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To cite this article: V L Chee *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **778** 012129

Combined natural and chemical coagulants to remove fluoride from wastewater

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Abstract. The combined chemical and natural coagulant showed greater fluoride ion removal in synthetic hydrofluoric acid wastewater when compared to natural coagulant or chemical coagulant treatment alone. The impact of applying fibrous thin film on the coagulation activity was assessed in this study. In this study, a new chemical coagulant called Ecogent F-Loc was introduced. It can increase 40% of fluoride removal when combined with sodium aluminate. Combined chemical and natural coagulants gave the highest fluoride reduction using the *Moringa Oleifera* seed and eggshell with dosage of 100 ppm were 57% and 73%, respectively. When the chemical coagulant added with *Moringa Oleifera* seed, the fluoride removal efficiency increased from 50% to 77%. This showed that the combined chemical and natural coagulant showed similar coagulation effect as conventional chemical coagulant. In term of fibrous thin film, there is no significant effect on the coagulation activity of coagulant, but it helped to reduce the turbidity and coagulant residue in the synthetic wastewater and used to produce ionic solution for fluoride removal. In addition, the direct contact between particles and the impeller of Jar Test equipment can destroy the surface morphology of coagulant particles. With the support of the fibrous thin film, this challenge can be solved. In conclusion, the combined natural and chemical coagulant solutions can be used to substitute existing chemical treatment in fluoride wastewater treatment.

1. Introduction

Coagulation and precipitation are the most common methods for wastewater treatment in beverage industry and fluoride removal in groundwater. Mahammerdrafi and Karthikeyan had compared the efficiency between chemical coagulant and electro-coagulation for hardness and fluoride ion removal from water [1]. Hardness of water was determined by the concentration of divalent ions (mainly calcium, Ca^{2+} and magnesium, Mg^{2+}). Under voltage of 5.0 V and contact time of 5 hours, 67 – 78% of hardness was removed from water for initial hardness concentration of 700, 1000, 1200 and 1300 mg/L using electro-coagulation. Under the same condition, 74-90% of fluoride was removed for initial fluoride concentration of 2.0, 3.0 and 5.0 mg/L. For comparison purpose, alum was used as chemical coagulant. It was found that alum was not effective in removing hardness, only 5 – 8% of hardness is removed. However, it showed satisfying results in fluoride removal, able to remove 80 – 90% of fluoride ions under pH value of 6.5. However, if hardness and fluoride ions are present together, with 1,300 mg/L of initial hardness concentration and 5.0 mg/L of initial fluoride concentration, the maximum efficiency of fluoride ion removal was reduced drastically from 90% to 65%. This was attributed to the interference of coagulation process with the presence of hardness ions (Ca^{2+} and Mg^{2+}), thus reducing the fluoride ion uptake efficiency.

In order to reduce the second pollutant resulted from chemical coagulant, there is a strong interest to seek for natural coagulants that could potentially replace chemical coagulants in groundwater treatment. Similar to chemical coagulant, natural coagulants were able to assist in forming interactions such as hydrogen bonding, ion exchange or covalent bonding, caused by the formation of hydrolysed species of positive charge in the compound, through adsorption or neutralization process [2]. This property allowed natural coagulants to possess active charges that lead to fluoride ion removal. Examples of natural coagulants include *Nirmali*, *Moringa Oleifera*, *Tannins*, *Cactaceos* and *Chitosan* [2]. Bazanella et al. had demonstrated the application of combination of *Moringa Oleifera* seed and ultrafiltration to remove fluoride from water. It was recorded that a reduction of 90.9 % from the initial fluoride content (10.0 ppm) in fluoridated water was achieved with a *Moringa Oleifera* seed dose of 2.5 ppm [3]. More importantly, it did not produce residue which was harmful to the environment or human being. However, the problem faced by using the *Moringa Oleifera* seed as coagulant is inadequate supply of the seed worldwide.

