

Soil remediation contaminated with phenanthrene by *in situ* chemical oxidation using modified clay as catalyst

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Abstract. Phenanthrene is a polycyclic aromatic hydrocarbons (PAH) listed as one of the 16 priority pollutants by the United States Environmental Protection Agency, which tends to be adsorbed to solid particles. Removing or treating soil contaminated by PAH is urgent as hydrocarbons can leach into groundwater and reach residential areas. This work aims to remediate the contaminated soil with phenanthrene by *in situ* chemical oxidation using sodium persulfate (SP) and hydrogen peroxide (HP) with activation by heterogeneous catalysis. The experiments were carried out using two types of soils named white soil (WS) and red soil (RS). For the catalyst synthesis, full factorial design was used varying the concentrations of sodium hydroxide, ferric sulfate and ferrous sulfate, totalizing 11 tests. The 11 catalysts were applied in batch tests lasting 72 hours for each oxidant in each soil, in order to evaluate the activation efficiency in phenanthrene removal. The results showed the efficiency of the catalysts in the *in situ* chemical oxidation for degradation of phenanthrene. It was possible to achieve about 70% removal of the contaminant in tests using sodium persulfate and between 55 and 60% removal in tests using hydrogen peroxide.

Keywords: advanced oxidation process, polycyclic aromatic hydrocarbon, priority pollutant, Fenton like, sodium persulfate.

1. Introduction

Large soil areas can be contaminated by different kinds of pollutants, considering that soil is treated as a complex media, the remediation of these fields is a significant issue (Romero *et al.*, 2011). For example, industrial wastes and accidents or leaks in underground tanks and pipelines can contribute to contamination problems. Thus, the soil becomes economically useless and hazardous to organism's health due to the high toxicity of some chemicals, as the polycyclic aromatic hydrocarbons (PAHs). Removing or treating soil contaminated by oil is especially urgent since hydrocarbons can leach into groundwater and reach residential areas.

PAHs are persistent organic pollutants from incomplete combustion process and fossil fuels processing. They contain from 2 to 6 aromatic rings, are highly toxic and tend to adsorb in solid particles due to their high hydrophobicity and low solubility in water (Peluffo *et al.*, 2016). Approximately 130 PAHs have already been identified, among which 16 are classified as priority pollutants by the US Environmental Protection Agency (US EPA) (Shih *et al.*, 2016).

Due to easy accumulation and their widespread occurrence in the environment, the degradation process of PAHs is challenging (Li *et al.*, 2016 and Mora *et al.*, 2014). Phenanthrene is a PAH listed as one of the 16 priority pollutants by the US EPA, obtained primarily from the fraction of coal tar oil. This substance is considered insoluble in water and tends to be adsorbed to solid particles.

Several technologies have been used in remediation of PAH-contaminated soils, like bioremediation, surfactant flushing, and chemical oxidation (Li *et al.*, 2016 and Yen *et al.*, 2011). *In situ* chemical oxidation (ISCO) is an advanced oxidation process (AOP) and has been widely considered as an alternative method to conventional treatments for soil remediation, mainly because it is able to degrade PAHs instead of merely transfer them to a different phase or converting them in harmless products (Mora *et al.*, 2004). This process is based on the injection of oxidants in contaminated environments in order to treat these areas through chemical reactions involving radicals with high oxidation power. However, the efficiency of the ISCO depends on soil characteristics and PAH properties (Gan *et al.*, 2009 and Mora *et al.*, 2014).

Among the most frequently used oxidants in ISCO are: permanganate (MnO_4^-), Fenton (hydrogen peroxide (H_2O_2) and iron (Fe)) and Fenton-like, persulfate ($S_2O_8^{2-}$) and ozone (O_3). The oxidative method most used and studied is based on Fenton reagents, where the hydrogen peroxide is activated by the iron as a catalyst generating the highly reactive hydroxyl radicals ($HO\bullet$) (2,8 V) (Romero *et al.*, 2011 and Shih *et al.*, 2016). Recently, chemical oxidation with persulfate has attracted many researchers' attention for treatments involving organic contaminants. It has been

shown that the sulfate radicals ($\text{SO}_4^{\bullet-}$) have high oxidative power (2.6 V) (Peluffo *et al.*, 2016; Shih *et al.*, 2016 and Yen *et al.*, 2011). The sulfate radical is more stable than the hydroxyl radical. Therefore, the first one is able to carry great distances in the subsurface and may persist for weeks. In addition, persulfate has a lower affinity for natural soil organic matter than other oxidants, being more efficient in soil with high content of organic matter. The methods of activation can be: UV light, heat, chelated iron, alkaline medium, hydrogen peroxide and ozone (Shih *et al.*, 2016 and Yen *et al.*, 2011).

