Optimizing Phenanthrene and Anthracene Oxidation by Sodium Persulfate and Fe-Modified Diatomite Using the Response Surface Method

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Abstract This study proposes an improved activation for hydrogen peroxide and persulfate using Fe-modified diatomite (MD) to favorably lead the reaction to generate hydroxyl and sulfate radicals to degrade the contaminants phenanthrene and anthracene. Diatomite was modified by impregnating it with a mixture of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in the form of precipitated iron oxides and hydroxides. The raw and synthesized materials were characterized by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), particle size by laser diffraction, chemical microanalysis of the elements by energy-dispersive X-ray, and scanning electron microscopy (SEM). Batch experiments were performed to compare the new activator material (modified diatomite) with traditional methods of activation for these oxidants and to statistically study the optimum ratio between the amount of this material and the concentration of one oxidant to the degradation of the contaminants phenanthrene and anthracene. The characterization results showed that the materials are amorphous and that the Fe ion concentration was 4.78 and 17.65 % for the raw and modified diatomites, respectively. This result shows a significant increase in the amount of iron ions after synthesis. Comparing the traditional activation method with the modified diatomite, the results of batch experiments showed that the synthesized material presents significant catalytic activity for the oxidation of these contaminants, using sodium persulfate and hydrogen peroxide as oxidants. The analysis of the variables results showed that the concentration of the oxidant has higher significance than the amount of the catalyst.

Keywords Modified diatomite · Polycyclic aromatic hydrocarbons · Oxidation

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1 Introduction

Soil and groundwater contamination by polycyclic aromatic hydrocarbons (PAHs) is a serious and widespread problem worldwide. Due to their resistance to natural degradation and potential damage to human health and ecosystems, PAHs have been classified as priority pollutants by the US Environmental Protection Agency (USEPA). The main sources of PAH in the environment are of anthropogenic origin, particularly the burning of fossil fuels, pyrolysis processes, spillage of petroleum products, disposal of industrial effluents, waste incineration, and wood preservatives (creosote) (Rivas 2006). In some cases, for the in situ treatment of groundwater and soil contaminated with PAH, it may require the use of more than one technology. In situ chemical oxidation

(ISCO) is a technology based on the injection of chemical oxidants into contaminated areas (be it groundwater, sediment, or soil), aiming to destroy the contaminant through chemical reactions and to convert its mass into inert compounds (Huling and Pivetz 2006). Different oxidants are used in ISCO; however, the four most commonly used oxidants are permanganate (MnO_4^-), hydrogen peroxide (H_2O_2), persulfate ($S_2O_8^{2-}$), and ozone (O_3). Recently, persulfate oxidation has emerged as an option for chemical oxidation of organic contaminants in soils and sediments (Liang et al. 2004, 2007; Ferrarese et al. 2008; Yen et al. 2011; Zhao et al. 2013). Persulfate salts dissociate in aqueous solution to the persulfate anion $S_2O_8^{-2}$ which is a strong oxidant (E_0=2.01 V) (Eq. 1).

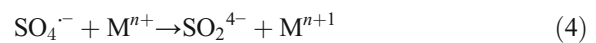$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad (1)$$

The reaction kinetics, however, is slow in destroying most of the recalcitrant organic contaminants (Usman et al. 2012). Persulfate can be activated using various initiators to form more powerful sulfate-free radicals ($SO_4^{-\bullet}$), which has a higher redox potential of 2.60 V (Osgerby 2006). Activation methods for this oxidant can be UV light, heat, alkaline, metal, hydrogen peroxide, and ozone. In the presence of high pH, persulfate is known to activate and to undergo the formation of sulfate radicals. It is a direct result of the requirement for the base in the chemical reaction to form sulfate radicals. This activation technique is widely practiced in ISCO remediation, generally by applying solutions of either sodium hydroxide or potassium hydroxide. Once activated, propagation continues through the formation of hydroxyl radicals (Eq. 2) (Liang et al. 2004).

$$SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \qquad (2)$$

Iron is a commonly used transition metal for chemical activation of persulfate anion Huling and Pivetz (2006). For in situ applications, the Fe^{2+} and Fe^{2+} are preferable as metal activators due to their abundance and the benign environmental repercussions of the process. Other transition metals have been studied to catalyze the radical production persulfate, such as Cu(I) and Ag(I), but these are undesirable for activating remediation applications due to their toxicity (Tsitonaki et al. 2010). In conventional hydrogen peroxide or sodium persulfate activation reaction, the regeneration of the radicals produced from activation by Fe^{2+} needs acidic pH. This low pH can adversely affect the natural soil systems and change their characteristics (Jorfi et al. 2013). Thus, the need to work with low pH can be considered as one of the disadvantages of the conventional method for activation using Fe^{2+}. During metal activation, the metal activator is involved in both radical generation (Eq. 3) and radical scavenging (Eq. 4); it is thus important to optimize the metal dosing to achieve effective activation without excess scavenging (Tsitonaki et al. 2010).