There are two general preparation method of natural coagulant, i.e. seed extraction method, and drying method. The seed extraction method includes cutting of plant material to small pieces, extraction of mucilage in distilled water for overnight, filtration, precipitation and oven drying. This method normally requires more time. Meanwhile, the drying method include drying of plant material in high temperature and grinding of the plant material into powder form, and this method is less time consuming. Seed extraction method aims to extract the active substances that normally possess active ions for the defluoridation process, while the drying process aims to remove the moisture content from the coagulant. Despite good fluoride removal efficiency shown by natural coagulant, they are usually highly biodegradable and have short shelf life [4]. Hence, combination of chemical and natural coagulant is suggested. Combined chemical and natural coagulant is expected to have reduction in the secondary pollutant or toxic residue, which is produced through coagulation activity of chemical coagulant, and increase in the shelf life of the coagulant.

The purpose of this research project is to determine the impact of the *Moringa Oleifera*, eggshell, calcium chloride, sodium aluminate, Ecogent E-floc and fibrous thin film (FTF) on fluoride removal efficiency from synthetic wastewater. This research project also serves to produce a combined natural and chemical coagulant, which possess extended shelf life and able to remove fluoride effectively.

2 Materials and Methodology

2.1 Materials.

The materials involved in this research project include sodium aluminate (consist of ≥ 92% $AlNaO_2$) (Industry grade, Platinum Strike Sdn. Bhd., Malaysia), poly aluminium chloride (Industry grade, Platinum Strike Sdn. Bhd., Malaysia), calcium chloride (Laboratory grade, Aplab Scientifik Sdn. Bhd., Malaysia), Ecogent F-Loc (10 – 30 % Aluminium Hydroxide, 1 -10 % Polyelectrolyte) (Industry grade, Platinum Strike Sdn. Bhd., Malaysia), hydrofluoric acid solution (Platinum Strike Sdn. Bhd., Malaysia), SPADNS2 Reagent for Fluoride, Arsenic-Free (AraChem (M) Sdn Bhd), sodium hydroxide, *Moringa Oleifera* seed, and eggshell.

2.2 Methodology

2.2.1 Preparation of sodium aluminate (SA) solution. 0.5 g of SA (consist of ≥ 92% $AlNaO_2$) was dissolved in 50 ml of 10 % caustic soda, before being added to 200 ml of distilled water and mixed together. Different formulation of chemical coagulant was used by modifying the concentration of SA. Different concentration of SA was prepared by replacing 0.5 g of SA to 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g.

2.2.2 Preparation of Poly Aluminium Chloride (PAC) solution. Poly Aluminium Chloride (15 % PAC) was prepared based on method described by Winston et al. and Goh et al. with some modification [4] [5]. It was prepared by dissolving 15.0 g of PAC in 100 ml of distilled water.

2.2.3 Preparation of calcium chloride ($CaCl_2$) solution. Calcium Chloride solution (35 % $CaCl_2$) was prepared based on method described by Winston et al. and Goh et al. with some modification [5] [6]. It was prepared by dissolving 35.0 g of $CaCl_2$ pellets in 100 ml of distilled water.

2.2.4 Preparation of chemical coagulant (SA + $CaCl_2$. Chemical coagulant (SA + $CaCl_2$) was prepared based on method described by Winston et al. and Goh et al. with some modification [5] [6]. 16.0 ml of prepared SA solution was mixed with 3.0 ml of prepared $CaCl_2$ solution.

2.2.5 Preparation of chemical coagulant (SA + Ecogent F-Loc). Chemical coagulant (SA + Ecogent F-Loc) was prepared based on method described by Winston et al. and Goh et al. with some modification [5] [6]. Similar to chemical coagulant (SA + $CaCl_2$), applying 16.0 ml of prepared SA solution, 3.0 ml of prepared $CaCl_2$ solution was replaced by 3.0 ml of Ecogent F-Loc (10 – 30 % Aluminium Hydroxide, 1 -10 % Polyelectrolyte).

