A COMPARISON STUDY OF TWO GRAVIMETRIC METHODS FOR OIL SPILLS CLEANUP BY MAGNETIC NANOMATERIALS: A METHODOLOGICAL DISCUSSION

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ABSTRACT: Magnetic nanoparticles have been successfully used to recover oil from water. In the present work, two different methods, with and without agitation by vortex, were employed to promote the interaction of three magnetic materials (magnetite nanoparticles, N; magnetic nanocomposites of yeast biomass, a byproduct from ethanol industry, Y; and cork powder, C), with oils with different API gravities (10, 20, 28 and 45) spilled on deionized water and real seawater. The magnetic materials exposed to oil on water were recovered by a simple magnet, and the oil recoveries were determined by gravimetric analyses before and after lyophilization. The lyophilization was determinant to guarantee the accuracy of the experiments. Only the API gravity affected the oil recovering, presenting a direct and negative correlation with the capacity of oil removal from water, enabling to predict the potential mass of oil to be removed by knowing the API.

KEYWORDS: oil spill, influence of water removal, bionanocomposite, API gravity, two-layers method, magnetic nanoparticles

1. INTRODUCTION

Oil spills are an environmental and public health issue due to their potential contamination of soils and water (surface and groundwater) and complicated remediation (Wang et al., 2010; Elias et al., 2015; Raj & Joy, 2015). Most of the oil spills occur during extraction, transportation, and transferring the oil between vessels (Berti et al., 2009). Oil spills generate tremendous environmental impacts. For example, it reduces the contact area between water and the atmosphere, which affects the biochemical demand for oxygen (BOD) and chemical oxygen demand (COD), thus hindering the photosynthesis by aquatic plants and respiration of aerobic marine organisms (Berti et al., 2009). The scale of devastation caused by oil spills, such as in Dalian-China (2010), Mexican Golf (2010), Campos-Brazil (2011), and Arkansas-USA (2013), symbolizes the necessity of new strategies for remediation. In this sense, Elias et al. (2015) and Raj & Joy (2015) point out that a relevant alternative is the development of a cost-effective, efficient, clean, recyclable and biocompatible techniques for the oil removal from aquatic systems. Moreover, treating the water co-produced with oil and gas is also an issue due to its contamination with emulsified oil and metals (Cakmakce et al., 2008).
Magnetic nanomaterials have stood out because they can be employed alone, functionalized or incorporated into different adsorbent materials, having the advantage of being easily removed from solution after use by the application of a magnetic field (Atta et al., 2015). Most studies estimate the removal capacity of a given material by comparing the weight before and after the removal of oil spilled. It may be appropriate because gravimetric methods are absolute and recognized for high reliability and accuracy (Hulanicki, 1995; Richter, 1997).

Despite the fact that various studies use gravimetric analysis to evaluate the removal of oil spilled in water by magnetic nanomaterials, there are no standard protocols of how this kind of experiment should be done. For example, the disposal of the oil on the water surface and the possible advantages of using or not using a vortex during the contact of the magnetic nanomaterial with the oil layer are still unclear.

Despite many works employed, the ASTM F 726-12 method is the standard method that is commonly used for such purposes (ASTM, 2012). However, this method has some limitations as it does not take into consideration the contribution of the water mass that may be removed with the oil, whether it is emulsified or simply dragged by the thrust provoked by the attraction of the magnetic particles and the magnet. As the procedure involves a gravimetric analysis, water masses and salt present in seawater can induce overestimations. Few papers reported a simple draining step of the magnetic material with the removed oil (Wu et al., 2014; Jiang et al., 2017; Cojocaru et al., 2017). However, most of papers ignored this step, which denotes that they possibly neglected the contribution of water mass on the estimated mass of oil removed by the evaluated magnetic material (Calgagnile et al., 2012; Grance et al., 2012; Gu et al., 2014; Mao et al., 2014; Elías et al., 2015; Ge et al., 2015; Yu et al., 2015; Pan et al., 2016; Tao et al., 2017). In the same way, the influence of oil API gravity remains unexplored.

At this moment, these methodological issues are the focus for developing new materials, which are related to the innovative conditions of the application of magnetic nanomaterials for the removal of spilled oils from water. Also, the multidisciplinarity of the researchers involved in the aforementioned studies, whose areas present different methodological practices, can also be a limiting factor for establishing principles for the development of a quantitative method.

A compromise with reproducibility and accuracy of measurements enables remedying the inconsistencies and methodological deficiencies (Richter, 1997), such as avoiding overestimation of the capacity of oil removal by the various materials and making possible comparisons of the removal capacity among materials to establish an efficiency gradient. Having these points in mind, we performed gravimetric studies simulating the removal of oils spilled on water in two-layer systems aiming to investigate the ways to establish a reliable and accurate methodology for the evaluation of the removal capacity of a selected sorbent.