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{-\bullet} + SO_4^{2-} + M^{n+1} \qquad (3)$$

$$SO_4^{-\bullet} + M^{n+} \rightarrow SO_2^{4-} + M^{n+1} \qquad (4)$$

The modeling of a process is required to reduce its multiple input variables into a desired smaller number with significant influence on the output response (Zafar et al. 2010). In industrial processes, homogeneous and heterogeneous catalysts are used (Schmal 2011). In the case of heterogeneous catalysis, iron minerals can be used to activate persulfate anion to produce sulfate radicals. The sulfate radicals are very reactive, rapidly oxidizing other compounds (Wilson et al. 2013). One of the most widely used types of catalysts consists of two phases: one phase support and the other active material obtained by impregnation, precipitation, or deposition by precipitation. The active phase may be a metal or metal oxide, which is the active component to interact with the molecules during the chemical reaction (Schmal 2011). The supports must be stable and constant properties resistant to acid attacks and the influence of temperature. Among the natural supports, diatomite and Kieselgur are based on silica and carbon, e.g., charcoal or natural coal. Studies have reported the modification of clay and other materials for treating organic compounds, such as naphthalene and toluene (Vianna et al. 2010a, b). Diatomite was used in other studies to investigate the potential application of this material as adsorbent for removing phosphorus, uranium, and metal ions from wastewater (Xiong and Peng 2008; Al-degs et al. 2001; Aytaş et al. 1999; Pookmanee et al. 2010, 2008). The high porosity of diatomite in 80–85 % voids makes it suitable for surface modification because highly porous diatomite can be an appropriate carrier material for some materials used for modifying diatomite (Xiong and Peng 2008).

In a previous study, the degradation of phenanthrene and anthracene in solid matrix using sand as soil model was evaluated. The sand was chosen to avoid the competition that may occur between the interfering materials and real soil. These interferences include the presence of organic matter, metals, and clay (Silva et al. 2014).

The application of modified diatomite to activate oxidants and to degrade PAH had not been documented before this study. The primary advantage of the material proposed herein is the activation of the oxidants in radical species without the need of a pH adjustment in the system. Some additional advantages for using diatomite for this activation are its low-cost, abundance, and high porosity. In addition, diatomite functions as a support to the iron which is to increase the distribution of iron ions on the surface of the support in order to have more active sites in contact with the pollutant molecules, rendering the treatment more effective.

In this context, the aim of this work was to prepare a heterogeneous material using diatomite as a support, to activate sodium persulfate and hydroxide peroxide, and to degrade organic contaminants. In addition, a statistic study to determine the optimum ratio between the amount of catalyst and the concentration of oxidant for degrading phenanthrene and anthracene was realized. The degradation of these contaminants was studied because they are considered PAH models to represent this group of contaminants for studies involving the interaction of PAH with the environment.

2 Materials and Methods

2.1 Materials

The soil model under study was acquired from Jacuzzi® manufacturer. This soil model was sand, with controlled particle size (particle diameter of 0.5 mm), composed predominantly of silica (SiO_2), with an apparent density of 1.4 g mL^{-1} and porosity of 0.26. The diatomite was acquired from BF-Clay Especialidades Ltda. The contaminant models were anthracene (high purity; Aldrich) and phenanthrene (98 % purity; Fluka Analytical).

2.2 Sample Preparation

The sand was first washed and then oven-dried at 60 °C for 24 h. The sand was contaminated in laboratory with anthracene and phenanthrene dissolved in dichloromethane (DCM) and homogenized using a glass rod.

2.3 Material Synthesis

The activator material was prepared using 100 g of diatomite added slowly to a mixture of 112 mL of aqueous solutions containing ferric sulfate (366 g L^{-1}) and ferrous sulfate (183 g L^{-1}) in an intensely stirred reactor. In this suspension, a solution of NaOH (5 mol L^{-1}, 220 mL) was added in four steps for 1 h. Each 15-min period, 55 mL of this solution was introduced. The mixture was homogenized for 1 h. The synthesized material was washed by vacuum filtration; after washing, the material was placed in an oven at 60 °C for 24 h. After drying, the catalyst was crushed (broken) with a mortar and a pestle and then sieved and stored in glass vials.

