Water Air Soil Pollut (2017) 228: 271
DOI 10.1007/s11270-017-3456-8

Remediation of Phenanthrene-Contaminated Soil by Persulfate Activated with Fe-Modified Diatomite: Kinetic and Statistical Approaches

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Received: 23 January 2017 / Accepted: 27 June 2017 / Published online: 10 July 2017

Abstract An innovative diatomite-supported iron catalyst has been developed by using an impregnation process with a mixture of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in the form of precipitated iron hydroxides. Raw and modified diatomite samples have been characterized by X-ray fluorescence and scanning electron microscopy. The main characterization results have revealed that modified diatomites are amorphous and have higher iron concentrations than raw diatomite. The results also indicate that the modified materials provided significant catalytic activity on phenanthrene degradation by using sodium persulfate. Satisfactory results were obtained with 45 g/L of sodium persulfate and 1 g of modified diatomite, thus degrading 98% of phenanthrene during 168 h of treatment. Kinetic and statistical approaches were developed for the remediation process herein, which have been validated with experimental data, thence yielding suitable results.

Keywords Advanced oxidation process · Phenanthrene · Diatomite · Modeling · Statistical · Kinetic · Persulfate · Soil

1 Introduction

Accidents caused by oil spills often occur in densely populated urban areas, which usually entail risks of fire and explosion in confined spaces (Favera 2008). Crude oil is physically, chemically, and biologically dangerous on account of its many toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs) (Abdel-Shafy and Mansour 2015). Incomplete combustion of fossil fuels or accidental discharge during transport and disposal of petroleum products can also cause contamination (Leneva et al. 2009).

Anjos (2012) has investigated possible soil contamination near a gas station in the urban area of Natal (Rio Grande do Norte - Brazil), thus detecting a few PAHs, such as phenanthrene, anthracene, and pyrene. The present results raise cause for concern due to the fact that 70% of Natal's water supply is from groundwater, therefore revealing that it is an area that requires further research. According to the US Environmental Protection Agency (USEPA), there are 16 PAHs, including phenanthrene, which are classified as priority pollutants due

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to their level of toxicity to humans and persistence in the environment. In the present study, phenanthrene degradation has been studied due to being regarded as a PAH model for studies involving its interaction with the environment.

The In Situ Chemical Oxidation (ISCO) technology is based on injecting chemical oxidants into the contaminated media (soil, groundwater or sediment) with the aim of destroying contaminants through chemical reactions, thus producing inert compounds (Huling and Pivetz 2006). Persulfate anion ($S_2O_8^{2-}$) is a new form of oxidant which has been under investigation due to being a strong oxidant, though it destroys most organic contaminants at a slow rate. Persulfate can be activated by different methods for generating a sulfate radical ($SO_4^{-\bullet}$) which is a stronger oxidant than $S_2O_8^{2-}$ (Osgerby 2006; Usman et al. 2012). Conventional activation with Fe^{2+} requires an acidic pH condition, which is disadvantageous since low pH values are detrimental in most soil systems (Jorfi et al. 2013). In heterogeneous catalysis with oxides or iron hydroxides, iron is stabilized within the porous catalyst structure and can produce radicals derived from hydrogen peroxide or persulfate under uncontrolled pH conditions without the occurrence of iron precipitation (Pouran et al. 2014). In soil slurry systems, there can be many reactions with synergistic and/or antagonistic effects on persulfate activation and persulfate oxidation reactions. All soil matrix factors could affect persulfate oxidation efficiency (Usman et al. 2012).