Herein, this work compares the oil removal by different in house prepared sorbents, namely: magnetite nanomaterial (N), magnetic nanocomposites of yeast biomass, a byproduct from ethanol industry (Y) and cork powder (C). Four oils with different API gravities (10, 20, 28 and 45) were used in oil spill simulations, which were spilled on deionized water and real seawater, using two different methods to promote the interaction of the materials with the oils (with and without agitation by vortex). Also, in commitment to the accuracy of the measures, we evaluated the influence of the insertion of a drying step to eliminate the water impact, which could be associated with oils and materials, as well as determine the solids dissolved in seawater, on the gravimetric results.

2. MATERIAL AND METHODS

2.1. Materials

Cork powder was obtained from an industry of cork artifacts in São Paulo (Brazil) and used as sorbent. Yeast Biomass was provided by Biorigin (Zilor Group Company, Lençóis Paulista, Brazil) and used to produce the composite with magnetic nanoparticles to be used as sorbent. All reagents employed to synthesize the magnetic materials like FeCl$_2$·6H$_2$O, FeCl$_2$·4H$_2$O, HCl, and NH$_2$OH were purchased from Merck (Germany). The oil removal studies were performed using four different oil samples, 10, 20, 28 and 45 API
2.2. Synthesis of Magnetite Nanoparticles and magnetic bionanocomposites

The magnetite nanoparticles (N) were synthetized by employing solutions of 200 mg L\(^{-1}\) FeCl\(_2\)-4H\(_2\)O and 134 mg L\(^{-1}\) FeCl\(_3\)-6H\(_2\)O prepared in 2.6 mol L\(^{-1}\) HCl, which were mixed together in proportion of 4:1. Following, this mixture was stirred for 30 min at room temperature, and 100 mL of 0.7 mol L\(^{-1}\) NH\(_2\)OH were slowly dropped into the mixture. The resulting suspension containing magnetic nanoparticles (N) of Fe\(_3\)O\(_4\) was centrifuged, and the magnetic precipitate was decanted with the help of a magnet, washed with purified water and rinsed with absolute ethanol before be stored in a desiccator to dry. As for the preparation of the magnetic nanocomposites, the same procedure was carried out except that the suspension was heated up to 80 °C before adding the cork powder or the yeast biomass and N in proportion of 8:1. This suspension was vigorously stirred for 30 min at 80°C, and the produced cork powder (C) or yeast biomass (Y) magnetic nanocomposites were washed with absolute ethanol and reserved in desiccator to dry for posterior use. The synthesized magnetic nanomaterials were previously characterized and employed for adsorptive removal of dye from textile wastewater as reported by Labuto et al. (2018).

2.3. Evaluation of Methods for Oil Spills Uptakes from Water by Magnetic Nanomaterials

The experiments were carried out to compare two different methods regarding the capacity of magnetic nanomaterials to remove oils dispersed in water. The oil spills were done performed two-layers, i.e., exposing the oil samples on water surface that resulted in two distinct phases to simulate an oil spill without emulsification between the aqueous phase and the oil. Around 300 mg of each oil was weighed and dropped on about 300 mL of deionized water (D) and seawater (S) at 25°C, at the time of weighing.

In the first oil removal method, called Two-Layers Floating (F), the oil remained floating on the surface of the D and S (Figure 1). Around 20 mg of the magnetic nanomaterials (N, C or Y) were spread over the oil spilled and left for 2 min without any additional action. Then the magnetic nanomaterials that interacted with the oil were removed from the water surface by approaching a magnet covered by a known mass of an aluminum foil. The aggregate formed by magnetic nanomaterials, the oil removed and the aluminum foil were weighed. The measured masses were recorded to evaluate how much the mass of water and salt from seawater during the dragging process influenced the results obtained from the gravimetric analysis. Subsequently, the aggregate was frozen, lyophilized by 24 h and weighed again to determine the masses of oil removed without the mass of water transported with the magnetic nanomaterials during magnet approach. For seawater, the values related to the contribution of the proportional salt present in the volume of water removed during lyophilization were discounted. Triplicates of 10 mL of seawater were also lyophilized and the solid residue was weighed to determine its contribution in g L\(^{-1}\).

In the second method, called Two-Layers Vortex (V), after exposing the oil on D or S at 25°C, a vortex was created with nearly 1.5 cm using a magnetic stirrer, which was held for 2 min avoiding the emulsification of the oil with water. Afterwards, the stirring was stopped and the magnetic nanomaterials were removed in the same way of the first method. All the experiments were conducted by triplicate to confirm reproducibility.