2.4 Material Characterization

To characterize the raw and modified diatomites, methods were employed and analyzed at the Institute of Geosciences at the University of São Paulo, Brazil. The analysis were powder X-ray diffraction (XRD) analysis, X-ray fluorescence (XRF) analysis, determination of particle size by laser diffraction, chemical microanalysis of the elements by energy-dispersive X-ray, and scanning electron microscopy (SEM). XRD analysis was performed using a model D5000 X-ray diffraction unit (Siemens/Brucker), with Cu K-alpha radiation (40 kV, 40 mA); the data were analyzed by Diffraction Plus Software. The diffractogram was recorded in the 3°–65° 2θ range, with a 0.02 step size and a collection of 1 s per point. X-ray fluorescence spectrometry was performed by Philips spectrometer model PW 2400 XRF. The X-rays were generated using a Rh-anode X-ray tube (Mori et al. 1999). The determination of particle size by laser diffraction was conducted using a Mastersizer 2000 (Malvern) analyzer. For the SEM analysis, samples of raw and modified diatomites were scanned with an EOL 440I scanning electron microscope. The samples were first mounted flat, using an adhesive, and then coated with a thin layer of gold.

2.5 Batch Experiment Treatment

To each glass reactor of 125 mL, 15 g of contaminated sand with 200 mg of phenanthrene and 25 mg of

anthracene per kg of soil was added. Then, the amount of the activator material and 30 mL of sodium persulfate or hydrogen peroxide solution were added. The temperature of the batch experiments was controlled using thermostatic bath at 32 °C. To all the experiments (control and reactions), the volume of the solution was 30 mL.

2.5.1 The effect of modified diatomite for activated sodium persulfate and hydrogen peroxide

Control assays were performed with contaminated sand and water (control), contaminated sand with 2.5 g of modified diatomite (control MD), contaminated sand and hydrogen peroxide at 0.1 mol L^{-1} without modified diatomite (control HP), and contaminated sand with sodium persulfate at 0.1 mol L^{-1} without modified diatomite (control SP).

Preliminary tests of the traditional method using Fe^{2+} were carried out in parallel to compare the efficiency of the catalyst proposed herein. These tests were conducted with the oxidants sodium persulfate and hydrogen peroxide activated with the conventional method by ferrous sulfate (Fe^{2+}) and compared with the activation promoted by the modified diatomite (containing Fe^{2+} and Fe^{3+}). The time of the tests was kept constant at 72 h. The conditions of preliminary tests for oxidants and activator material are shown in Table 1. To evaluate the efficiency of the modified diatomite, traditional activation tests by ferrous sulfate were carried out at

approximately the same iron concentrations in the systems that were used with modified diatomite. The experiments were carried out in duplicate, and the experimental errors were lower than 5 %.

2.5.2 Experimental Designs

The experimental design allows the estimation of how a certain response is influenced by one or more variables, called factors, and how these factors, in turn, affect each other. The first experimental design (design A) was carried out according to the central composite design, and the experimental points used according to this design are shown in Table 2. The factors were concentration of sodium persulfate oxidant and catalyst amount (modified diatomite). The design software used in the study was Statistica software 12. The tests were conducted using sodium persulfate concentrations ranging from 1 to 29 g L^{-1} and catalyst amount ranging from 0.1 to 2.9 g. The central points were 15 g L^{-1} for the concentration of the oxidant and 5.0 g for the amount of catalyst. The remediation time was kept constant at 168 h. The pH of the reactions was around 9–11 (natural pH with the catalyst).

The second experimental design (design B) was performed according to Table 3. In this design, sodium persulfate concentrations ranged from 21 to 49 g L^{-1} and the catalyst amount ranged from 0.1 to 2.9 g. The central points were 35 g L^{-1} for the oxidant concentration and 1.5 g for the amount of catalyst. The

Table 1 Preliminary tests: concentrations of oxidants, ferrous sulfate, and catalyst

Oxidants	Oxidants (g L^{-1})	Ferrous sulfate (g L^{-1})	Catalyst amount (g)[a]	pH
Hydrogen peroxide (HP)	3.4	0.03	–	3
Sodium persulfate (SP)	25	0.40	–	3
Hydrogen peroxide+ modified diatomite (HP+MD)	3.4	–	2.5	11
Sodium persulfate+ modified diatomite (SP+MD)	25	–	2.5	11

[a] Each 2.5 g of catalyst is equivalent to 0.4 g of ions Fe^{2+} and Fe^{3+}; $C=13$ g L^{-1}

