Research Article

Removal of Fluoride from Aqueous System Using Moringa oleifera Seed Cake and its Composite Coagulants

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Abstract

The seeds from the Moringa oleifera tree contain 35-45\% of oil. The seed oil, known as “Ben oil” can be used for the production of biodiesel. The Moringa oleifera biodiesel is an environmentally sustainable fuel. The residue originated from the oil extraction (cake), can be used as fertilizer and animal feed. Currently another significant use of this byproduct concerns to the removal of pollutants in aqueous systems for their coagulant, clarifier and adsorbent properties due to the presence of some functional group such as hydroxyl, carboxyl, amines, phenolic, methoxyl, hydroxyl aliphatic groups etc. The adsorbed particles coagulate and settle down as precipitate in the process of purification of water. Coagulation with aqueous extract of Moringa oleifera seed cake powder reduced the fluoride concentration of fluoridated water below 1mg/L but the turbidity after coagulation was very high which was removed by double filtration. When composite coagulants prepared by adding alum and starch with Moringa oleifera was used for coagulation of fluoridated water, the fluoride concentration reduced below 1mg/L and the turbidity is within the standard limit of drinking water. So the composite coagulant helps to remove fluoride effectively without any significant increase in turbidity of the de-fluoridated water.

Keywords: Moringa oleifera, Oil extraction, Biodiesel, Seed cake coagulation, Composite coagulants, fluoride removal, Aluminium.

1. Introduction

Access to fresh water is a human right, yet more than 780 million people, especially in rural areas, rely on unimproved sources and the need for finding ways of treating water is crucial (Ida Bodlund, 2013). In India, endemic fluorosis affects more than one million populations and is a major problem in 17 of the 29 states. Similar health problems due to high fluoride content in ground water have also been reported worldwide and it is estimated that around 260 million people are adversely affected in 30 countries of the world (Neelo Razbe et al., 2013). The Bureau of Indian Standard which is the main regulatory agency for drinking water in India specifies that the desirable limit of fluoride in drinking water is 0.6-1mg/L. In Kerala, the condition of fluoride is reported to be endemic in the districts of Alappuzha and Palakkad (Tomas Blom et al., 2009; P. Gopalakrishnan et al., 1999). Fluoride is considered as a “two edged sword” because deficiency of fluoride intake leads to dental caries while excess consumption leads to dental and skeletal fluorosis (P. Gopalakrishnan et al., 1999). Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity which results in dental, skeletal and non skeletal forms of fluorosis (Vaishali Tomar et al., 2013). One of the most popular techniques for defluoridation that is used in India is Nalgonda technique. In this technique, calculated quantities of alum, lime and bleaching powder are mixed with water followed by flocculation, sedimentation, filtration and disinfection. Disadvantage of this technique is that treated water has high residual aluminium concentration (2-7 mg/L) than the WHO standard of 0.2 mg/L (Vaishali Tomar et al., 2013). Alum coagulant can be used to remove fluoride selectively from aqueous solutions. Even at 60-70\% removal, the left over fluorides were within the permissible limit for drinking water (V. Subhashini et al., 2012). Aluminum in drinking water poses possible risks to humans. Aluminium is strongly neurotoxic and may be involved in the development of Alzheimer’s disease (R. Rajendran et al., 2013). Previous studies indicate that MO is an efficient coagulant for the removal of turbidities in both water and waste water treatment (K. Ravikumar et al., 2012).

The Moringa oleifera (MO) tree grows in tropical and subtropical region around the world and its seeds have been used for drinking water treatment in small scale in Sudan and India for generations. The potential uses of this wonderful tree includes (a) water purification (b) a very good source of nutrient for man (c) a component of drugs
for man and animals (d) a sure source of 2nd generation biodiesel and (e) act as sinks for carbon dioxide in the atmosphere (K. Ravikumar et al, 2013). Biodiesel derived from MO seed oil is an acceptable substitute for petrodiesel, also when compared to biodiesel fuels derived from other vegetable oils (Umer Rashid et al, 2008). MO will yield at maturity as high as 3 tons oil/hectare with proper nutrition, and irrigation and that it could be used for food in times of shortages. Also the byproduct seedcake after oil extraction can be used as a coagulant for water treatment. MO coagulant is biodegradable, non-toxic, non-corrosive and easy to use (Patrick Niquette et al, 2004). Sludge produced from clarification processes using natural organic coagulants does not contain added metals or toxic compounds (Patrick Niquette et al, 2004). The trees will act as sinks for carbon dioxide and hence the MO plantation will reduce the amount of this green house gas in the atmosphere (K. Ravikumar et al, 2013; Wahidul K. Biswas, 2008). Thus MO is a sustainable solution to food, water and energy crisis.

