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Evaluation of Coagulation/ Floculation Process for Water Treatment using Defatted Cake from Moringa *oleifera*

Andressa C. Feihrmann[a], Aline T. A. Baptista[a], João P. Lazari[b], Mariana O. Silva[b], Marcelo F. Vieira[b], Angélica M. S. Vieira*[a]

[a]Department of Food Engineering, State University of Maringá. Av. Colombo, 5790. 13, 87020-900. Maringá,Paraná, Brazil
[b]Department of Chemical Engineering, State University of Maringá. Av. Colombo, 5790. Block D90, 87020-900. Maringá, Paraná, Brazil
amsvieira@uem.br

The *Moringa oleifera* Lam belongs to Moringaceae family and is native to India and widely cultivated in the tropics all over the world.Their seeds are a good source of oil with an excellent quality and protein that present potential coagulant for water treatment. Studies reported that even after the removal of the oil from the seed, the defatted cake keeps its coagulant properties. The aim of this study was to evaluate the Moringa seed as coagulant in the treatment of surface water, after the removal of its oil. Saline coagulants were prepared in concentrations range of 3.45 - 75.8 mg / L, using seed (unprocessed) and defatted cake using mechanical and chemical extraction process with the solvents hexane and ethanol. The different coagulants were evaluated in the Jar test to verify their power to treat water with low turbidity. The results showed that both the defatted coagulants and the integral coagulant (unprocessed seeds) obtained similar results in the removal of approximately 83%, 90% and 69% for color, turbidity and UV_{254nm}, respectively. However, the defatted coagulants (hexane and mechanical) that presented the low lipids content showed better results in the removal of dissolved organic carbon present in the raw water. The high efficiency in water treatment and decreased concentration in organic matter in the water, open new perspectives in the use of defatted coagulant of *Moringa oleifera* as a natural coagulant for the treatment of supply water. In addition, it is possible to extract oil from *Moringa oleifera* seeds that have several applications and use the defatted cake in the water treatment process without losing its ability to coagulate.

1. Introduction

Obtaining drinking water in a scenario where the contamination of the aquatic environments is increasing has increasingly become a subject of global interest. About 1.2 billion of people does not have access to potable water and more than 6 millions of children die as a result of waterborne diseases each year (Ali et al., 2010).
Nowadays aluminum sulfate is one of the most largely used compounds in water treatment, although it produces a large amount of a non-biodegradable mud, generating concerns regarding public health due to high levels of aluminum remaining in the treated water (Huang et al., 2000, Camacho et al. 2015). For these reasons, some countries such as Japan, China, India and the USA have been adopting the use of natural polymers in the treatment of surface water for the production of water for human consumption (Kawamura, 1991).
Among the most studied natural coagulants *Moringa oleifera* (MO) is one of them, it is from a plant native to India, belonging to the Moringaceae genus and which develops throughout the tropic region. Its seeds have a protein, which when solubilized in water can lead to coagulation/flocculation of compounds that promote color and turbidity of surface waters (Okuda et al., 2001).
Another factor that contributes to a better surface waters treatment is the oil removal from the seeds before the coagulant extraction process, once the earlier oil removal reduces the organic load that the seeds could consequently add to the treated water. Moreover, the previous oil extraction generates a co-product with application in several areas of the industrial sector (Ndabigengesere e Narasiah, 1995).

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As for the extraction of cereal oil and other vegetable raw materials the hexane is widely used by the industry. However, because of its toxicity and non-renewable character, oils technology has been looking for other extraction techniques either by use of supercritical or the substitution of hexane by other solvents such as ethanol (considered a 'green solvent'), there is also being carried out studies with enzymes for this purpose (Da Porto et al., 2016; Silva et al. 2016, Latif and Anwar, 2008; Li et al., 2004; Oliveira et al., 2013).The use of the ultrasonic bath in the processes is considered a method called clean because it minimizes the use of organic solvent, along with reduction in the time of extraction (Metherel et al., 2009; Chemat et al., 2011).
In view of the fore going, the present work aims to characterize and evaluate the potential of partially defatted cake of MO seeds in the treatment of surface waters using extraction in NaCl 1M solution and express in protein concentration.

