An evaluation of different preparation methods of the M. Oleífera-based natural coagulating agent in the treatment of produced water from petroleum

Avaliação de diferentes métodos de preparo do agente coagulante natural à base de M. Oleífera no tratamento de água produzida de petróleo

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Abstract

Before the petroleum produced water can be rejected or disposed of, it must undergo a series of treatments. Among these is coagulation, which is an important stage for the removal of organic and inorganic materials from the water. The use of environmentally friendly coagulants has become a viable alternative for the treatment of water, and has shown advantages, as opposed to inorganic chemicals, specifically in terms of biodegradability, low toxicity, and a low production index of residual mud. As such, this work's objective is to evaluate different preparation methods for a moringa-based coagulant and to determine its efficacy in removing the oils and gravels present in the produced water. Five preparation methods of the moringa-based coagulant were proposed. The coagulation/flocculation tests were conducted varying the concentration of Moringa oleifera Lam between 50 ppm to 300 ppm, with samples of synthetic produced water (SPW) in order to determine the best concentration in each preparation method. In general, the results proved effective, reaching a maximum removal of oil of 96%, in the concentration of 100 ppm, for the coagulant prepared mesh 20 (S₂₀).

Resumo

A água produzida de petróleo antes de ser condicionada ao descarte ou rejeição, necessita passar por uma série de tratamentos, dentre estes a coagulação, etapa importante para a remoção de material orgânico e inorgânico. O uso de coagulantes ambientalmente corretos apresenta-se como uma alternativa viável para o tratamento de água e tem mostrado vantagens em relação aos químicos, especificamente em relação à biodegradabilidade, baixa toxicidade e baixo índice de produção de lodos residuais. Sendo assim, este trabalho tem como objetivo avaliar diferentes métodos de preparo do coagulante à base de moringa e determinar a sua eficiência de remoção de óleo e graxas presentes na água produzida de petróleo. Cinco métodos de preparo do coagulante à base de moringa foram propostos. Os ensaios de coagulação/floculação foram realizados variando a concentração de Moringa oleifera Lam entre 50 ppm a 300 ppm, com amostras de água produzida sintética (APS) a fim de determinar a melhor concentração do coagulante em cada método de preparo. De maneira geral, os resultados mostraram-se eficientes, alcançando uma remoção máxima de óleo em água de 96%, na concentração de 100 ppm, para o coagulante preparado na forma mesh 20 (S₂₀).

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1. INTRODUCTION

Produced water (PW) is the water retained in subterranean formations which is brought the surface together with petroleum and gas (THOMAS, 2004). When petroleum is produced, the flow of the well normally contains produced water associated with hydrocarbons. The water must be separated from the hydrocarbons and disposed of in a way that does not pollute the environment. The produced water is separated from the petroleum through processing equipment by gravity, such as three-phase separators, heaters, and free water disposal vessels. Generally, in onshore systems, the national volume of petroleum is approximately 23% (SANTOS E WESNER, 1997; STEWART E ARNOLD,
According to Brazil (2016a) the production of petroleum in Brazil was around 54,357 thousand barrels from onshore fields and 8,300 thousand barrels from offshore fields, totaling 864,043 thousand barrels in 2015. By that name was of volume of produced water of 220,024,430.1 m³.

The state of Sergipe has 22 onshore fields in production and 8 maritime fields, totaling 1,711 productive onshore wells and 35 offshore wells. In 2016, the production of petroleum generated 8,187 thousand barrels from onshore fields and 2,717 thousand barrels from offshore fields (BRASIL, 2016a). The onshore field at Carmopolis is considered the largest productive field in Brazil and the fourth in terms of oil production. Carmopolis has an average daily production of 28,000 m³ of produced water (RIBEIRO, 2013).

The resolution by the National Council on the Environment CONAMA nº 393/2011 established that produced water must adhere to a maximum value of contained oil and gravel of 42 ppm and that the pH must be between 5 and 9. As such, treatment is inevitable to establish and maintain the control of this effluent (BRASIL, 2011).

