EVALUATION OF THE PROCESS OF COAGULATION / FLOCCULATION OF PRODUCED WATER USING *Moringa oleifera* Lam. AS NATURAL COAGULANT

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ABSTRACT

In the lifetime of an oil well, there comes a moment when a lot of water begins to be produced along with oil, either by the conditions of the reservoir, or as a result of water injection in the secondary recovery of the well. An important step in such process involves the treatment of the produced water by means of coagulation techniques. Therefore, the use of environmentally correct coagulants is presented as a viable alternative and has demonstrated advantages over the use of chemical coagulants. The plant of the genus *Moringa*, whose species is *oleifera* Lam, stands out as one of the most promising natural coagulants. The present study investigated the evaluation of the coagulation/flocculation of produced water, using seeds of *Moringa oleifera* Lam. as coagulant. The results were very significant, demonstrating that *Moringa oleifera* Lam. can be used as a natural coagulant in this type of treatment.

KEYWORDS

Moringa oleifera Lam.; produced water; coagulation/flocculation; natural coagulant; oil/water emulsion

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1. INTRODUCTION

The production of oil and gas is accompanied by significant production of water, commonly known as “produced water”, which is the waste that has the highest volume during the production and exploration of oil (Henderson et al., 1999). According to Thomas (2001), water is one of the most undesired contaminants in the production of oil. The amount of produced water associated with several types of hydrocarbon varies depending on a number of factors, such as the characteristics of the reservoir from which fluids are produced, age of the producing wells and the recovery methods used. The development of new technologies for the treatment of produced water or the optimization of existing ones is extremely important for the continuous expansion of the oil industry, whilst minimizing impacts to the environment. According to Spinelli (2001), when water needs to be treated by means of a coagulation technique, this becomes an important step in any treatment technology.

The terms coagulation and flocculation are used as synonyms, since they both mean the whole process of agglomeration of particles. Specifically, coagulation is a chemical process used to destabilize the colloidal particles. The addition of a chemical agent generates positively charged ions in water, which contains negatively charged colloids. As a result, there is a reduction in the repulsion between the particles (Silva, 2005). The flocculation is the aggregation of particles in suspension. This agglomeration is a function of the van der Waals forces. The formation of flakes can occur spontaneously only through the successive collisions between the several particles, if the system has energy available to do so, due to the agitation of the system. However, very intense stirring can disaggregate the flakes that are spontaneously formed, in which case there would be no need of such strong agitation as that used in the mixing operation.

Many coagulating agents are used in processes for treating water, such as inorganic coagulants (salts of aluminum and iron), synthetic and natural organic polymers (Cardoso, 2007). Aluminum sulfate is widely used worldwide as a coagulant, but recently its use has been questioned due to evidence that Alzheimer’s disease may be associated with aluminum in the water intended for human consumption. Moreover, aluminum is

not biodegradable, and can cause disposal problems and require treatment of the generated sludge (Moraes, 2004).

Many developing countries cannot afford the high costs of imported chemicals for water treatment. In this context, a coagulant which is environmentally friendly and inexpensive can be introduced as a viable alternative for the treatment of wastewater. Thus, in several countries, many plants are being used as sources of natural coagulants and flocculants. In particular, some biopolymers have been investigated more intensely than others, such as those found in *Moringa oleifera* Lam. (Silva et al., 2004).

This study proposes the evaluation of the coagulation / flocculation of produced water using *Moringa oleifera* Lam. in order to verify its effectiveness as a coagulant agent for this type of effluent.

2. MATERIALS AND METHODS

2.1 Preparation of synthetic produced water

Synthetic Produced Water was prepared using oil samples from the field of Bonsucesso, Carmópolis/SE (Northeastern Brazil). To each liter of distilled water, 35 g of NaCl P.A (Synth) and about 100 drops of oil were added. The generation of the emulsion was performed using the Ultra Turrax T50 homogenizer at a speed of 6,000 rpm, for 15 minutes.