2. Materials and Methods

2.1 Defatted cake obtainment and characterization

The MO defatted cakes were obtained through mechanical and chemical processes using hexane and ethanol as solvents. For the chemical extraction was used an ultrasonic bath UltraCleaner 800 with a 40 kHz frequency in erlenmeyers of 125 mL. The bath water was maintained at a temperature of 25°C. Previous studies showed of the highest oil removes occurs with 30 and 120 minutes of extraction for hexane and ethanol, respectively. The mechanical process was performed using a hydraulic press Bovenau, the employed pressure was 26.63MPa, and 75g of seed approximate was extracted during a 2-hour period, after that period of time variation of extracted oil content was not observed. After the oil extraction using chemical compounds the residual of solvents was eliminate with washing the defatted cakes with water at 40 °C and drying process in same temperature. Moisture and ash were determined by AOAC (1997), crude protein by Micro-Kjeldahl, as described by AOAC (1997), fat/oil by Bligh and Dyer (1959) and total carbohydrate by difference.

2.2 Obtaining the coagulant

The coagulants were obtained using MO seed (unprocessed) and defatted cakes using mechanical and chemical extraction process with the solvents hexane and ethanol, being respectively called coagulant integral, coagulant mechanical, coagulant hexane and coagulant ethanol respectively. For the coagulants preparation 1 gram of seeds were weighed, which were ground in a blender and added to 0.1 L of saline solution (NaCl 1M), corresponding to a concentration of 1% m/v. Than the solution was stirred for 30 minutes and vacuum filtered. The content of soluble proteins present in the coagulants was determined by the method of Lowry et al. (1951).

2.3 Surface water coagulation/flocculation

The coagulation/flocculation assays were performed using simple six-prove Jar test Milan (Model JT 101/6), with rotating regulator of the mixer rods. For the assays was used low turbidity surface water collected at the Maringá Sanitation Company (SANEPAR).These tests were carried out adopting as condition the natural pH of the raw water, since no correction or adjustment of it was made, the pH was around 7.91. Dosage of the coagulants in the coagulation/flocculation processes was determined by protein concentration in each coagulant. The dosages used were 3.45; 13.78; 34.46; 55.14 and 75.8, according with Baptista et al. (2015). The Jar test operating conditions were fast mixing time of 3 minutes with rapid mixing gradient of 100 rpm and slow mixing time of 15 minutes with mixing gradient of 15 rpm (Madrona et al., 2010), followed by a 30 minutes decantation at the end of the process.
In order to evaluate the efficiency of the coagulation/flocculation process, the color, turbidity and UV_{254nm} analyses were performed according to the methodology described in the Standard Methods (Apha, 1995).

2.4 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) was analysed in raw water, defatted coagulants and in the water treated by them. Prior to DOC determination, the samples were filtered in a Millipore cellulose ester membrane, average pore diameter 0.45 μm, by a vacuum pump. DOC concentration was determined by TOC Analyser (Shimadzu 5000ª), in mg/L, following Standard Methods (APHA, 2005).

3. Results and Discussion

3.1 Characterization of Defatted Cakes

The defatted cakes studied by the present project were all obtained by cold extraction processes, using a hydraulic press and ultrasonic extraction using ethyl alcohol and hexane as solvents. The integral seed of MO was also used for comparison purposes in the coagulation / flocculation process. The data of the centesimal composition of the seeds and defatted cakes used are shown below in Table 1.

Table 1: Composition of Defatted Cake and seed of Moringa oleifera

	Moisture	Ash	Fat/oils	Crude Protein	Carbohydrates
Integral	10.09±0.40	3.42±0.15	24.84±0.65	33.20±0.55	28.44±2.47
Mechanical	9.52±0.18	4.79±0.04	11.45±0.50	40.91±0.46	33.33±1.68
Hexane	7.07±0.10	5.20±0.03	10.93±2.56	47.79±1.02	29.00±5.25
Ethanol	5.98±0.05	4.09±0.15	26.25±1.28	32.37±0.77	31.31±3.18

The composition of the integral seed found is according to data reported in the literature for MO (Anwar et al., 2005; Silva et al., 2016).With the data presented in Table 1 it is still possible to notice a great similarity between the composition of the seed integral and the defatted cake obtained with ethanol, except for moisture, a factor that is due to the drying process at which the lees obtained by extraction with solvent were submitted after washing the removal of possible traces of it. Another factor to be highlighted is that the extraction of the lipophilic compounds did not cause a significant loss of protein content found in the bran, and it is still possible to observe an inversely proportional relation between the oil and protein content.

3.2 Coagulation / flocculation

As for the coagulation/flocculation assays performed in jar test the crude water used in the experiments presented average parameters of 340 mgPtCo/L of color, turbidity of 75 NTU and 0,305 cm^{-1} of compounds with absorption in UV_{254nm}. The results obtained for the removal of the parameters color, turbidity and UV_{254nm} with the use of the different coagulants are expressed on Figure 1.

