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SYNTHETIC WASTEWATER DE-FLUORIDATION USING CHEMICAL COAGULANTS

ZHEN JIE GOH[1], CHIEN HWA CHONG[2,*],
RAJESH NITHYANANDAM[1], WINSTON LIM[1]

[1]School of Engineering, Taylor's University, Taylor's Lakeside Campus,
No. 1 Jalan Taylor's, 47500, Subang Jaya, Selangor DE, Malaysia
[2]School of Engineering and Physical Sciences, Heriot-Watt University, Malaysia Campus,
No 1 Jalan Venna P5/2, Precinct 5, 62200 Putrajaya, Malaysia
*Corresponding Author: chien_hwa.chong@hw.ac.uk

Abstract

The objective of this research is to reduce fluoride concentration to a maximum target of 5.0 ppm (standard B). The scopes of this research include the effect of different coagulant dosages, coagulant types and pH effects. Poly-aluminium chloride (PAC) and mixture of sodium aluminate (SA) with sodium hydroxide (NaOH) were used as chemical coagulants. Samples of synthetic fluoride with concentration of 100 ppm were used in this research. It was found that increasing coagulant dosage enhances the de-fluoridation performance. 85.9 % of de-fluoridation efficiency was achieved using a 3.0 g/L of PAC with mixture of SA with NaOH at optimum pH of 7. Statistical analysis using ANOVA one-way test showed that the p value is 5.53×10-12 ($p < 0.05$), which concluded the chemical coagulant dosage provides significant effect on de-fluoridation performance.

Keywords: Coagulant, Concentration, De-fluoridation, Fluoride, pH.

1. Introduction

Fluoride have both positive and negative effects on human. It is widely used in dental application for tooth decay prevention especially in higher sugar intakes areas. It is often presented in the form of tablets, mouthwashes, toothpastes, and other soluble gels with respective applications. It is evidently shown that at low concentrations of fluorides, human can benefit from its bone and tooth strengthening effect [1]. However, upon excessive intake via drinking water in the long run can lead to wide occurrence of dental and skeletal fluorosis diseases. In worldwide, there are approximately 500 million people are contracted to suffer fluorosis and these phenomena had been considered as major issues which would eventually affect the global population of people, economic and social aspect [1]. Hence, the removal of fluoride from portable water has received great attention in the past few years.

The existence of fluoride in the environment occurs through natural presence in the earth's crust and industrial activities during disposal of waste products, especially semiconductor, electroplating, glass, steel etc. which lead to fluoride contamination on the surface and ground water. Hence, fluoride removal in wastewater treatment engineering has become popular topic and draws much interest by society nowadays. Water scarcity has been known as one of the greatest global challenges because of the rapid elevation in world's population, which leads to continuous growth of water consumption rates [2]. Current wastewater treatment could be categorised into three main groups: physical, chemical, or biological processes; and a typical wastewater treatment consists of combination of all wastewater treatment types to maximise de-fluoridation performance. Referring to World Health Organisation (WHO) standard, the optimum fluoride level in portable water is between 0.5 mg/L to 1.0 mg/L and the effluent discharges standard for fluoride in wastewater industries are different with respect to countries. For instances, the wastewater effluent discharge standard for fluoride content in Malaysia is 5.0 ppm (standard B), whereas United State (US) recently established the effluent charge standard of 4.0 ppm for fluoride content in wastewater treatment [3, 4]. The general fluoride concentration in actual industrial wastewater ranged between 250 ppm to 1500 ppm, depending on the operating condition.

De-fluoridation was being accomplished by various techniques such as an adsorption, an electro-coagulation, a membrane separation, an ion-exchange, and the Nalgonda technique. Among the techniques used for fluoride removal, a chemical coagulation method has been widely used due to its simplicity and high effectiveness of removing the fluoride content. In general, coagulation can be classified into chemical and natural coagulation. Aluminium chloride ($AlCl_3$) and aluminium sulphate are known as alum and poly-aluminium chloride (PAC) is commonly used as the chemical coagulant for fluoride removal.

Extensive studies were discovered by researchers and scientists regarding chemical coagulation for de-fluoridation. Gong et al. [5] stated that the formation of Al-F complexes involves the fluoride removal using AlCl3, and this effect improves the de-fluoridation efficiency to a large extent compared to aluminium hydroxide, Al(OH)3 adsorption. Bi et al. [6] concluded that Al-F complications influenced the hydrolysis of aluminium salts and their respective distribution and transformation afterwards as the hydrolysis of Al salts tended to form a series of Al composition with respective structures, charges, and polymerisation characters.

