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Oil sludge treatment by photocatalysis applying black and white light

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ABSTRACT

Soil contamination by non-aqueous phase liquid compounds (NAPLs), mainly from petroleum hydrocarbons, has been a matter of great concern, especially due to aromatic and polycyclic aromatic hydrocarbon contamination, which can pose a health risk due to its carcinogenic and mutagenic properties. In this study, oil sludge treatment was carried out using heterogeneous photocatalysis (H_2O_2/UV/TiO_2). A 2^3 factorial design experimental plan was used, applying black and white light reactors; in addition the effects of hydrogen peroxide (H_2O_2) concentration, TiO_2 mass and irradiation time were evaluated using TOC removal as a response. Heterogeneous photocatalysis provided efficient degradation and mineralization of a large part of the organic matter. Moreover, the method also proved to be an alternative treatment for removing PAH from oil sludge, eliminating 100% of all PAH content from the oil sludge sample after 96 h of irradiation.

1. Introduction

Oil spills cause significant environmental and economic damage to a wide variety of natural resources. The degree of this damage depends on where the spill occurs, type and discharge volume, season and environmental conditions [1,2]. In recent decades, soil contamination by non-aqueous phase liquid compounds, specifically oil hydrocarbons from oil spills has been a matter of great concern [3,4]. This concern is justified because polycyclic aromatic hydrocarbons (PAH), an oil contaminant, pose a risk to human health due to its carcinogenic and mutagenic properties [5–8]. According to Faria and Rosa [9], the complexity of PAH mixtures depends on their emission sources. Generally, these mixtures have a wide variety of PAH at different concentrations. Thus, the knowledge of the presence of these compounds in environmental samples and the search for suitable treatment methods are of great interest to governments worldwide. Although the remediation for PAH-contaminated soil has been extensively investigated by various research groups, especially in terms of biological treatment, few works were found in the literature on treating PAH with advanced oxidation processes (AOPs) [10,11].

PAH concentrations of ng L^{-1} have been detected in soil, water and plant samples [12,13]. In addition, due to their physical–chemical properties and their wide environmental distribution, the risk of contamination by these substances is significant. Indeed, because of their lipophilic nature, PAH and their derivatives can be absorbed by the skin, ingested or inhaled, and quickly spread throughout the organism [8].

Advanced oxidation processes are defined as processes that can generate radicals in a sufficient amount to oxidize most of the complex chemicals present in environmental matrices. Hydroxyl radicals ($^*OH$) are powerful oxidizing reagents with an oxidation potential of 2.8 V [14]. Furthermore, they react with most organic and many inorganic compounds, exhibiting faster oxidation reaction rates than those of conventional oxidants [15]. The main advantage of these processes is that the contaminant is destroyed and not transferred to another phase [16,17]. Among the AOPs, heterogeneous photocatalysis stands out as a promising technology in the treatment of environmental pollutants [18–21]. The photocatalytic oxidation enables the utilization of near UV and sunlight for irradiation, thus, resulting in a considerable saving especially for large-scale operations [22]. These processes entail a photochemical degradation of a lot of compounds present in wastewater, capable of achieving total mineralization at mild conditions of temperature and pressure [23]. In these processes, the chemical reactions are characterized by a free radical mechanism, thus radicals such as "$^*OH$ and $^*HO_2$" can be produced by the homogeneous radiations degradation of oxidizing compounds like hydrogen peroxide (H_2O_2) and ozone. Another method to achieve and at the same time enhance the production of free radicals is the photocatalytic oxidation mechanism occurring at the surface of semiconductors e.g., TiO_2 [24].

The aim of this work was to study the oil sludge treatment by photocatalysis using titanium dioxide (TiO_2) as catalyst, hydrogen

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peroxide, black and white light. During the experiments, PAH concentration and total organic carbon (TOC) were monitored. In order to determine the best operational conditions for this treatment, factorial plans were used. H_2O_2, TiO_2, irradiation time and radiation sources were studied using TOC removal as response.

