OIL SLUDGE TREATMENT BY SOLAR TiO_2 -PHOTOCATALYSIS TO REMOVE POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

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ABSTRACT

The objective of this study is to explore the treatment of oil sludge by heterogeneous photocatalysis ($\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$) using solar radiation. Comparisons of total organic carbon (TOC) and polycyclic aromatic hydrocarbons (PAH) removal from the sludge, before and after photodegradation, proved the efficiency of the treatment. The EPA 3540 - Soxhlet extraction method was used to determine PAH. The quantification of PAH was performed by the EPA 8270 - semi-volatile organic components identification method- using chromatography/mass spectrometry (GC/MS). The methodology for determining the TOC was the Walkey-Black modified method. The treatment method removed 90.7% of TOC after 144 hours of exposure to solar radiation, eliminating 100% of PAH after 96 hours using 5 mg of TiO_2 and 0.8 mol.L^{-1} of hydrogen peroxide.

KEYWORDS

heterogeneous photocatalysis; PAH; oil sludge; solar radiation

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1. INTRODUCTION

The soils or sediments contaminated with oil are mixtures composed by numerous chemical species, with diverse physicochemical properties, which present an extensive range of toxicity to organisms (Tang et al., 2011). Among the harmful chemical species present in this type of waste, the polycyclic aromatic hydrocarbons (PAH) are a group of chemicals known for being genotoxic. The relevance of studying PAH in light of environmental regulations is due to their potential hazardous effects on public health (Yang et al., 1991; Tarantini et al., 2011).

The main emissions of PAH result from anthropogenic sources such as the burning fossil fuels, atmospheric carriage by adsorption by soot or particulate matter, drag and deposit of the abrasion products from asphalt and tires, vehicle emissions, oil spills, and byproducts containing complex mixtures of PAH (Kibble & Harrison, 2005; Martins et al., 2007; Audebert et al., 2012). The composition and complexity of PAH mixtures generated through these different processes, which depend on the emission sources (USEPA, 1995), justify the growing interest in researching them (Faria & Rosa, 2004; Reynaud & Deschaux, 2006; Alomirah et al., 2011).

PAH have a tendency to persist in the environment and natural resources, such as sediments, soil, water, and air, resulting in a widespread distribution; in water, because of its hydrophobic characteristic and low solubility, being also able to pollute sediments (Ferrarese, 2008). The interaction of these pollutants in the soil occurs by attractive forces such as dipole-dipole, induced dipole, and hydrogen bonds (Pignatello & Xing, 1996).

Oil pollution in soils can be produced by accidental spills and the leakage in underground storage tanks (Khamsehchiyan et al., 2007).

The efficiency of bio-remediation methods is affected by a number of physical, chemical, and environmental issues, in example, soil pore-structure, aeration, toxic oil constituents, and nutrient availability. Further, the chemical oxidation processes may offer a better solution for partial or even complete contaminant degradation (Hamed et al., 1991).

The majority of the methods devoted to oil sludge treatment are based on biodegradation. However, biodegradation cannot remove some of the toxic or low biodegradable contaminants. Literature addressing the chemical and/or physical transformation of oil sludge is sparse. Some methods used in the treatment of oil sludge, which have been cited are pyrolysis (Liu et al., 2009), microwave (Jiang et al., 2012), thermal-oxidative (Shie et al., 2004), flotation (Sokolov et al., 1979), and UV-TiO₂ (Da Rocha et al., 2010). These treatments are effective in removing recalcitrant organic matter and decreasing toxicity. The costs, however, remain as the main problem in chemical treatment, especially those based on oxidative methods. In our research, we investigate the use of solar radiation in an attempt to reduce the overall cost of oxidative treatments.

Conventional oxidation processes use oxygen as the oxidant, ozone, chlorine, sodium hypochlorite, chlorine dioxide, potassium permanganate, and hydrogen peroxide. However, some of these processes are resistant to the direct action of conventional oxidizing agents. In these cases, it is necessary to use advanced oxidation processes, which are methods based on the formation of hydroxyl radicals (HO•), which have an increased oxidation potential and are capable of reacting with practically all organic compounds' classes (Béltran et al., 1997; Higarashi et al., 2000).

Regardless of the various reaction systems, Advanced Oxidation Processes (AOP) are characterized by the same chemical process, which is a hydroxyl radical production (HO•). Its versatility is due to their ability to produce hydroxyl radicals by different means, depending on specific requirements of each treatment (Amiri et al., 1997; Fernández-Alba et al., 2002).

Treatment processes using AOP are considered as promising methods for industrial waste remediation, as well as cleaning up contaminated soils and wastewaters containing non-biodegradable organic pollutants (Muneer et al., 1997; Chen & Ray, 2001; Bandala et al., 2008; Da Rocha et al., 2010; Dantas et al., 2010). Fenton's reaction has been used in the chemical remediation of contaminated soil (Mater et al., 2007; Ndjou'ou & Cassidy, 2006). However, according to Sirguey et al. (2008), the use of

Fenton reaction in the treatment of petroleum contaminated soil may cause the inhibition of plant growth due the reduction in the pH of the soil. To attenuate this possible problem, one can use the stabilization with lime.