2.2.6 Preparation of natural coagulant (Moringa Oleifera). Moringa Oleifera was purchased from a local market. The preparation of *Moringa Oleifera* seed coagulant is based on Dehghani and Alizadeh with some modification [7]. The seeds of *Moringa Oleifera* were extracted out and being dried with temperature of 80 °C for 5 hours inside the oven (HWU/LE174/WG.66/UF55). If temperature of higher than 80 °C was used, the structure of protein inside *Moringa Oleifera* seeds were altered, and this affected the coagulation activity of it. The dried seeds were ground into powder form (< 600 μm) using a blender (Panasonic MX-GM1011). 10.0 g of *Moringa Oleifera* was measured and wrapped in FTF before immersed in 100 ml of distilled water.

2.2.7 Preparation of natural coagulant (Egg Shells). The eggshell coagulant is prepared based on method described by Bhaumik et al. with some modification [8]. The egg shells were washed using distilled water, following by drying in the hot oven (HWU/LE174/WG.66/UF55) (110 °C) for 24 hours. If temperature higher than 110 °C was used, the surface morphology of eggshell particle was altered, and this affected the coagulation activity of it. The dried egg shells were ground into powder form (< 600 μm) using a blender (Panasonic MX-GM1011). 10.0 g of eggshell powder was measured and wrapped in FTF before immersed in 100 ml of distilled water.

2.2.8 Preparation of synthetic fluoride wastewater. Synthetic fluoride wastewater (SFW) was being prepared by diluting 55 % hydrofluoric acid solution (Platinum Strike Sdn. Bhd., Malaysia) to 100 ppm. 0.9 μL of 55 % hydrofluoric acid solution was mixed with 5.0 L of distilled water.

2.2.9 pH Measurement. The pH was measured using a pH meter (ECPHWP30002K). The pH meter was inserted into the centre of beaker, the reading was taken after the solution inside the beaker was stabilised.

2.2.10 SFW analysis. The SFW analysis was measured using the Jar Test ET 740, based on Ren et al. with some modification [9]. Various dosage (4.0 ml, 8.0 ml, 12.0 ml, 16.0 ml, 20.0 ml, and 24.0 ml) of natural coagulant 1 were added into 6 different beakers with 400 mL of SFW. The samples were stirred at 120 revolutions per minute (rpm) for 2 min, before 3.0 ml of PAC solution was added to each beaker. The samples were stirred at 20 rpm for 5 min and allowed to be settled for 30 min. Samples were extracted, and the concentration of fluoride in the samples were analysed using a UV/VIS spectrophotometer (DR 6000). 2.5 ml of samples were mixed with 250 ml of distilled water to dilute the sample by 100 times before measurement due to the limitation of spectrophotometer up to 2 ppm only. The SFW analysis was repeated by changing the *Moringa Oleifera* seed with eggshell, Sodium Aluminate with various SA concentration, combined sodium aluminate and calcium chloride with various SA concentration, combined sodium aluminate and Ecogen F-Loc with various SA concentration, coagulant combining sodium aluminate, calcium chloride and *Moringa Oleifera* seed ionic solutions (SACMO) at various dosage (4.0 ml natural coagulant + 12.0 ml chemical coagulant, 8.0 ml natural coagulant + 8.0 ml chemical coagulant, 12.0 ml natural coagulant + 4.0 ml chemical coagulant), coagulant combining sodium aluminate, Ecogen F-Loc and *Moringa Oleifera* seed (SAEMO) at various dosage. All these experiments were carried out under room temperature (25 °C).

2.2.11 Fluoride removal efficiency calculation. The fluoride removal efficiency of coagulant was calculated using the formula:

$$\text{Fluoride removal} = \frac{(C_i - C_f)}{C_i} \, x \, 100\%$$

Where C_i is the initial fluoride concentration, and C_f is the final fluoride concentration.