2. Materials and methods

2.1. Oil sludge characterization and methods

The oil sludge used in this research was collected from the bottom of oil storage tanks (Petrobras S. A., Brazil). These reservoirs are located in the State of Rio Grande do Norte, Brazil. The oil sludge was initially characterized in terms of pH and metals. The metals, including iron, were analyzed by flame atomic absorption spectrometry (Varian AA240FS) following standard methodology [25].

The method used for PAH extraction followed EPA 3540 protocol (Soxhlet extraction), using 300 mg of oil sludge (before or after treatment). For PAH quantification, EPA 8270 was applied. The method uses a gas chromatography column coupled to a mass spectrometer, Shimadsu models GC-17A and QP5050A, respectively. A DB-5 MS capillary column (length = 30 m, inner diameter = 0.25 and film thickness = 0.25 μm) was used. The injector temperature was 280 °C (splitless). Chromatographic conditions included an initial oven temperature of 80–120 °C with a program rate of 20 °C min^{-1}, and 120–285 °C with 2.8 °C min^{-1}. The detection limit was 0.25 mg kg^{-1}.

The methodology used to measure TOC was the modified Walkley Black method [26]. This method consists of oxidizing the organic carbon from the soil with potassium dichromate ($K_2Cr_2O_7$, 0.4 N) in sulfuric acid, forming carbonic gas and water.

2.2. Photocatalysis using white and black light (TOC and PAH removal)

Photocatalytic experiments were carried out in Petri dishes with a surface area of 63.6 cm^2 placed into photocatalytic reactors. The reactors were equipped with black and white lamps placed on the reactors lid. Each reactor was made up of three lamps and had the capacity to irradiate four Petri dishes. The light sources used in this study were a UV-365 black light mercury lamp (UV-A, Higuchi, F20T10 20W) and a white light lamp (Philips, 20 W). The black light reactor was able to emit 98 lux and 373 μW cm^{-2} at the wavelength range from 290 to 390 nm and 10.4 μW cm^{-2} at 254 nm, while the write light reactor emitted 1900 lux and 74 μW cm^{-2} at wavelength range from 290 to 390 nm and 11.2 μW cm^{-2} at 254 nm. To carry out the experiments, 300 mg of samples were irradiated by black and white light inside the reactors (Fig. 1). To verify the influence of the experimental conditions on process efficiency, a 2^3 factorial plan was used and the UV radiation source (white and black), H_2O_2 (30%, w/w, Merck, Brazil) concentration (0.4 and 0.8 mol L^{-1}), titanium dioxide (Degussa P25) mass (5 and 6 mg) were the studied variables. TOC removal was the response used in this experimental plan. The comparison between TOC measurements before and after photodegradation shows the efficiency of each individual experiment. The hydrogen peroxide concentration cited to in this work refers to the volume of 21 mL added every 24 h for a period of 96 h.

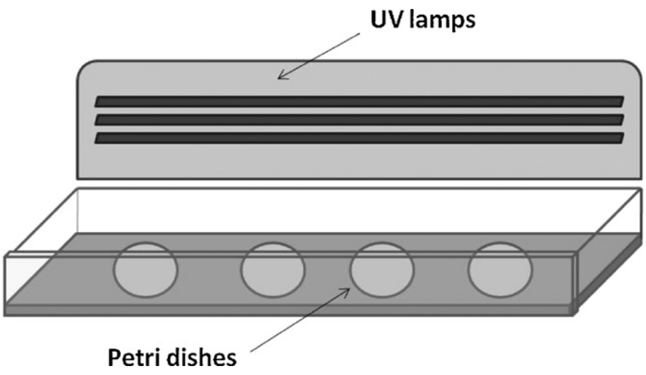

Fig. 1. Photocatalytic reactor.

2.3. Photocatalysis using white light (TOC removal)

The second experimental plan was performed only with experiments using the white light reactor; thus, the variable time was added to the factorial plan. Hydrogen peroxide H_2O_2 (0.4 and 0.8 mol L^{-1}), TiO_2 mass (5 and 6 mg), and radiation time (96 and 144 h) were used in different combinations to determine the optimal operating condition.