Among the various AOP, the heterogeneous photocatalysis has emerged as a suitable alternative to treat a large quantity of organic pollutants (Esplugas et al., 2002). Heterogeneous photocatalysis involves the photocatalyst irradiation of a semiconductor (inorganic). TiO_2 is used widely in this process due to its efficiency, stability, and solubility in water (Percherancier et al., 1995). The objective of this work is to study the degradation of total organic carbon (TOC) and PAH present in oil sludge using heterogeneous photocatalysis ($\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$).

2. MATERIALS AND METHODS

2.1 Oil sludge characterization

The samples used in this investigation were withdrawn from oil storage tanks located in the State of Rio Grande do Norte, Brazil (Petrobras S. A., Brazil). First, the samples were examined for metals and pH. Flame Atomic Absorption Spectrometry was used to analyze metals, including iron (Varian AA240FS), using standard methodology (Lenore et al., 1998).

Measurements of PAH and TOC were performed as described in the following sections.

2.2 PAH analysis

The PAH extraction method used the EPA protocol 3540, utilizing Soxhlet extraction and 300 mg of oil sludge (before or after treatment). The PAH quantification was performed employing gas chromatography following the EPA 8270 method. The method was replicated using a GC/MS (Shimadzu models GC-17A and QP5050A, respectively). It used was a DB-5 MS capillary column (length = 30 m, inner diameter = 0.25, and film thickness = 0.25 μm) with an injector temperature of 280°C in split less mode. Other chromatographic conditions were: initial oven temperature of 80-120°C, with a ramp of 20°C min⁻¹, and 120-285°C, with 2.8°C min⁻¹. The detection limit was 0.25 mg kg⁻¹.

2.3 Total Organic Carbon (TOC) analysis

The methodology employed to determine the TOC was the Walkey-Black modified method, described by Embrapa (Embrapa, 1997).

The methodology is based on the oxidation of the present organic carbon by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 4N) in acidic medium, thus, forming carbon dioxide and water.

2.4 Photocatalytic experiments

To perform the experiments, 300 mg of samples were exposed to solar radiation in Petri dishes with a surface area of 63.6 cm². To obtain the best experimental conditions, a 2³ factorial design was used with radiation time (96 and 144 hours), 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) as the variables. The TiO_2 P25 presented a specific surface area (BET) of 50±15 m² g⁻¹, and an average primary particle size of 21nm (EVONIK, Germany). The TOC removal was the response for this experimental plan. The hydrogen peroxide concentration used refers to a volume of 21mL, added every 24 hours. The experiments were exposed to solar radiation for 12 hours and, then, another 12 hours without radiation. To verify the efficiency of each individual experiment, the comparison between TOC measurements before and after photodegradation was carried out.

The experiments were performed in duplicate, yielding a pure error of 0.5%. Experiments were conducted during the month of October, in Recife, Brazil (8° 04'03" S; 34° 55'00" W), at the same time every day in order to avoid incidental radiation variance. The average solar radiation was approximately 17 mJ m⁻²s⁻¹ in the wavelength range of 380-780 nm.

3. RESULTS AND DISCUSSION

3.1 Characterization of sludge

By quantifying the metals it is possible to discover the inorganic portion of the sludge that, inevitably, will be left over after organic degradation. From Table 1, one can see that, among the metals analyzed, only cadmium was not detected. Iron stood out significantly in terms of

Table 1. Quantities of metals present in the oil sludge.

Metal	mg kg ⁻¹	Metal	mg kg ⁻¹
Cadmium	-	Iron	3500
Lead	565	Manganese	542
Cobalt	100	Nickel	125
Copper	214	Zinc	769
Chrome	119		

quantity (34.5 mg kg⁻¹), which is justified because of the specific composition of the material (oil sludge) and the manner in which it is stored. The material used in this study was taken from oil tanks, and possible corrosion in these tanks may explain the great amount of iron found, if compared to other metals.

The sample showed a pH around 5, and had an appearance similar to a very viscous black grease, presenting an oil-like strong odor.

The PAH present in the untreated oil sludge are shown in Table 2.

The literature describes PAH soil levels in environmental samples in the range of 0.8 mg kg⁻¹ to 100 mg kg⁻¹ (Pereira Netto et al., 2000). Compared to those found in the untreated sludge used in this study (218.22 mg kg⁻¹), the high potential for contamination by PAH (polyaromatic hydrocarbons) was confirmed.

3.2 Removal of total organic carbon

The TOC analysis of the sample of oil sludge without treatment obtained 547.27 g of carbon kg⁻¹ initial content in the sample. To corroborate the accuracy of the data, blank tests were performed and no significant removal was achieved by any single element of the photocatalysis, such as solar radiation, hydrogen peroxide, or TiO₂ alone. The levels of the variables of this factorial design were determined by the experience acquired during these preliminary tests.

