Remediation of petroleum contaminated soil by photo-Fenton process applying black, white and germicidal light

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Tratamiento de suelos contaminados con petróleo por el proceso foto-Fenton con aplicación de luz negra, blanca y germicida

Tractament de sòls contaminats amb petroli, pel procés foto-Fenton amb aplicació de llum negra, blanca i germicida

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RESUMEN

El objetivo de este trabajo fue estudiar la aplicación del proceso de foto-Fenton para tratar suelos contaminados con petróleo. En este trabajo se ha investigado la influencia del tiempo de irradiación, la concentración de peróxido de hidrógeno y el uso de la luz visible, UV-A y UV-C. Además, se evaluó la presencia de un catalizador externo (Fe^{2+}). El tratamiento fotocatalítico del suelo contaminado con petróleo ha demostrado ser un método eficaz para eliminar el carbono orgánico total (COT), alcanzando aproximadamente 50% de eliminación de COT al final del tiempo de reacción. El uso de luz UV-A ha promovido mayor eliminación de COT que las otras fuentes de irradiación, aumentando cerca de 17 y 10 % la eliminación de COT en comparación a la luz UV-C y visible, respectivamente. En el caso del tratamiento utilizando lámparas UV, la adición de Fe no ha sido necesaria para lograr altos niveles de eliminación de COT.

Palabras clave: residuos de petróleo, oxidación avanzada, suelo contaminado, foto-Fenton.

SUMMARY

The aim of this work was to study the application of photo-Fenton process to remediate oil contaminated soil. In this work, the influence of irradiation time, hydrogen peroxide concentration and the use of visible, UV-A and UV-C light were investigated. In addition, the presence of external catalyst (Fe^{2+}) was assessed. The photocatalytic treatment of petroleum contaminated soil was an efficient method for removing the total organic content, achieving about 50% of TOC removal at the end of the reaction time. The use of UV-A light promoted higher TOC removal than other irradiation sources, increasing 17 and 10% the TOC removal when compared to UV-C and visible light, respectively. In the case of treatment using UV lamps, the addition of external Fe was not necessary to achieve high levels of TOC removal.

Keywords: petroleum waste; advanced oxidation; contaminated soil; photo-Fenton.

RESUM

L'objectiu d'aquest treball va ser estudiar l'aplicació del procés de foto-Fenton per tractar sòls contaminats amb petroli. En aquest treball s'ha investigat la influència del temps d'irradiació, la concentració de peròxid d'hidrogen i l'ús de la llum visible, UV-A i UV-C. A més, es va avaluar la presència d'un catalitzador extern (Fe^{2+}). El tractament fotocatalític del sòl contaminat amb petroli, ha demostrat ser un mètode eficaç per eliminar el carboni orgànic total (COT), assolint aproximadament un 50% d'eliminació de COT al final del temps de reacció. Amb l'ús de llum UV-A s'aconsegueix una eliminació de COT més gran que amb les altres fonts d'irradiació, augmentant prop del 17% i del 10%, l'eliminació de COT en comparació a la llum UV-C i visible, respectivament. En el cas del tractament utilitzant làmpades UV, l'addició de Fe no ha estat necessària per aconseguir alts nivells d'eliminació de COT.

Paraules clau: Residus de petroli, oxidació avançada, sòl contaminat, foto-Fenton.

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1. INTRODUCTION

A significant portion of soil contamination is generally attributed to oil refinement and its derivatives. This contamination often occurs during extraction, transport, refining or disposal (Freire , 2000, Tam , 2005).

Despite technological advances, processes are susceptible to flaws. With regard to the oil industry, these faults may contaminate water in offshore drilling, as well as the soil during onshore extraction. Another source of contamination are leaks, thus a substantial part of organic matter, primarily the hydrophobic fraction, is adsorbed in soil, These compounds slowly desorb and may reach the water table, promoting significant contamination levels over time (Robinson , 1990).

In recent years, advanced oxidative processes (AOP) have gained importance for their effectiveness in degrading organic compounds (Da Rocha , 2010; Dantas 2010). They have also been employed as promising alternatives in waste treatment and/or remediation of soils contaminated with highly toxic and recalcitrant substances (Legrini, 1993; Kanel ., 2003; Kim , 2006).