2.4. PHA removal by photocatalysis with white light

After investigating oil sludge mineralization obtained by heterogeneous photocatalysis, the individual removal level of each PAH was also studied. Therefore, in this part of the study, experiments were carried out using 5 mg of TiO_2, and an H_2O_2 concentration of 0.8 mol L^{-1} for 24, 72 and 96 h of irradiation. Each PAH concentration was determined before and after irradiation and the results are expressed as individual PAH removal.

3. Results and discussion

3.1. Oil sludge characterization

The first part of this study deals with the characterization of raw oil sludge. Table 1 presents the metal content revealed by the flame atomic absorption spectrometry analysis. According to Table 1, the iron content (34,500 mg kg^{-1}) was significant, which could be explained due to the origin of the sludge. It came from cleaning (scraping) oil storage tanks, which explains the high iron content found in the sample. The considerable presence of iron would contribute to the development of Fenton and photo-Fenton reactions. However, as the pH of the samples was around 5.0, these reactions were not favored. To verify this point, a previous experiment only with H_2O_2 was carried out. Nevertheless, no significant degradation took place. Once dissolved in water, the sample also had a pH of around 5 and resembled black grease, exhibiting high viscosity and a strong odor. PAH concentration in three different oil sludge samples was measured and the mean concentration of each PAH is given in Table 2. Two of the PAH listed in the analytical method (acenaphthylene and anthracene) were not detected because their concentration was lower than the quantification limit of 0.83 mg kg^{-1}. The results are presented along with their standard deviations.

It should be pointed out that in order to confirm the reliability of the characterization method in terms of PAH concentration, GC–MS

Table 1
Metal content in the raw oil sludge.

Metal	mg kg^{-1}
Cobalt	100
Lead	565
Copper	213.5
Iron	34,500
Nickel	125
Zinc	769
Manganese	542
Chrome	119

Table 2
PAH concentration in the raw oil sludge.

PAH	mg kg^{-1}	σ
Naphthalene	6.34	±1.54
Acenaphthylene	<LQ[a]	–
Acenaphthene	7.99	±0.34
Fluorene	21.29	±0.22
Phenanthrene	40.90	±0.68
Anthracene	<LQ[a]	–
Fluoranthene	20.68	±0.50
Pyrene	23.70	±0.52
Benzo(a)anthracene	21.29	±0.05
Chrysene	26.07	±0.63
Benzo(b)fluoranthene	29.41	±3.80
Benzo(k)fluoranthene	4.61	±1.36
Benzo(a)pyrene	10.42	±0.74
Indeno(1,2,3-cd)pyrene	4.56	±0.96
Dibenzo(a,h)anthracene	7.02	±1.70
Benzo(ghi)perylene	8.58	±0.91
Total	218.22	±1.54

[a] LQ, lower than the quantification limit of 0.83 mg kg^{-1}.

analysis was performed after extraction in three different oil sludge samples, as described in the experimental section. The low standard deviations obtained in PAH measurements ensure the reliability of the values.

3.2. *Oil sludge mineralization using white and black light*

To study the influence of hydrogen peroxide, catalyst mass and UV source on oil sludge mineralization, a 2^3 experimental plan was used. Accordingly, a group of eight experiments using different factor combinations were carried out and the results are presented in Fig. 2. The responses, in terms of TOC removal percentages, were used to determine the optimal operating conditions of this treatment method. It is important to remark that preliminary experiments (blank tests) were carried out and no significant degradation was obtained by single elements of the used photocatalysis such as UV light, hydrogen peroxide and TiO_2. In addition, the levels of the variables used in this factorial plan were based on the experimental experience acquired during these preliminary tests.

Fig. 2 shows that the organic matter content in the oil sludge waste undergoes a high level of mineralization, which was around 81% on average. Besides, it was observed that the white light reactor (WLR) removed TOC more efficiently than the black light reactor (BLR). The values ranged between 75.32% and 80.35% for the BLR, and between 82.93% and 86.99% for the WLR. Considering that the two photocatalytic reactors used have similar irradiance power, it can be suggested that the visible wavelength emitted by white light lamps can promote better oil sludge photocatalytic degradation when compared with the UV-A wavelength emitted by black light lamps.

