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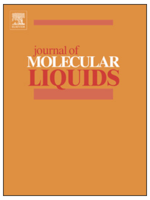

Experimental investigation of Al-F species formation and transformation during coagulation for fluoride removal using alum and PACl

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ABSTRACT

Aluminium salts are widely investigated for the coagulation process for removal of fluoride, but the residual Al above the acceptable limit is the main concern which is mainly due to the formation of soluble and colloidal Al-F complexes of aluminium and fluoride. Hence, it is necessary to investigate the nature and mechanism of formation of colloidal, dissolved and precipitated Al-F complexes and other Al associated species, that govern the concentration of residual Al in the defluoridated water. In the present study, experiments were performed to find the optimized dosage of aluminium sulfate (alum) and polyaluminium (PACl) for removal of fluoride from drinking water. Residual fluoride, turbidity and TDS were found to be 1.3 ppm, 7 NTU & 280 ppm respectively, for alum and 0.48 ppm, 4 NTU & 200 ppm respectively for PACl for initial fluoride concentration of 4 ppm. Residual Al was found to be above the acceptable limit (0.2 ppm), but it was less for PACl as compared to alum, however, after the subsequent microfiltration, residual Al was 0.268 & 0.13 for alum & PACl respectively that almost met the acceptable limit. Characterization of the treated water before and after filtration by using microfiltration membrane was done through electrospray ionization mass spectroscopy (ESI-MS) to identify the colloidal, dissolved Al-F species. Aluminium species in the form AlF_5^{2-},AlF_2^{+}, AlF_4^{-}, $Al_2(OH)_2^{2+}$, $Al(OH)_2^{+}$, Al $(OH)_2F_2^{-}$, $AlOHF^{+}$ etc. as Al-F were recognised. From the ESI-MS results, it was observed that only a few Al-F complexes with lesser concentrations were formed in case of PACl, which confirmed the fact that PACl worked better for the fluoride removal with low residual Al. The settling of the Al-F complexes for PACl was better than alum due to the difference in flocculation mechanism bridging in case of PACl and sweep flocculation for alum. XRD, SEM & FT-IR analysis of alum and PACl sludge was done to identify the precipitated species.

1. Introduction

Fluoride is useful to human health in strengthening bones and in preventing tooth decay at low concentrations [1]. Though, the consumption of fluoride above the permissible limit (>1.5 mg/L) via drinking water can result in severe fluorosis, of which over millions of people are suffering [2]. In the recent times, fluoride removal has received consideration, and it can be accomplished by various processes including adsorption, membrane separation, electrocoagulation and coagulation process [3–6]. Among the mentioned technologies, coagulation process has been extensively applied because of its simplicity and high efficacy [7]. Commonly used coagulants include aluminium sulfate (alum) and polyaluminium chloride (PACl) which have been examined well concerning the removal of fluoride [8]. But the main limitation of the technique is the high amount of residual aluminium left in the treated water, which is due to high concentration of suspended solids that primarily comprise alumino-fluoro complexes not being able to settle under plain sedimentation [7, 9]. In the recent years, some researchers have tried defluoridation of water using poly aluminium chloride (PACl) [10, 11]. These studies indicated that the use of PACl could be a good alternative to alum for the defluoridation purpose [12]. Removal of fluoride content from synthetic water using coagulation technique by adding PACl dosages in varying percentages has also been reported [13]. Since high fluoride is present in relatively deep groundwater that carries low suspensions, application of PACl may have the advantage that its coagulation mechanism of bridging would prove better than the sweep floc mechanism of alum, which has limitations under such conditions [12, 14, 15]. However, in both the cases, the treated water was not able to meet the residual aluminium standards of 0.2 ppm and a subsequent microfiltration membrane can be integrated to meet this target [12]. Effective removal of residual Al-F complexes was expected to achieve, as the sizes of these particles are in micrometre range (≈2 μm) thereby causing almost no suspensions and very low aluminium in output water [16]. Hence, it is necessary to understand the basic mechanism involved in the flocculation mechanism of fluoride removal so that the suspended particles would not be present in the treated water.

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Previous studies reveal that $Al(OH)_3$ flocs are formed in the course of hydrolisation of aluminium salt, fluoride removal is done through adsorption on these flocs [17]. In the above process, aluminium fluoride complexation, exchange of ions, the attraction of electrons and physical adsorption are involved [18]. But the main flocculation mechanism of fluoride removal is still not clear. Literature indicates that the fluoride removal process is strongly dependent on coagulant dosage and a decrease in pH due to this treatment is inevitable [6, 19]. It has been reported that the residual aluminium and fluoride in the treated water is because of the presence of colloidal and dissolved alumino-fluoro complexes [20]. The transformation of various species specifically free fluoride, complex fluoride and adsorbed fluoride have an influential role. In addition to this hydrolysis, distribution and transformation of aluminium salts are greatly affected by complexation of aluminium and fluoride. However, hydrolysis of aluminium salts tends to generate a sequence of aluminium species having various structures, charges & degree of polymerization [21]. Hence the complexation of aluminium and fluoride is greatly influenced by the assemblage of aluminium species. Various models have been introduced that are based on the surface complexation model to understand the coagulation mechanism for alum [22–24]. But these models failed to explain the diversity in the Al species formed after the coagulation treatment. A model has been developed to determine the nature and distribution of Al species in various forms that are present in alum-treated water, which helps simulate the chemical processes and explains the concentration of residual Al [20]. Moreover, this model predicted that the optimum alum dosage for treating high fluoride waters around 5.5–7.5 pH is lower than that suggested in conventional coagulation process for conditions of minimum dissolved and colloidal aluminium concentrations in treated water.