2.2 Preparation of coagulant agent

Throughout the experimental part of this study, seeds of *Moringa oleifera* Lam. were provided by *Ambiental: Produto Natural e Orgânico*, a company located in the city of Aracaju, in the Brazilian State of Sergipe, in order to maintain the quality standards of the seeds and ensure that the results were not compromised by loss of effectiveness of the active coagulant.

Initially, the wings and the barks of the seeds were removed, and the remaining parts were crushed in a mill, so that a homogeneous material was obtained. The oil contained in the seeds was collected in an extraction system using n-hexane

P.A (Synth). After three hours of extraction, the *Moringa* pie was placed in a drying oven (model TECNAL TE 397 / 5) at 40 °C, for a period of 24 hours, until the mass became constant. The maximum temperature supported by the vegetable proteins before they are degraded is 60 °C (Heredia and Martín, 2008), so in this work all coagulation assays were carried out at 40 °C. Granulometric characterization was made by means of the sieving method, using 6 sieves with meshes of 1.18 mm, 0.59 mm, 0.42 mm, 0.25 mm, 0.149 mm and 0.074 mm.

2.3 Coagulation process

Tests to determine the optimal concentration of *Moringa* were conducted using a Jar-Test equipment (model analog HD-110 A6, six assays), with controlling rotation of mixers rods. During the mixing process, we varied the concentration of the *Moringa* in the synthetic produced water, at ambient temperature (25 °C), prepared with and without NaCl. The system was submitted to rapid rotation (120 rpm) for 10 minutes, and then to slow rotation (60 rpm) for 20 minutes, after which it was allowed to rest for 1 hour and 30 minutes, to enhance the process of decantation and/or particle flotation. A 25-mL aliquot was collected from the center of the jar, avoiding minimum disturbance, and the concentration of oil present in each sample was measured. Concentration levels of *Moringa* for emulsions with and without NaCl were 0.1, 0.5, 1.0, 1.5 and 2.0 g/L. The concentration of NaCl used was 30,000 ppm.

Using the optimal concentrations of *Moringa* determined in the previous tests performed without NaCl (0.1 g/L) and the tests performed with NaCl (2.0 g/L), a new study was carried out using *Moringa* concentrations close to these values, namely 0.25, 0.20, 0.15, 0.10 and 0.05 g/L, for the emulsion without NaCl addition, and 0.50, 1.00, 1.50, 2.00 and 2.50 g/L for the emulsion with NaCl, aiming to verify the existence of a point of maximum efficiency of oil removal.

Assays were performed by fixing the concentration of *Moringa* and varying the concentration of NaCl at 30,000, 35,000, 40,000, 45,000 and 50,000 ppm, to verify the behavior of the coagulant at different concentrations of NaCl.

After determining the best concentration of NaCl, the previous step was repeated, by varying

the concentration of *Moringa* to 1.5, 2.0, 2.5, 3.0 and 3.5 g/L in the sample of synthetic produced water (SPW). The same procedure was performed to determine the optimal concentration for the sample of real produced water (RPW).

Subsequent tests were carried out to adjust the pH of the synthetic emulsion, by setting the optimal concentration of *Moringa*, as found earlier, and varying the pH in each jar in the Jar-Test. The initial pH of the emulsion was measured and then corrected accordingly either with a 0.1-M hydrochloric acid solution or a 0.1-M sodium hydroxide solution, for values around the initial pH.

The assessment of the kinetics in the Jar-Test was made with the synthetic emulsion, using the optimal *Moringa* concentrations in each of the six jars. This test involved rapid rotation (120 rpm) for 10 min and then slow rotation (60 rpm) for 20 min. Once the mixing stopped, samples were collected at 0, 5, 10, 20, 30 and 60 min for each jar, respectively.