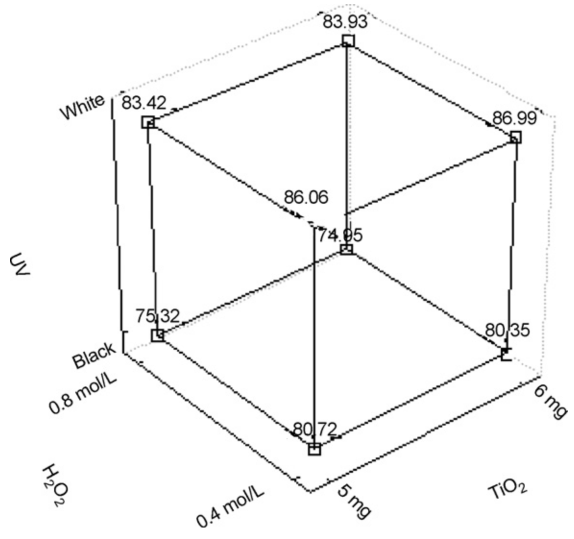

Fig. 2. Cube showing the results in terms of % of the removal of TOC, for the eight experiments carried out within 144 h.

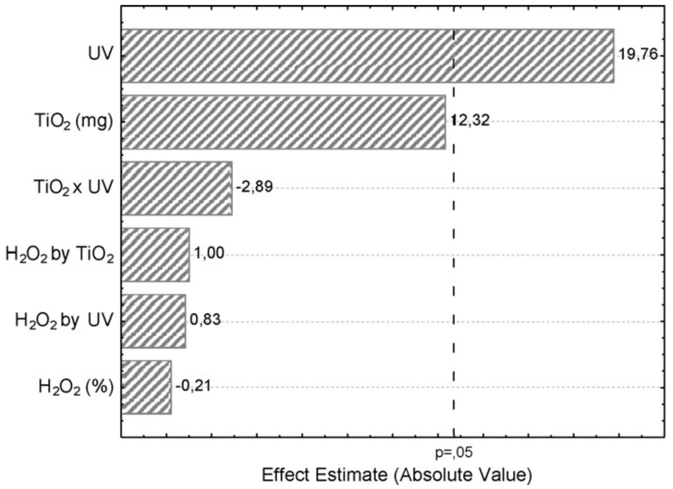

Fig. 3. Pareto chart of the variable effects and their interactions for the experimental plan using black and white light.

Fig. 3 shows the Pareto chart for all study variables and their interactions for the planned usage of black and white light. The independent variables and their interactions are on the *Y* axis, while the estimated absolute effect is shown on the *X* axis, and calculated from the ratio between the estimated effect and its respective standard deviation. All Pareto chart values greater than the *P* value (0.05) are statistically significant. Thus, it can be observed in Fig. 3 that UV light is the only statistically significant effect. In this case, the other variables and their interaction are not statistically significant.

3.3. *Oil sludge mineralization using white light*

Since the experiments carried out with white light showed the best TOC removal results, the second experimental plan was carried out using data from this group of experiments. Thus, another 2^3 experimental plan was performed and the responses were in terms of TOC removal. The data obtained was useful for studying the effect of hydrogen peroxide concentration, catalyst mass and irradiation time. Fig. 4 shows a group of eight experiments using different factor combinations. To ensure reproducibility, all experiments were conducted in duplicate.

Fig. 5 illustrates the Pareto diagram, which shows the effects of study variables and their interactions. The graph demonstrates that irradiation time, H_2O_2 concentration, TiO_2 mass and the interaction between TiO_2 and time was statistically significant. However, irradiation time proved to be the most important experimental factor for oil sludge mineralization. The interaction between TiO_2 and H_2O_2 and between H_2O_2 and time was not statistically significant. The overall results also demonstrate that TiO_2 mass had not significant effect on the final TOC removal using black light, as showed in the previous section. In the case of write light, this factor has significance. Besides, the fact that the oil sludge degradation increased with the augment of TiO_2 mass only with 96 h (Fig. 4) and not with 144 h of irradiation might be because higher quantity of catalyst accelerates the degradation mainly in the early step of degradation.