2.4. Statistical Analyses
All the statistical analyses were executed using Minitab 18®. When necessary, data were transformed if distribution did not fit the normal curve or did not present homoscedasticity (Shapiro-Wilk and F tests, respectively). The type of water, removal method, material, and oil were compared by paired tests (t-test or Kruskal-Wallis test, depending on distribution and homoscedasticity). Pearson correlation was employed to verify the association between the type of oil and removal capacity.

3. RESULTS AND DISCUSSIONS

3.1. Evaluation of Methods for Oil Spills Uptakes from Water by Magnetic Nanomaterials

Oils disperse differently in water depending on the API grade and the type of water (Figure 1). It is notorious that increasing API promotes higher dispersion of the oil; it is less intense in seawater. This dispersive behavior may be related to the chemical composition of each oil; the weaker the intermolecular cohesion forces, the more dispersed will be the oil (Israelachvili, 2011). Thus, both the type of oil and the type of water may influence the quantity of the spilled oil removed.

3.1.1. Influence of lyophilization and salt on accuracy of gravimetric oil removing by magnetic nanomaterials analyses

Lyophilizing prior to the gravimetric determination seems to be crucial to producing accurate results obtained for oil removal, independent of the API grade, magnetic material used and the mechanism of contact between the magnetic material and the oil to be removed (Figure 2). Lyophilization may be the best method because it eliminates water in low temperate, which prevents losing volatile substances and preserves the oil (Cetin et al., 2003). In this study, estimates of oil removal without prior lyophilization ranges from 1.4 to 8.6 times greater than the mass determined with lyophilization. Thus, it is relevant to remark that if a given investigation did not eliminate water prior determination of oil removed, it probably overestimated the capacity of removing oil from water because some mass of water is incorporated to the final mass recovered. Also, it is possible to state that the lower the API grade, the higher the relative standard deviations and the quantities of water carried with the oil during the magnetic removal process. This fact is probably related to the forces of cohesion between the molecules that compose the oil, which intensify the buoyancy process caused by the attraction of the magnetic materials, and the magnet, favoring the transport or water and oil together (Israelachvili, 2011).

Figure 1. Aspect of the different oils spilled on deionized water and seawater at 25 ºC. Poderia reduzir um pouco estas imagens. Parecem um pouco distorcidas!
3.1.2. Evaluation of methods for oils spills uptakes from water by magnetic nanomaterials

Among all the results of variables and treatments evaluated (Table 1), only the type of oil differs significantly from each other (Figure 3, Table 2), which is directly and inversely correlated to the capacity of oil removal (Figure 4). Therefore, it is possible to predict the potential mass of oil to be removed knowing its API; as the lower the API the more oil will be removed. These observations reinforce the conclusion that oil removal mechanism by magnetic nanomaterials cannot be described only by adsorption, because it is not only associated with the type of material used and the physical or chemical interactions between their functional groups and the molecules of oil. The main contribution in the removal process is the action of the thrust caused by the attraction of the magnetic material impregnated with oil as the magnet approaches, with the additional contribution of the intermolecular forces of the oil molecules, such as London interactions (Israelachvili, 2011).
Table 1. Oils spilled recovery from water with diverse salinities employing three different magnetic nanocomposites and two contact methods between the magnetic materials and oils, n = 3.