Table 2 Experimental design A

Trials	Catalyst	Oxidant	Catalyst (g)	Oxidant (g L^{-1})
	Normalized values		Absolute values	
1	−1	1	0.5	25
2	−1	−1	0.5	5
3	1	1	2.5	25
4	1	−1	2.5	5
5	0	0	1.5	15
6	0	0	1.5	15
7	0	0	1.5	15
8	1.4	0	2.9	15
9	0	1.4	1.5	29
10	−1.4	0	0.1	15
11	0	−1.4	1.5	1

Table 3 Experimental design B

Trials	Catalyst	Oxidant	Catalyst (g)	Oxidant (g L^{-1})
	Normalized values		Absolute values	
1	−1	−1	0.5	25
2	1	1	2.5	45
3	−1	1	0.5	45
4	1	−1	2.5	25
5	0	0	1.5	35
6	0	0	1.5	35
7	0	0	1.5	35
8	1.4	0	2.9	35
9	0	1.4	1.5	49
10	−1.4	0	0.1	35
11	0	−1.4	1.5	21

Table 4 X-ray fluorescence results

Compound	Raw diatomite (%)	Modified diatomite (%)
SiO_2	63.71	41.73
Fe_2O_3	4.79	17.60
Al_2O_3	12.54	8.80
Na_2O	1.31	13.39
TiO_2	0.56	1.00
MnO	0.09	0.63
MgO	2.84	2.56
CaO	3.53	2.87
K_2O	1.13	1.31
P_2O_5	0.32	0.75
LOI	9.18	9.36

LOI loss on ignition

remediation time was kept constant at 168 h. The pH of the reactions was around 9–11 (natural pH with the catalyst).

2.6 Extraction and Analytical Methods

For quantifying the residual contaminants in the solid phase, aliquots of 2.5 g were withdrawn from each reactor. Each aliquot was added to a vial of 40 mL, to which 10 mL of solvents were added, hexane/ketone (1:1). *Fisher Scientific* FS110 Ultrasound was used for extracting the contaminants (EPA Method 3550). The extracts were analyzed by mass spectrophotometry and gas chromatography (Shimadzu GC-MS GC-17A, DB-5MS capillary column). This analysis method was used to identify and quantify the contaminants. The quantification of phenanthrene and anthracene was conducted using a five-point calibration method. The chromatographic analysis was performed at an injection temperature of 250 °C, using helium as a carrier gas and injecting of 2 μL of the sample (EPA Method 8270).

3 Results and Discussion

3.1 Diatomite Characterization

The X-ray fluorescence analysis shows that the concentration of total iron ions (expressed in terms of oxides) was 4.78 and 17.65 % for the raw diatomite and the modified one, respectively (Table 4). The result

indicates a significant increase in the amount of iron ions after synthesis. The iron ions in this study are the metals responsible for activating the oxidant.

From analyzing the results of the X-ray diffraction, it was not possible to detect iron oxides or hydroxides formed in the modified diatomite, indicating that the material formed is amorphous which is a characteristic of iron hydroxides (Figs. 1 and 2). In this case, further analysis is needed to adequately specify these hydroxides as amorphous materials.

The average particle size of raw diatomite and modified diatomite was 29 and 65 μm, respectively. The analysis of SEM was used to determine differences in the structures of the surfaces of raw diatomite and modified diatomite. The microscopy shows that the raw diatomite has a porous structure and a large void
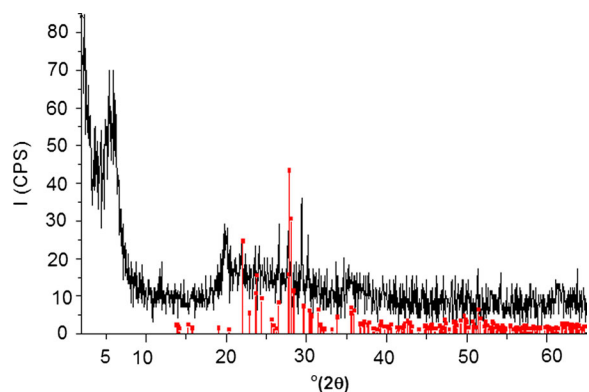
Fig. 1 X-ray diffraction for the raw diatomite (JCPDS card no. 01-083-1939)—albite, calcian—$Na_{0.685}Ca_{0.347}Al_{1.46}Si_{2.54}O_8$
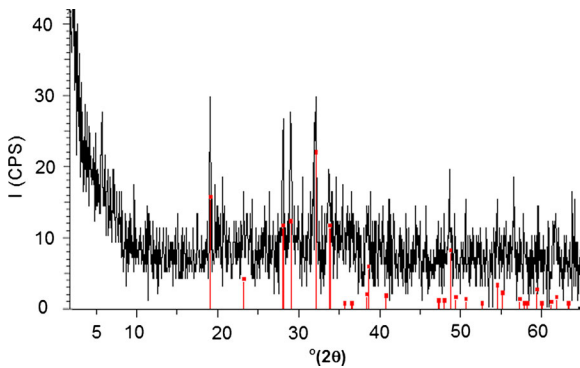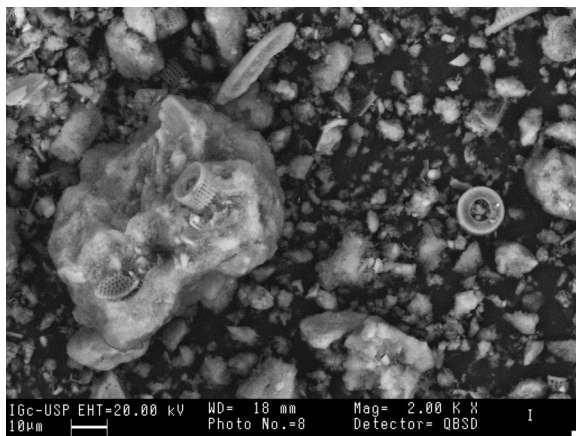
Fig. 2 X-ray diffraction for the modified diatomite (JCPDS card no. 37-1465)—thenardite, syn—Na$_2$SO$_4$