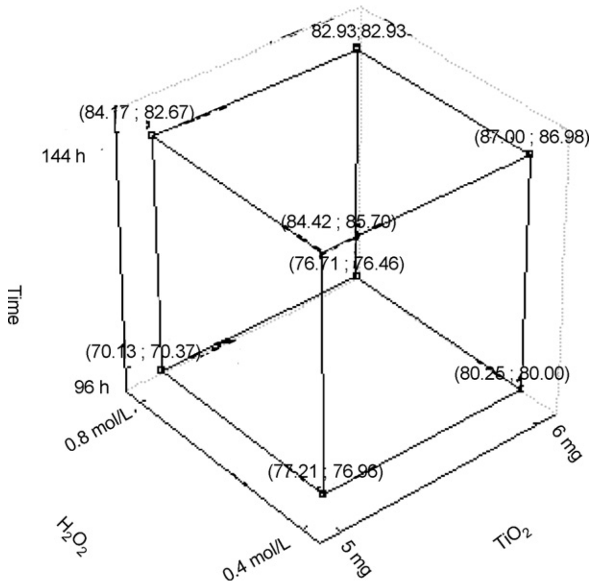

Fig. 4. Cube showing the results in terms of % of the removal of TOC, for the eight duplicate experiments using the white light reactor.

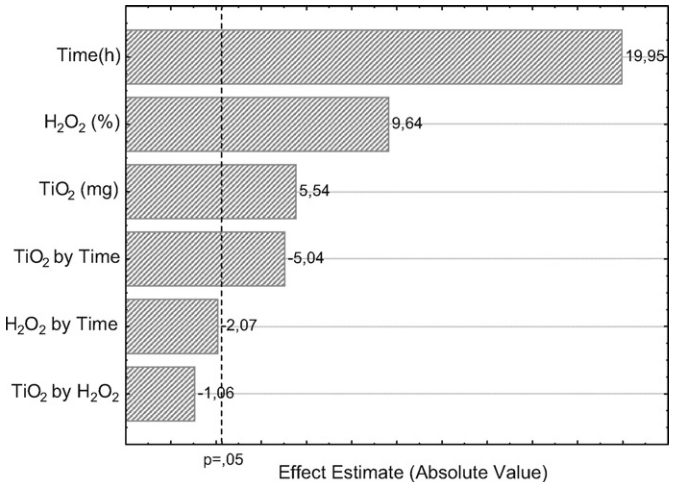

Fig. 5. Pareto chart of the variable effects and their interactions for the factorial plan using white light.

The next step in this study was to observe the behavior of the experimental data on the response surface methodology. Fig. 6 presents three different surface response graphics, which represent the behavior of overall factor influence on oil sludge mineralization. Response surface graphics explore the relationship between two variables and one response.

From the obtained data, an empirical model capable of predicting the system efficiency in terms of TOC degradation (%), applying the studied variables, was generated with the help of the Statistica Experimental Design programme (Eq. (1)).

$$D = 80.43063 + 1.22688\,X_{\mathrm{TiO_2}} + 2.13438\,X_{\mathrm{H_2O_2}} + 4.41938\,X_{\mathrm{Time}} - 0.23437\,X_{\mathrm{TiO_2}}\,X_{\mathrm{H_2O_2}} - 1.11687\,X_{\mathrm{TiO_2}}\,X_{\mathrm{Time}} - 0.45938\,X_{\mathrm{H_2O_2}}\,X_{\mathrm{Time}} \quad (1)$$

The analyses of the response surfaces are from the Statistica Experimental Design programme. In Fig. 6a the response surface using the variation of H_2O_2 and TiO_2 can be observed. It was found

