



## Petroleum oxidation using Fenton's reagent over beach sand following a spill

Valéria S. Millioli<sup>a,b</sup>, Denize D.C. Freire<sup>a</sup>,  
Magali C. Cammarota<sup>a,\*</sup>

<sup>a</sup> Department of Biochemical Engineering, School of Chemistry,  
Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

<sup>b</sup> Mineral Technology Center (CETEM/MCT), Rio de Janeiro, Brazil

Received 29 November 2002; received in revised form 4 July 2003; accepted 8 July 2003

---

### Abstract

Removal and oxidation of petroleum adhered onto the beach sand after a spill over Guanabara Bay in Rio de Janeiro (Brazil) have been studied using Fenton's reagent ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ). Jar tests were done on 5 and 20 g sand suspended in 200 ml aqueous solution containing iron(II) salt and hydrogen peroxide under constant stirring. The  $\text{H}_2\text{O}_{2(\text{g})}:\text{Fe}_{(\text{g})}^{2+}$  ratio varied from 0.5:1 to 50:1, pH was 2.0 and 6.0 and reaction time 1 and 3 h. Initially, the contaminated sand content of oil and grease (O&G) was 32 g/kg sand. The statistical analysis showed time and iron–sand and  $\text{H}_2\text{O}_2$ –iron–sand interactions to be the most significant variables, with an average O&G removal from the contaminated sand being just 30% after 3 h reaction. However, oil was removed from the sand (by up to 97%) and passed to the aqueous phase, making waste final disposal easier. The post-reaction analysis showed the supernatant to be biodegradable. Chromatographic analysis results were that the Fenton's reaction favored both the change and reduction of oil saturated and aromatic fractions.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Fenton's reagent; Petroleum; Beach sands; Spill

---

### 1. Introduction

Pollution caused by spills of petroleum and its derivatives over coastal areas is a serious threat to the environment. Thus, an adequate treatment of these areas is called for, considering that when a petroleum spill reaches the beaches, there may be deeper penetration in the soil, which depends on sand grain size, so causing serious damages to the ecosystem.

---

\* Corresponding author. Tel.: +21-2562-7568; fax: +21-2562-7567.  
E-mail address: christe@eq.ufrj.br (M.C. Cammarota).

Many have been the studies conducted in order to investigate means of treatment capable of eliminating or recovering the oil adhered to the grains of sand.

A major leak out of a pipe occurred in the Guanabara Bay in January 2000 during which around 1.3 million liters of crude oil reached beaches and mangrove areas. From the beaches the oil was removed together with sand by using shovels, thus forming a hazardous residue. This residue has been in store until a means of treating or recovering the oil at a reasonable cost is found. Chemical oxidation using the Fenton's reagent has been promising in precipitating and/or mineralizing various organic contaminants [1–4] and in decontaminating soils as an alternative remedy for polluted sites. The means of obtaining a powerful oxidant ( $\text{OH}^\bullet$  radical) capable of destroying or hydrolyzing various compounds in contaminated soils by decomposing  $\text{H}_2\text{O}_2$ , is shown next:



At first, Fenton reaction was used to oxidize water soluble compounds such as alcohols and phenols. In the case of contaminated soils, the contaminant is adsorbed on the soil matrix [5]. The physical state of the contaminant is a hindrance to the treatment conditions and requires a more stringent process than that applied to the classical Fenton's reaction [6].

The objective of this work is to study the chemical oxidation process by Fenton's reagent (a mix of ferrous sulfate and hydrogen peroxide) for removing and degrading the oil adhered to contaminated sand.

## 2. Materials and methods

### 2.1. Contaminated beach sand

The oil contaminated sand collected after the spill was provided by CENPES (Leopoldo Miguez Research Center of Petrobras). The sand presented an initial O&G content of 32 g/kg sand. Before the analysis the sand was quartered so as to obtain a representative sample as per the Brazilian Technical Standards Association recommendation [7]. According to Petrobras [8], the oil was 44% aromatic compounds, 31% resins, 14% asphaltenes and 11% saturated hydrocarbons.

### 2.2. Fenton's reagent tests

The tests of Fenton's reagent were jar tests under constant stirring (70 rpm) at room temperature ( $25 \pm 2^\circ\text{C}$ ). The glassware consisted of 1000 ml glass beakers, 12 cm in diameter. To the beakers masses of 5 or 20 g sand were added. The beakers contained 200 ml of 1N ferrous sulfate and hydrogen peroxide (30% (v/v)) at varied proportions. All the testing started with weighing the contaminated sand, transferring to the beaker, adding distilled water to make to final volume, adding the ferrous sulfate solution and, finally, adding the hydrogen peroxide solution. From that point on, the oxidation reaction started and the time was counted.