3.2.12 Statistical analysis. All data was analysed using One-way ANOVA test followed by post-hoc test with Microsoft Excel 2016.

3. Results and Discussion

3.1 Coagulation activity of chemical coagulant in synthetic fluoride wastewater.
Sodium aluminate showed good fluoride removal efficiency, mainly due to the presence of aluminum ions (Al^{3+}). Refer to Figure 1, 46% of fluoride was removed when dosage of the sodium aluminate used was 6000 mg/L. The dissociation of the sodium aluminate to caustic soda and aluminum hydroxide provided aluminum ions, which were responsible in removing fluoride through ion-exchange with fluoride ions. However, a drastic drop of fluoride efficiency to 14% was observed when the coagulant dosage was increased to 12000 mg/L, which implied that 86 ppm of fluoride was left in the synthetic wastewater. This was best explained by the stabilisation of coagulant particles caused by overdose of positive aluminum ions, which hindered the effect of defluorination process [10].

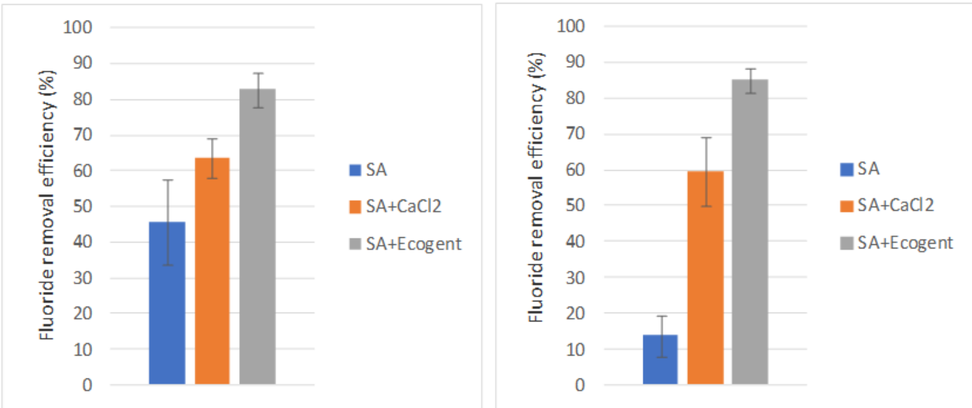


Figure 1. Coagulation activity of chemical coagulants on the synthetic wastewater at a) coagulant dosage of 6 g/L and b) 12 g/L

An improvement of fluoride removal efficiency by 8% and 37%, implying that 46 ppm and 17 ppm of fluoride were left in the synthetic wastewater respectively, were observed when the sodium aluminate of dosage 6000 mg/L was combined with calcium chloride and Ecogent F-Loc. This is mainly attributed to the introduction of calcium ions and aluminium ions from calcium chloride and Ecogent F-Loc, which increased the maximum fluoride uptake of the coagulant. It was observed that the decrease in fluoride removal efficiency of combined solidum aluminate and calcium chloride coagulant was relatively lesser when the sodium aluminate dosage used was doubled. This was due to the presence of chloride and hydroxide anions that served as co-existing anions that prevented the coagulant particle from being stablised [11]. Meanwhile, the fluoride removal efficiency of combined sodium aluminate and Ecogent F-Loc increased slightly from 83% to 85%, implying that 15 ppm of fluoride was left in the synthetic wastewater, due to the presence of polyelectrolyte present in Ecogent F-Loc. It served as promising flocculants that undermined the negatively charged fluoride anion. The polyelectrolyte enhanced the flocculation process by providing particle attraction, thus providing cleaner water [12]. These results showed that sodium aluminate was a decent coagulant for fluoride removal in wastewater treatment when combined with another chemical such as the Ecogent F-Loc. However, aluminum residue was produced as second pollutant during the coagulation activity, which might require secondary treatment.