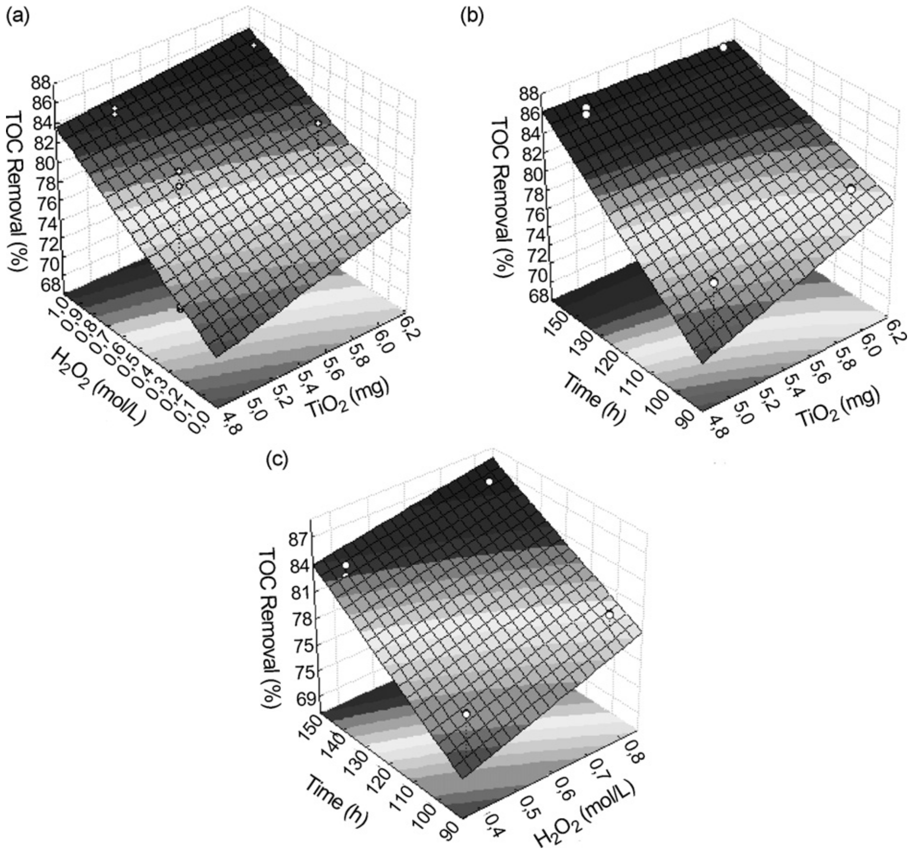

Fig. 6. Response surface graphics for the mineralization of oil sludge sample, using white light. (a) H_2O_2 (%) vs. TiO_2 (mg); (b) time (h) vs. TiO_2 (mg); (c) time (h) vs. H_2O_2 (%).

Table 3
PAH removal using different irradiation times and lamps (%).

	White light			Black light		
	24 h	72 h	96 h	24 h	72 h	96 h
Naphthalene	26.4	100.00	100.00	36.90	50.04	50.04
Acenaphthylene	–	–	–	–	–	–
Acenaphthene	27.03	100.00	100.00	38.79	100.00	100.00
Fluorene	21.72	100.00	100.00	37.38	65.15	100.00
Phenanthrene	36.43	42.95	100.00	38.88	42.95	42.95
Anthracene	–	–	–	–	–	–
Fluoranthene	36.33	59.70	100.00	27.46	46.81	59.79
Pyrene	52.17	65.54	100.00	29.67	55.69	66.4
Benzo(a)anthracene	14.68	100.00	100.00	19.37	29.55	100.00
Chrysene	5.39	100.00	100.00	0.00	58.45	62.86
Benzo(b)fluoranthene	39.94	100.00	100.00	32.00	45.60	100.00
Benzo(k)fluoranthene	100.00	100.00	100.00	0.00	0.00	100.00
Benzo(a)pyrene	0.00	100.00	100.00	0.00	100.00	100.00
Indeno(1,2,3-cd)pyrene	0.00	100.00	100.00	0.00	100.00	100.00
Dibenzo(a,h)anthracene	100.00	100.00	100.00	0.00	100.00	100.00
Benzo(ghi)perylene	0.00	0.00	100.00	0.00	100.00	100.00
Total removal	24.69	76.89	100.00	15.74	50.49	75.52