Fig. 4 Scanning electron micrograph for the modified diatomite with magnification of ×2000 (*scale*=10 μm)

volume. The SEM of raw diatomite shows that there are two main types of structures: centric and pennate (Fig. 3). The results agree with other studies (Xiong and Peng 2008). The SEM of the modified diatomite (Fig. 4) shows that the original geometry of diatoms was destroyed by treatment with NaOH and deposition of oxides and/or hydroxides of iron.
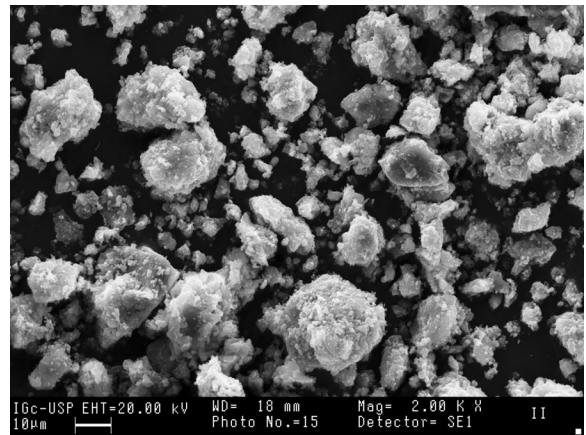
3.2 Batch Experiment Results

3.2.1 The Effect of Modified Diatomite for Activated Sodium Persulfate and Hydrogen Peroxide

Figure 5 shows the results of testing with sodium persulfate and hydrogen peroxide oxidants with the conventional activation method and with the method proposed herein. The reaction time was kept constant at 72 h, and the temperature was controlled at 32 °C.

Fig. 3 Scanning electron micrograph for the raw diatomite with magnification of×2000 (*scale*=10 μm)

Comparing the control (test without the addition of catalyst or oxidant) test result, with the control MD (test with catalyst, and without oxidant), the material showed the property/capacity of adsorbing the contaminants. Control experiments using only oxidants, at pH 11, did not result in the decomposition of phenanthrene and anthracene. Figure 5 shows that verifying that the tests using the oxidant sodium persulfate and hydrogen peroxide activated with the modified diatomite had better results than those obtained using conventional activation methods. The degradation percentages for the total contamination (phenanthrene+anthracene) using hydrogen peroxide were 20.5 and 43.5 % for conventional and modified diatomite activation, respectively. In the treatments with the sodium persulfate activation, the degradation percentages for the total contamination were 35.5 and 59 % for conventional and diatomite activation, respectively. In accordance with these results, shown in Fig. 5, the sodium persulfate activated with the modified diatomite was selected for further investigation. Other advantages of this oxidant are low affinity for organic matter in the soil and persistence in the environment, and it may be transported over long distances (Usman et al. 2012). Formation of the anthraquinone, intermediate from anthracene degradation, was detected experimentally; however, the amount observed was insignificant to be quantified.