Fenton's reaction is obtained by the combination of hydrogen peroxide and iron salt (Fe^{2+} or Fe^{3+}) in aqueous acidic medium. This reaction produces hydroxyl radicals with oxidizing power to degrade a large number of contaminants (Fenton, 1876; Chamarro , 2001; Watts , 2002; Lundstedt , 2006). Several studies report the use of inorganic minerals present in the soil, mainly magnetite, hematite and geotite, with the exception of ferrihydrite, as iron source for the Fenton reaction (Watts and Dilley, 1996; Kanel 2003; Baciochi , 2004; Flotron , 2005). In the last decade, the Fenton's reaction has been applied in the chemical remediation of contaminated soil (Mater ., 2007; Ndjou'ou and Cassidy, 2006), however according to Sirguey ., (2008), the application of Fenton processes for the remediation of petroleum contaminated soil may cause the inhibition of plants growing due the reduction in the pH of the soil. However, this problem can be attenuated by stabilization with lime.

The aim of this study is to assess the application of photo-Fenton process to remediate oil contaminated soil. To determine the best experimental condition for each system, the influence of the following variables were studied: irradiation time, irradiation source (visible, UV-A and UV-C light), catalyst presence (Fe^{2+}) and hydrogen peroxide concentration. To analyze the data, a factorial plan was applied using the total organic carbon (TOC) removal as response.

2. MATERIAL AND METHODS

The soils samples used in this work came from the area where the "Abreu and Lima" oil refinery (Pernambuco, Brazil) (8° 23' 37.20" S, 34° 58' 37.95" W) will be built.

Soil characterization assays were conducted according to EMBRAPA methodology (1997). The following physical and chemical characteristics of the soil were measured: granulometry, pH, electrical conductivity ($dS.m^{-1}$), organic matter ($g.kg^{-1}$), nitrogen ($g.\ kg^{-1}$), C/N ratio, assimilable phosphorous ($g.kg^{-1}$) and sorptive complex (Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, H^+ (cmol(+). kg^{-1}). The used methodology to measure total organic carbon ($g.kg^{-1}$) was the modified Walkley Black method. This method consists of oxidizing the organic carbon from the soil with potassium dichromate ($K_2Cr_2O_7$, 0.4 N) in presence of sulfuric acid, forming carbonic gas and water.

Soil samples were artificially contaminated at a ratio of 20 mL of crude oil for every kilogram of soil and then the samples were submitted to a photochemical advanced oxidation process (H_2O_2/ Fe^{2+}/UV).

Photochemical oxidation assays were carried out in Petri dishes with a surface area of 63.6 cm^2. To perform the runs, Petri dishes containing 2 g of soil were placed into photochemical reactors. Three reactors with different irradiation sources were used: visible light (Philips, 20W), UV-A (Higuchi, F20T10 20W) and UV-C (Philips, 20W). Each reactor had three lamps, able to irradiate four Petri dishes. A schematic drawing of the photocatalytic reactor is shown in Figure 1.

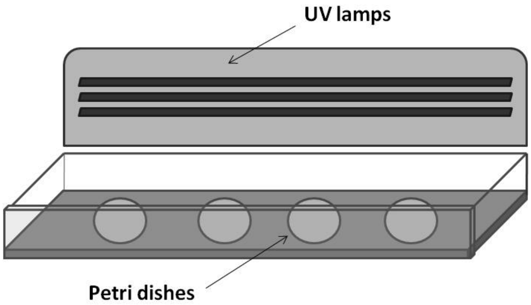


Figure 1 *– Photochemical reactor (Rocha , 2010)*

The UV-A reactor emitted 98 lux and radiation of 373 $\mu W\ cm^{-2}$ in the wavelength range between 290 and 390 nm, and 10.4 $\mu W\ cm^{-2}$ at a wavelength of 254 nm. The visible light reactor produced 1900 lux and radiation of 74 $\mu W\ cm^{-2}$ in wavelengths ranging from 290 to 390 nm and 11.2 $\mu W\ cm^{-2}$ at 254 nm. The UV-C reactor emitted 2500 lux and radiation of 53 $\mu W\ cm^{-2}$ at a wavelength between 290 and 390 nm and 18.6 $\mu W\ cm^{-2}$ at 254 nm.

A 2^3 factorial plan was applied to evaluate the influence of the following experimental conditions: external catalyst concentration (Fe^{2+}) (0; 0.17 and 0.34 mmol L^{-1}), hydrogen peroxide concentration (68; 102 and 136 mmol L^{-1}) and irradiation time (6; 9 and 12 h). Process efficiency was assessed as a function of TOC removal. Analysis of total organic carbon was conducted according to the modified Walkley-Black method (EMBRAPA, 1997).