that the percentage of TOC removal increases with TiO_2 mass and H_2O_2 concentration. The calculus of the effects showed that a rise in TiO_2 mass from 5 to 6 mg promoted a mean TOC removal increase of 2.45% and the increment in hydrogen peroxide promoted a removal increase of 4.27%.

Fig. 6b presents the response surface for TOC removal with the TiO_2 and irradiation time. The results show that time has a significant influence on TOC removal. It was observed that for high values of time, TiO_2 mass became statistically irrelevant.

The last surface response relates the influence of H_2O_2 and time on TOC removal, and follows the trend of previous results. Fig. 6c shows that the best TOC removal outcomes are related to high irradiation times; however, H_2O_2 concentration was also statistically significant. The time increment from 96 to 144 h promoted an augment of 8.84% on the TOC removal, while the H_2O_2 increase from 0.4 to 0.8 mol L^{-1} resulted in a TOC removal increment of 4.27%. These results confirm the irradiation time dependence of oil sludge mineralization using photocatalysis.

3.4. PAH removal

The previous experimental design was useful to obtain the optimal operating conditions for mineralizing oil sludge. According to the previous factorial plan, the best TOC removal results were obtained using 6 mg of TiO_2 and H_2O_2 concentration of 0.8 mol L^{-1}. These experimental conditions were used to perform the irradiation experiments with black and white light using irradiation times of 24, 72 and 96 h. Table 3 shows the removal of 16 PAH after the respective irradiation times.

It was observed that the best results were obtained with the WLR, following the trend of the TOC removal study. Moreover, increased PAH removal as a function of irradiation time, occurred even at 24 h, where considerable removal was observed for most of the studied PAH. With respect to total PAH removal, the white light reactor removed 76.89% after 72 h of irradiation, similar to the percentage obtained by the BLR (75.52%) after 96 h of treatment. In addition, after 96 h of treatment, the WLR achieved a 100% removal rate for all the PAH studied.

4. Conclusions

The results obtained from the present study allow observing the following conclusions:

1. The experiments using white light generally achieved higher mineralization than those carried out with black light.
2. Concerning the irradiation time, although higher PAH removal was obtained with 96 h, in order to find a suitable treatment, the good results obtained at shorter irradiation time should be taken into account.
3. The experimental plan carried out only with the WLR demonstrated that irradiation time is the most important experimental variable for TOC removal.
4. Photocatalysis proved to be an efficient method for removing PAH from oil sludge waste, and due to the high performance of the photocatalytic treatment with visible wavelength (white light), it is possible that the use of solar radiation would be a good alternative for cost reduction.
5. Photocatalytic treatment proved to be a suitable alternative to remove and mineralize PAH from oil sludge and to reduce its harmfulness to humans and the environment.

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References

[1] H. Chapman, K. Purnell, R.J. Law, M.F. Kirby, The use of chemical dispersants to combat oil spills at sea: a review of practice and research needs in Europe, Mar. Pollut. Bull. 54 (2007) 827–838.

[2] C.A. Silva, C.A. Oliveira Ribeiro, A. Katsumiti, M.L.P. Araújo, E.M. Zandoná, G.P. Costa Silva, J. Maschio, H.H.C. Roche, S. de Assis, Evaluation of waterborne exposure to oil spill 5 years after an accident in Southern Brazil, Ecotoxicol. Environ. Saf. 72 (2009) 400–409.

[3] B. Mrayyan, M.N. Battikhi, Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge, J. Hazard. Mater. B120 (2005) 127–134.

[4] C.E. Cerniglia, Biodegradation of polycyclic aromatic hydrocarbons, Biodegradation 3 (1992) 351–368.