However, conventional activation methods involving Fenton and persulfate reagents require low pH, which makes the process disadvantageous because it might have a strong environmental impact with the alteration of its natural conditions. In order to avoid acidification of the medium, the oxidative process involving heterogeneous catalysis allows the use of neutral conditions (Romero *et al.*, 2011). In heterogeneous catalysis by iron oxides or hydroxides, iron is stabilized within the porous structure of a catalyst, and can effectively produce the radicals without pH adjustment (Pouan, Raman & Daud, 2014). For this reason, iron oxides have been used lately in oxidation process, which has resulted in an advantageous technology when compared to traditional oxidant activation methods (Usman *et al.*, 2012; Xue, Hanna & Deng, 2009; Zhong *et al.*, 2013).

This work aimed to investigate the remediation of contaminated soil with phenanthrene by ISCO using sodium persulfate (SP) and hydrogen peroxide (HP) oxidants with activation through heterogeneous catalysis, employing modified clay by iron and sodium hydroxide as catalyst.

2. Materials and methods

2.1. Materials

In order to study soil samples with different iron and organic matter, two types of soil were collected in the campus of Federal University of Rio Grande do Norte (Natal/RN, Brazil), at 30 cm depth. Samples were screened in a sieve (8 Mesh), in order to remove coarse material, homogenized and stored. Soils properties are presented in Table 1. Phenanthrene (98%; Sigma Aldrich) was selected as the target pollutant. The soils were contaminated in the laboratory at a concentration of 200 mg of phenanthrene per kg of soil, using hexane (Dinâmica) as solvent.

Table 1. Properties of white soil and red soil.

Analytical items	WS	RS
pH	5,70	5,56
Water contente (%)	1,45	2,91
Soil Organic Matter (mg/kg)	0,13	3,86
Total Iron (%)	8,63	15,36

For the catalyst synthesis, smectitic clay was supplied by Bentonisa industry. Sodium hydroxide (Êxodo), ferric sulfate (Dinâmica) and ferrous sulfate . 7 H₂O (Neon) were also used. 30% hydrogen peroxide (Synth) and sodium

persulfate (Dinâmica) were applied as oxidants. Acetonitrile for analysis (Merck) was used as extraction solvent.

2.2. Catalyst synthesis

The trials for the catalyst synthesis were carried out based on full factorial design, varying the concentrations of NaOH, Fe²⁺ and Fe³⁺, with three center points, totalizing 11 trials. The purpose of the planning was evaluating the optimal activation condition and to select the best catalyst for each oxidant.

The iron solution and the smectitic clay were homogenized in an intensive mixture reactor where the NaOH solution was dripped for one hour. The synthesized material was placed in an oven at 60 °C for 48 hours. After drying, the catalyst was disaggregated with mortar and pestle, screened in a sieve (140 Mesh), and finally conditioned in glass vials.

2.3. Batch experiments

For the batch runs, 15 g of contaminated soil were weighed in each reactor; next, 1.5 g of the catalyst and 30 mL of the oxidant solution were added. Control trials (soil + water; soil + oxidant; soil + oxidant + raw clay) were carried out under the same treatment conditions. All the experiments were performed without pH adjustment at room temperature (around 28 °C) for 72 hours.

2.4. Analytical methods

In order to quantify the residual contamination, aliquots of 2.5 grams of soil sample were taken from each reactor and added in 40 mL vials along with 10 mL of acetonitrile. The vials were then exposed to ultrasound during 30 minutes for solid-liquid extraction. After this procedure, the filtration was performed in 0.45 µm filters. The extract was added in 1.5 ml vials and analyzed by High-Performance Liquid Chromatography coupled with ultraviolet detection (HPLC-UV) (Shimadzu).

3. Results

With the purpose of evaluating the best percentage of phenanthrene removal, advanced chemical oxidation tests were performed for both types of soil (WS and RS) and two oxidants were used: sodium persulfate (SP) and hydrogen peroxide (HP). The 11 catalysts synthesized under different concentrations of NaOH, Fe²⁺ and Fe³⁺ were analyzed in the oxidants activation.

Figure 1 presents the phenanthrene removal results for both control tests (soil + water; soil + oxidant; and, soil + oxidant + raw clay) and tests using the catalysts for each soil and each oxidant (white soil with sodium persulfate - WSSP, red soil with sodium persulfate - RSSP, white soil with hydrogen peroxide - WSHP and red soil with hydrogen peroxide - RSHP).

The control trials are presented at the zero point of the graphs in Figure 1. The removal percentage around 20% for all soil and water controls occurs due to the amount of phenanthrene transferred naturally to the solution, which is related to the effect of the partition coefficient octanol-water ($\text{Log } K_{ow} = 4,62 \pm 0,01$) of the studied contaminant (Jonker, 2016). The soil + oxidant control proves the need of the oxidant activation by the catalyst, since the percentage of removal obtained did not varied considerably when related to the soil + water control. Finally, the results for soil + oxidant + raw clay control show that the clay did not contribute to the oxidant activation. Besides, for the red soil tests, the clay leads to a reduction in the percentage of contaminant removal, which decreases the oxidation process efficiency.