<table>
<thead>
<tr>
<th>Oil API</th>
<th>Oil removal method</th>
<th>Water kind</th>
<th>Yeast biomass nanocomposite (Y)</th>
<th>Cork powder nanocomposite (C)</th>
<th>Magnetite nanoparticles (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oil removed (kg/kg)</td>
<td>Oil removed (%)</td>
<td>Oil removed (kg/kg)</td>
</tr>
<tr>
<td>10</td>
<td>Vortex (V)</td>
<td>Deionized (D)</td>
<td>16.98 ± 1.49</td>
<td>109 ± 9</td>
<td>14.77 ± 1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>16.59 ± 0.91</td>
<td>107 ± 5</td>
<td>14.26 ± 0.87</td>
</tr>
<tr>
<td></td>
<td>Floating (F)</td>
<td>Deionized (D)</td>
<td>15.98 ± 0.20</td>
<td>101 ± 1</td>
<td>14.65 ± 0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>15.16 ± 0.33</td>
<td>99 ± 4</td>
<td>15.28 ± 0.80</td>
</tr>
<tr>
<td>20</td>
<td>Vortex (V)</td>
<td>Deionized (D)</td>
<td>12.36 ± 1.59</td>
<td>83 ± 10</td>
<td>11.71 ± 0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>13.88 ± 2.42</td>
<td>90 ± 16</td>
<td>11.83 ± 0.92</td>
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<tr>
<td></td>
<td>Floating (F)</td>
<td>Deionized (D)</td>
<td>13.34 ± 0.77</td>
<td>84 ± 4</td>
<td>10.37 ± 0.85</td>
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<td></td>
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<td>Seawater (S)</td>
<td>13.99 ± 0.41</td>
<td>91 ± 3</td>
<td>12.37 ± 0.62</td>
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<tr>
<td>28</td>
<td>Vortex (V)</td>
<td>Deionized (D)</td>
<td>6.80 ± 1.73</td>
<td>39 ± 5</td>
<td>8.29 ± 0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>10.37 ± 3.37</td>
<td>55 ± 8</td>
<td>5.53 ± 0.58</td>
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<tr>
<td></td>
<td>Floating (F)</td>
<td>Deionized (D)</td>
<td>7.88 ± 0.72</td>
<td>54 ± 5</td>
<td>8.88 ± 0.56</td>
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<td>Seawater (S)</td>
<td>8.04 ± 0.44</td>
<td>55 ± 2</td>
<td>8.56 ± 0.73</td>
</tr>
<tr>
<td>45</td>
<td>Vortex (V)</td>
<td>Deionized (D)</td>
<td>5.93 ± 1.20</td>
<td>37 ± 8</td>
<td>2.01 ± 0.25</td>
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<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>4.68 ± 0.24</td>
<td>31 ± 1</td>
<td>1.04 ± 0.21</td>
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<tr>
<td></td>
<td>Floating (F)</td>
<td>Deionized (D)</td>
<td>5.56 ± 0.63</td>
<td>37 ± 4</td>
<td>5.58 ± 0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Seawater (S)</td>
<td>6.18 ± 4.69</td>
<td>23 ± 1</td>
<td>5.16 ± 0.80</td>
</tr>
</tbody>
</table>
Figure 3. Box-plot of each type of oil (A) material (B), water (C) and removal method (D). Letter over each box-plot indicates if the respective mean differs significantly to other ($\alpha = 0.05$).

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Type of test</th>
<th>Test value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionised x Seawater (water)</td>
<td>$t$-test*</td>
<td>2.62E-14</td>
<td>1.000</td>
</tr>
<tr>
<td>Floated x Vortex (removal)</td>
<td>$t$-test*</td>
<td>2.98E-15</td>
<td>1.000</td>
</tr>
<tr>
<td>Y x N x C (material)</td>
<td>Kruskal-Wallis</td>
<td>1.66</td>
<td>0.437</td>
</tr>
<tr>
<td>10 x 20 API (oil)</td>
<td>$t$-test</td>
<td>9.34</td>
<td>4.86E-11</td>
</tr>
<tr>
<td>10 x 28 API (oil)</td>
<td>Kruskal-Wallis</td>
<td>5.26</td>
<td>2.92E-13</td>
</tr>
<tr>
<td>10 x 45 API (oil)</td>
<td>Kruskal-Wallis</td>
<td>5.23</td>
<td>2.92E-13</td>
</tr>
<tr>
<td>20 x 28 API (oil)</td>
<td>Kruskal-Wallis</td>
<td>5.29</td>
<td>3.45E-13</td>
</tr>
<tr>
<td>20 x 45 API (oil)</td>
<td>Kruskal-Wallis</td>
<td>5.23</td>
<td>2.92E-13</td>
</tr>
<tr>
<td>28 x 45 API (oil)</td>
<td>Kruskal-Wallis</td>
<td>4.82</td>
<td>3.68E-12</td>
</tr>
</tbody>
</table>

* transformed data

Table 2. Paired comparison between variable/treatments (types of water, removal method and types of oil).

Figure 4. Scatterplot of API degree versus oil mass removal (mean ± standard deviation), using Pearson correlation.

4. CONCLUSIONS

The removal of oil by magnetic based nanomaterials using a magnet field is believed to be influenced not only by adsorption, but also can be due to the phenomenon of pushing the oil by the thrust caused by the magnetic attraction associated with the intermolecular interaction between the oil molecules. Eliminating water before the determination of the removal capacity is critical for the correct inference of the mass of oil removed when using composite materials loaded with magnetic nanoparticles. On the contrary, an overestimation of removal capacity may take place if water presents. Results reported in percentage of
oil removal support this fact. The type of magnetic material, the mechanism of contact with the oil spill and the water salinity are not major factors that affect the removal efficiency of the oil. Among the evaluated parameters, the API gravity is inversely proportional to the amount of oil removed, enabling the prediction of removal based on the high and significant correlation observed.

5. REFERENCES


6. ACKNOWLEDGEMENTS

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