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Removal of fluoride and aluminium using plant-based coagulants wrapped with fibrous thin film

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ABSTRACT

The coagulation activity of *Moringa oleifera* seed and *Hibiscus esculentus* (okra) mucilage were assessed for their ability to remove both anionic and cationic contaminants in aluminium sulphate and hydrofluoric acid synthetic wastewater. The effect of encasing these coagulants in a fibrous thin film along with their effect on pH and concentration were also assessed. Assessment using the jar test showed a 79.9% aluminium reduction and 91.7% fluoride reduction using okra mucilage and *Moringa oleifera*, respectively. Besides that, there was no effect on both the pH and coagulation activity in the application of fibrous thin film. The plant-based coagulation activity is comparable with conventional coagulant as fluoride removal treated by polyaluminium chloride formulation was 85.3 ± 0.8% with the optimum dosage of 3 g/L. The significance of these findings in the application of fibrous thin film with plant-based coagulants could be an advantage for industries to commercialise mechanically prepared coagulants, which has a much longer shelf life as compared to chemically prepared coagulants, as it has the potential to reduce the turbidity associated with mechanically prepared coagulants. Also, these results indicate the possibility of having a cost-effective yet environmentally friendly water treatment solution that combines the application of both plant-based and conventional coagulants.

1. Introduction

Fluoride is a common element use in our daily application. It is widely used as a prevention for tooth decay. Fluoride can be in mouthwashes, toothpastes, tables and other soluble gels form for various applications. However, fluoride has both positive and negative effects on human; at low concentration, it helps strengthen bone and teeth (Elemental fluorine market: Global industry analysis and forecast 2016–2026, 2016). On the other hand, excessive intake of fluoride in drinking water over a prolong period can lead to dental and skeletal fluorosis. According to (World Health Organization, 2011), more than 260 million people around the world have been found to be affected by dental and skeletal fluorosis caused by long term exposure to groundwater containing fluoride in excess of 1.5 ppm. The formation of fluoride in groundwater is common in Asia, especially in places where crystalline basement rocks with fluoride ions are present (Raj and Shaji, 2017). Although there is no proven efficient treatment for fluorosis, the best approach would be to maintain fluoride concentration in wastewater and/or potable water at a safe level. In Malaysia, the maximum allowable fluoride concentration in the wastewater effluent is 2 ppm and 5 ppm for Standard A and Standard B respectively (Department of Environment, Malaysia, 2010).

A common method for treating fluoride-rich wastewater uses conventional coagulants such as alum and poly-aluminium chloride (PAC). Yang et al. (2010) demonstrate an effective defluoridation method using alum and PAC at the dosage of 15 ppm Al_2O_3 and at a pH of 6. Additionally, Ahmad et al. (2008) found that the application of PAC could remove turbidity, total dissolved solid (TDS) and chemical oxygen demand (COD) by 99.8%, 99.4% and 91% respectively. The high removal rate is mainly due to the effective adsorption and/or chemisorption through mechanism of charge neutralisation, polymer bridging and electrostatic patch (Mishra et al., 2006; Sharma et al., 2006). However, the aluminium residue in the treated wastewater using PAC introduces a secondary pollutant. It is a potential hazard to the environment as the study of coagulant residue in treated wastewater is rather limited. The

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National Priorities List (NPL), a register of hazardous waste sites in the United States maintained by the Environmental Protection Agency (EPA), indicates that of the 1699 sites in the list, 569 contain hazards related to aluminium (Agency for Toxic Substance and Disease Registry, 2008). Long term exposure to aluminium can lead to metal fume fever which causes fever, cold and coughing (New Jersey Department of Health and Senior Services, 2017). Other than health hazards, aluminium also leads to low production yield in Al-sensitive crop like cocoa and paddy. This causes growth retardation among the crops when the Al^{3+} ion in the soil exceeds 100 μM and 900 μM for cocoa and paddy respectively (Cate and Sukahi, 1964; Auxtero and Shamshuddin, 1991). Even though alum-based coagulant is much preferred by the industry for being cost-effective, the usage of the inorganic coagulants has also affected the pH value of the treated water. A large amount of non-biodegradable sludge is also produced leading to additional costs for pH adjustment and sludge process and disposal (Ahmad et al., 2008; Matilainen et al., 2011; Matilainen et al., 2005; Gidde et al., 2012). This would suggest that the usage of PAC is not environmentally sustainable.

Studies have found that plant-based coagulants have the potential to replace conventional inorganic coagulants. This is due to the active ingredients in these plant-based coagulants containing charges similar to conventional coagulants. *Moringa oleifera* has the ability to remove 80% of lead ions and okra mucilage is able to reduce total dissolved solids (TDS) and turbidity up to 37.5% and 93%–97.3%, respectively (Veronica et al., 2012; Anastasakis et al., 2009; Srinivasan and Mishra, 2008). From the pH perspective, plant-based coagulants tend to have less effect on the water pH. Ndabigengesere and Narasiah (1998) showed that *Moringa oleifera* had no effect on the pH water (7.6) after treatment whilst the application of alum would reduce the pH of the treated water to 4.2. It was concluded from this finding that plant-based coagulants would require less pH adjustment as compared to conventional coagulants. Though, from experiments with synthetic wastewater, it was found that plant-based coagulants tend to neutralise the pH of the water. An advantage due to its intrinsic pH which ranges from 7.5–7.7 under 35° C (Ndabigengesere and Narasiah, 1998; Georgiadis et al., 2011; Wadiwsky et al., 1985).