Diatomite ($SiO_2 \cdot nH_2O$) is a special material formed from diatom remains which grows and is deposited on seas or lakes (Pookmanee et al. 2010; Xiong (2009). Diatomite is an abundant material that can be found in many areas worldwide, which is easily available in large quantities at extremely low cost. It has favorable physical characteristics, such as high porosity, low thermal conductivity, and high adsorption capacity (Zhaolun et al. 2005; Bakr 2010). Diatomite-based products can be applied in a variety of ways, e.g., as filter aids, thermal insulators, absorbents, and catalyst carriers (Reza et al. 2015). Previous studies have demonstrated that Fe-modified diatomite was effective at promoting oxidants activation aiming at perfluorooctanoic acid degradation by reductive species (Silva-Rackov et al. 2016) as well as phenanthrene and anthracene degradation by oxidative species (Silva et al. 2015). The produced radical species (reductive or oxidative) depend upon pH conditions and oxidant concentrations. In addition, other studies have reported the modification of clay and other materials for treating organic compounds. The mixture of Fe^{2+}/Fe^{3+} oxides was found to be the most effective catalyst in comparison with only Fe^{2+} oxide for the chemical oxidation of petroleum hydrocarbons and other organic pollutants (Usman et al. 2012; Kong et al. 1998; Vianna et al. 2010a, 2010b).

From a theoretical standpoint, the degradation of PAHs via oxidation consists in a complex system of reactions, in which kinetics and thermodynamics play pivotal roles. Previous studies have reported anthracene and phenanthrene degradation modeling (Forsey et al. 2010; Silva et al. 2014). Nevertheless, its use is still scarce in literature.

This work mainly aims to evaluate the remediation of soil contaminated with phenanthrene by using advanced oxidation processes in a heterogeneous system. In addition, it was sought to find optimal experimental conditions for catalyst synthesis by using a smaller amount of reagent in order to make the process technically and economically feasible. Another important aspect is the effectiveness of evaluating sodium persulfate in the presence of a synthesized catalyst under optimal conditions for the phenanthrene-contaminated soil treatment. A mathematical model based on reaction kinetics and soil/solution partition has been developed and validated through experimental data obtained herein in order to broaden the understanding of the process.

2 Methodology

2.1 Material Preparation

The innovative activation method for the present advanced oxidation process consists in the preparation of diatomite-supported iron ions. Four catalysts were prepared at different sodium hydroxide (NaOH) concentrations (1, 2, 5, and 20 mol/L), named, CAT-1 CAT-2, CAT-5, and CAT-20, respectively. The iron ion solution was composed of 366 g/L of ferric sulfate ($Fe_2(SO_4)_3$) and 183 g/L of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). For the catalyst preparation, 100 g of diatomite was slowly added to the aforementioned iron solution (112 mL) under mechanical stirring. Then, a solution of NaOH (220 mL) at its respective concentration was added to this suspension. The mixture was homogenized for 1 h. The prepared material was washed and placed in an oven at 60 °C for 24 h. After drying, the catalyst was ground with a mortar and a pestle, and then sieved and conditioned in glass vials.

2.2 Characterization

Characterization and analyses of raw and modified diatomite samples were carried out by standard methods. For quantifying the iron content in each sample, X-ray fluorescence spectrometry (XRF) was performed by using a Philips spectrometer, model PW 2400 XRF. X-rays were generated by an Rh-anode X-ray tube. For the scanning electron microscopy (SEM) analysis, raw and modified diatomite samples were scanned with an EOL 440I scanning electron microscope, and the samples were coated with a thin layer of gold.

2.3 Remediation of Phenanthrene-Contaminated Soil

The present work was carried out with an uncontaminated soil sample which was collected in the city of Natal (State of Rio Grande do Norte, Brazil) at 30 cm deep. It consists of a sandy soil with low organic matter content (0.13% of total organic carbon).

The experiments were carried out in a batch system by using sodium persulfate (Synth, 99%) for treating the contaminated soil with 200 mg of phenanthrene (98% purity, Fluka Analytical) per kg of soil, whose contamination was carried out in laboratory.