3. RESULTS AND DISCUSSION

The first section of the investigation focused the soil characterization. Table 1 illustrates its physical and chemical properties. The studied soil was slightly acidic, with pH of 4.7. Most of the sample consisted of coarse sand (2-0.2 mm, 487 $g.kg^{-1}$) and clay (<0.002 mm, 300 $g.kg^{-1}$). Due natural iron presence in the soil, the photo-Fenton-like reaction may occur with H_2O_2 addition and irradiation.

After soil artificial contamination, the TOC increased from 0.20 $g.kg^{-1}$ to 13.61 $g.kg^{-1}$. Before experimentation, blank experiments were performed to evaluate the influence of H_2O_2 oxidation and direct photolysis. Nevertheless, no significant degradation was observed.

The influence of hydrogen peroxide concentration, external catalyst concentration and irradiation time were evaluated using a 2^3experimental plan. Response in terms of TOC removal percentage was used to assess the process efficiency as well as identify the best experimental conditions. TOC removals obtained with visible, UV-A and UV-C light for the photo-Fenton process ($H_2O_2/Fe^{2+}/UV$) are shown in Table 2. According to the obtained data, the TOC removal achieved using the UV-A was about 17 and 10 % higher than those achieved by germicidal and write light, respectively.

Table 1 *- Physical and chemical characteristics of the soil.*

Properties	Values
Soil	
Total Organic Carbon (g kg$^{-1)}$	0.20
Electrical conductivity (dS m^{-1})	0.21
pH	4.7
Organic matter (g kg^{-1})	0.34
Nitrogen (g kg^{-1})	0.1
C/N Ratio	2.0
Sand 2-0,2 mm (g.kg^{-1})	487
Fine sand 0,2-0,05 mm (g.kg^{-1})	105
Silt 0,05-0,002 mm (g.kg^{-1})	108
Clay <0,002 mm (g.kg^{-1})	300
Textural	Sandy clay loam
Extractable phosphorus (mg kg^{-1})	2.0
Easily extractable Fe (g kg^{-1})	9.1
Exchangeable cátions (nmol (+) kg $^{-1}$)	
Ca	0.10
Mg	0.10
K	0.00
Na	0.00
H	0.37
Al	1.17
Contaminated soil	
Total Organic Carbon (g kg-1)	13.61

Figure 2 shows the Pareto chart for all studied variables and their interactions for experiments using the white light photo reactor. The Y axis contains the independent variables or inter-variable interactions. The X axis represents the absolute value of the estimated effect, calculated from the ratio of estimated effects and their respective standard deviations. All variables on the Pareto chart to the right of p-value = 0.05 show statistical significance. Figure 2 demonstrates that all effects were statistically significant. However, for this type of irradiation, irradiation time and hydrogen peroxide concentration were the most significant. In this case, the only variable that was not significant was the presence of external catalyst.

Table 2 *- Results of a 2^3 factorial plan with different types of radiation.*

Experiment	Time (h)	Fe^{2}+ (mmol L^{-1})	H_2O_2 (mmol L^{-1})	TOC removal - visible light (%)	TOC removal – UV-A light (%)	TOC removal – UV-C light (%)
1	6	0.00	68	14.3	22.0	27.0
2	12	0.00	68	19.7	18.5	25.0
3	6	0.34	68	16.5	15.1	11.5
4	12	0.34	68	21.9	20.7	33.7
5	6	0.00	136	21.4	20.6	25.1
6	12	0.00	136	38.4	42.7	38.5
7	6	0.34	136	25.6	27.2	29.8
8	12	0.34	136	38.8	50.3	31.0
9	9	0.17	102	41.2	36.4	30.0
10	9	0.17	102	40.1	36.3	29.5
11	9	0.17	102	39.5	34.8	33.3

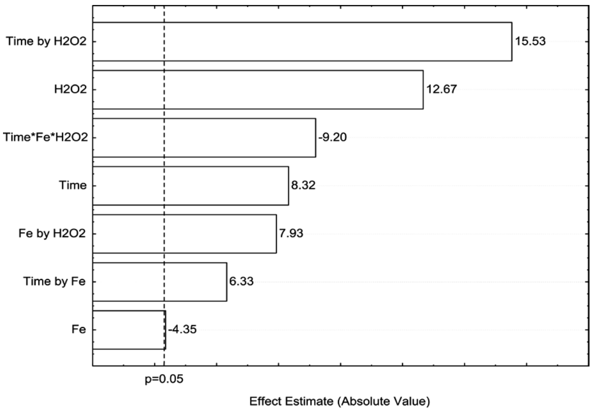


Figure 2 *- Pareto chart of the values of the effects of all the variables studied for the visible light reactor using the $H_2O_2/Fe^{2+}/UV$ process.*