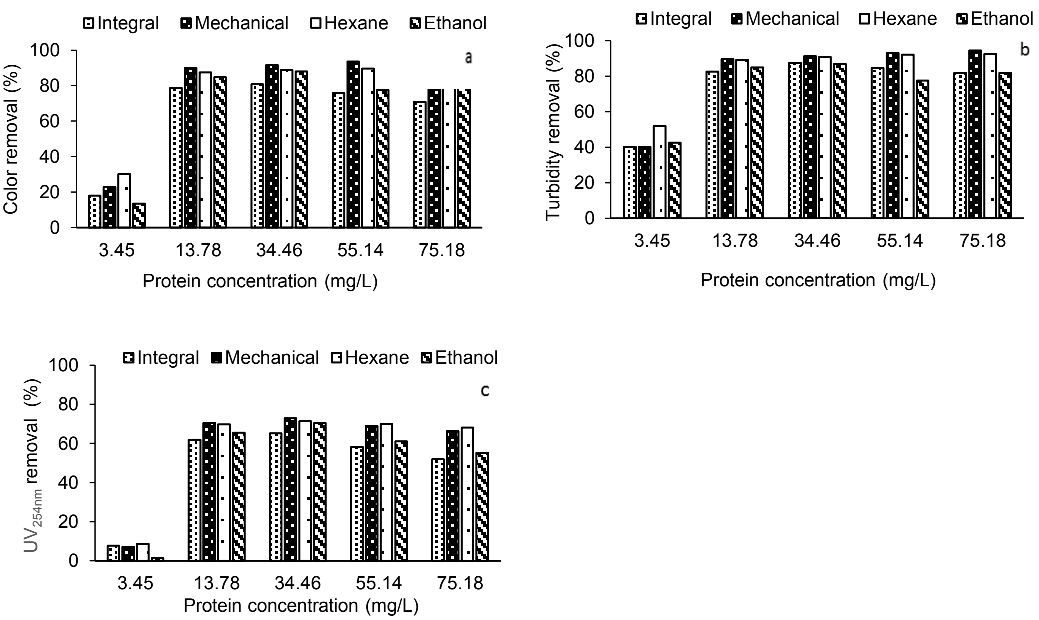

Figure 1: Percentage of color removal (a), removal of turbidity (b) and removal of UV_{254nm} (c) for the studied coagulants.

As can be observed, the removal of the three parameters was very similar among the different coagulants employed. Analyzing individually the color removal, represented by Figure 1 (a), it was verified an increase in the percentage of removal up to the concentration of 34.46 mg/L, from which it was possible to verify two different behaviors. The percentage of removal with the use of mechanical and hexane coagulants presented small increase according to the increase in concentration of coagulant, reaching removals above 91%.

Opposite behavior was observed for integral and ethanol coagulants which presented the removal of color reduced with increasing concentration of coagulant.
The results obtained were consistent with Baptista et al. (2015) that also found near 90% removals for color using MO saline coagulant in the same concentration range in low turbidity surface waters.
The turbidity removal, Figure 1 (b), showed a similar profile to the color removal, with an increase in turbidity removal for all coagulants up to a concentration of 34.46 mg/L. Bongiovani et al. (2014) conducted studies using defatted coagulants with ethanol and hexane reaching removal of 70% and 84% respectively at a dose of 15 mg/L of coagulating. In the present work the coagulants defatted with hexane and ethanol with the use of the ultrasound reached greater removals than the one obtained by Bongiovani et al. (2014) with percentages of 89% and 84% respectively in a lower dosage, of 13 mg/L. As far as the turbidity removal is concerned, similar results are found by Madrona et al. (2012) who also used MO saline coagulants, but with protein concentrations higher than 50 mg/L.
In relation to the removal of UV_{254nm} in Figure 1 (c), it was observed that the highest percentages were obtained in the concentration of 13.78 mg/L e 34.46 mg/L for the mechanical and hexane coagulants, reaching percentages close to 70%. Differently from the other parameters, the increase of the coagulant concentration above 34 mg/L necessarily implied the reduction of the percentages of removal. Among the evaluated parameters, the removal of the compounds with absorption in UV_{254nm} was inferior to the others since the parameter of UV_{254nm} is related to the presence of organic matter in the medium, although defatted Moringa still carries to the medium organic compounds that are solubilized and eventually lead to lowest removals (Baptista et al., 2015; Madrona et al., 2012; Bongiovani et al., 2015).
In general, the dosages of 13.78 mg/L and 34.46 mg/L showed superior performance in the removal of the parameters, however, the similar percentages of removal, suggest the lowest concentration of 13.78 mg/L was the best dosage. Thus, the parameters of color, turbidity and residual UV obtained using the dosage of 13.78 mg/L of coagulant together with the values of the raw water are expressed in Table 2.