All experiments were conducted in batch reactors (125 mL) at 25 °C. Ten grams of contaminated sandy soil and 20 mL of an oxidant solution were added into each glass flask (reactor). Three control experiments were performed: one without any oxidant or diatomite (control); a second one with soil, water, and 1.0 g of diatomite (control-CAT); and a third one with soil and sodium persulfate (45 g/L) without diatomite (control-PS). In addition, control tests (without oxidant) were performed for all reactions under the same experimental conditions. To ensure good homogenization, the batch reactors were capped and manually shaken twice a day, as recommended by PSOD-1 (2006). All experiments were conducted in duplicate, and the results showed that there were less than 5% of experimental errors.

Experimental tests were conducted with 45 g/L of sodium persulfate and 1 g of catalyst (CAT-1 CAT-2, CAT-5, and CAT-20) for 168 h of reaction time in order to find the optimal condition in terms of oxidation efficiency. After identifying the most desirable synthesized catalyst, a factorial experimental design 2^2 was carried out at 24, 48, 72, 120, and 168 h of experiment. The investigated experimental variables were oxidant concentration and amount of catalyst, whose experimental conditions are shown in Table 1. The concentrations listed in Table 1 were chosen according to an earlier work, whose results had indicated that sodium persulfate concentrations should be higher than 25 g/L (Silva et al. 2015). For the statistical data analysis, the Statistica v. 13 software package (StatSoft, Tulsa, OK, USA) was used for conducting the experimental design.

2.4 Extraction and Analysis

Aliquots of 2.5 g of solids were taken from each reactor in order to quantify residual contamination. After sample collection at pre-determined times (each reactor is represented by a dot in the degradation profiles), the remaining soil sample in the reactors was discarded. Each aliquot was added to a 40-mL vial containing 10 ml of acetonitrile. Each vial containing the sample and solvent was submitted to ultrasound for 30 min, according to 3550 USEPA Method. After this stage, the extract was filtered with a syringe filter. The filtered material was then placed in a 1.5-mL vial for a subsequent analysis with a High Phase Liquid Chromatograph (HPLC) equipped with UV-Visible detector (HPLC-UV) (Shimadzu) under the following conditions: λ = 254 nm, flow rate = 1 mL/min, and acetonitrile/water at a ratio 70:30 (*v*/*v*) as mobile phase.

Table 1 Factorial experimental design 2^2

Trials	Normalized values		Absolute values	
	Catalyst	Persulfate	Catalyst (g)	Persulfate (g/L)
1	−1	1	0.5	45
2	1	1	1	45
3	−1	−1	0.5	25
4	1	−1	1	25
5	0	0	0.75	35
6	0	0	0.75	35
7	0	0	0.75	35

2.5 Mathematical Modeling

The present system is composed of two solid phases and an aqueous phase. Instantaneous equilibrium was considered for phenanthrene concentrations in soil and solution (partition). The following reaction mechanism is valid for pH values ranging between 3 and 7 through Fenton-like steps (Kwan and Voelker 2003) and persulfate decomposition steps (Yang and Yeh 2011; Samarghandi et al. 2017) (Eqs. 1–4).

$$S_2O_8^{2-}+2H_2O\rightarrow 2HSO_4^{-}+H_2O_2 \tag{1}$$

$$HSO_4^{-}\rightarrow H^{+}+SO_4^{-2} \tag{2}$$

$$\equiv Fe^{3+}+H_2O_2\rightarrow \equiv Fe(HO_2)^{2+}+H^{+} \tag{3}$$

$$\equiv Fe(HO_2)^{2+}\rightarrow \equiv Fe^{2+}+HO_2 \tag{4}$$

From Eqs. 1 to 4, the following overall reaction is obtained (Eq. 5):

$$\equiv Fe^{3+}+S_2O_8^{2-}+2H_2O\rightarrow 3H^{+}+2SO_4^{2-} + \equiv Fe^{2+}+HO_2 \tag{5}$$