### 2.3. Oil degradation tests

For this study a complete factorial design  $2^5$  was used with 5 variables (pH, iron(II) concentration, hydrogen peroxide concentration, sand mass, and time) and 2 levels (−1 and +1). The reagents ratio under study in the Fenton's reaction were 5:1, 50:1, and 0.5:1 of  $\text{H}_2\text{O}_2(\text{g}):\text{Fe}_{(\text{g})}^{2+}$  using  $\text{H}_2\text{O}_2$  at 0.4 M (13.6 g/l) or 4 M (136 g/l) concentrations and 2.7 or 27.2 g/l  $\text{Fe}^{2+}$ . At this phase, after the sand was mixed with the  $\text{Fe}^{2+}$  solution and distilled water, pH was adjusted with 1N  $\text{H}_2\text{SO}_4$  or 1N NaOH solutions in order to achieve the desired initial values (2.0 or 6.0). The  $\text{H}_2\text{O}_2$  required for each test was added during the first 10 min and the reaction time count (1 and 3 h) started right after the first dosage of  $\text{H}_2\text{O}_2$  added to the reactional medium. At this phase, the tests were carried out without controlling the pH throughout the reaction time. These experiments analyzed oil total degradation in the solution. The entire beaker contents (aqueous phase + sand) were analyzed in order to obtain the total O&G content. The oxidation results in terms of O&G were analyzed using the Statistica 5.1 software for determining the most significant factors and/or interactions.

### 2.4. Tests of oil detachment from the sand

These tests were intended to investigate just the oil that remained in the sand following chemical oxidation. To analyze oil detachment from the sand the same factors as those in the complete factorial design were evaluated, except for pH, the latter being initially adjusted to 3.0 and kept constant throughout the reaction (it was adjusted at every 1 h of reaction). The levels under evaluation were the same, except for time the levels of which were increased to 3 and 6 h. Reaction time was lengthened in function of this variable having been pointed out to be the most significant in the total process of oxidation evaluated in the first phase of this work.  $\text{H}_2\text{O}_2$  was added slowly to the medium for 3 h. This manner of adding  $\text{H}_2\text{O}_2$  was preliminarily evaluated and showed the best detachment efficiency when gradually added to the reactional medium. The effect of the various factors on the process of oil detachment from the sand was evaluated through an experimental fractional design  $2^{4-1}$  with three central points [9]. The variable for response to these experiments was O&G contents, which kept adhered to the sand after oxidation.

### 2.5. Aqueous phase degradability analysis

Degradability assays, on the aqueous phase separated after chemical oxidation, were performed in a bioreactor 500 ml in usable volume. Activated sludge from a municipal sewage treatment plant was employed as inoculum (volatile suspended solids = 2210 mg/l) being gradually acclimated to the aqueous phase separated after chemical oxidation. Following addition of nutrients (chemical oxygen demand (COD):nitrogen:phosphorus = 100:5:1) and pH adjustment to values close to neutrality, the aqueous phase was mixed to the sludge and then aerated through a sintered glass air distributor. Aliquots were taken from the aqueous phase at every 2 h for the determination of soluble COD.

## 2.6. Analytical methodologies

H<sub>2</sub>O<sub>2</sub> was quantified by a titrimetric method with permanganate [10]. To analyze O&G contents the Soxhlet extraction method adapted for soil sample was used [11]. COD was analyzed using the closed reflux method [11] and H<sub>2</sub>O<sub>2</sub> interference was corrected using Talini and Anderson's equation [12]. The chromatographic analyses were conducted on a HP 5890 A chromatograph using a SE-54 column (5% phenyl, 95% methylsilicone). Following Fenton reaction, the oil was extracted from the sand and the saturated and aromatic fractions were separated according to a methodology by Olson et al. [13]. After the solvent evaporated, the oil was diluted in dichloromethane (1 mg/10 ml) and injected in the chromatograph.

## 3. Results and discussion

### 3.1. Oil degradation analysis

This analysis was performed in order to investigate whether the oil was mineralized by Fenton's reagent. At this step, 32 trials were done to a complete factorial design 2<sup>5</sup>. The results showed a maximum degradation efficiency of O&G of just 31% and in many trials little or no degradation was observed. The software used generated a linear regression curve with a 0.948 correlation coefficient for a 95% confidence interval. To check which effects were significant or not on oil degradation efficiency as measured by O&G analysis, the Student's *t*-test was used. The tabulated Student's *t*-value is obtained through the number of degrees of freedom for the trials that is provided by the software (error's degree of freedom in complete factorial design 2<sup>5</sup> was 6). Assuming a confidence interval of 95% and 6 degrees of freedom, a value of  $t = 2.447$  was obtained from tables in statistical books. From that value, the effects were analyzed for their significance on O&G oxidation process. For an effect or interaction to be considered important, its value should be greater than the tabulated one (2.447). These analyses are best visualized by using Pareto's graph where the dotted black vertical line ( $P = 0.05$ , the tabulated Student's *t*-value) indicates the minimum magnitude of the statistically significant effects for a 95% confidence level for the system under analysis. The effects of factors and interactions surpassing that line indicate that they are important to the analysis in question. Fig. 1 on the manuscript shows the effect analysis of the 32 trials using Pareto's graph. The values shown in the horizontal columns of Pareto's graph correspond to calculated Student's *t*-test of each factor or interaction ( $t = \text{coefficient of each factor/standard error}$  provided by the software). The effects of these factors can be classified as main or interaction effects. The main positive effects indicate that the factors should be used at their highest level so as to provide the best response to the system; the negative effects indicate that they should be used at their lowest level. The interactions can also be positive or negative. An negative BE interaction (as shown in Fig. 1) indicates that if one shifts from +B to -B, the E effect increases, and if one shifts from +E to -E, the B effect increases. Thus, Pareto's graph shows that the main effect for O&G degradation efficiency that was found in the sample was "time" (positive) followed by iron-sand (negative) and H<sub>2</sub>O<sub>2</sub>-iron-sand (negative) interactions. The effects of H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, and pH, analyzed separately, were not significant to a 95% confidence level in Student's *t*-distribution.