[5] R.E. Lehr, D.M. Jerina, Metabolic activations polycyclic hydrocarbons, Arch. Toxicol. 39 (1977) 1–6.

[6] K.L. White, An overview of immunotoxicology and carcinogenic polycyclic aromatic hydrocarbons, Environ. Carcinog. Rev. 2 (1986) 163–202.

[7] R.C. Sims, M.R. Overcash, Fate of polynuclear aromatic compounds in soil–plant system, Residue Rev. 88 (1988) 1–68.

[8] A.D. Pereira Netto, J.C. Moreira, A.E.X. Dias, G. Arbilla, L.F.V. Ferreira, A.S. Oliveira, J. Barek, Assessment of human contamination by polycyclic aromatic hydrocarbons (HPAs) and their nitrate derivatives (NPAH): a methodological revision, Quim. Nova 23 (2000) 765–773.

[9] P.M. Faria, H.V. Rosa, Polycyclic aromatic hydrocarbons (PAH): a revision of their toxicological aspects, Revista Brasileira de Toxicologia 17 (2004) 61–70.

[10] F.J. Rivas, F.J. Beltrán, B. Acedo, Chemical and photochemical degradation of acenaphthylene. Intermediate identification, J. Hazard. Mater. 75 (2000) 89–98.

[11] J.S. Levitt, A.L. N'Guessan, K.L. Rapp, M.C. Nyman, Remediation of α-methylnaphthalene-contaminated sediments using peroxy acid, Water Res. 37 (2003) 3016–3022.

[12] M. Kanaki, A. Nikolaou, C.A. Makri, D.F. Lekkas, The occurrence of priority PAHs, nonylphenol and octylphenol in inland and coastal waters of Central Greece and the Island of Lesvos, Desalination 210 (2007) 16–23.

[13] N Cardellicchio, A. Buccolieri, S. Giandomenico, L. Lopez, F. Pizzulli, L. Spada, Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy), Mar. Pollut. Bull. 55 (2007) 451–458.

[14] F.J. Beltrán, M. González, P. Alvarez, Tratamiento de águas mediante osidación avanzada (II): procesos com peróxido de hidrogeno, Ingenieria Química 332 (1997) 165–169.

[15] W.H. Glaze, An overview of advanced oxidation processes: current status and kinetic models, Chem. Oxid. 2 (1994) 44–57.

[16] M. Pera-Titus, V. Garcia-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[17] I. Arslan, A.I. Balcioglu, Degradation of Remazol black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogenous media, Color. Technol. 117 (2001) 38–42.

[18] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[19] A.O. Ibhadon, G.M. Greenway, Y. Yue, P. Falaras, D. Tsoukleris, The photocatalytic activity and kinetics of the degradation of an anionic azo-dye in a UV irradiated porous titania foam, Appl. Catal. B: Environ. 84 (2008) 351–355.

[20] B. Bayarri, M.N. Abellan, J. Gimenez, S. Esplugas, Study of the wavelength effect in the photolysis and heterogeneous photocatalysis, Catal. Today 129 (2007) 231–239.

[21] B. Pare, S.B. Jonnalagadda, H. Tomar, P. Singh, V.W. Bhagwat, ZnO assisted photocatalytic degradation of acridine orange in aqueous solution using visible irradiation, Desalination 232 (2008) 80–90.

[22] A.A. Yawalkar, D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Solar assisted photochemical and photocatalytic degradation of phenol, J. Chem. Tech. Biotech. 76 (2001) 363–370.

[23] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Behnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 93 (1995) 69–96.

[24] I. Mazzarino, P. Piccinini, Photocatalytic oxidation of organic acids in aqueous media by a supported catalyst, Chem. Eng. Sci. 54 (1999) 3107.

[25] S.C. Lenore, E.G. Arnold, D.E. Andrew, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA and WEF, New York, 1998.

[26] Embrapa, Manual de métodos de análise de solo, Centro Nacional de Pesquisa de Solos, 2nd ed., Rio de Janeiro, 1997.