INTRODUCTION

In January 2000, there was a large-scale oil spill in Guanabara Bay, when around 1.3 million barrels of crude oil leaked out of a pipeline, affecting beaches and mangroves. After it reached the beaches, the oil was removed together with the sand with spades, constituting a hazardous waste. This waste is being stored until a treatment method or means of recuperating the oil is found at a reasonable cost. One of the treatment processes that seems promising for the precipitation and/or mineralization of various organic contaminants is chemical oxidation using Fenton’s reagent 1, 2, 3, 4.

The decontamination of soils with Fenton’s reagent has been investigated as an alternative process in the remediation of sites contaminated with organic compounds. The obtainment of a strong oxidant (radical OH•) capable of destroying or hydrolyzing many of these compounds in contaminated soils by decomposing H2O2 is shown as follows:

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH• + OH^- 
\]

Initially, Fenton’s reaction was employed in the oxidation of compounds soluble in water, like alcohols and phenol. The greatest difference when it comes to contaminated soils is the physical state of the contaminant. While in aqueous systems the contaminant is soluble in water, in soil it is adsorbed or present as particles into soil matrix 5. The physical state of these contaminants hampers treatment conditions, requiring a more rigorous process than that applied in the classic Fenton’s reaction, which involves the addition of diluted hydrogen peroxide 6.

MATERIALS AND METHODS

Contaminated beach sand: The beach sand contaminated with petroleum collected after the spill was granted by CENPES (Centro de Pesquisas Leopoldo Miguez – Petrobrás). The sand’s initial O&G content was 32 g/kg sand. Before being analyzed, the sand was quartered to obtain a representative sample 7. According to the PETROBRÁS data, the oil contained 44% aromatic compounds, 31% resins, 14% asphaltenes and 11% saturated hydrocarbons.

Analytical methodology: The H2O2 was quantified by titrimetric analysis with permanganate 9. To analyze the O&G levels, a Soxhlet extraction method was used, adapted for the soil sample 10. To analyze the COD, the closed reflux method was used 10. The interference of H2O2 in determining the COD was corrected using the equation by Talini & Anderson 11. The chromatographic analyses were conducted in an HP 5890 A chromatograph, using an SE-54 column (methyl 5% phenyl silicone). After Fenton’s reaction, the oil was extracted from the sand and the fractions of saturated and aromatic hydrocarbons were separated according to the methodology employed by Olson et al. 12. After the solvent was evaporated, the oil was diluted in dichloromethane (1mg/10mL) and injected into the chromatograph.

Analysis of biodegradability of the aqueous phase: Biodegradability tests on the aqueous phase separated after
chemical oxidation were carried out using a bioreactor with a working volume of 500 mL, using activated sludge from a sewage treatment plant (VSS= 2210 mg/L) that had been adapted previously. After nutrients KH₂PO₄ and urea were added (COD:N:P = 100:5:1) and the pH adjusted to 7.0, the aqueous phase was mixed with the sludge and aerated. Samples of the aqueous phase were taken every 2h to measure the soluble COD.

Tests with Fenton’s reagent: The experiments carried out with Fenton’s reagent were conducted at ambient temperature (25 ± 2 °C), with constant shaking (70 rpm) in a jar test. They were done in 1000 mL glass beakers with a 12 cm diameter. To these beakers were added 5 g or 20 g sand in 200mL of a solution containing iron (II) sulfate heptahydrate 1N and hydrogen peroxide (30%, v/v) in different proportions. The concentrations of H₂O₂ used were 0.4 M or 4.0 M and of Fe²⁺ were 2.7 g/L or 27.2 g/L. The reaction time investigated for the removal of oil from the sand was 3 h and 6 h. The pH, was initially adjusted to 3.0, and was thereafter adjusted each hour. The H₂O₂ was added to the medium slowly for 3h.

Experimental design: The effect of the different factors on the removal of oil from the sand was evaluated through a fractionary experimental design 2⁴⁻¹ with three central points, developed in accordance with the methodology proposed by Montgomery ¹³. The factors selected were: H₂O₂ concentration, Fe²⁺ concentration, mass of contaminated sand and reaction time. The O&G removal results were analyzed using Statistica 5.5 software to determine the most significant factors and/or interactions involved in the removal of oil from the sand.

RESULTS AND DISCUSSION

Analysis of the Experimental Design: A statistical analysis of the results generated linear regression with a correlation coefficient of 0.99 for a confidence level of 95%. The 11 experiments with their respective results are presented in Table 1. It can be seen that the O&G removal efficiency varied between 54% and 97%. These results show that the oil came away well from the sand, moving to the aqueous phase, which reduced the toxicity of this residue and made its final disposal easier.