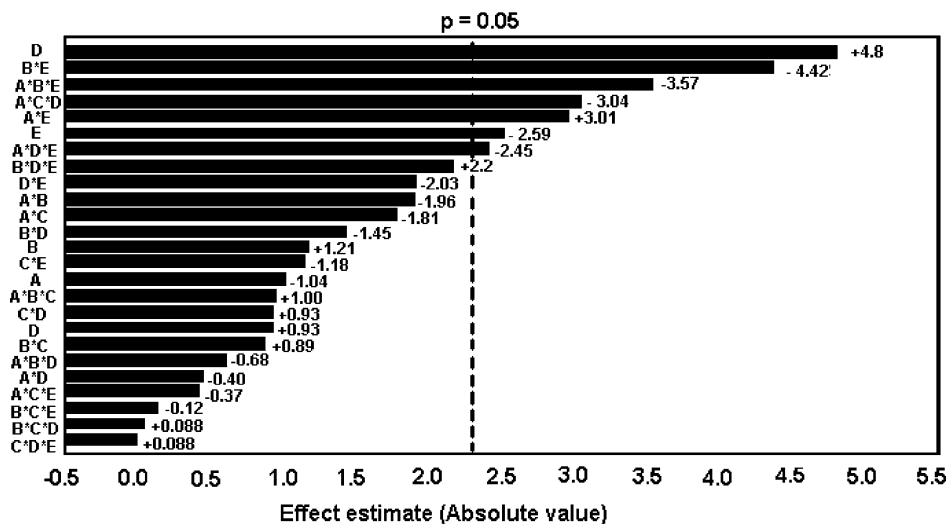


Fig. 1. Pareto graph for O&G degradation efficiency using Fenton's reagent. The letters A–E represent the factors and interactions (A, H<sub>2</sub>O<sub>2</sub>; B, Fe<sup>2+</sup>; C, pH; D, time; E, sand mass). The values appearing the horizontal columns of the graph correspond to Student's *t*-value generated for each factor and the dotted black vertical line indicates the tabulated Student's *t*-test value (2.447). The factors and interactions surpassing that vertical line indicate that they are important to the analysis in question.

H<sub>2</sub>O<sub>2</sub> showed not to be significant to O&G degradation within the concentration range evaluated (0.4–4.0 M) and O&G degradation efficiency figures were very low ( $\leq 31\%$ ). This suggests that, within that range, there was no H<sub>2</sub>O<sub>2</sub> enough for the Fenton reactions to take place in an efficient fashion. Watts and Stanton [14] studied oxidation and mineralization of hexadecane in sandy mud (0.1 mmol/kg) with Fenton reaction and found that 83% hexadecane found sorbed and in the NALP (nonaqueous liquid phase) was mineralized to CO<sub>2</sub> and H<sub>2</sub>O under more severe conditions, that is, with H<sub>2</sub>O<sub>2</sub> at a 10 M concentration. Low concentrations of H<sub>2</sub>O<sub>2</sub> have been used in most studies of Fenton's reagent [14]. Notwithstanding, high concentrations of H<sub>2</sub>O<sub>2</sub> appear to be required to oxidize sorbed contaminants. That tendency was documented by Watts et al. [1] who found that H<sub>2</sub>O<sub>2</sub> at elevated concentrations was required to oxidize sorbed hexachlorobenzene.

As far as time is concerned, Kong et al. [4] observed through gas chromatographic analyses diesel oil and kerosene degradation levels in a sandy soil close to 50% only at 72 h after the experiment which is indicative that time is really an important factor.

The factor sand presented a significant and negative effect so showing that, in the assays with smaller soil mass, O&G degradation efficiency was higher. This is probably due to the better mix obtained under that condition that made hydroxyl radicals' action easier, obtaining better oxidation and degradation efficiency from O&G adhered to the sand.

Nonsignificance of the pH can be explained by its decrease following addition of H<sub>2</sub>O<sub>2</sub> to the reactional medium. Because no pH adjustment was made, it kept within the 1.5–2.5 range at the end of the trials. Chamarro et al. [15] also observed in their experiments that pH dropped with H<sub>2</sub>O<sub>2</sub> addition to the reaction.