Recently, Sarpola et al., 2007 has performed for the identification of aluminium complexes with the help of electrospray ionization mass spectrometry (ESI-MS) method [25]. Emphatical analysis and identification of the hydrolysis products of aluminium chloride ($AlCl_3$) at various concentrations using ESI-MS method have been examined by several researchers [26–28]. In addition to this, salts of aluminium salts such as sulfate, nitrate/perchlorate were investigated by ESI-MS [27, 29, 30]. Also, Rämöet et al., 2008 established the variations in aluminium species of PACl with different basicities at various pH values with the help of ESI-MS method [31]. Hence, based on detection of mass to charge ratio (*m*/*z*) of complexes, the ESI-MS method has been proved as an important analysis for the detection of species [32]. In a study, the attempt was made to detect aluminium species from a mass spectrum, based on inferring changes in *m*/*z* and molecular formulas of oligomers in five typical polyaluminium chloride coagulants [33]. The chemical species with three types of charges (i.e., +1, +2, +3) were calculated and described as $Al_{13}O_{12}(OH)_{14}^{+}$, $Al_{13}O_{12}(OH)_{13}{}^{2+}$, and $Al_{13}O_{12}(OH)_{12}^{3+}$, respectively. Aluminium species of coagulants having low concentration was examined comprehensively using ESI-MS [32]. The results depicted that solution pH greatly affected the hydrolyzed aluminium species dispersion having a low concentration. Analysis of several hydrolyzed monomers, dimers, trimers and tetramers of aluminium species could be performed with the help of ESI-MS method. ESI-MS was much superior to ^{27}Al NMR and Ferron method in recognizing aluminium species at low concentrations accurately. Gong et al., 2012 studied the Al-F complexation and fluoride removal in coagulation at various pH and concentrations of fluoride [34]. It was concluded that Al-F-OH coprecipitate formed with Al-F complexes in coagulation followed by coprecipitation with complexation which enhanced the removal of fluoride. He et al. explained the consequences of fluoride on the transformation & distribution of various aluminium species formed after the interaction of coagulant and fluoride [8]. It was reported that hydrolysis of aluminium generates a sequences of aluminium species including bimomers, oligomers, aluminium polymers, sol/gel in addition with monomeric form of aluminium depicted as $Al(OH)_n{}^{(3-n)+}$ $(0 \le n \le 2)$ which are critically different in structures of their molecules & charge density and their F^- removal capacity was also unlike afterwards. Moreover, the interactions involving aluminium and fluoride impact distribution and transformation of aluminium species and subsequently influence removal of fluoride. However, studies have not been performed for the differentiation of Al-F complexes distribution in treated water that comprises colloidal, dissolved and precipitated species.

Thus, the present study is focused on investigating the transformation and distribution of various aluminium species through ESI-MS method, consequently identifying the various species formed during the defluoridation process. Lastly, the dominating mechanism responsible for the removal of fluoride by various aluminium species was suggested. The identification of the dissolved, colloidal and precipitated species formed was performed through characterization of samples using ESI-MS, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) techniques.

2. Materials and methods

2.1. Chemicals and reagents

All the reagents in the experiments namely sodium fluoride (NaF), aluminium sulphate ($Al_2(SO_4)_3.18H_2O$) were of analytical grade obtained from ACS. Calcium oxide (Hi-media) was used to maintain proper pH in the coagulation experiments. A stock solution of fluoride was prepared by weighing 2.21 g of NaF and dissolving it in 1 L of deionized water. The reagent was oven dried at 60 °C, and the concentration of fluoride ion was measured by Orion Star A214 Fluoride Ion Meter. Total ionic strength adjustment buffer (TISAB) was prepared by taking 58 g of NaCl, 4 g CDTA, and 57 mL of glacial acetic acid. 5 M NaOH solution was used for adjustment of the pH of the buffer to 5.0 to 5.5. TISAB was used to measure fluoride ion. De-ionized water was used for all experiments to avoid any ionic contamination.

2.2. Batch experiments

In a typical experiment, 1 L of 10 mg/L of fluoride solution was prepared by diluting the appropriate amount of stock solution. Different working solutions of fluoride were obtained by appropriate dilution from the stock solution. The optimum dose of alum was found out by carrying out experiments for different doses of alum. CaO was added to maintain the pH at 6.5. The beaker containing the solution was placed on a magnetic stirrer, and all the reactants were flash mixed for 10. After 10 min of flash mixing at 500 rpm, 20 min of slow mixing at 70 rpm was done to minutes to accomplish flocculation. Finally, the flocs were allowed to settle down for 30 min, and the supernatant was collected, and a part was filtered through 0.2 μ membrane and analyzed further. Similar experiments were carried using PACl as coagulant which was obtained from Aditya Birla group, with the aluminium content of 11% as Al_2O_3 as per the specifications provided by the supplier.

Table 1
Parameters permissible limit for drinking water.

S. No.	Parameters	Permissible limit (WHO, 2011)	Residual parameters of treated water (with alum)
1.	Fluoride(ppm)	1.5	1.3
2.	Aluminium (ppm)	0.2	0.411
3.	Turbidity (NTU)	5	7
4.	Total dissolved solids (ppm)	600	280
5.	Sulfate (ppm)	80	123.9
6.	Chloride (ppm)	200	–