In the conventional treatment of produced water, the brute water is captured and then sent to a rapid mix unit where the processes of coagulation/flocculation and sedimentation occur (ROLA et al, 2016). The process of coagulation can be used as an important preliminary or intermediate step among other treatment methods for produced water. It is also considered an important step in the treatment of effluents due to its simplicity, efficacy, and low energy consumption (ZAHRIM et al, 2017).

The most used coagulants for the treatment of PW are inorganic, among them aluminum sulfate, ferric chloride, and ferric sulfate. Despite their clear efficiency in the removal of contaminants, these coagulants are not biodegradable and can create problems in the treatment and disposal of residual mud (DOS SANTOS et al., 2016).

As such, in the last few years the extracts of various plants have been used as natural coagulants, in which a small number of biopolymers have been applied and studied more in-depth than others. Such is the case of the Moringa oleifera (M. oleifera), the chitosan and the tamarind (DOS SANTOS et al., 2016; MERAS et al, 2016).

The M. oleifera is a native Indian northeast species and belongs to the family Moringaceae. Colloquially known as the white lily, this species contains cationic proteins in its seeds with low molecular weight, which are responsible for the coagulation process (ARANTES et al., 2015; GUALBERTO et al., 2015).

In light of the petroleum industry’s preoccupation with the large volume of produced water, especially in mature onshore fields, this study’s aim is to evaluate the different preparation methods the M. oleifera-based coagulating agent’s efficiency in coagulation.

2. MATERIALS AND METHODS

2.1. Obtaining the Moringa Seeds

The seeds of the M. oleifera used in this study were taken from plants located on the Federal University of Sergipe campus in Sergipe, Brazil. All of the steps in the experiments were undertaken at the same university, at the Characterization and Biofuels Processing Laboratory (LCPB) in the Competency in Petroleum and Gas Center of Sergipe (NUPEG/SE). Five preparation methods of the moringa-based coagulating agent were proposed, as shown in Figure 1.

![Image: Flow chart of the different preparation methods of the moringa-based coagulating agent](https://via.placeholder.com/150)

Figure 1 - Flow chart of the different preparation methods of the moringa-based coagulating agent
2.2. Preparation of the moringa oleifera-based coagulant in natura

The preparation of the natural coagulant in natura without a specific granulometry ($S_{int}$) was adapted based on the methodology described by Valverde et al. (2014). 50g of moringa seeds with the shells removed were ground in a mill (Tecnal TE 633), to obtain a homogenous material, which was then placed on a stove (BRASDONTO-Mod. 2) with circulation and air renewal at 40°C until it reached a consistent texture. After the drying stage, the material was then analyzed based on its granulometry, as described in the following procedure.

2.3. Preparation of the moringa oleifera-based coagulant in natura with specific granulometry

In order to obtain the specific granulometry of the coagulant, 100g of the prepared seeds as described above (in natura) were homogenized in a set of sieves over the course of one hour. Granulometries of mesh 35 and mesh 20 were chosen, named $S_{int-35}$ and $S_{int-20}$, respectively. After this stage the seeds were separated according to their granulometries in two closed recipients.

2.4. Preparation of the moringa oleifera-based coagulant in defatted form

An extraction of the oil of the M. oleifera seeds was conducted using a mechanical press in order to obtain the defatted coagulant ($S_{dnu}$). 15 g of the M. oleifera seeds in natura was collected manually in the press and left there for a period of 24h. After this stage, the defatted seeds were stored in closed recipients.

2.5. Preparation of the Moringa oleifera-based coagulant in a liquid médium

A 100 mL beaker was used to add 50 mL of distilled water and 1g of in natura seeds. Soon after, the solution was homogenized using an agitation of 1000 rpm over 30 minutes. The mixture obtained was then separated using vacuum filtration, where the filtrate behaved similarly to the M. oleifera extract in the liquid medium ($S_{aquo}$) used as a natural coagulant for the treatment of produced water.

2.6. Preparation of the Synthetic Produced Water

The samples of petroleum for the development of this project came from the Sergipe / Alagoas basin.