3.2.2 The Effect of the Concentrations of Sodium Persulfate and Catalyst

According to design A, the conditions that had the lowest levels of residual contaminants were concentration of
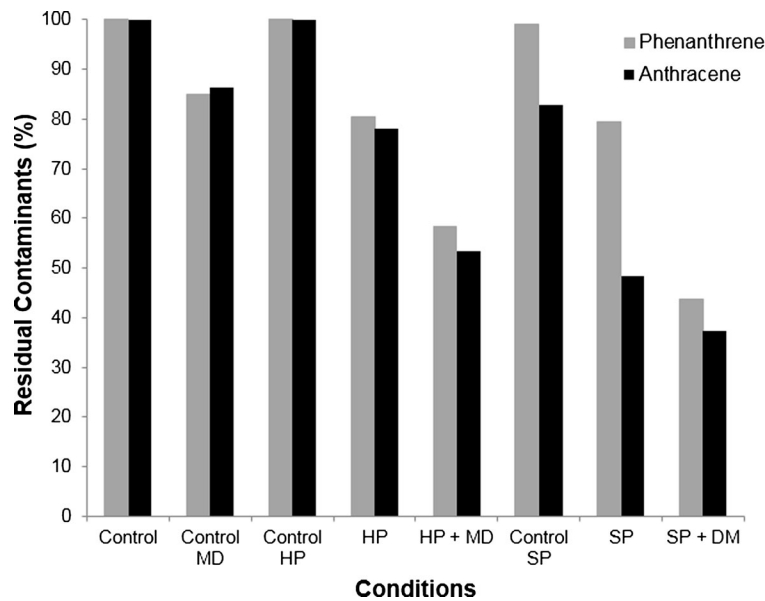
Fig. 5 Phenanthrene and anthracene oxidation during the experiments by hydrogen peroxide (*HP* and [ferrous sulfate]= 0.03 g L^{-1}, at pH 3), hydrogen peroxide and modified diatomite (*HP+MD*, at pH 11), sodium persulfate (*SP* and [ferrous sulfate]= 0.40 g L^{-1}, at pH 3), and sodium persulfate and modified diatomite (*SP+MD*, at pH 11). Controls are as follows: *control* contaminated sand and water; *control MD* contaminated sand, modified diatomite, and water; *control HP* contaminated sand and solution of hydrogen peroxide without modified diatomite; and *control SP* contaminated sand and solution of hydrogen peroxide without modified diatomite. Experimental conditions were [anthracene]= 25 mg kg$_{sand}$$^{-1}$ and [phenanthrene]=200 mg kg$_{sand}$$^{-1}$, [HP]= 3.4 g L^{-1}, [SP]=25 g L^{-1}, contaminated sand=15 g, MD=2.5 g, volume of solution=30 mL, temperature=32 °C, and constant time at 72 h

oxidant to 25 g L^{-1} and 2.5 g of catalyst. Accordingly, the degradation rate was 77 and 95 % for contaminants phenanthrene and anthracene, respectively (Table 5). The residual contaminants in these conditions were

36 mg of phenanthrene per kg of soil and 0.6 mg of anthracene per kg of soil.

Analyzing the response variable average degradation of the contaminants in the concentration of the sodium

Table 5 Results of design A

Trials	Catalyst	Oxidant	Catalyst (g)	Oxidant (g L^{-1})	Degradation (%)		
	Normalized values		Absolute values		Phenanthrene	Anthracene	Average
1	−1	1	0.5	25	71	91	81
2	−1	−1	0.5	5	65	81	73
3	1	1	2.5	25	77	95	86
4	1	−1	2.5	5	45	79	62
5	0	0	1.5	15	50	86	68
6	0	0	1.5	15	43	74	59
7	0	0	1.5	15	59	90	75
8	1.4	0	2.9	15	50	87	68
9	0	1.4	1.5	29	59	89	74
10	−1.4	0	0.1	15	34	55	45
11	0	−1.4	1.5	1	42	55	48
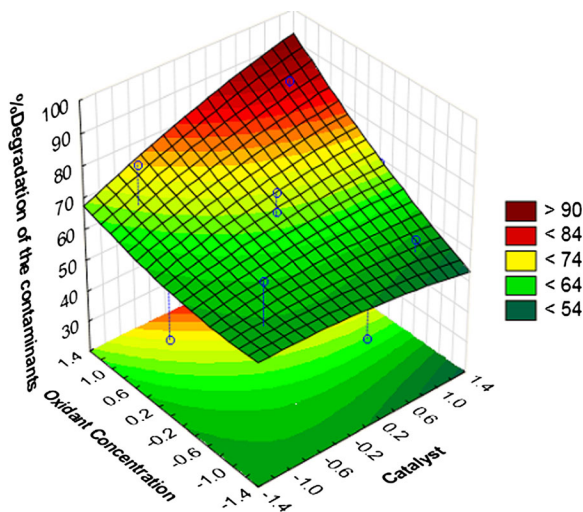
Fig. 6 Response surface of contaminant degradation in design A. Experimental conditions were as follows: persulfate concentrations of 1 to 29 g L^{-1}, catalyst amount of 0.1 to 2.9 g, and central points of 15 g L^{-1} and 1.5 g for the persulfate concentration and catalyst amount, respectively. The constant time was set at 168 h, and the temperature was set at 32 °C

