, turbidity 10 NTU, 10 mg/L PACl at pH 4 and turbidity of 20 NTU, 20 mg/L ferric chloride at pH 8 and turbidity of 15 NTU).

3.4. Effect of fluoride concentration

The effect of initial fluoride concentration ranging from 4 to 20 mg/L on the fluoride removal has been investigated by keeping other variables constant. The initial fluoride concentration of 4, 8, 12, 16, and 20 mg/L was tested according to Fig. 4. Results indicated that the increase of initial concentration of fluoride has slight effect on the removal of fluoride for all three coagulants. The highest fluoride removal occurred when the initial fluoride concentration was 20 mg/L for all three coagulants and the percentage removals were 83%, 63%, and 50% for Al^{+3}, PACl, and Fe^{3+}, respectively. The effect of initial fluoride concentration on the removal of fluoride was investigated in the study by Dargahi et al. [33]. The initial fluoride concentration varied from 3 to 10 mg/L. The results showed that the fluoride removal efficiency decreased at all three settling times (10, 30, and 45 min) with increasing initial fluoride concentration [33].

4. Conclusion

In this study, three types of coagulants; $Al_2(SO_4)_3 \cdot 14H_2O$, $(Al_2(OH)_5Cl_{2.6})$, and $FeC1_3$, have been studied for the removal of fluoride. Results showed that parameters; pH, coagulants dosage, turbidity, and initial concentration of fluoride significantly affected the fluoride removal. The maximum removal efficiency of fluoride at the pH 4 for alum, and PACl were 57%, 50%, respectively and for ferric chloride was 53% at pH 8. The effect of coagulant complexations showed that the dosage of coagulants has different effects on the removal of process and the maximum removal (83%) was achieved for aluminum salt at 30 mg/L. Furthermore, the residual fluoride in water mainly depends on the initial fluoride contamination. In brief, the process showed suitable ability for removing F^- for aqueous solutions.

Acknowledgments

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