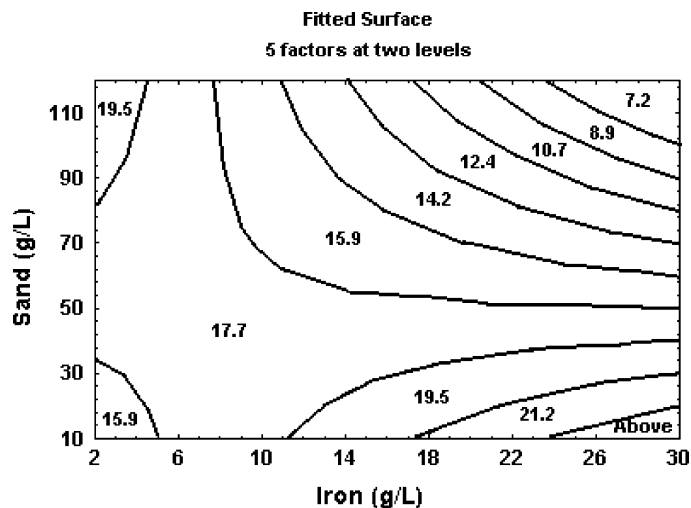


Fig. 2. Response surface describing the interaction of sand mass (vertical axis) and  $\text{Fe}^{2+}$  concentration (horizontal axis). Contour lines represent percent value of O&G degradation efficiency obtained for each combination.

The iron–sand and  $\text{H}_2\text{O}_2$ –sand interactions also appear as significant and one can see that for a better degradation efficiency, the trials of Fenton oxidation should be conducted with the highest level of iron and the lowest level of sand or conversely (Fig. 2). This result seems to indicate presence of low iron concentrations in the contaminated sand and existence of an optimum level of iron(II), since with small sand masses, the sand level of iron is not sufficient and degradation efficiency increases with iron concentration, and that as the sand mass is increased, the situation starts to invert, that is, the increase in iron concentration begins to reduce efficiency. On the other hand, the  $\text{H}_2\text{O}_2$ –sand interactions (Fig. 3) showed that efficiency increased with a higher level of  $\text{H}_2\text{O}_2$  and sand or with a lower level of both, again indicating the importance of  $\text{H}_2\text{O}_2$  concentration in respect of the oil mass to be oxidized. In smaller sand masses there was less oil to be oxidized in the reaction, thus requiring low concentrations of  $\text{H}_2\text{O}_2$ . With larger masses of sand, that is, in the presence of higher concentrations of oil, efficiency appears to be closely related to  $\text{H}_2\text{O}_2$  concentration in the reactional medium.

An experimental condition was randomly selected and three assays were conducted under that condition for investigating oil fractionation. After chemical oxidation the solution phases separated: the supernatant (aqueous phase with dissolved and emulsified oil + oily phase with free oil) and the sand (with adhered oil) that were analyzed for O&G contents. Table 1 has the results for the different fractions. Observed is that little oil remained on the sand following chemical oxidation (only 19% total O&G content), that is, 81% oil was removed from the sand. Most of the oil remained emulsified which made its removal from the medium easier. Oil total oxidation efficiency was obtained over the total oil content (the sum of the three fractions) remaining in the solution after Fenton's reagent treatment. Thus, one sees that, on the average, just 35% of O&G found on the sand was mineralized by Fenton's reagent under the analysis conditions.

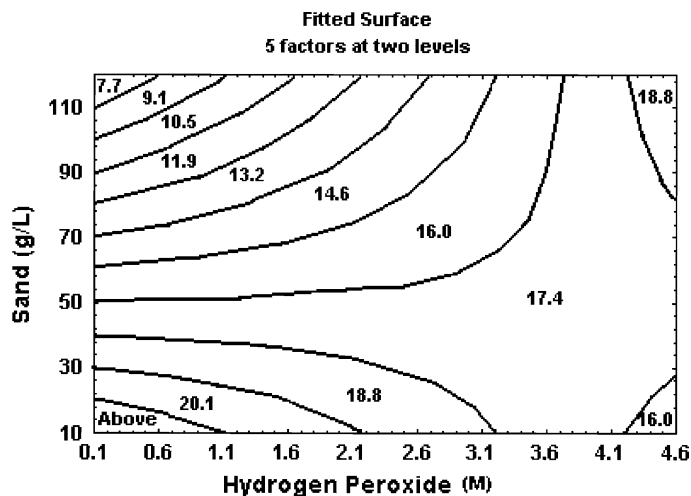


Fig. 3. Response surface describing the interaction of sand mass (vertical axis) and  $\text{H}_2\text{O}_2$  concentration (horizontal axis). Contour lines represent percent value of O&G degradation efficiency for each combination.

Analyses were carried out under different conditions:  $\text{H}_2\text{O}_2$  addition to the solution (without iron), iron addition (without  $\text{H}_2\text{O}_2$ ), and water addition to the solution (without iron and  $\text{H}_2\text{O}_2$ ). The third assay was done in order to check whether oil would detach from the sand only under jar test stirring at 70 rpm and in an acidic medium (pH 3.0) after a 3 h trial. pH was adjusted right after water and/or iron addition.  $\text{H}_2\text{O}_2$  addition took place right at the first 20 min of reaction. Fig. 4 presents the results of these assays where a better oil detachment from the sand (83%) is observed when using Fenton's reagent.  $\text{H}_2\text{O}_2$  resulted in an elevated detachment (60%), as it is an excellent oxidant and provided detachment when added to the solution.

In view of the results in the first step of this work having produced low mineralization levels and that the oil did detach from the sand, as confirmed by preliminary fractionation tests, a decision was made for a more detailed study of the process of oil detachment from the sand.