In the preparation of the synthetic produced water (SPW), 35 g of NaCl were added to each 1-liter of distilled water and close to 0.5 g of petroleum. These concentrations are based on the report of the analysis by Petrobras of produced water in the Sergipe-Alagoas basin (Brasil, 2016b). The mixture was made using a homogenizer from the FISATOM brand, 713D model, at a rotation of 2,500 rpm over the course of 30 minutes.

2.7. Determination of the Best Concentration of the Moringa-based Coagulant

The determination of the best concentration of the M. oleifera-based coagulant was conducted by means of a jar test with the analogue model JT-112 A6 in six tests. In this stage, the system was submitted to a rapid rotation of 100 rpm for 3 minutes and then followed by a slow rotation of 15 rpm in 15 minutes, as in the methodology described by Madrona et al. (2012). With the objective of consolidating the coagulation/flocculation, the synthetic produced water (SPW) was later left to sit for 60 minutes. This phase is necessary for the decantation and/or flotation of the particles. Finally, an aliquot of 25 mL was taken from the center of the beaker, avoiding the minimum suspension of the decantation, and which was then analyzed to determine the concentration, and the Oil and Gravel Content (OGC) post-treatment. The concentrations of M. oleifera-based coagulant used in the coagulation/flocculation tests, and sedimentation was: 50; 100; 150; 200; 250; and 300 ppm.

2.8. Analysis of the Oil and Gravel Content (OGC)

The dependent variable of this study was the efficacy of the process based on the analysis of the initial and final oil and gravel contents. This analysis was conducted using the INFRACAL apparatus (Wilks Enterprise brand, CVH model). The solvent used in these tests was tetrachloroethylene (Neon brand, 99.99%). All of the results obtained were analyzed in duplicates.

After measuring the OGC, the data was validated by means of analysis of the variance (ANOVA) and the average comparison test, using the Tukey test, with 95% accuracy ($p$-value<0.05) to verify the significant differences.

2.9. Monitoring the pH

The pH was monitored via an immersion of the pHmeter electrode (Hanna pH 21 model) directly into the sample, after calibration. The electrode was washed with deionized water between samples. After each test, the values were noted for each sample.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the Different Preparation Methods for the Moringa-based Coagulant

The coagulation/flocculation tests were conducted using the jar test, utilizing a volume of 200 mL of SPW, in the concentrations of 50; 100; 150; 200; 250; and 300 ppm. In order to have greater confidence in the obtained results, a variance analysis was conducted (ANOVA) and an average comparison test, using the Tukey test, which resulted in 95% accuracy ($p$-value<0.05) through the SISVAR 5.6.
Table 1 shows the averages of the obtained results in the efficacy of the removal of the OGC, considering the preparation methods of the moringa coagulating agent in the $S_{\text{int}}, S_{\text{int}-20}, S_{\text{int}-35}$, $S_{\text{int}-20}$ e $S_{\text{aq}}$ forms in a function of the concentrations of 50; 100; 150; 200; 250; and 300 ppm.

Table 1 - Efficacy of the removal of the OGC for the different methods of the preparation of the moringa-based coagulating agent

<table>
<thead>
<tr>
<th>Coagulant Concentration (ppm)</th>
<th>Efficacy of the removal of OGC %</th>
<th>Preparation Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{int}}$</td>
<td>$S_{\text{int}-35}$</td>
<td>$S_{\text{int}-20}$</td>
</tr>
<tr>
<td>50</td>
<td>90.9 ± 0.49&lt;sup&gt;a&lt;/sup&gt;</td>
<td>82.1 ± 0.39&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>100</td>
<td>92.3 ± 0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>90.7 ± 0.37&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>150</td>
<td>95.2 ± 0.37&lt;sup&gt;c&lt;/sup&gt;</td>
<td>92.4 ± 0.65&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>200</td>
<td>94.3 ± 0.24&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>89.0 ± 0.58&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>250</td>
<td>93.10 ± 0.49&lt;sup&gt;b,d&lt;/sup&gt;</td>
<td>88.8 ± 0.97&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

(1) Percentages of the OGC’s presented in values of averages ± standard deviation. Within the same column, the averages followed by the same letter do not differ statistically in and of themselves via the Tukey test at a 5% level of significance.