2.4 Determination of oil and grease (TOG)

The amount of oil contained in the RPW and SPW samples was determined using an Infracal TOG/TPH Analyzer, Model CVH from Wilks Enterprise, which measures the total recovery of oil and lubricants by the method of transmission or attenuated total reflection, obtained by infrared spectroscopy, whereby the result, given in mg/L, is calculated from the difference in the intensity of light absorbed by the sample.

3. RESULTS AND DISCUSSION

3.1 Determination of the optimal concentration of *Moringa*

This section discusses the tests carried out in order to determine the optimal concentration of the coagulant agent.

3.1.1 Variation of *Moringa* mass in the synthetic emulsion prepared with and without NaCl

The assays were conducted with a SPW sample with initial TOG of 627 ppm for the two emulsions

(with and without NaCl). The concentration of NaCl used was 30,000 ppm. The analysis for the samples without *Moringa* showed a final TOG of 620 and 615 ppm for the emulsion prepared with and without NaCl, respectively. Figure 1 shows the variation in the percentage of oil removal versus the concentration of *Moringa* with and without NaCl.

Figure 1. Percentage of oil removal as a function of concentration of *Moringa* with and without NaCl.

From the experimental results presented above, it was observed that, upon increasing *Moringa* concentration without NaCl, the removal efficiency of oil decreases until a minimum point is reached, from which the efficiency increases again. In the presence of salt, the phenomenon is reversed. Higher *Moringa* concentrations are required to increase oil removal. Within the scope of this investigation, it could be observed that the best concentrations of *Moringa* are 0.1 g/L in non-saline

Figure 2. Effect of the influence of salt (S) concentration compared to non-saline (NS) systems in the process of oil removal (RO).

systems and 2.0 g/L in salt-containing solutions. It was verified that salinity has a negative effect on the removal process, but the effect is opposite when the coagulant concentration is equal to or higher than 1.5 g/L, as shown in Figure 2.

In the experiments with NaCl, different emulsion behaviors were noticed as compared to the non-saline systems. The color of the emulsion without NaCl is darker, and the speed of separation was quite low. According to [Okuda et al. \(1999\)](#), the salt itself has a clarification effect, which explains the difference in color between the two emulsions. A simple increase in ionic strength of the solution already started the process of coagulation. Probably, the phenomenon of compression of the electrical double layer contributed to this effect, i.e. there is a balance of ionic strength between the coagulant and saline-solution, reaching the point where the ionic strength of the coagulant agent is higher than that of the saline-solution, obtaining a positive value in the removal of oil. The highest efficiency was observed with a coagulant concentration of 2.0 g/L.

3.1.2 Refinement of the range of concentration of *Moringa* for synthetic emulsion prepared with and without NaCl

From the results obtained previously, a refinement of the values of concentration of *Moringa* around the optimum value was made. The concentration of *Moringa* was varied in the amounts of 0.05, 0.10, 0.15, 0.20 and 0.25 g/L for the SPW samples without NaCl, and amounts of

Figure 3. Variation in the percentage of oil removal versus the concentration of *Moringa* with and without NaCl.

0.5, 1.0, 1.5, 2.0 and 2.5 g/L for the SPW samples with NaCl at a concentration of 30,000 ppm, both with a initial TOG of 328 ppm. The analysis for the samples without *Moringa* gave a final TOG of 320 ppm. Figure 3 shows the variation in the percentage of oil removal based on the finest ranges of *Moringa* mass with and without NaCl.

The main purpose of this step was to verify the existence of a point of maximal efficiency of *Moringa* coagulant in the emulsions mentioned above. Once the concentrations were established and tested, one could observe that the mass of 0.15 g of *Moringa* provided the best percentage of oil removal for the emulsion without salt, and 2.5 g of *Moringa* were necessary to provide the same result for the salt-containing emulsion. The same behavior detected previously was observed here.

3.1.3 Variation of NaCl concentration

In view of previous results, another test was made to check the best rate of oil removal by varying the salt concentration, keeping constant the initial concentration of oil (292 ppm) and *Moringa* (2.5 g/L). Figure 4 shows the percentage of oil removal with the aid of coagulant / flocculant studied, for different concentrations of NaCl.