persulfate at 5 g L^{-1} and increasing the amount of the modified diatomite from 0.5 to 2.5 g, the degradation was observed to decrease by 11 % (Table 5, Fig. 6). This factor can be explained by the fact that, in these conditions, there was excess catalyst, making the iron ions present in the material scavenge the radical sulfate, transforming it into persulfate ion again, hence decreasing the efficiency of the degradation. Calculating the variables effect of design A, the effect of the catalyst

presented a negative value (−3), which indicates that by increasing the amount of catalyst, in these conditions, the treatment efficiency decreases, as already explained with the results shown in Table 5. The effect of the oxidant showed a value of 16, which indicates that the degradation efficiency increases by 16 %, on average, when the concentration of sodium persulfate varies from a lower level (5 g L^{-1}) to a higher level (25 g L^{-1}).

Figure 6 shows the response surface, related to the degradation of phenanthrene and anthracene, according to the experimental design described in Table 1 using Statistica software 12.

According to Fig. 6, the response surface of design A, obtained using Statistica software 12, shows that the optimal conditions were not obtained. Therefore, another experimental design, design B, was accomplished by increasing the concentration of oxidant and in the same amounts as the catalyst. According to the results of design B, shown in Table 6, the conditions with the lowest levels of contaminants were detected in the analysis at a 45 g L^{-1} concentration and 2.5 g of catalyst, which had removal rates of 86 and 96 % for phenanthrene and anthracene, respectively (Table 7). The residual contaminants in these conditions were 14.5 mg of phenanthrene and 0.5 mg of anthracene per kg of dry soil. Values under the intervention were limited for total PAH according to the Dutch regulation for soils (40 mg of total PAH per kg of soil).

To represent the behavior of the remediation of soils contaminated with phenanthrene and anthracene with sodium persulfate oxidation coupled to the catalyst

Table 6 Results of percentage degradation obtained in design B

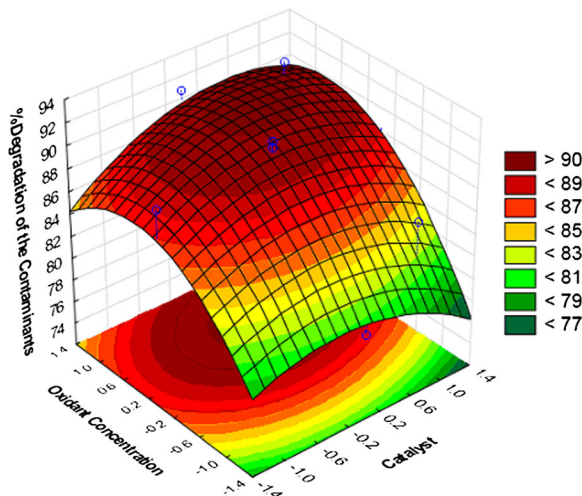| Trials	Catalyst	Oxidant	Catalyst (g)	Oxidant (g L^{-1})	Degradation (%)		
	Normalized values		Absolute values		Phenanthrene	Anthracene	Average
1	−1	−1	0.5	25	75	89	82
2	1	1	2.5	45	87	96	91
3	−1	1	0.5	45	80	90	85
4	1	−1	2.5	25	76	93	84
5	0	0	1.5	35	83	95	89
6	0	0	1.5	35	85	96	90
7	0	0	1.5	35	86	96	91
8	1.4	0	2.9	35	76	94	85
9	0	1.4	1.5	49	84	96	90
10	−1.4	0	0.1	35	83	95	89
11	0	−1.4	1.5	21	67	92	79

Table 7 Percentage of degradation observed and calculated in design B

Trials	Catalyst	Concentration of oxidant	Experimental contaminants degradation (%)	Model contaminants degradation (%)
1	−1	1	85	88
2	−1	−1	82	83
3	1	1	92	91
4	1	−1	84	82
5	0	0	90	90
6	1.4	0	85	88
7	0	1.4	90	89
8	−1.4	0	89	86
9	0	−1.4	79	80