3.2 Coagulation Activity of Natural Coagulant in Synthetic Fluoride Wastewater
The Moringa Oleifera seed was proven to be a decent coagulant to remove fluoride due to its high porosity, surface texture and presence of coagulant protein. It contained 31.4% of protein [13]. According to Ndabigengesere et al. and Gassenschimidt et al. the protein in *Moringa Oleifera* seed was charged with cationic dimmers (6.5 to 13 kDa and it is an iso-electric point above 9.6 with positive charge. The interaction between fluoride and *Moringa oleifera* seed was occurred through ion adsorption mechanism because fluoride ion is negative charge [14][15]. Table 1 showed the effect of *Moringa Oleifera* seed on the coagulation activity of synthetic wastewater. Refer to Figure 2, *Moringa Oleifera* seed had increased in fluoride removal efficiency from 42% to 57% when the amount of

coagulant increased from 4.0 ml to 16.0 ml. This could be due to the increase in positive charged surface for binding of negatively charged fluoride ions due to electrostatic forces. Compaoré, et al. found that the most abundant nutrients composition in *Moringa Oleifera* seeds are protein (35 ± 0.07 g/ 100 g) and lipids (43 ± 0.03 g/ 100 g) which are rich in zinc cation (Zn^{2+}) and magnesium cation (Mg^{2+}) [16]. The positive charged protein and lipids created electrostatic attraction with negatively charged fluoride ion, and form zinc fluoride and magnesium fluoride which were slightly soluble and insoluble in water respectively. This ion exchange process helped in the formation of flocs which settled due to gravity. Furthermore, Sasikala and Muthuraman found that the *Moringa Oleifera* particles are loosely agglomerated upon dispersed in water [17]. This loose agglomeration of *Moringa Oleifera* particles provided a large surface area which ease the fluoride removal process. The optimum coagulant dosage is 16.0 ml. Beyond the optimum coagulant dosage, a sharp drop of fluoride removal efficiency from 57% to 43% is observed, which was attributed to saturation and agglutination of *Moringa Oleifera* particles. This substantially reduced the total surface area available for fluoride removal. Thus, the fluoride removal efficiency of *Moringa Oleifera* seed was reduced by 14% [18].

Table 1. Observation of effect of the *Moringa Oleifera* seed on coagulation activity of synthetic wastewater

	Before treatment	After treatment	
Top view of synthetic fluoride wastewater			
Observation	No residue is observed after the wastewater treatment. Macroflocs are noticed.		

Besides the *Moringa Oleifera*, eggshell is also proven to show good capability in fluoride removal, mainly credited to the presence of positive charged calcium ion (Ca^{2+}). Table 2 showed the effect of eggshells on the coagulation activity of synthetic wastewater. Referring to Figure 3, with an increase in amount of eggshell coagulant (dosage 100 g/L) used, the fluoride removal efficiency increased until it reached its peak of 73%. Calcium ion is more electronegative than hydrogen ion and it replaced the hydrogen ion (H^{+}) in hydrofluoric acid to form insoluble calcium fluoride precipitate with an electrochemical potential of -2.868 V with respect to hydrogen ion [19]. According to Tsai et al., the composition of eggshell consists of high amount of calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [20]. Kashi et al. found that the surface of eggshell particle is non-adhesive, porous, irregular and agglomerating before any fluoride treatment [21]. An enhancement of fluoride removal efficiency from 69% to 73% is observed when an optimum coagulant dosage of 16 ml was used. This was mainly attributed to agglomeration of eggshells, which increased the total surface area for the ion-exchange process. However, beyond the optimum coagulant dosage, a slight decline of fluoride removal efficiency from 73% to 69% is observed. This was best explained by the wastewater medium reaching its saturation point of coagulant, inducing the agglomeration of eggshell particle, thus reducing the voidage available for fluoride uptake.