Table 1

Oil fractionation results in the different phases, right after Fenton reaction on a sample with initial O&G content of 32 g/kg sand

Assays <sup>a</sup>	1	2	3	Average
Oil on sand <sup>b</sup> (fraction A) (%)	18.0	22.0	17.0	19.0
Soluble oil in aqueous phase <sup>b</sup> (fraction B) (%)	1.5	1.0	2.5	1.2
Free and emulsified oil in aqueous phase <sup>b</sup> (fraction C) (%)	48.0	41.0	44.0	44.3
Oil after Fenton treatment <sup>b</sup> (fraction D = A + B + C) (%)	67.5	64.0	63.5	64.7
Overall efficiency of O&G oxidation <sup>b</sup> (100-D) (%)	32.5	36.0	36.5	35.3

<sup>a</sup> Assays conducted with addition of  $\text{H}_2\text{O}_2$ : 4 M,  $\text{Fe}^{2+}$  (2.7 g/l), time (3 h), pH 3.0 and sand mass (25 g/l).

<sup>b</sup> Relative to initial O&G contents of 32 g/kg sand.

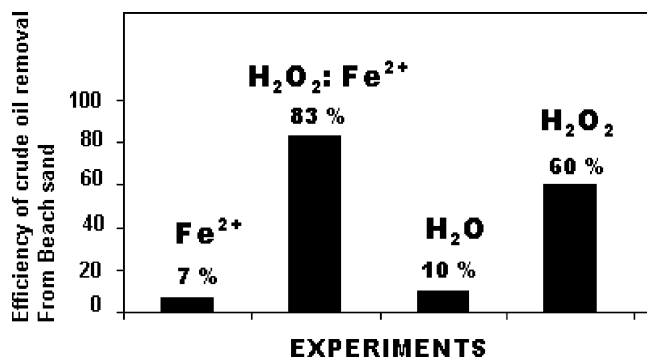


Fig. 4. Assays conducted in order to compare efficiency of oil detachment from the sand under different conditions: Fe<sup>2+</sup> (27.2 g/l); H<sub>2</sub>O<sub>2</sub> (136 g/l); H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> (5:1) in solution containing 100 g of contaminated sand.

### 3.2. Analyzing oil detachment from the sand

The statistical analysis of the results generated a linear regression with a 0.993 correlation coefficient for a 95% confidence interval, meaning that the experimental values were very close to those values predicted by the model. The 11 trials and respective results are tabulated in Table 2. Efficiency of O&G detachment from the sand is seen to have varied from 53.5 to 97%. These figures show that the oil detached well the sand and entered the aqueous phase and made waste final disposal easy.

Again, in order to check whether the effects were significant for the efficiency of oil detachment from the sand, Student's *t*-test was used. A tabulated value of Student's *t* = 4.303 was obtained, assuming a confidence interval of 95% and 2 degrees of freedom provided by the software (error's degree of freedom in experimental fractional design 2<sup>4-1</sup> was 2). From that value, effects were evaluated for significance. These analyses are best visualized on Pareto's graph which shows the analysis of factor effects and their interactions. The analysis of the Pareto graph plotted in this step (Fig. 5) indicated that in order to achieve better oil

Table 2

Results for efficiency of O&G detachment from the sand under the experimental fractional design 2<sup>4-1</sup>

Trial	H <sub>2</sub> O <sub>2</sub> (M)	Fe <sup>2+</sup> (g/l)	Sand (g/l)	Time (h)	Detachment (%)
1	4.0	27.2	100	6.0	95.0
2	4.0	2.7	25	6.0	97.0
3	0.4	27.2	25	6.0	62.0
4	0.4	2.7	100	6.0	78.0
5	4.0	27.2	25	3.0	79.0
6	4.0	2.7	100	3.0	91.0
7	0.4	27.2	25	3.0	60.0
8	0.4	2.7	25	3.0	53.5
9	2.2	14.5	62.5	4.5	65.0
10	2.2	14.5	62.5	4.5	68.0
11	2.2	14.5	62.5	4.5	62.5



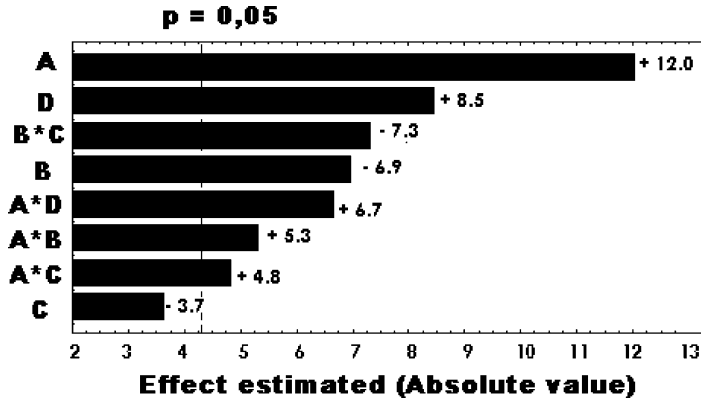


Fig. 5. Pareto graph plotted for efficiency of O&G detachment from the sand using Fenton’s reagent. The letters A–D represent the factors and interactions (A, H<sub>2</sub>O<sub>2</sub>; B, Fe<sup>2+</sup>; C, sand mass; D, time). The values appearing the horizontal columns of the graph correspond to Student’s *t*-value generated for each factor and the black vertical line indicates the tabulated Student’s *t*-test value (4.303). The factors and interactions surpassing that vertical line indicate that they are important to the analysis in question.

detachment from the sand, the reaction should have been conducted with higher concentrations of H<sub>2</sub>O<sub>2</sub>, lengthier reaction time and lower concentration of Fe<sup>2+</sup>. The mass of sand analyzed in these trials was not significant, however, presenting a negative effect. This pointed to a tendency of working with smaller masses in order to have more oil detached from the sand.