Literature survey reveals that MO plant is the most inexpensive credible alternative for providing good nutrition and to cure and prevent a lot of diseases (Ritu Paliwal et al, 2011). Aqueous extract of MO showed strong and superior antibacterial activity against bacterial strains such as Staphylococcus aureus, Bacillus subtilis, Escherchiasia coli and Pseudomonas aeruginosa (M. Abdulmoneneim et al, 2011). MO is the best natural coagulant that can replace aluminium sulphate (alum) which is widely used all around the world (Eman N. Ali et al, 2009). Removal of turbidity and hardness can simultaneously be done by using MO seed extract with 1.0M sodium chloride solution (MO-Nacl) (Muhammad Ridwan Fahmi et al, 2011). MO seed extract against E. coli by TVC method reduced >99.9% E.coli count (Jadhav Swapnali Mohan et al, 2008). Efficient reduction (80.0% to 99.5%) of high turbidity produces an aesthetically clear supernatant, concurrently accompanied by 90.00% to 99.99% bacterial reduction (Michael Lea, 2010). Distilled water extract of MO seed powder achieved 90 to 95% sedimentation of the suspended particles in underground and surface water samples (A.O Oluduro et al, 2007). Increased dose of MO seed powder showed reduction in turbidity, TDS, TS, hardness, chlorides, alkalinity, acidity, MPN and SPC in ground water samples (M. Mangale Sapanha et al, 2012). Shelled blended MO seed as a biosorbent removes C.I. Acid Orange 7 from the aqueous systems (Reza Marandi et al, 2011). The percentage removals by MO seeds were 90 % for copper, 80 % for lead, 60 % for cadmium and 50 % for zinc and chromium (Vikashni Nan et al, 2012). MO has been applied in many water purification studies to remove heavy metals such as Ni, Cu, Zn, Pb, Cr and Cd with success. The active sites hypothesized to be responsible for the observed adsorptive capability of MO contain functional groups such as hydroxyl, carboxyl, amines, phenolic, methoxyl, hydroxyl-aliphatic groups (Peter Papoh Ndibewu et al, 2011). MO seeds are capable of adsorbing the fluoride and heavy metals from aqueous systems. The removal of MO seeds were 88% for fluoride, 90 % for copper, 80 % for lead, 60 % for cadmium and 50 % for zinc and chromium (R. Sowmeyan et al, 2011). Acid extract of natural polyelectrolyte MO seed is very effective as a coagulant for removal of fluoride from water (C.M Vivek Vardhan et al, 2011). Alum is presently used as a coagulant in water treatment for removing turbidity. One of the most important polysaccharides is starch. Application of starch as a coagulant aid accompany with coagulant ferric chloride in water turbidity removal and found that the starch as a coagulant aid plays an important role in turbidity elimination (T Shahriari, et al, 2012). Composite coagulant of MO with alum and Starch in various proportions will effectively remove the fluoride without enhancing the turbidity considerably.

MO is a natural coagulant having potential to remove turbidity and other toxic materials from water. Compared to turbidity, the removal of toxic materials such as heavy metal, fluoride etc required more coagulant dosage. So the turbidity is increased during the period of coagulation and adsorption process. The objectives of the study was to identify a sustainable, low cost, locally available, simple, reliable, acceptable, eco-friendly, household level point of use water treatment technology most suitable for rural population of developing countries. This study is an attempt to remove the fluoride from water by using two methods (a) coagulation with MO for fluoride removal and double filtration for excess turbidity removal (b) Preparing suitable composite coagulant of MO that will reduce the fluoride concentration without enhancing the turbidity.

2. Materials and methods

2.1 Preparation of MO seed powder

Dry MO pods were collected from Varkala, Trivandrum, India. Pod shells were removed manually; kernels were grounded in a domestic blender and sieved through 600 micro meter stainless steel sieve.

2.2 Oil Extraction and Biodiesel Production

Oil was removed by mixing the seed powder in ethanol. This was mixed with a magnetic stirrer for 30-45 min and subsequently separation of the residue from the supernatant was done by centrifuging for 45 min at 3000 rpm. The supernatant was decanted and the residual solid was dried (seed cake) at room temperature. The supernatant containing oil and ethanol when mixed with potassium hydroxide catalyst, the chemical reaction produces biodiesel and glycerol.