Usman et al. (2012) described the radical generation from persulfate through the following step (Eq. 6):

$$\equiv Fe^{2+}+S_2O_8^{2-}\rightarrow SO_4^{2-} + \equiv Fe^{3+}+SO_4^{-\cdot} \tag{6}$$

Phenanthrene degradation reaction was taken into account, as shown in Eq. 7:

$$C_{14}H_{10}+66SO_4^{-\cdot}+28H_2O\rightarrow 66HSO_4^{-}+14CO_2 \tag{7}$$

where $\equiv Fe^{3+}$ and $\equiv Fe^{2+}$ are iron ions supported on diatomite. The following assumptions were considered in the model:

- Resistance to mass transfer is negligible
- Phenanthrene concentrations in the soil and solution are determined through a partition coefficient.
- Kinetics is of first order for each species involved in the reactions
- There is excessive water which has no effect on reaction rates.

Since resistance to mass transfer was considered negligible, the aqueous phase and catalytic sites ($\equiv Fe^{3+}$ and $\equiv Fe^{2+}$) were considered to be homogeneously distributed along the solution/diatomite system. In order to reduce the number of parameters of the model, the overall reaction (Eq. 5) was considered together with Eq. 6 and Eq. 7 (rate coefficients: k_1, k_2, and k_3, respectively). Molar balances can be described as follows (Eqs. 8–12):

$$\frac{d\left[Fe^{3+}\right]}{dt}=-k_1\left[Fe^{3+}\right]\left[S_2O_8^{2-}\right]+k_2\left[Fe^{2+}\right]\left[S_2O_8^{2-}\right] \tag{8}$$

$$\frac{d\left[S_2O_8^{2-}\right]}{dt}=-k_1\left[Fe^{3+}\right]\left[S_2O_8^{2-}\right]-k_2\left[Fe^{2+}\right]\left[S_2O_8^{2-}\right] \tag{9}$$

$$\frac{d\left[Fe^{2+}\right]}{dt}=k_1\left[Fe^{3+}\right]\left[S_2O_8^{2-}\right]-k_2\left[Fe^{2+}\right]\left[S_2O_8^{2-}\right] \tag{10}$$

$$\frac{d[C_{14}H_{10}]_s}{dt}=-\left[\frac{1}{\left(\frac{m}{V}+K_{PP}\right)}\right]k_3[C_{14}H_{10}]\left[SO_4^{-\cdot}\right] \tag{11}$$

$$\frac{d\left[SO_4^{-\cdot}\right]}{dt}=k_2\left[Fe^{2+}\right]\left[S_2O_8^{2-}\right]-66k_3[C_{14}H_{10}]\left[SO_4^{-\cdot}\right] \tag{12}$$

where k_1, k_2, and k_3 are the rate constants of reactions 5, 6, and 7, respectively; m is the catalyst mass (g), V is the solution volume (L), and K_{PP} is the partition coefficient which is defined as follows (Eq. 13):

$$K_{PP}=\frac{[C_{14}H_{10}]}{[C_{14}H_{10}]_s} \tag{13}$$

where $[C_{14}H_{10}]$ and $[C_{14}H_{10}]_s$ are phenanthrene concentrations in the solution and soil, respectively. The set of differential Eqs. 8–12 was numerically solved through MATLAB® with the ODE45 algorithm. The model has been validated through the experimental data shown in Table 2.

3 Results and Discussion

3.1 Characterization

Results of iron content obtained by X-ray fluorescence (expressed in wt.%) were raw diatomite (4%), CAT-1 (21%), CAT-2 (22%), CAT-5 (17%), and CAT-20 (25%), thus indicating that a decrease in NaOH concentration (CAT-20 to CAT-1) caused no significant decrease in the amount of iron in the material composition. Thus, it can be considered economically and environmentally feasible, since a lower concentration of reagent (NaOH) can be used without compromising the synthesized material quality. X-ray fluorescence analysis showed that diatomite is mainly composed of SiO_2, besides iron and other elements in lesser amounts in the sample, such as Ca, Ti, O, Al, Na, Mg, Ba, and S.