In order to better evaluate the results, response surfaces generated by the Statistica Experimental Design program were built (Figure 3). A response surface is obtained when a response variable, in this case TOC removal, is graphically represented in function of two or more factors of the process in order to obtain its optimization. Figure 3a in-

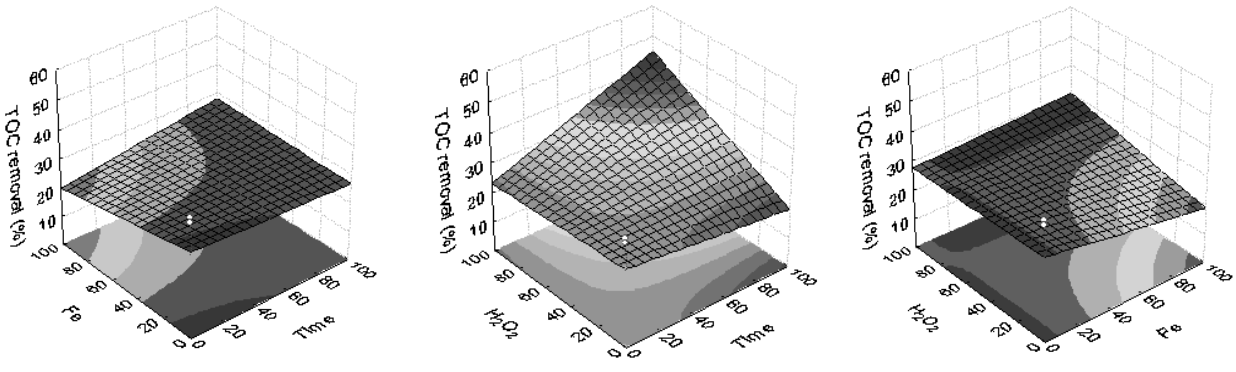


Figure 3 *- Response surface graphics based on TOC removal for visible light experiments. (a) = Fe (mmol) vs time (h); (b) = H_2O_2 (mmol) vs time (h); (c) =H_2O_2 (mmol) vs Fe (mmol).*

dicates that TOC removal increases with the augment of hydrogen peroxide concentration, however, this effect is only noticeable at higher Fe concentration. Figure 3b put in evidence the importance of irradiation time. This graphic demonstrates that at lower irradiation time H_2O_2 concentration is not statistically significant, thus high TOC removals are only obtained with the increase of both H_2O_2 and irradiation time. Finally, Figure 3c illustrates that even at longer irradiation time Fe concentration increase did not promote an important augment on TOC degradation.

Figure 4 presents the Pareto chart for the effects of the studied variables and their interactions using the UV-A reactor. Results were similar to those obtained with visible light. The majority of the variables and their interactions were significant, except Fe concentration. The response surface generated, based on TOC removal was used to analyze the influence of irradiation time, H_2O_2 and Fe concentrations (Figure 5).

Figure 5 corroborate with the previous conclusions obtained for the visible light photo reactor. As in the previous results, the higher TOC removal was achieved by the combination of higher quantity of H_2O_2 treated at higher irradiation time. Moreover, the absence of Fe concentration significance should be point out.

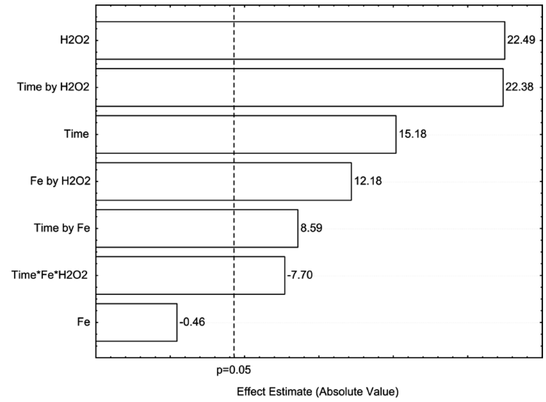


Figure 4 - *Pareto chart of the values of the effects of all the variables studied for the UV-A light reactor using the $H_2O_2/Fe^{2+}/UV$ process.*

The final section of this study deals with the use of the UV-C photo reactor. Figure 6 shows the Pareto chart for the effects of all studied variables and their interactions. In this case, the only statistically significant effect was the irradiation time and the interaction between the three variables. Thus, due to the absence of interactions significance, the response surfaces were not evaluated. This set of experiments demonstrated that photo-Fenton process using UV-C light was not suitable for this type of contamination. In this case, the augment of oxidant did not promotes significant increase of TOC removal, thus it can be suggested that the use of more energetic radiation is not necessary for the treatment of oil contaminated soils.