2.3 Preparation of seed cake coagulant of MO

Aqueous seed cake extract was prepared by using 200ml of distilled water and 25 g of MO seed cake powder, mixed by a magnetic stirrer for 60 minutes and settled for 20 minutes. MO aqueous extract is finally filtered through 20µm paper filter. The optimum dosage of MO was determined by coagulation, flocculation and sedimentation using jar test and obtained as 2.5g/L for various initial fluoride concentrations of 2,4,6,8 and 10 mg/L.
2.4 MO seed cake coagulation and double filtration

MO seed cake coagulation effectively remove the fluoride within the standard limits (<1mg/L) but the turbidity after coagulation increase to very high value, so that it can be removed effectively by double filtration (roughing filtration followed by rapid sand filtration). Double filtration is an efficient and effective drinking water treatment technique for source water with high turbidity, organic matter, and suspended solids.

Jar tests were performed in synthetic fluoride water with different initial concentrations of 2, 4, 6, 8 and 10mg/L for coagulation flocculation and sedimentation with optimum MO seed cake coagulant dosage of 2.5g/L. The standard procedure was 1 min of rapid mixing (120 rpm) followed by 15 minutes of slow mixing (30 rpm) for flocculation and 60 minutes of settling. Roughing filtration was conducted directly after the coagulation and flocculation processes with MO and separates the suspended solids.

2.4.1 Filtration test with roughing filter

In vertical-flow roughing filters the water to be treated flows in sequence through the three filter compartments filled with coarse, medium and fine filter material. The size of the three distinct filter material fractions were between 25 and 3 mm, and graded in to fractions of 25-16mm, 16-8mm and 8-3mm. Vertical-flow roughing filter was operated at 0.3 to 1.0 m/h filtration rates.

Rapid sand filtration was conducted directly after the roughing filtration and separates the last remaining flocs that failed to disappear during roughing filtration.

2.4.2 Filtration test with rapid sand filter

In rapid sand filters the water to be treated flows in sequence through the three filter compartments filled with coarse, medium and fine filter materials. The size of the three distinct filter material fractions were between 50 and 0.5 mm, and graded into fractions of 25-50mm, 13-25mm and 0.5-13mm. The washing of the roughing filter was carried out through lower drainage, and the washing of the rapid filter was counter current.

2.5 Preparation of composite coagulant of MO

Composite coagulant of MO was prepared by adding starch and alum as a coagulant aid that will reduce the turbidity of de-fluoridated water after coagulation. Combinations of alum and starch dosages of 0.5g/L, 1g/L and 2g/L in varying proportions such as 100% starch, 20% of alum and 80% of starch, 40% of alum and 60% starch, 60% of alum and 40% of starch, 80% of alum and 20% of starch and 100% of starch for finding the optimum dosage with 2.5g/L of MO seed cake extract using jar test. The dosage of 1g/L (composition of 40% alum and 60% starch) of coagulant aid in 2.5g/L of MO seed cake extract was the optimum dosage of composite coagulant obtained. Advantages of using MO composite coagulant are that removal of fluoride from water effectively without significant increase in turbidity.

2.6 Coagulation with Composite coagulant of MO

Jar tests were performed in synthetic fluoride water with different initial concentrations of 2.4, 6.8 and 10mg/L for coagulation, flocculation and sedimentation with MO composite coagulant. The standard procedure was 1 min of rapid mixing (120 rpm) followed by 15 minutes of slow mixing (30 rpm) for flocculation and 60 minutes of settling.

3. Result and Discussions

3.1 Coagulation activity test results of synthetic fluoridated water samples after coagulation with seed cake coagulant of MO

Coagulation- flocculation was done using aqueous extract of MO seed cake powder. First the optimum dose was determined. Various dosages of MO seed coagulants were used for different initial fluoride concentrations of 2, 4, 6, 8 and 10 respectively. The optimum dosage is the minimum dosage of coagulant corresponding to the removal of fluoride within the standard limits. The optimum dose was 2.5g/L. But the turbidity increased to very high value in the case of MO seed cake coagulant in all five de-fluoridated water samples as shown in Table 1.