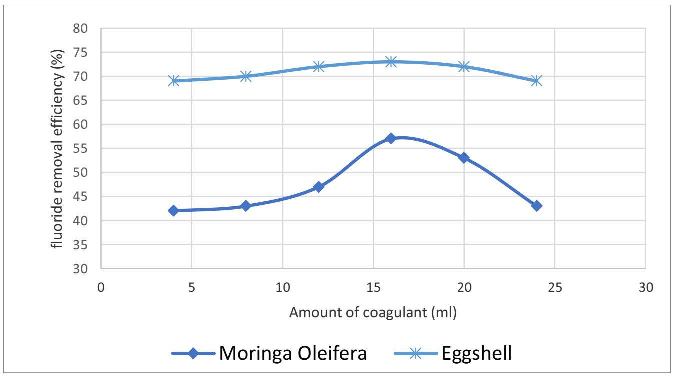
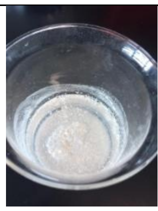


Figure 2. Coagulation activity of natural coagulants on synthetic wastewater

Over 50% fluoride removal was shown by the *Moringa Oleifera* seed and eggshell, indicating their potential of replacing chemical coagulant in fluoride removal process in wastewater treatment. However, natural coagulants showed limitations of relatively low efficiency when compared to chemical coagulants. Compared to eggshell, the *Moringa Oleifera* seed has inadequate supply. On the other hand, eggshells were waste from hatcheries, restaurants or fast food industries and they were readily available [22]. Using eggshells as coagulant not only helped in wastewater treatment, but also reduced the eggshells waste disposed.

Table 2. Observation of effect of eggshells on coagulation activity of synthetic wastewater

	Before treatment	After treatment	
Top view of synthetic fluoride wastewater			
Observation	Eggshell residue is observed after the wastewater treatment. Macroflocs are noticed.		

3.3 Coagulation activity of combined natural and chemical coagulant in synthetic fluoride wastewater. The combination of chemical and natural coagulants had shown significant effect on fluoride removal efficiency. Table 3 showed the fluoride removal efficiency of two different coagulant combinations using different amount of chemical and natural coagulant at various volume ratio. A small increment was observed when the amount of chemical coagulant used in both combination of coagulants (SACMO and SAEMO) increased from 4.0 ml to 12.0 ml. This was mainly due to the chemical properties of aluminium cation that formed ligands through covalent coordinate bond, to induce the formation of more complex structure such as Al-OH-F complex after the formation of aluminium-fluoride (Al-F) complex. The increase in fluoride removal efficiency would eventually be smaller despite the increase in amount of chemical coagulant used [5]. Another possibility that the increase in amount of chemical coagulant used have minimal effect on the fluoride removal efficiency was due to some unexpected interruption that limits or hinders the formation of Al-F complex. When there was an elevated aluminium ion (Al^{3+}), the growth of flocs was inhibited, the aluminium cation available decreased, and the charge neutralization between fluoride ion (F^{-}) and aluminium ion (Al^{3+}) decreased [23].

Table 3 showed that natural coagulants had the same capability to remove fluoride ions as chemical coagulant. Although there was a small increment being observed when the amount of chemical coagulant was increased by 300% (4.0 ml to 12.0 ml), the change in fluoride removal tendency was

minimal, which was less than 10%. This implied that there was insignificant difference in fluoride removal efficiencies between chemical coagulants and natural coagulants.
Recently, there were a lot of research regarding chemical and natural coagulants composite in wastewater treatment, such as poly-aluminium chloride chitosan composite [24] and poly-aluminium chloride poly-acrylamide composite [25]. This was because, chemical and natural coagulants composite were relatively more environmental friendly as natural coagulants were biodegradable and did not produce toxic sludge as chemical coagulants did. Furthermore, natural coagulants were also more cost effective than chemical coagulants.