According to Figure 4, the most efficient removal was obtained with the NaCl concentration of 35.000 ppm.

3.1.4 Optimum concentration of *Moringa*

In order to compare the SPW and RPW samples, we developed a chart of the normalization (C/C_0) versus the concentration of *Moringa*, because,

Figure 4. Percentage of oil removal as a function of NaCl concentration.

when working with oil, it is virtually impossible to keep the same concentration in all samples. Figure 5 shows the results of the optimal concentration of *Moringa* with a weight change of 1.5 g, 2.0 g, 2.5 g, 3.0 g and 3.5 g. When the SPW sample was tested, the NaCl concentration was 35.000 ppm, with an initial TOG of 390 ppm. With the RPW sample, the initial TOG was 492 ppm. In both cases, the required normalization was made. The readings of blank samples in both cases were 387 and 489 ppm for the RPW and SPW systems, respectively.

Figure 5. Comparison of normalization (C/C_0) for SPW and RPW versus the concentration of *Moringa* (g/L).

According to Figure 5, it was observed that the condition of equality between the two experiments lies in the range between 2.0 and 2.5 g/L. The best concentration of *Moringa* in SPW samples continues to be 2.5 g/L. For the RPW system, the best concentration was 1.5 g/L.

3.2 pH tests

In the experiment, within the range studied, it was observed that *Moringa* acts without significant variation in the percentage of oil removal, at a concentration of 2.5 g/L of the biopolymer *Moringa oleifera* Lam., in an emulsion with 505-ppm initial TOG. This is shown in Figure 6, where it is clearly shown that the percentage of oil removal in the presence of coagulant is independent on the pH of the emulsion.

According to **Muyibi and Evison (1995)**, *Moringa oleifera* Lam. does not change the pH of the treated water because it does not affect the alkalinity of the solution. **Ndabigengesere and**

Narasiah (1996) argue that this fact is typical of polyelectrolytes, due to the mechanism of reactions that occur.

Figure 6. Percentage of oil removal at different pH values.

Figure 7. Variation of $(-\ln C/C_0)$ with time in the integral method for the determination of the reaction order.

3.3 Kinetic test in Jar-test

The kinetics tests were performed using the Jar-Test equipment, for a sample of SPW with an initial TOG of 359 ppm, concentration of *Moringa* coagulant of 2.5 g/L and NaCl concentration of 35.000 ppm. Using the integral method, the order of reaction was assessed from the results shown in Figure 7, from which it was possible to conclude that the reaction is first order ($n = 1$) with a speed constant (k) equal to 0.0487 min^{-1} . This means that the speed of reaction ($-r_A$) is proportional to concentration (C_A), as described by equation (1).

$$-r_A = 0.0487 C_A \quad (1)$$

According to Levenspiel (1974), for first-order reactions the half-life ($t_{1/2}$) is directly related to the speed constant, as shown by equation (2).

$$t_{1/2} = 0.693/k \quad (2)$$

Therefore, the half-life for the reacting systems described in this work is 14.23 min^{-1} .

4. CONCLUSIONS

The efficiency of oil removal initially decreases with increasing *Moringa* concentration in a non-saline environment, and then increases again. In the presence of salt, the opposite phenomenon is observed. Within the limits of this work, it could be determined that the best *Moringa* concentration in non-saline systems is 0.1 g/L, whilst in saline environment the best concentration is 2.0 g/L. The optimal *Moringa* concentrations were 2.5 g/L for SPW samples, and 1.5 g/L for RPW samples, probably due to the interaction of coagulant agent with the other components of the RPW. With respect to pH, we could see that there was no influence in the process of coagulation/flocculation when using *Moringa*. Overall, the use of *Moringa oleifera* Lam. as a coagulant agent in the process of coagulation/flocculation of produced water provided significant results, which justify its use as an alternative coagulant in the treatment of produced water.

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