Table 1 Final fluoride concentration and the respective turbidity after coagulation treatment with different concentrations of filtrated MO seed cake coagulant

<table>
<thead>
<tr>
<th>Initial fluoride concentrations mg/L</th>
<th>Final fluoride concentrations mg/L</th>
<th>Final turbidity NTU</th>
<th>Final fluoride concentrations mg/L</th>
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<th>Final fluoride concentrations mg/L</th>
<th>Final turbidity NTU</th>
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<td>0.88</td>
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<tr>
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</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>0.89</td>
<td>47</td>
<td>0.83</td>
<td>65</td>
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<tr>
<td>10</td>
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<td>49</td>
<td>0.77</td>
<td>65</td>
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</tbody>
</table>

3.2 Coagulation activity test results of synthetic fluoridated water sample after coagulation with composite coagulant of MO

In the case of composite coagulant turbidity after de-fluoridation is almost within the standard limit of drinking water. This is due to the presence of alum and starch which act as a coagulant aid that helps to remove the turbidity of the de-fluoridated water. So there is no need of double filtration. Hence the composite coagulant helps to remove fluoride effectively without any significant increase in turbidity of the de-fluoridated water.

At optimum coagulant dosage the final fluoride concentrations reduced below 1mg/L in all the five de-fluoridated water samples. But the turbidity was very low in all the five de-fluoridated water samples as shown in Table 2. The composition of 0.4g alum and 0.6g starch (1g/L) in 2.5g/L of MO was the optimum dosage of composite coagulant obtained as shown in figure 2. In the
optimum dosage of composite coagulant the residual aluminium concentrations present were BDL (below detection level) in the treated drinking water.

Table 2 Final fluoride concentration and the respective turbidity after coagulation treatment with different concentrations of filtrated MO composite coagulant

<table>
<thead>
<tr>
<th>Initial fluoride concentration mg/L</th>
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<th>Final fluoride concentration mg/L</th>
<th>Final turbidity NTU</th>
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<tr>
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<td>10</td>
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3.3 Comparison of fluoride removal efficiency of MO seed cake coagulant and composite coagulant

The de-fluoridation efficiency increases as the initial fluoride concentration increases and the final concentrations of fluoride in all the five de-fluoridated water samples after coagulation with MO seed cake coagulant and its composite coagulant were within the desirable limit (0.6-1mg/L) as shown in Table 3.

The best coagulation condition was reached using MO composite coagulant of alum (0.4g) and starch (0.6g) in 2.5g/L of MO with 10 mg/L of fluoride in the water, achieving 92.5% of fluoride reduction in the treated water. The final turbidity obtained was within acceptable limits for drinking water production in all the five de-fluoridated water samples (<5 NTU).

3.4 Comparison of turbidity removal efficiency of de-fluoridated water sample after roughing filtration, double filtration and MO composite coagulant

MO seed cake is used as a coagulant for fluoride removal additional filtration is needed for reducing the turbidity to the limits (<5NTU). But in the case of composite coagulant no need of filtration because simultaneous removal of turbidity and fluoride obtained due to the activity of optimum coagulant aid (alum and starch) as shown in Table 4. Turbidity removal efficiency of de-fluoridated water using MO composite coagulant is more than that of double filtration efficiency as shown in Table 5.
The maximum turbidity removal efficiency of roughing filtration, double filtration and composite coagulant were 87.50%, 96.82% and 96.87% respectively for de fluoridated water. The final turbidity obtained was within acceptable limits for drinking water production in all the five de-fluoridated water samples (<5 NTU).

Conclusions

MO is an eco-friendly natural coagulant most suitable for the treatment of water containing undesirable fluoride concentrations. From one kg of MO seed 360g of biodiesel can be produced and 610g of seedcake is obtained as a byproduct.

Coagulation with aqueous extract of MO seed cake coagulant was reduced the fluoride concentration of fluoridated water below 1mg/L. But the turbidity after coagulation was very high which was removed by double filtration.

When composite coagulants prepared by adding alum and starch with MO seed cake coagulant was used for coagulation of fluoridated water, the fluoride concentration reduced below 1mg/L and the turbidity is within the standard limit of drinking water (<5NTU). So the composite coagulant helps to remove fluoride effectively without any significant increase in turbidity of the de-fluoridated water. The reagent cost of composite coagulant is low, and treatment effect is good. Besides, its “no or low aluminum (< 0.1mg/L)” characteristics reduce the harm to human body. So the novel composite coagulant prepared by itself can be used in drinking water treatment field in the fluoride affected areas of Alappuzha and Palakkad districts of Kerala.

References