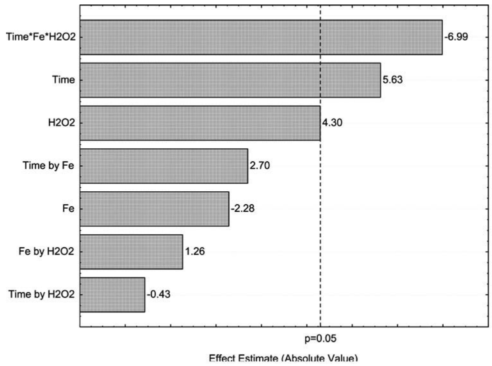
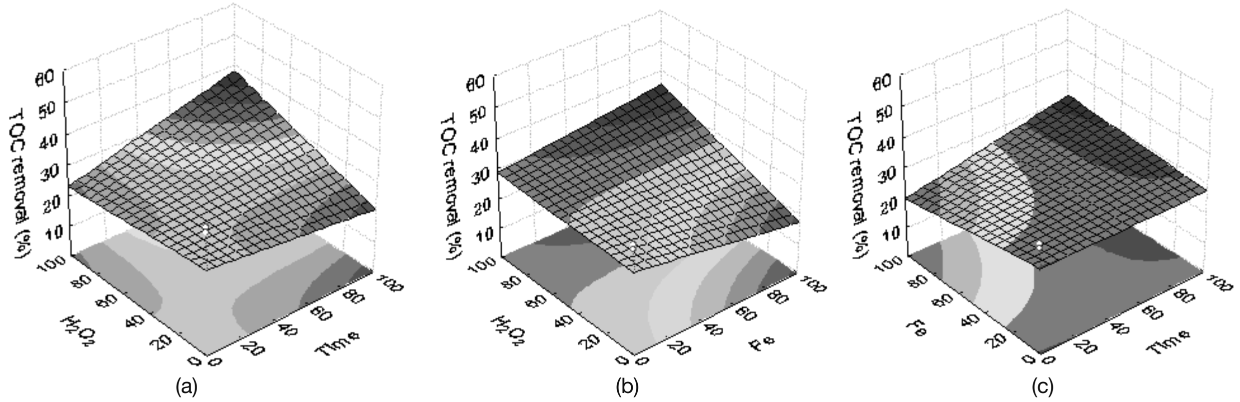


Figure 6 - *Pareto chart of the values of the effects of all the variables studied for the UV-C light reactor using the $H_2O_2/Fe^{2+}/UV$ process.*

An overall evaluation of the three radiations sources (visible, UV-A and UV-C light) indicates that the use of UV-A light would achieve best results in terms of TOC removal. This fact could be explained by the higher radiation intensity in the range between 300 and 400 nm emitted by the UV-A lamps. According to literature, in the case of soil treatment, the natural iron can form complexes with organic matter such as humic substances. Thus, iron species may exist as iron-humates, which absorbs at wavelength range from 300 to 400 nm (Aguer and Richard,1996; Fukushima 2000; Fukushima and Tatsumi, 2001).

4. CONCLUSIONS

The study demonstrated that the photochemical oxidation treatment of petroleum contaminated soil was able to achieve high levels of TOC removal. Visible UV-A, and



(a) (b) (c)

Figure 5 *- Response surface graphics based on % TOC removal for UV-A light experiments. (a) = H_2O_2 (mmol) time (h); (b) = H_2O_2 (mmol) vs Fe (mmol); (c). = Fe (mmol) vs time (h).*

UV-C light achieved higher TOC removal between 6 and 12 hour of treatment. The treatment using UV-A light produced higher TOC removal than other irradiation sources. However, additional factors such as the cost of the lamps must be taken into account when selecting the best irradiation source. The addition of external catalyst (Fe) was not necessary, which would simplify the treatment since only the addition of hydrogen peroxide would be mandatory.

5. ACKNOWLEDGEMENTS

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