Table 3. Comparison of fluoride removal efficiency between different combination of natural and chemical coagulants

Coagulant combination	Amount of chemical coagulant (ml)	Amount of natural coagulant (ml)	Final fluoride concentration (ppm)	Fluoride removal efficiency (%)
Sodium Aluminate +	4.0	12.0	29	71 ± 0.58
Calcium chloride +	8.0	8.0	28	72 ± 0.33
***Moringa Oleifera* seed (SACMO)**	12.0	4.0	23	77 ± 0.33
Sodium Aluminate +	4.0	12.0	26	74 ± 1.16
Ecogent F-Loc + *Moringa*	8.0	8.0	19	81 ± 0.88
***Oleifera* seed (SAEMO)**	12.0	4.0	18	82 ± 0.88

3.4 Effect of fibrous thin film in coagulation activity. The application of FTF had no significant effect on the coagulation activity of coagulant. A comparison between presence and absence of fibrous thin film in the aspect of fluoride removal efficiency for *Moringa Oleifera* seed and Eggshell are shown in Table 4. With the absence and presence of the FTF, the coagulants performed similarly in term of fluoride removal efficiency. This was because despite trapping the insoluble ground solid particles of coagulant inside the FTF, the active ions possessed in water soluble protein of coagulants were still able to dissolve and diffused though the FTF. The FTF is useful in preparing ionic solution for fluoride removal without any cleaning or particle removal process.

Table 4. Comparison between presence and absence of fibrous thin film in the aspect of fluoride removal efficiency

Coagulant	Coagulant activity	Final fluoride concentration (ppm)	Fluoride removal efficiency (%)
Moringa	With fibrous thin film	30	70 ± 0.33
Oleifera	Without fibrous thin film	26	74 ± 1.33
Eggshell	With fibrous thin film	32	68 ± 0.88
	Without fibrous thin film	29	71 ± 0.88

Table 5 showed the top view of synthetic wastewater before and after the treatment by *Moringa Oleifera* with the presence and absence of FTF. From Table 5, it was observed that some particles were diffused out of the FTF. This was probably due to the irregular size of pore of FTF. Some of the pore of FTF was greater than the particle size of *Moringa Oleifera* seed (600 µm). This made the treated synthetic wastewater harder to be cleaned. This problem could be countered by using FTF of smaller and more regular pore sizes. The pore size must be greater than the size of solid particle, but smaller than the size of active protein, to allow the diffusion of the active ions for coagulation activity to occur. Nevertheless, although there was no significant difference on the coagulation activity of coagulant with the absence and presence of FTF, the usage of FTF was also beneficial for natural coagulant prepared using drying and grinding process. This was because lesser time was required for natural coagulant to be prepared mechanically and wrapped with FTF than chemically (chemical extraction method) [26].

IOP Conf. Series: Materials Science and Engineering **778** (2020) 012129 doi:10.1088/1757-899X/778/1/012129

3.5 Effect of direct contact in coagulation activity.

The coagulation activity of the *Moringa Oleifera* seed was greatly influenced by the presence of direct contact, but not eggshell. Table 6 showed the comparison between presence and absence of direct contact in aspect of fluoride removal efficiency for the *Moringa Oleifera* seed and eggshell coagulant. The top view of synthetic fluoride wastewater before and after the treatment by the *Moringa Oleifera,* with and without direct contact is shown in Table 7. With the presence of direct contact, *Moringa Oleifera* seed showed a sharp decrease in fluoride removal efficiency from 74% to 44%, while there was no significant change in fluoride removal efficiency for eggshell. A possible explanation was that the surface morphology of *Moringa Oleifera* seed was destroyed by the shear force produced from the rotating blade of the jar test equipment. The solid density of *Moringa Oleifera* seed and eggshell are 4.77 g/cm$_3$ [27] and 1.148 g/cm$_3$ [21], respectively. The *Moringa Oleifera* sinked to the bottom of synthetic wastewater while eggshell floated on surface of synthetic wastewater more due to small difference in density with water. This made the *Moringa Oleifera* seed closer to the impeller blade than eggshell during the Jar Test. With a higher agitation speed, the *Moringa Oleifera* seed experienced greater shear force formed from the rotating impeller than eggshell. This increased the chance of collision between particles and the blades or within particles, which might alter the surface morphology of *Moringa Oleifera* particles by destroying the active sites for fluoride removal. Thus, the coagulation activity of coagulant was greatly reduced. Furthermore, with direct contact, the turbidity of synthetic wastewater increased, with more secondary product being produced, which made the water cleaning process harder. This problem could be countered by wrapping the natural coagulant inside FTF to prevent direct contact between the rotating impeller and the coagulant. This method can be used to produce ionic solution for fluoride removal.