Table 2: Residual of color, turbidity and UV254nm in coagulation/flocculation assays for the best conditions available

	Concentration of coagulant (mg/L)	Color (mgPtCo/L)	Turbidity (NTU)	UV_{254nm} (cm^{-1})
Integral	13.78	71.74±1.15	13.10±0.45	0,117±0.005
Mechanical	13.78	34.03±0.96	7.91±0.28	0.090± 0.003
Hexane	13.78	42.74±0.73	8.18± 0.46	0.092±0.002
Ethanol	13.78	51.75±0.25	11.43±1.38	0.105±0.007
Raw water	0.00	340.00±2.03	75.00±1.10	0.305±0.009

According to Table 2 it is possible to verify that the removal of the studied parameters is superior for the defatted coagulants, as already emphasized by Ndabigengesere and Narasiah (1995). The ones with the best performance, hexane and mechanical coagulants, were those obtained from the lees with the lowest percentage in remaining lipids, as shown in Table 1. The oil contained in MO seeds may lead to the formation of an emulsion or coating film, which inhibits contact with the reaction surface and thus reduces the formation of flakes, making the process of coagulation / flocculation difficult to occur (Ali et al., 2010; Baptista et al., 2015). Another possible explanation is that the removal of lipophilic compounds from the seeds reduces the interactions between lipids and active proteins, thus explaining the improvement in the coagulation potential of the coagulant obtained from defatted seeds.
As for the dissolved organic carbon, it was analyzed in the integral coagulants, mechanical coagulant, hexane and ethanol coagulants and are expressed in Table 3.

Table 3: Dissolved organic carbon present in coagulants.

	Integral	Mechanical	Hexane	Ethanol
DOC (mg/L)	1746.00	1355.00	1294.00	1693.00

Table 3 shows that the DOC values were consistent with the lipid content of the coagulants and the integral coagulant was the one with the highest amount of lipids, which presented the highest DOC value with 1746.00 mg/L and the lowest values of DOC 1355.00 mg/L and 1294.00 mg/L for the coagulants obtained by pressing and hexane extraction with lower lipid content. Thus, in view of the quantities of organic matter present in the coagulants given in Table 3, the treatment of water with defatted coagulants could result in less organic matter being added to the treated waters compared to the integral coagulant. In order to confirm this hypothesis the water samples treated with the aforementioned coagulants in dosage 13.78 mg/L were also analyzed for DOC and their results expressed in Table 4.

Table 4: Dissolved organic carbon present in the raw water and in the waters after treatment with the coagulants.

DOC (mg/l)	Raw water	Water treated with different coagulants			
		Integral	Mechanical	Hexane	Ethanol
	15.40	24.63 ± 1.02	9.12 ± 0.89	8.85 ± 0.76	11.10 ± 0.97

Table 4 shows a similar behavior to the removal with the mechanical and hexane coagulants, these being the ones that obtained the highest removals and presented lower DOC values with 9.12 mg/L and 8.85 mg/L, respectively. In general, it was possible to observe that the process of withdrawing the oil present in the seed before the preparation of the coagulant contributed to the DOC removal. This improvement in DOC removal can be confirmed when the DOC values of the waters treated with defatted coagulants are compared with the one treated with the integral coagulant. Due to the high concentration of organic matter added to the water treated with the integral coagulant there are concerns about the formation of trihalomethanes (THMs). During the disinfection process of water with chlorine the presence of organic matter can act as a precursor in the formation of THMs that are harmful to health due to their high toxicity and high carcinogenic and mutagenic potential (Brown et al., 2015; Niu et al., 2015; Gough et al., 2014; Bongiovani et al., 2015). The use of defatted coagulants has a further advantage with respect to the formation of trihalomethanes, since these coagulants provide lower amounts of organic matter dissolved in the treated water. In addition, the presence of smaller amounts of organic matter in the water after its treatment may reduce problems with taste, odor and the development of microorganisms during storage.

4. Conclusion

The use of coagulants produced from seeds with a reduced content of lipids resulted in an improvement in the process of surface water treatment, reaching color removal and turbidity above 90% and with a performance superior to the integral coagulant. Further, the use of defatted seeds coagulants presented the advantage of decreasing DOC of the treated water differently from the use of the MO coagulant in its integral form. Considering that the MO coagulant is natural and biodegradable, the use of this coagulant in its defatted form presents itself as a good alternative in the water treatment.

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