Following Table 1 and evaluating the five preparation methods of the moringa-based coagulating agent, it was possible to observe a removal efficiency between 68% and 99% for the OGC parameter.

Using the moringa seed in natura ($S_{\text{int}}$), we observed a variation in the efficacy of the removal of the OGC between 85% and 95%. The best performance was seen in the concentration of 150 ppm, which obtained a removal of OGC of 95±0.37%. The statistic analysis revealed the augmentation of the concentration of moringa-based coagulant in the $S_{\text{int}}$ form, which implies the augmentation of the efficacy of the removal of the OGC, and confirms that for the approximate concentration of 200 ppm, is exists a maximum level of OGC removal, thus indicating an excess of coagulant in the treatment of SPW.

Daud et al. (2015) used different inorganic coagulants in concentrations varying from 300 ppm to 500 ppm for the removal of OGC in produced water. The authors reached a removal percentage of 97% using the aluminum polychloride, 99% with aluminum sulfate, and 97% with ferric chloride. In light of this, it's clear that the moringa-based coagulant in the $S_{\text{int}}$ form is a viable alternative for the treatment of produced water. In all of the experiments conducted, the $S_{\text{int}}$ coagulant did not meet the environmental requirement described by the CONAMA Resolution number 430 in relation to the OGC (<20 ppm) in the following conditions: (1) concentration = 50 ppm (final OGC = 26 ppm); (2) concentration = 100 ppm (final OGC = 22 ppm); (3) concentration = 250 ppm (final OGC = 21 ppm) and (4) concentration = 300 ppm (final OGC = 42 ppm).

For the moringa coagulating agent with a specific granulometry of mesh 35 ($S_{\text{int}-35}$), a Better performance of 150 ppm was observed, presenting the removal of 92 ± 0.65% of the OGC parameter, which, when analyzed statistically using the program SISVAR, it was verified that there were no significant differences between the concentrations of 100 and 150 ppm, which makes it possible to use the 100 ppm concentration or the 150 ppm concentration. In this way, keeping in mind the cost of the treatment, it is more advantageous to use the 100 ppm concentra-
concentrations of 150 ppm and 250 ppm were similar, showing that the concentration of coagulant is an important factor in the removal of OGC. It was also observed that an increase in the concentration of coagulant starting at 250 ppm did not imply a better percentage of OGC removal in the SPW. According to Baptisa et al. (2015), the moringa-based coagulant prepared in the liquid medium has limited use, seeing as the increase in the concentration of the coagulant can cause a greater organic weight in the treated water, which contributes negatively to the process of coagulation/flocculation and sedimentation. Of all of the tests performed, the coagulant prepared in the form $S_{aquoso}$ was successful in meeting the standards of the Brazilian legislation in relation to OGC ($<$20 ppm) in only two conditions: (1) concentration = 100 ppm (OGC= 10ppm), and (2) concentration = 200 ppm (OGC= 1ppm).

Figure 2 shows the monitored values of the pH after the coagulation/flocculation process using the natural moringa-based coagulant in the $S_{int}$, $S_{des}$, $S_{int-35}$, $S_{int-20}$ e $S_{aquo}$ forms.

Using Figure 2, it was possible to see that the moringa-based coagulant in the $S_{int}$, $S_{des}$, $S_{int-35}$, $S_{int-20}$ e $S_{aquo}$ forms did not alter the pH significantly to the point of compromising the disposal of produced water, remaining within the parameters established by CONAMA law number 430/2011. In other words, the pH remained between 5 and 9 (BRASIL, 2011). This fact implies that the direct application of the moringa coagulant in a produced water treatment station contributes to the additional costs for the process of the correction of the pH of the water, as normally occurs when using inorganic coagulants (MAGESHKUMAR E KARTHIKEYAN, 2016).