The removal of TOC values obtained in the experimental design varied from 84.7% to 92.2%.

The experiments used the Statistical Experimental Design program, which treated the

Table 2. PAH identified in untreated sludge.

PAH	mg kg ⁻¹	Σ
Naphthalene	6.34	±1.54
Acenaphthylene	<LQ *	-
Acenaphthene	7.99	± 0.34
Fluorene	21.29	± 0.22
Phenanthrene	40.90	± 0.68
Anthracene	<LQ *	-
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

Where * LQ = quantity less than the quantification limit of 0.83 mg kg⁻¹.

obtained data, and an empirical model capable of predicting the system's efficiency in terms of TOC degradation (%). By applying the studied variables, Equation 1 was generated:

$$D = 89.02 + 1.1812 X_{\text{Time}} - 0.8312 X_{\text{TiO}_2} X_{\text{H}_2\text{O}_2} + 0.8563 X_{\text{H}_2\text{O}_2} X_{\text{Time}} + 0.8063 X_{\text{TiO}_2} X_{\text{H}_2\text{O}_2} X_{\text{Time}} \quad (1)$$

With the possibility of making use of a source of clean energy, free of cost, with increased response in the degradation of organic substance present in sludge, the process symbolizes a new alternative to the use of present methods.

The significance of all variables studied, and their interactions, are represented in Figure 1, in the Pareto chart. According to the graphic, the Pareto chart values greater than the P value (0.05) are statistically significant. The estimated absolute effect is shown on the X-axis, while the independent variables and their interactions are on the Y-axis. The effect is calculated from the ratio between the estimated effect and its respective standard deviation.

Figure 1 demonstrates that the effect with the highest statistical significance was the main variable, Time. The effects of interactions H₂O₂ x Time and TiO₂ x H₂O₂ were also statistically significant, indicating that the greater the amount

Figure 1. Pareto chart of the variables effect and their interactions.

Figure 2. Response surface graphics for the mineralization of oil sludge sample, using solar radiation. (a) = H₂O₂ (mol.L⁻¹) vs. TiO₂ (mg), (b) = Time (h) vs. TiO₂ (mg).

of time of exposure to solar radiation, the better the result were.

The following steps were to build the response surface graphics using the experimental data and to evaluate their behavior. In this case, the response surface graphics describe the relationship between three variables and one response. The behavior of overall factor influence on oil sludge mineralization is presented in Figure 2.

It can be observed in the first figure that the

highest values of degradation of TOC are obtained with a greater amount of TiO₂ and a lower concentration of H₂O₂, or with a lower amount of TiO₂ and greater concentration of H₂O₂. Under the conditions studied, these conditions are consistent with the Pareto chart, where the interaction effect TiO₂ x H₂O₂ is negative.

In Figure 2b one can see that the best results for removal of TOC are obtained by using a longer Time and a higher concentration of H₂O₂.

Table 3. Results in removing the PAH (%) using solar radiation.

Compound	Sun radiation		
	24 h	72 h	96 h
Naphthalene	50.00	50.04	100.00
Fluorene	37.45	37.45	100.00
Phenanthrene	50.69	58.51	100.00
Fluoranthene	42.95	43.0	100.00
Pyrene	0.00	0.00	100.00
Benzo (a) anthracene	51.64	56.48	100.00
Chrysene	57.80	63.43	100.00
Benzo (b) fluoranthene	3.71	100.00	100.00
Benzo (k) fluoranthene	53.97	56.53	100.00
Benzo (a) pyrene	46.73	100.00	100.00
Total	45.70	68.08	100.00

3.3 Removal of PAH

The previous experimental design was performed to obtain the optimal operating conditions of the treatment. Thus, the best results of TOC removal were achieved using 6 mg of TiO₂ and 0.4 mol.L⁻¹ concentration of H₂O₂. These experimental conditions were used to perform the irradiation experiments with solar radiation using times of 24, 72, and 96 h. The results are shown in Table 3.

It is observed that, after 96 h, the degradation of HPA was 100%. This result is promising because the radiation source used in this work was the sun, making the process less costly.

4. CONCLUSIONS

The results obtained from the present study lead to the following conclusions:

1. Remediation of oil sludge was efficiently achieved in 96 h, under the experimental conditions tested (5 mg TiO₂ concentration and H₂O₂ 0.8 mol.L⁻¹), obtaining 100% removal of PAH using solar radiation.
2. The application of sunlight as the source of UV radiation obtained a success rate of 90.7% in TOC degradation at 144 h, being cost-effective. However, reaction time should be reduced.
3. The mineralization of organic compounds in the sludge, in response to the TOC degradation with consequent degradation of PAH, indicates the efficiency of the process, and can be

considered technically feasible in the remediation of similar environmental matrices.

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