Table 5. Top view of synthetic fluoride wastewater before and after treatment by *Moringa Oleifera* seed a) with fibrous thin film b) without fibrous thin film

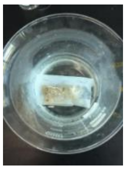
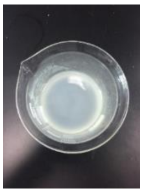
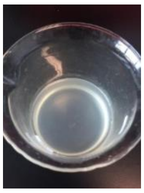
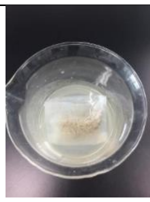
	Before treatment	After treatment	
a) Top view of synthetic fluoride wastewater (with fibrous thin film)			
b) Top view of synthetic fluoride wastewater (without fibrous thin film)			
Observation	With fibrous thin film, small amount of the *Moringa Oleifera* seed residue is observed after wastewater treatment. Macroflocs are observed after wastewater treatment regardless of the presence or absence of FTF.		

Table 6 Comparison between presence and absence of direct contact in the aspect of fluoride removal efficiency

Coagulant	Coagulant activity	Final fluoride concentration (ppm)	Fluoride removal efficiency (%)
***Moringa Oleifera* seed**	With direct contact	56	44 ± 3.38
	Without direct contact	26	74 ± 1.33
Eggshell	With direct contact	30	70 ± 1.53
	Without direct contact	29	71 ± 0.88

Table 7 Top view of synthetic fluoride wastewater before and after treatment by *Moringa Oleifera* seed a) without direct contact b) with direct contact and eggshell c) with direct contact

	Before treatment	After treatment	
a) Top view of synthetic fluoride wastewater when *Moringa Oleifera* is added (without direct contact)			
b) Top view of synthetic fluoride wastewater when *Moringa Oleifera* seed is added (with direct contact)			
c) Top view of synthetic fluoride wastewater when eggshell is added (with direct contact)			
Observation	With direct contact, the *Moringa Oleifera* seed and eggshell residues are observed. Macroflocs are observed after wastewater treatment regardless of the presence or absence of direct contact		

4. Conclusions

Comparison was made between chemical coagulants, natural coagulants and combined natural and chemical coagulants. Combined chemical and natural coagulant can be used for fluoride removal. The combined sample like SACMO shows fluoride removal efficiency as high as 77%. This is because overdose of Aluminium ion (Al^{3+}) hinders the formation of Al-F complex, which limits the floc formation and reduces the Aluminium cation available for fluoride removal. The addition of the *Moringa Oleifera* seed prevents overdose of Al^{3+}. Furthermore, SACMO have greater shelf life and higher fluoride removal efficiency than the *Moringa Oleifera* seed coagulant alone. The application of FTF reduces the turbidity and prevents the solid particle of coagulant from diffusing out of the FTF during the coagulation activity. It prevents direct contact between the coagulant and the agitating impeller that the surface morphology of coagulant from being destroyed. From this research, it was found that natural coagulant has capability to replace chemical coagulant in term of fluoride removal efficiency although higher dosage is required.

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6. Acknowledgments

This work was supported by the Marketing Director of Platinum Strike Sdn. Bhd. Mr. Goh C.L for sponsoring chemicals for this research project. The authors extend their appreciation to Universiti Putra Malaysia (UPM) for funding this research work through GP-IPB/2016/9515200).