Plant-based coagulants can be prepared through (i) chemical extraction and (ii) drying and grinding (Agarwal et al., 2003; Srinivasan and Mishra, 2008; Mishra et al., 2002; Mishra et al., 2003; Mishra et al., 2004; Mishra et al., 2006). Chemical extraction involves extracting the active substance using chemical e.g. alcohol from raw material. On the other hand, drying and grinding, as the name suggests, involves drying the part of the plant to remove most of the moisture and further grinding it into powder form. In comparison, chemically extracted plant-based coagulant e.g. *Moringa oleifera*, has been found to be better at reducing lead ions concentration compared with its mechanically prepared counterpart but both have similar electric conductivity reduction and pH effect (Basra et al., 2014). Despite the amazing coagulation activity, chemically prepared coagulant generally have a much shorter shelf life as it is in liquid form. In contrast, mechanically prepared coagulant have a similar shelf life as compared to commercial coagulant. For example, no deterioration were found in the active protein in dried *Moringa oleifera* for period time of 12 months (Helene et al., 2015). Mechanically prepared coagulants, however, could cause high turbidity in treated wastewater.

In order to solve the turbidity challenge, this study introduces the use of fibrous thin film (FTF) in the application of mechanically prepared plant-based coagulants. FTF was used as a filtration system to prevent inactive substances from causing the secondary effect of turbidity while the water-soluble active substances dissolve in the water and thus perform similarly as chemically prepared coagulant. The typical pore size for FTF used in this study ranges from 1 to 5 μm which is very different from membrane which has a more uniform pore size and typically in the nanometre range making it not suitable for this application.

Recent plant-based coagulant development took on the approach of grafting it into synthetic polymer. This is done by placing both the coagulant and the polymer through energy waves to generate free radical sites on the polymer backbone where the coagulant would attach to. With this, the shelf life of these plant-based coagulant is extended while the environmental impact of the synthetic polymer is reduced. However, the cost-associated with this approach remains high despite the various approaches to reduce cost (Mishra et al., 2011; Sen et al., 2009; Wang et al., 2008). This has impeded the development in commercialising grafted coagulants.

With the objective of prolonging the shelf life of plant-based coagulants, the work detailed in this paper focuses on approach to improve the performance of mechanically prepared plant-based coagulant. As such, it focuses on the coagulation activity of *Moringa oleifera* and okra mucilage and their effect on pH and turbidity in the treated wastewater. The effect of these plant-based coagulant wrapped in FTF on these parameters were also studied. PAC coagulant mixture, which acts as a conventional coagulant, was also applied to treat fluoride with different concentration to determine its optimum dosage and the results were compared with plant-based coagulant.

2. Materials and methods

2.1. Preparation of moringa oleifera seed powder

Dried *Moringa oleifera* seeds were purchased from a local market (GPS coordinate 3°11′36.9″N 101°40′48.3″E) in Selangor, Malaysia. The dried seeds were ground to fine powder (<500 μm) using a domestic grinder (Lebensstil Stainless Steel Coffee Grinder LKCG4012SS, Germany).

2.2. Preparation of okra mucilage

Okra mucilage purchased from a local market (GPS coordinate 3°11′36.9″N 101°40′48.3″E) in Selangor, Malaysia was prepared using the method described by Agarwal et al. (2003) with some modifications. The okra samples were cut longitudinally and seed pods were obtained by separating from the skin. These seed pods were dried in the oven at a temperature of 70° C for 14 h and were then ground to fine powder (<500 μm) using a domestic grinder (Lebensstil Stainless Steel Coffee Grinder LKCG4012SS, Germany).

2.3. Preparation of PAC formulation

This coagulation mixture formulation was prepared based on Aoudj et al. (2015) with some modification. The PAC formulation consists of poly-aluminium chloride (PAC) (15 ±0.5% Al_2O_3) (Industry grade, Platinum Strike Sdn. Bhd., Malaysia), sodium aluminate (SA) (Consist of 92% of 41–44% of Na_2O + 51–53% of Al_2O_3) (Industry grade, Platinum Strike Sdn. Bhd., Malaysia) and sodium hydroxide (NaOH) (Analytical grade, R&M). A dosage of 3.0 mL of 15% PAC and various concentrations (0.5 g/L, 1 g/L, 2 g/L and 3 g/L) of SA and NaOH coagulant mixture are prepared for fluoride treatment. The coagulant mixtures are prepared from dissolution of SA powder and NaOH pellet into distilled water.

2.4. Preparation of wastewater

The effect of coagulation was investigated using synthetic wastewater. Synthetic aluminium wastewater (SAW) and synthetic fluoride wastewater (SFW) were prepared by diluting 8% Alum