However, limited studies had been made on the effects of Al species distribution whereas the transformation on fluoride removal performance using Al coagulation is more focused and evaluated in this research.

Despite coagulation provides cost effective performance with low equipment and capital costs, the main drawback using this conventional method is its low efficiency on removing contaminations, which causes severe environmental issues such as water pollution, which endangered marine habitants. Hence, many researchers and scientists were investigating on methods to improve efficiency of de-fluoridation either in portable water or wastewater effluent. One of the methods in optimising fluoride removal performance was membrane separation otherwise known as nanofiltration (NF) as it could achieve high inorganic removal like fluoride due to the involvement of combination of separation mechanisms including solution diffusion, size exclusion, and charge repulsion adsorption [7].

Ayoob et al. [8] reported that improvement of fluoride removal using nanofiltration (NF) and reverse osmosis (RO) was successful as total of more than 96 % and 90 % of fluoride rejections were being accomplished respectively. Pontie et al. [9] claimed that fluoride removal performance by the NF/RO could reduce fluoride concentration in wastewater effluent up to 15 mg/L to meet WHO guideline with lower energy consumption. Possible drawbacks of using the NF are membrane fouling and scaling, which inherent in fluoride removal through the separation process. As the NF technology remain sophisticated in current studies, more research and investigation are necessary to explore the potential of using the NF in improving fluoride removal.

The research question is how much fluoride concentrations can be reduce using sodium aluminate as a chemical coagulant. It is hypothesised that suitable adjustment of studied parameters (chemical coagulant dosage, type of coagulants, and presence of fibrous thin film) enhance coagulation performance for wastewater de-fluoridation and meet wastewater effluent discharge standard (A and B) as high conversion rate of Al-F complexes can be achieved to remove fluoride content at specified studied condition. The research objectives are to investigate the effect of coagulant dosages, coagulant types on fluoride removal performance and pH effect after coagulation at desired conditions and evaluate the final fluoride concentration.

2. Methodology

2.1. Material preparation

Hydrofluoric acid, HF was used as the synthetic wastewater sample for the de-fluoridation process. The HF concentration is 550000 ppm at purity of 97%. 148 μl of HF 55% was diluted with distilled water in a 1000 ml flask.

Coagulants used were poly-aluminium chloride (PAC) and sodium aluminate, $NaAlO_2$ (SA). PAC 30 % (15000 ppm, 95% purity, boiling point of 100-120˚C with complete solubility in water at 20˚C) and $NaAlO_2$ (white powder, minimum of 80% purity, optimal range of more than pH 12). The mixture coagulation solution with 1.0 g/L was prepared. It has 1.0 g of $NaAlO_2$ powder was weighted and diluted with 1000 ml of distilled water together with 1.0 g of NaOH powder and same steps were repeated for preparation of 2.0 g/L, 3.0 g/L and 0.5 g/L of mixture coagulant solution based on the formulation provided by Aoudj et al. [10].

2.2. Methods

2.2.1. Jar test

The coagulation tests were conducted using a jar tester (Lovibond® ET 750, USA) at ambient condition (25 ± 2˚C) with optimum pH value of 7 [10]. The procedure of this test was modified according to the journal reported by Aoudj et al. [10]. 148 μl of synthetic wastewater, hydrofluoric acid (550000 ppm) was transferred into 2000 ml corrosive resistant beaker and diluted with distilled water with a total volume of 1000 ml. The chemical coagulant, PAC with mixture of $NaAlO_2$ and NaOH were added to the diluted HF solution. After addition of aluminium-based coagulant, the following steps consisted of 2 min of standard mixing at 100 rpm with an adjustment of desired pH value, then 15 min for slow mixing at 40 rpm, and 30 min for settling and stabilisation. Then, the supernatants were filtered using a 0.45 µm thickness membrane to analyse the final concentration of fluoride and aluminium residues in the filtrate.

2.2.2 pH test

A pH meter (Eutech PC 700, Insearch Scientifix Sdn. Bhd., Malaysia) was used to analyse the final pH of the filtered substance from the jar test. The procedure was conducted using the manual provided by Hu et al. [11] with some modification applied.