The iron–sand interaction which also showed to be significant, can be better evaluated in Fig. 6. To have better efficiency of oil detachment, oxidation should be conducted with a

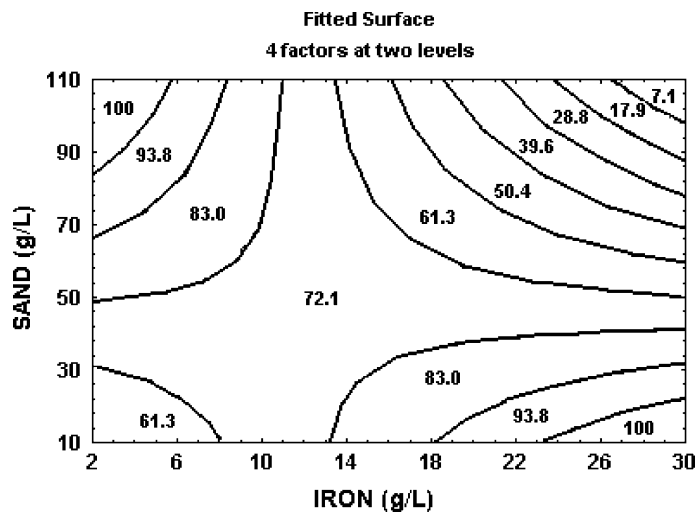


Fig. 6. Response surface describing the interaction between sand mass (vertical axis) and Fe<sup>2+</sup> concentration (horizontal axis). Contour lines represent percent value of O&G detachment efficiency for each combination.

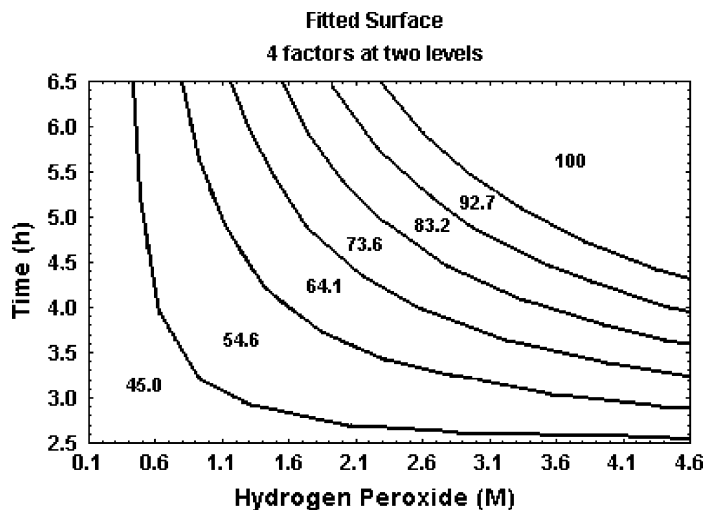
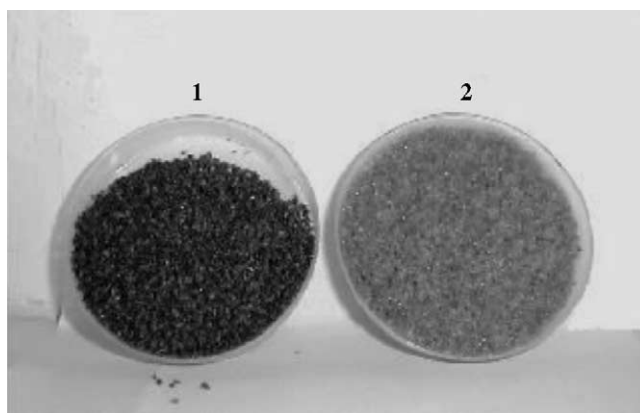


Fig. 7. Response surface describing the interaction between  $\text{H}_2\text{O}_2$  concentration (horizontal axis) and time (vertical axis). Contour lines represent percent value of O&G detachment efficiency for each combination.

higher level of sand and a lower level of iron or vice versa. The  $\text{H}_2\text{O}_2$ –time interaction was also significant and indicated that, while working with the highest level of both, detachment efficiency was greater as depicted in Fig. 7. These results demonstrate that in order to remove oil from the sand,  $\text{H}_2\text{O}_2$  should be at high concentrations in the reactional medium, however, without high concentrations of iron. Scheme 1 depicts the sand before and after Fenton treatment.