SEM micrographs of raw and modified diatomite samples are shown in Fig. 1. Pores and cylindrical shapes can be observed on their surface. After the treatment with an NaOH and Fe^{2+}/Fe^{3+} solution, the shape and pores of CAT-1, CAT-2, and CAT-5 samples were preserved, but some changes were detected on the diatomite structure for CAT-20 (see Fig. 1e). SEM images of raw diatomite and CAT-20 showed a considerable difference in their textures. This might have occurred due to a high NaOH concentration used for preparing CAT-20, which leads to a change in SiO_2 content on account of its partial dissolution in NaOH. Similar diatomite structures were observed in literature (Xiong and Peng 2008). The modified diatomite surface was covered with layers of Fe hydroxides. It is understood that Fe layers are accountable for persulfate activation (Silva-Rackov et al. 2016). Moreover, the porous structure of diatomite provides access to catalytic sites for phenanthrene degradation. Other characterization analysis for raw diatomite and CAT-5 can be found elsewhere (Silva-Rackov et al. 2016; Silva et al. 2015).

Table 2 Experiments used for model validation

Run	Initial $Na_2S_2O_8$ (g/L)	Initial mass of CAT-1 (g)
1	45	1.0
2	45	0.5
3	25	1.0
4	25	0.5

3.2 Soil Treatment with Different Catalysts

In a previous study, the effectiveness of conventional persulfate activation by a solution of Fe^{2+} and CAT-5 in a solid matrix has been evaluated, where the modified diatomite CAT-5 showed higher efficiency at PAHs degradation (Silva et al. 2015). The present work shows a comparison of the efficiencies of catalysts prepared at different NaOH concentrations for treatment of soil from Natal contaminated with phenanthrene. In order to investigate optimal conditions for the phenanthrene-contaminated soil treatment, tests were conducted with 45 g/L of sodium persulfate and 1 g of catalyst (CAT-1, CAT-2, CAT -5 and CAT-20).

Figure 2 shows that the phenanthrene was degraded in all reactions with activated persulfate by different types of catalyst. CAT-1, CAT-2, CAT-5, and CAT-20 samples provided phenanthrene degradations of 98, 97, 93, and 94%, respectively, at 168 h of treatment. Different synthesized catalysts provided similar efficiencies, which can be explained by similar iron contents in the catalysts, although they were prepared at different NaOH concentrations. The system's pH varied according to the kind of catalyst being used in the reaction. CAT-1, CAT-2, CAT-5, and CAT-20 showed pH values of 4, 4, 8, and 9, respectively (no pH adjustment required). This effect was caused by the differences in NaOH concentrations for each catalyst. By comparing the control test result (test with no addition of catalyst or oxidant) to the control-CAT (test with catalyst, but without oxidant), it was observed that the catalyst showed only 15% of contaminant adsorption capacity after 168 h of treatment. Control-PS (test with only soil and oxidant) results showed negligible contaminant consumption, which indicate that sodium persulfate must be activated by the catalyst in order to obtain considerable degradation, as observed for CAT-1 to CAT-20 samples.

After analyzing the results presented in Fig. 2, it was concluded that CAT-1 showed better results despite being prepared at a lower NaOH concentration. An excessive amount of NaOH and other undesirable products, such as sodium sulfate (Na_2SO_4) (Eqs. 14 and 15), can hinder contaminant degradation efficiency. Based on this finding, CAT-1 was chosen for conducting a detailed study:

$$FeSO_4 + 2NaOH \rightarrow \mathrm{Fe(OH)_2} + \mathrm{Na_2SO_4} \quad (14)$$

$$\mathrm{Fe_2(SO_4)_3} + 6NaOH \rightarrow 2\mathrm{Fe(OH)_3} + 3\mathrm{Na_2SO_4} \quad (15)$$

Figure 3 shows phenanthrene degradation along the reaction. According to these results, satisfactory degradation values were obtained with 45 g/L of sodium persulfate and 1 g of CAT-1 at 120 and 168 h of reaction time, thus degrading about 90 and 98% of phenanthrene, respectively.