2.2.3 Fluoride test

A spectrophotometer (Spectroquant® Prove 300 UV/VIS, Merck KGaA, Germany) was used to determine the final concentration of fluoride content within the filtered product. A test kit with full set of reagents, corrosive resistant test tube and stirrer were supplied by Merck for fluoride concentration test. The experiment procedures were set by referring to He et al. [12] with some modification. Firstly, 2.0 ml of reagent was added into a 25 ml test tube followed by 5.0 ml of distilled water and 0.5 ml of the stock solution. The synthetic wastewater samples after the coagulation process was mixed with the reagent in the test tube. Lastly, a scoop of reagent powder with 0.1 g was added into the test tube and shake well until no precipitation. After letting it settled for 5.0 min, the mixture was poured into a cuvette and ready to be measured using the spectrophotometer.

2.3. Statistical analysis

All data were tabulated for statistical analysis as well as comparison. Statistical analysis was used to evaluate how significant of the parameter affected the desired result. The statistical analysis focused on the effect of coagulant dosage on fluoride removal performance and therefore, ANOVA one-way test was selected to verify the significance of only parameter, coagulant dosage on de-fluoridation efficiency by comparing theoretical results obtained from respective coagulant dosage. All experiments were conducted in triplicates.

3. Results and Discussion

Effect of chemical coagulant dosage on de-fluoridation efficiency

The effect of chemical coagulant dosage on fluoride removal performance is shown in Table 1. Four sets of different coagulant dosages were formulated to treat fluoride.

Table 1. Final fluoride concentration at respective coagulant dosage.

Coagulant Dosage, g/L	1st Average Value, ppm	2nd Average Value, ppm	3rd Average Value, ppm
0.5	HI	HI	HI
1.0	19.2 ± 1.2	19.0 ± 1.1	18.5 ± 1.0
2.0	14.7 ± 1.5	15.8 ± 1.6	14.2 ± 1.2
3.0	14.5 ± 2.3	14.4 ± 2.0	14.5 ± 1.3

*HI indicates fluoride concentration, which exceeds from 20.0 ppm

Coagulant dosage showed significant effect on de-fluoridation efficiency. Referring to Table 1, the final fluoride concentration at coagulant dosage of 0.5 g/L showed "HI" symbol for three average reading, which indicated that the remaining fluoride content after chemical coagulation still exceeded the amount of 20.0 ppm. This occurrence is because of aluminium compositions (Al_3, Al_7 etc.) binding with fluoride ions within the stock solution become a limiting factor. The HF to form aluminium-fluoride complexes, which are commonly known as flocs [13]. As a result, incomplete de-fluoridation process might have occurred causing high fluoride contents contamination at the surface of stock solution, the HF after settlement, which caused failure to achieve the standard of industrial effluent from wastewater (5.0 ppm for Standard B and 2.0 ppm for Standard A). The fluoride concentration was reduced to more than 20.0 ppm to a range of 18.5 ppm – 19.2 ppm with average standard deviation of 1.5 ppm using coagulant dosage of 1.0 g/L. For the coagulant dosage of 2.0 g/L and 3.0 g/L, the final fluoride concentration are 14.7 ± 1.5 g/L, 15.8 ± 1.6 g/L and 14.2 ± 1.2 g/L and 14.4 ± 2.3 g/L, 14.5 ± 2.0 g/L and 14.4 ± 1.3 g/L, respectively.

The remaining fluoride content after the coagulation process decreased with increased of concentration 1.0 g/L to 2.0 g/L and then 3.0 g/L but with a slower reducing rate. It was notably observed that the elevated coagulant dosage become less significant to the changes on the final remaining fluoride, until a point where the effect became non-apparent when a constant value is observed despite the continuous increased of the coagulant dosage. Due to lack of fluoride ions, F^- to bind with aluminium composition, Al to form Al-F complexes as the initial concentration of stock solution was 100.0 ppm and eventually act as the limiting substances for the formation of Al-F complexes after coagulation [6]. Hence, fluoride removing rate would eventually achieve a constant value even though the coagulant dosage kept increased.

However, Liu et al. [14] claimed that the elevated Al concentration might inhibit the attachment of fluoride ions, F^- onto Al flocs to form Al-F complexes and adversely inhibited fluoride removal by Al coagulation thereafter. Hence, the efficiency of fluoride removal would increase with a slower increasing rate and held constant at higher coagulant dosage and then kept elevated due to the inhibition of F^- attached onto Al flocs to form Al-F complexes for maximising fluoride removal rate.

The trend of de-fluoridation efficiency with respective chemical coagulant dosage was investigated. As shown in Table 2, first average reading presented the efficiency of removing fluoride was increased from 80.8 % to 85.3 % and eventually to 85.5 % when coagulant dosage increased linearly from 1.0 g/L to 3.0 g/L. The efficiency of fluoride removal using chemical coagulation for second and third set of average data had similar behaviour and trend with the first set of average reading, with a value from 81.0 % to 84.2 % and elevated to 84.4 % as well as from 81.5 % to 85.8 % and increased to 85.9 %, respectively.