In their experiments, Watts et al. [1] determined the need for high concentrations of  $\text{H}_2\text{O}_2$  to provide desorption of the contaminant hexachlorobenzene from a sandy soil. This



Scheme 1. Sand before (1) and after (2) Fenton treatment under the best conditions obtained in the experimental design.  $\text{H}_2\text{O}_2 = 4 \text{ M}$ ;  $\text{Fe}^{2+} = 2.7 \text{ g/l}$ ; sand = 25 g/l; time = 6 h; pH = 3.

desorption was necessary in order to have better chemical oxidation of the medium. Watts and Stanton [14] studied a ratio of  $\text{H}_2\text{O}_{2(\text{g})}:\text{Fe}_{(\text{g})}^{2+}$  of 364:1 and observed the contaminant hexadecane desorb from the soil and its later chemical oxidation.

### 3.3. Analyzing aqueous phase degradability

New trials were carried out under the best conditions provided by the Pareto graph. The resulting aqueous phase was analyzed for degradability. Characterization of the aqueous phase containing only dissolved and emulsified oil presented a residual concentration of  $\text{H}_2\text{O}_2$  of 500 mg/l and a COD (corrected) value of 542 mg/l. Fig. 8 shows an aqueous phase soluble COD drop with time.

From Fig. 8 one can verify that the resulting aqueous solution following Fenton reaction was biodegradable considering that in around 7.5 h COD reduction had already reached 60%. Chamarro et al. [15] also observed COD reductions following Fenton reaction with different organic compounds (formic acid, phenol, 4-chlorophenol, 2,4-dichlorophenol, and nitrobenzene).

### 3.4. Analyzing oxidation by gas chromatography

A gas chromatographic investigation was made into oil oxidation on the extracts obtained after Fenton reaction conducted under the best (Experiment 2) and worst (Experiment 8) conditions of oil removal from the sand (Table 2). These analyses were meant to check whether oil oxidation by Fenton's reagent was or not closely connected to oil removal from the sand.

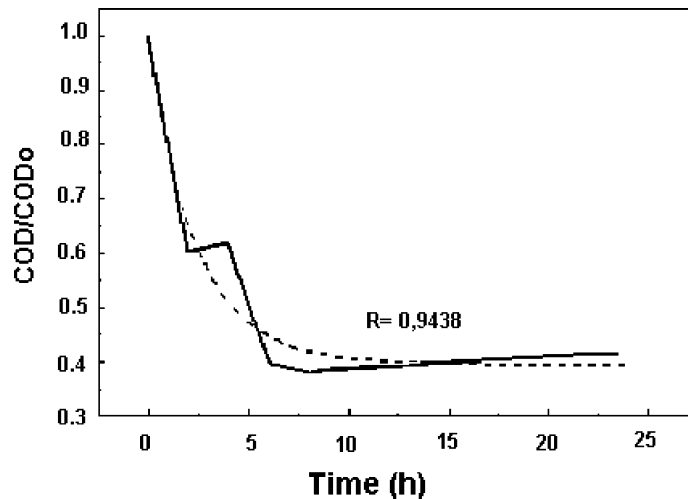


Fig. 8. Aqueous phase degradability curve following Fenton reaction. Inoculum: activated sludge from a municipal sewage treatment plant (VSS = 2210 mg/l); aqueous phase supplemented with nutrients (COD:N:P = 100:5:1), pH adjusted to 7.0. COD<sub>0</sub> = initial soluble chemical oxidation demand; COD = soluble chemical oxidation demand at every 2 h.