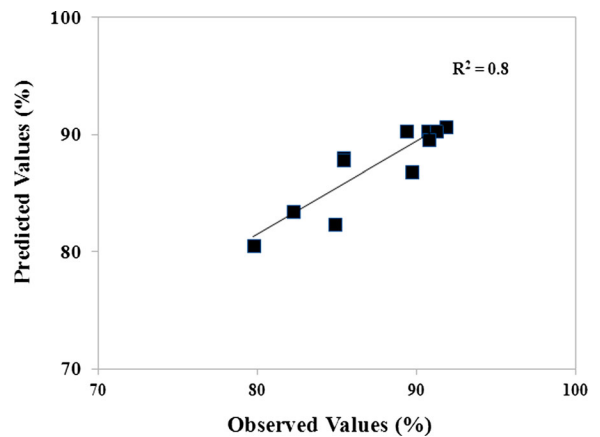Fig. 8 Observed values versus predicted values in design B

proposed herein, using the experimental design described in Table 3, a second-order polynomial model was proposed (Eq. 5).

$$Z = a_0 + a_1 x + a_2 x^2 + a_3 y + a_4 y^2 + a_5 xy \qquad (5)$$

In this model, the variables a_0, a_1, a_2, a_3, a_4, and a_5 are parameters, where a_0 represents the overall average of the degradation of contaminants and a_5 represents the

Fig. 7 Response surface of contaminants degradation in design B. Experimental conditions were as follows: persulfate concentrations at 21 to 45 g L^{-1}, CAT-5 amount of 0.1 to 2.9 g, and central points of 35 g L^{-1} and 1.5 g for the persulfate concentration and catalyst amount, respectively. The constant time was set at 168 h, and the temperature was set at 32 °C

effects and interactions. The normalized variables are represented by x (amount of catalyst) and y (oxidant concentration), and Z is the percentage of degradation of the contaminants. Equation 6 shows the model proposed for degrading phenanthrene and anthracene in design B.

$$Z = 90.42 + 0.38x - 1.53x^2 + 3.22y - 2.70y^2$$
$$+ 0.95xy \qquad (6)$$

The response surface of design B (Fig. 7) was obtained from Eq. 6, varying the amount of catalyst and concentration of the oxidant, along their minimum and maximum levels. To calculate the optimal obtained by design B, we used the MATLAB software. It showed that the peak for the model equation obtained is 1.56 g of catalyst and the oxidant concentration at 41 g L^{-1} (optimum ratio). Studies suggest that for a good fit of a model, the correlation coefficient (R^2) should be at least 0.80 (Joglekar and May 1987; Fua et al. 2007). The R^2 values for the response variables of design B, shown in Table 7 and Fig. 8, were approximately 0.80, indicating that the regression models explained the reaction well.

Calculating of the effect of the variables of design B, one verifies that the effect of the catalyst and the oxidant, in the employed conditions of this design, showed both positive values for the variables, differently from design A, in which the catalyst effect calculation showed a negative value. It can be inferred that in design B, the concentration of the

oxidant employed was higher than that of design A to the same catalyst amounts. Thus, in the conditions of design B, the catalyst was not excessively used as in design A. In design B, the effect of the oxidant showed a value of 2, which indicates that the degradation efficiency increases by 2 %, on average, when the concentration of sodium persulfate varies from lower level (25 g L^{-1}) to higher level (45 g L^{-1}); the catalyst showed a value of 4.5, which indicates that the degradation efficiently increases by 4.5 %, on average, when the amount of the catalyst varies from lower level (0.5 g) to higher level (2.5 g).

4 Conclusions

The results of the evaluation of the catalyst efficiency showed that the synthesized material has significant catalytic activity for phenanthrene and anthracene oxidation, using sodium persulfate and hydrogen peroxide as oxidants. The treatment with sodium persulfate demonstrates advantages over hydrogen peroxide activation. Among the reasons is that the activated persulfate with the modified diatomite can produce sulfate and hydroxyl radicals. Thus, it can degrade a wide range of the different classes of contaminants. According to the analysis of the variables of experimental designs, it showed that a relational amount of catalyst and oxidant concentration should be optimized to use the right amount of catalyst. The use of excess iron ions may cause scavenging of the sulfate radicals, decreasing the efficiency of degradation. Experimental design B to the degradation of phenanthrene and anthracene with sodium persulfate and modified diatomite showed that the optimal degradation can be achieved under the conditions at 41 g L^{-1} and 1.56 g of catalyst, which indicates an optimal mole ratio of sodium persulfate and iron ions present on the surface of the material, from 1:1, to produce, oxidative radicals effectively. These optimal conditions are within of the experimental domain carried out.

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