Table 2. Fluoride removal efficiency.

Coagulant Dosage, g/L	1st Average Value, %	2nd Average Value, %	3rd Average Value, %
0.5	>80.0	>80.0	>80.0
1.0	80.8	81.0	81.5
2.0	85.3	84.2	85.8
3.0	85.5	84.4	85.9

It was clearly observed that at higher fluoride removal efficiency, further increment of the coagulant dosage produces less drastic changes on the removal rate. It also shown clearly that the maximum curve of the data lies between the ranges of 2.0 g/L to 2.5 g/L of coagulant dosage, where the fluoride removal efficiency started to decrease with further addition of the coagulant. The trend of the results above showed similar agreement with the journal provided by Liu et al. [14]. Hence, it can be concluded that results obtained were legit and suitable to be evaluated and discussed.

4. Statistical Analysis

ANOVA one-way test was selected to verify the significance of only parameter, coagulant dosage on de-fluoridation efficiency. Results obtained for verifying the significance between parameter are shown in Table 3.

Table 3. Statistical analysis of respective chemicalcoagulant dosage on de-fluoridation efficiency using ANOVA-1 way test.

Comparison between Chemical Coagulant Dosage, g/L	*p* value	Indication
1 with 2	1.18×10^{-9}	$p < 0.05$
2 with 3	0.65	$p > 0.05$
1 with 3	1.5×10^{-9}	$p < 0.05$
All	5.53×10^{-12}	$p < 0.05$

The effect of chemical coagulant dosage on de-fluoridation efficiency using ANOVA 1-way method. Referring to Table 3, it was observed that p value between chemical dosage of 1.0 g/L to 2.0 g/L and 1.0 g/L to 3.0 g/L were found to be 1.18×10^{-9} and 1.5×10^{-9}, respectively. The p value for coagulant dosage between 1.0 g/L and 2.0 g/L as well as 1.0 g/L and 3.0 g/L were fall under the same category of $p<0.05$. This indicated that the coagulant dosage increased from 1.0 g/L to 2.0 g/L, there was a significant effect and great impact on fluoride removal efficiency. This same applies to coagulant dosage of 1.0 g/L to 3.0 g/L. However, it showed p value of 0.65 when the coagulant dosage was increased from 2.0 g/L to 3.0 g/L, which fall under the category of $p>0.05$. This implied that there was no significant effect on fluoride removal performance when coagulant dosage was increased from 2.0 g/L to 3.0 g/L.

This could be because of the elevated coagulant dosage causes the increases of aluminium composition, which might inhibit the formation of aluminium-fluoride complex (Al-F), also known as flocs, for fluoride removal purpose [15]. Thus, the decreased in fluoride removing rate have less significant effect on de-fluoridation performance at coagulant dosage of 2.0 g/L to 3.0 g/L. In overall, the elevated coagulant dosage from 1.0 g/L to 3.0 g/L showed a significant effect on fluoride removal efficiency as the p value showed $5.53x10^{-12}$, which is less than 0.05 and hence, the effect of coagulant dosage range from 1.0 g/L to 3.0 g/L is worth to investigate. This is also in agreement with Lim et al. [16] where fluoride removal increased from less than 80% to 85% for coagulant dosage ranged from 0.5 to 3.0.

5. Conclusions

The above results gave a conclusive idea that physical parameters are crucial and the most effective factors on enhancing fluoride removal efficiency under specified circumstances. With respect to the above, it is important to comprehend the effect of chemical coagulant dosage and the type of coagulant on fluoride removal performance, along with the evaluation of de-fluoridation performance with fibrous thin film to improve the current existing technologies. With the results obtained, the highest fluoride removal efficiency of 85.9 % was achieved when 3.0 g/L of chemical coagulant with formulation provided previously was used to treat 100.0 ppm of synthetic wastewater sample, HF at pH 7 in room condition. The study also stated that the higher the coagulant dosage, the higher fluoride removal performance could be accomplished but with a decreasing of elevation rate because of the inhibition of de-fluoridation efficiency by elevated aluminium composition.

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Nomenclatures

NaOH	Sodium hydroxide
PAC	Poly-aluminium chloride
SA	Sodium aluminate

Abbreviations

NF	Nanofiltration
RO	Reverse osmosis
WHO	World Health Organisation

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