The Student t-test was used to verify which effects were significant in the oil removal efficiency, the results of which are presented as a Pareto graph in Figure 1. An analysis of the Pareto graph indicated that to obtain greater oil removal, the reaction must be conducted with higher H₂O₂ concentrations, a longer reaction time and lower Fe²⁺ concentration. Watts & Stanton ¹⁴ observed that high H₂O₂ concentrations, of around 10M, brought about a greater desorption and oxidation of hexadecane in sand (silica). The mass of sand analyzed in these experiments was not significant, yet it had a negative effect, indicating that it could be advantageous to work with smaller masses to achieve better oil removal from the sand.

In other tests, the fractions of oil were analyzed (oil adhered on the sand + dissolved oil + emulsified and free oil), after the treatment with Fenton, as shown in Table 2. It can be seen that little oil remained in the soil after the chemical oxidation (only 19% of the total O&G content), i.e. 81% of the oil was removed from the sand.

Table 1 - Results referring to the O&G removal efficiency from sand in the fractionary experimental design 2⁴⁻¹:

<table>
<thead>
<tr>
<th>RUN</th>
<th>H₂O₂(M)</th>
<th>Fe²⁺(g/L)</th>
<th>SAND(g/L)</th>
<th>TIME(h)</th>
<th>REM. EFF.(%)</th>
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<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>27.2</td>
<td>100</td>
<td>6</td>
<td>95</td>
</tr>
<tr>
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<td>4</td>
<td>27.2</td>
<td>100</td>
<td>6</td>
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</tr>
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<td>25</td>
<td>6</td>
<td>62</td>
</tr>
<tr>
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<td>14.5</td>
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<td>4.5</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 2 - Results showing fractions of oil in the different phases, soon after the Fenton reaction, in a sample with an initial O&G level of 32g/kg sand.
remained emulsified (44.3%), which made its removal from the medium easier. The total oil oxidation efficiency was obtained for the total oil content (100% - à A + B + C) that remained in the solution after treatment with Fenton’s reagent. In this way, it was verified that on average only 35.3% of the O&G present in the sand was mineralized by Fenton’s reaction under the conditions analyzed.

Analysis of biodegradability in the aqueous phase: New experiments were held under the best conditions supplied by the Pareto graph (Run 2 – Table 1). The resulting aqueous phase was analyzed as to its biodegradability. The aqueous phase, which contained only dissolved and emulsified oil, presented a residual H₂O₂ concentration of 500 mg/L and COD of 542 mg/L (corrected value). Figure 2 shows the decay of soluble COD from the aqueous phase with time.

It can be seen in Figure 2 that the aqueous solution that resulted from Fenton’s reaction was biodegradable, since by around 7.5 h, the COD level had already been reduced by 60%. Chamarro et al. also observed reductions in COD after Fenton’s reaction with different organic compounds (formic acid, phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene).

Analysis of the oxidation by gas chromatography: The oxidation of the oil was investigated using gas chromatography of the extracts obtained after Fenton’s reaction, conducted under the best (Run 2) and worst (Run 8) oil removal conditions (Table 1). The purpose of these analyses was to verify whether the oxidation of the oil by Fenton’s reaction was closely related to the oil removal from the sand.

Figure 3 shows the fractions of saturated and aromatic hydrocarbons before and after Fenton’s reaction under the best and worst experimental conditions. The chromatograms of the oil treated under the best removal conditions (chromatograms S₁ and A₁) show that there was a greater modification in the composition of the oil and a greater reduction in the fractions of saturated and aromatic hydrocarbons than was observed under the worst removal conditions (chromatograms S₂ and A₂), when both are compared with the chromatograms obtained for the untreated oil (S₀ and A₀). These modifications could be closely related to the removal of oil from the sand. In other words, for there to be a greater oxidation of the hydrophobic contaminants present in the soil, it is necessary for the oil to be removed from the sand so it can be in contact with the reactive species in the solution and the oxidation process can begin. The need for there to be oil removal for there to later be oxidation was reported by other authors.

CONCLUSIONS

In the analysis of the removal efficiency of oil from the sand, efficiency levels of between 54% and 97% were achieved, indicating that Fenton’s reaction was effective in cleaning the beach sand. Analyses made on the supernatant after Fenton’s reaction indicated a 60% COD reduction after around 7.5 h, which implies that the effluent generated was biodegradable. The chromatographic analysis indicated that Fenton’s reaction made it possible to modify the fractions of saturated and aromatic hydrocarbons when there was a higher proportion of oil removed from the sand.

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REFERENCES


4 - Kong, S.; Watts, R.J.; Choi, J. *Chemosphere.* 1998. 37(8), 1473.