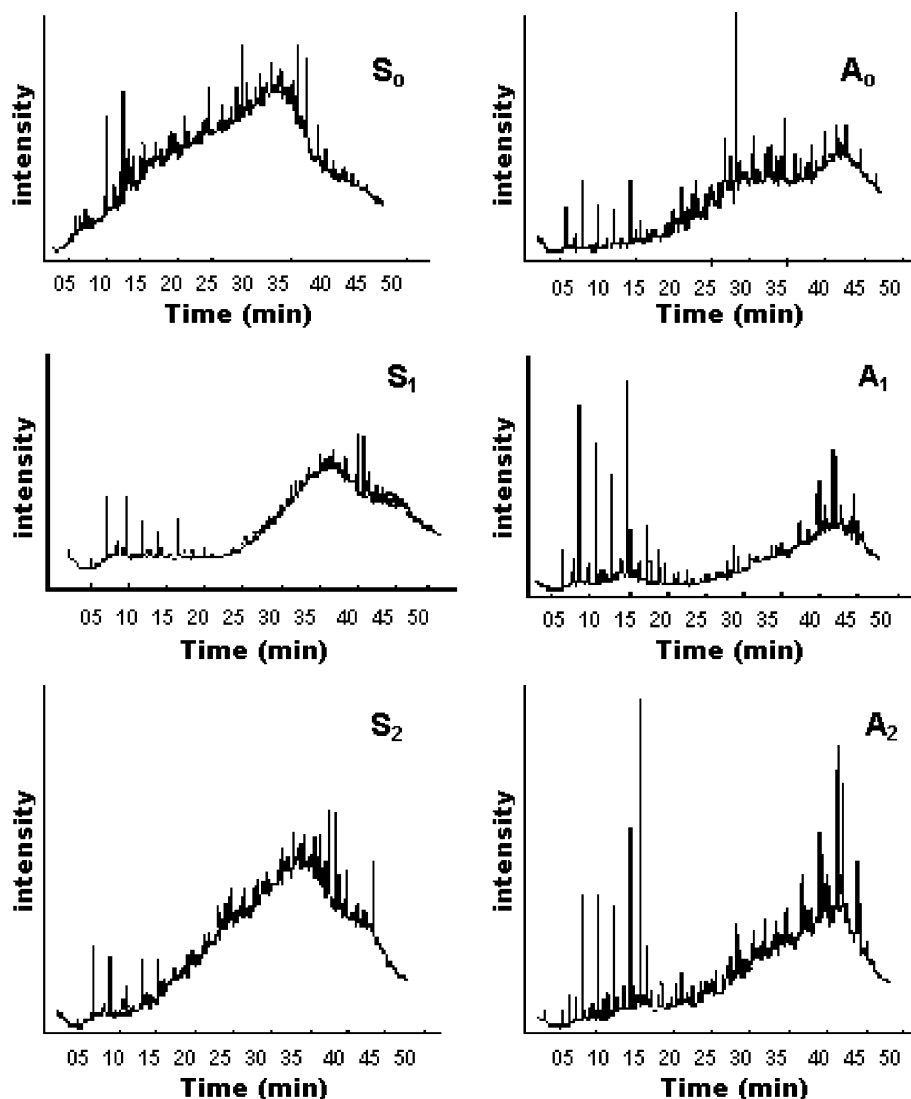


Fig. 9. Chromatographic analysis of the oil before and after Fenton reaction under those conditions where the best and worst oil removal occurred. Indices: S, saturates; A, aromatics; 0, before reaction; 1, after reaction under best removal condition; 2, after reaction under worst removal condition.

Fig. 9 shows saturated and aromatic fractions before and after Fenton reaction under both the best and worst conditions. On the chromatograms for the oil treated under the best removal condition (S.1 and A.1) one can observe that there was better modification of oil composition and greater reduction of saturated and aromatic fraction than those observed under the worst removal condition (chromatograms S.2 and A.2), when compared with the chromatograms produced for untreated oil (S.0 and A.0). These changes may be

closely connected to oil removal from the sand. That is to say that, for a better oxidation of hydrophobic contaminants found in the sand to take place, oil must be removed from the sand so that it will contact with the solution's reactive species and that the oxidation process can start. The necessity of an oil removal for an oxidation to take place was reported by Watts and Stanton [14] and Watts et al. [1].

#### 4. Conclusions

In the oil degradation analysis low removal efficiencies (31% at maximum) were obtained which indicated that applying Fenton's reagent for decontaminating oil impacted soils requires high concentrations of  $H_2O_2$  and longer reaction times. However, following oxidation the oil was found to be in solution (free, emulsified, or dissolved). Efficiencies of oil removal from the sand were achieved between 54 and 97% so indicating that Fenton reaction was efficacious in cleaning the beach sand. Analyses performed on the supernatant following Fenton reaction revealed a drop in COD of 60% after circa 7 h that showed that the effluent generated is liable to biodegradation. The chromatographic analysis indicated that Fenton reaction allowed modification of saturated and aromatic fractions when a better oil removal from the sand was observed.

#### Acknowledgements

The authors are indebted to CENPES (Petrobras) for the sand samples and the provision of the required experimental data and to Mr. Alberto dos Santos (LADETEC/IQ/UFRJ) for the gas chromatographic analyses and to the José Bonifácio University Foundation (FUJB) and to CAPES for the funding.

#### References

- [1] R.J. Watts, S. Kong, M. Dippre, W.T. Barnes, *J. Hazard. Mater.* 41 (1994) 105.
- [2] R.J. Watts, M.K. Foget, S.H. Kong, A.L. Teel, *J. Hazard. Mater.* B69 (1999) 229.
- [3] R.J. Watts, D.R. Haller, A.P. Jones, A.L. Teel, *J. Hazard. Mater.* B76 (2000) 73.
- [4] S. Kong, R.J. Watts, J. Choi, *Chemosphere* 37 (1998) 1473.
- [5] R.J. Watts, M.D. Udell, R.M. Monsen, *Water Environ. Res.* 65 (1993) 839.
- [6] C. Walling, *Accounts Chem. Res.* 8 (1975) 125.
- [7] NBR 10007, Amostragem dos resíduos, ABNT–Associação Brasileira de Normas Técnicas, 1987.
- [8] Petrobrás, Caracterização preliminar do impacto do vazamento acidental de óleo ocorrido em 18/01/2000 na Baía de Guanabara, Fev. 2000.
- [9] D.C. Montgomery, *Design and Analysis of Experiments*, third ed., Wiley, New York, 1991.
- [10] T. Morita, R.M.V. Assumpção, *Manual de Soluções, Reagentes and Solventes*, second ed., Edgard Blucher Ltda., 1981, p. 630.
- [11] APHA, AWWA, WPCF, *Standard Methods for the Examination of Water and Wastewater*, 18th ed., New York, 1992.
- [12] I. Talini, G.K. Anderson, *Water Res.* 26 (1993) 107.
- [13] J.J. Olson, G.L. Mills, B.E. Herbert, P.J. Morris, *Environ. Toxicol. Chem.* 18 (1999) 2448.
- [14] R.J. Watts, P.C. Stanton, *Water Res.* 33 (1999) 1405.
- [15] E. Chamorro, A. Marco, S. Espulgas, *Water Res.* 35 (2001) 1047.