Analyzing the results for the trials using sodium persulfate (Figure 1) it can be seen that for the WSSP trials, the effects were very similar when the catalysts 1 to 11 were applied, achieving a removal between 60 to 70%. For the same oxidant, in the RSSP trials, although the catalyst 7 stands out for the removal percentage (approximately 73%), this catalyst requires a greater amount of reagents when compared to the catalyst 11, which still reaches about 70% removal of the phenanthrene. Analyzing the results for the runs using hydrogen peroxide (Figure 1), catalyst 10 promoted about 55% removal in the WSHP trials and catalysts 3 and 9 promoted a removal percentage of approximately 62% in the RSHP trials.

Comparing the results regarding to the characteristics of the soil types in study, it was expected that the red soil would have a better performance than the white soil in the oxidative processes, due to its higher iron content, since iron is the main choice for oxidants activation in

environmental applications (Shih *et al.*, 2016). Nevertheless, comparing the soils concerning to the same oxidant, there was no significant variation in the percentages of contaminant removal. This can be explained by the presence of more organic matter in the red soil than in the white soil, a quality known as a negative interference in the chemical oxidation. This discussion is consistent with Romero (2011), which reports that the soils' natural organic matter can consume and compete for the oxidant during a Fenton reaction.

In addition, Usman *et al* (2012) describes that persulfate has a lower affinity to the soils' natural organic matter. Therefore, it has greater efficiency in soils with a higher content of organic matter when compared to the process using permanganate as oxidant, which shows the interference of organic matter in the advanced oxidation processes.

4. Conclusion

The application of advanced oxidative processes using sodium persulfate and hydrogen peroxide as oxidants with activation by catalysts produced in the contaminated soils treatment with phenanthrene presented significant results, leading to degradation of the contaminant.

The catalysts used in this study are supported by smectite clay, a low cost material which can be found naturally in the environment. Moreover, since heterogeneous catalysis is involved, there is no need for pH adjustment, differently of the conventional methods application using Fe^{2+}

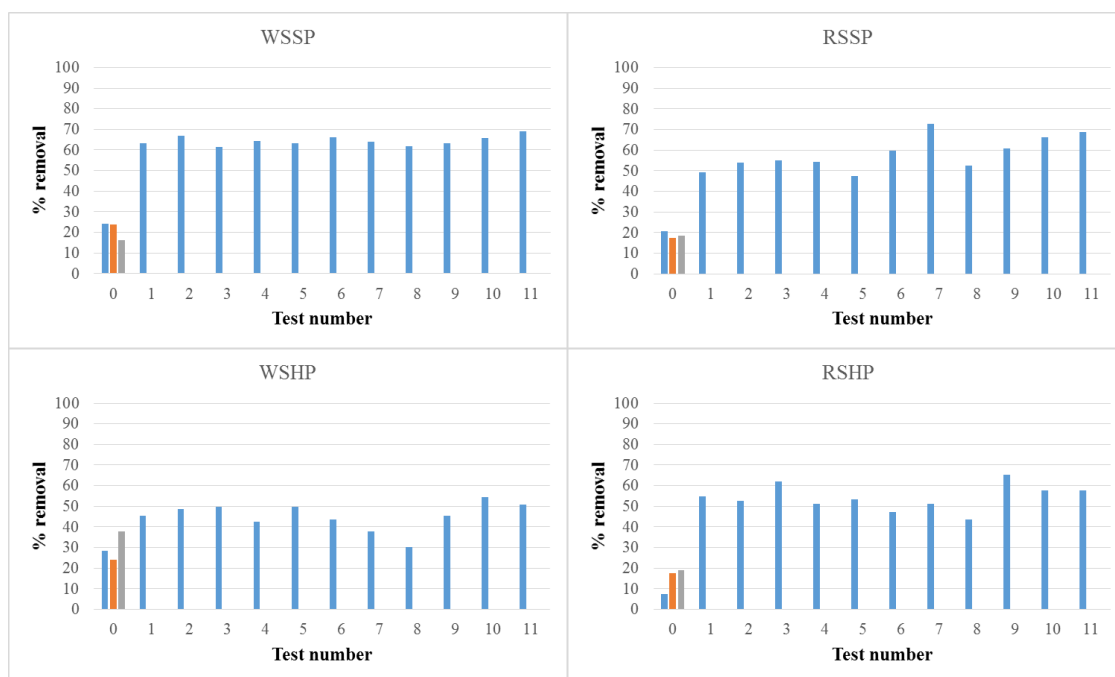


Figure 1. Results for the percentage of phenanthrene removal for the control trials showed at zero (soil + water, soil + oxidant; soil + oxidant + raw clay) and for the 11 different catalysts using the two different types of soil (white soil (WS) and red soil (RS) and oxidant (sodium persulfate (SP) and hydrogen peroxide (HP)).

activated sodium persulfate and hydrogen peroxide, which require acidic pH, which is characterized as disadvantage of this type of process.

Therefore, the use of clay in the heterogeneous catalysis process applied to ISCO is advantageous as it does not affect the natural conditions of the medium.

According to the results obtained in this study, it was observed that sodium persulfate is a better oxidant when activated by the catalysts produced compared to the tests using hydrogen peroxide, for both soils selected. Finally, the catalysts that obtained the best percentage of contaminant removal will be used for further studies.

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