### 3.2. Comparison between the efficacies of the different preparation methods of the moringa-based coagulant

Using Figure 2, it was possible to see that the moringa-based coagulant in the $S_{int}$, $S_{des}$, $S_{int-35}$, $S_{int-20}$ e $S_{aquo}$ forms worked with synthetic produced water made it difficult to maintain the same initial concentration of OGC in the water in each of the 5 methods studied. A graph was created to show the normalization ($C/C_0$) versus the concentration of coagulant.

The results of Figure 3 illustrate that the concentration of 100 ppm generally proved more effective in the removal of OGC. As such, it was used to test this concentration to determine which method was most effective among the five studied. Table 2 shows the comparative results of the five methods in the efficacy of the reduction of OGC present in the SPW.
Figure 3 - Normalization ($C/C_0$) of the tests with SPW using different methods versus the concentration of coagulant

Table 2 - Comparative between the efficacies of the different methods of preparation of the moringa-based coagulant in the concentration of 100 ppm

<table>
<thead>
<tr>
<th>Preparation methods</th>
<th>Efficacy of Removal of OGC (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{int}$</td>
<td>92% ± 0,12 a</td>
</tr>
<tr>
<td>$S_{int-35}$</td>
<td>91% ± 0,37 a</td>
</tr>
<tr>
<td>$S_{int-20}$</td>
<td>96% ± 1,06 b</td>
</tr>
<tr>
<td>$S_{des}$</td>
<td>76% ± 1,16 c</td>
</tr>
<tr>
<td>$S_{aquo}$</td>
<td>96% ± 0,41 b</td>
</tr>
</tbody>
</table>

(1) Efficacy of the removal presented in average values ± standard deviation. In the same column, the averages followed by the same letter do not differ statistically among themselves as per the Tukey test at a 5% level of significance.

Table 2 shows that the preparation methods of the moringa-based coagulant in the $S_{int}$, $S_{int-35}$, $S_{int-20}$ and $S_{aquo}$ forms presented the best results in the removal of OGC and obtained, in general, an efficacy above 90%. Using statistical analysis, it was observed that there were expressive variations among the methods studied, especially in the preparation method of the coagulant in $S_{des}$ form. The jar tests for the removal of OGC demonstrated that considering the economic side of the process, as well as the ease in preparation of coagulant, the most advantageous method was in the $S_{int-20}$ form and the least recommendable preparation method was the $S_{des}$ form.

4. CONCLUSIONS

In light of these results, it is possible to conclude the following.

1. Among the five preparation methods of the *moringa oleifera*-based coagulant, four proved themselves effective and promising alternatives to the use of inorganic coagulants for the treatments of the effluents in produced water, with the advantages of being a natural, biodegradable, non-toxic agent with an easy preparation method and a low production cost.

2. The concentration and the preparation method significantly influenced the removal of OGC in produced water.

3. Statistically, the preparation methods in the forms: in the liquid medium ($S_{aquo}$) and with a specific granulometry of mesh 20 ($S_{int-20}$) did not present significant variations. Similar behavior was observed in the preparation methods with the specific granulometry of mesh 35 ($S_{int-35}$) and *in natura* ($S_{int}$).

4. In terms of the percentage of OGC reduction, the recommended methods are in the liquid medium ($S_{aquo}$) and that with a specific granulometry of mesh 20 ($S_{int-20}$). Both of these methods obtained a removal efficacy of 96% at a concentration of 100 ppm.

5. The preparation method of the defatted form ($S_{des}$) had the least efficacy in terms of OGC removal among the five methods studied. Even though it achieved a maximum efficacy of 76%, it was unable to meet the legislation requirements in terms of OGC (<20 ppm), which is the lowest quantity required.

6. The pH's monitored after the coagulation process remain...
within the guidelines established by the CONAMA law number 393/2007, in other words, between 5 and 9. As such, the use of the natural moringa-based coagulant does not compromise the disposal of produced water and does not even require the correction of pH.

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