3.3 Model Predictions

The kinetic model was validated by using degradation data obtained from CAT-1 sample (Table 2). Results of degradation as a function of time are shown in Fig. 4. Satisfactory trends were obtained with the present mathematical model in comparison with the experimental data. An average correlation of $R^2 = 0.92$ was reached, thereby indicating reasonable prediction through using three adjustable parameters (k_1, k_2, and k_3), whose values are $k_1 = 500$, $k_2 = 800$, and $k_3 = 110$ L mol^{-1} h^{-1}, corresponding to reactions 5, 6, and 7, respectively. k_2 has the highest value, which corroborates the catalytic nature of the reaction with Fe^{2+}. The partition coefficient used in the simulation was $K_{PP} = 1.62$ g/L (Silva et al. 2014). Despite being validated with relatively few experimental results, the curve-fitting study presented coherent values among the rate constants of the proposed reaction mechanism. Another mathematical equation involving fewer parameters may also be suitable to predict the cases

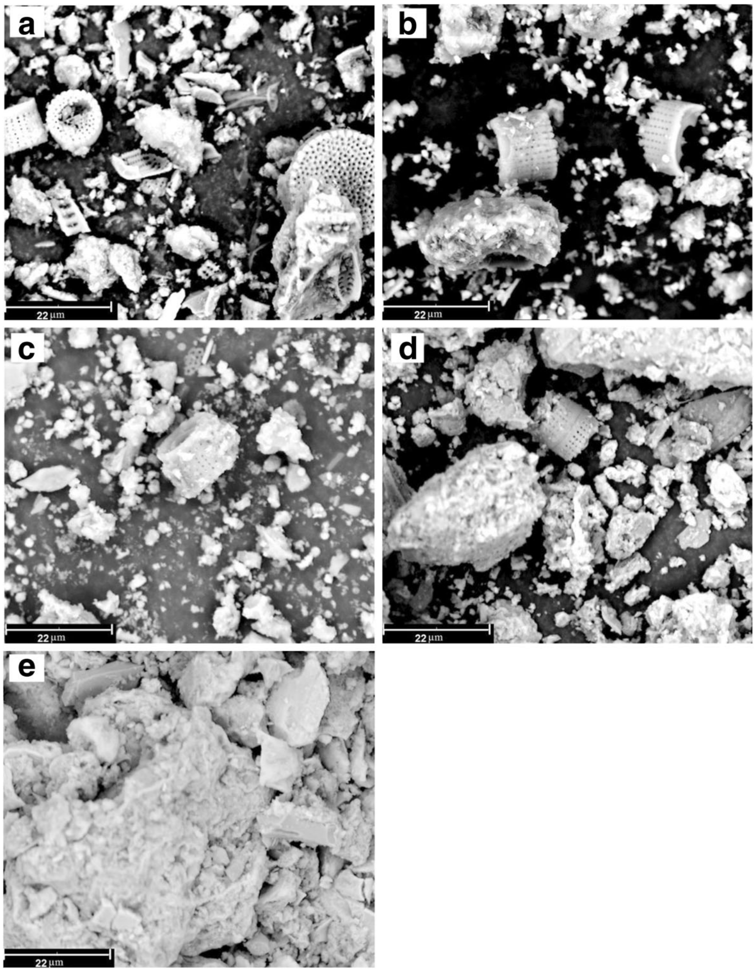


Fig. 1 Scanning electron micrograph for raw (**a**) and modified diatomites (CAT-1 (**b**), CAT-2 (**c**), CAT-5 (**d**) and CAT-20 (**e**)). Magnification = ×3900

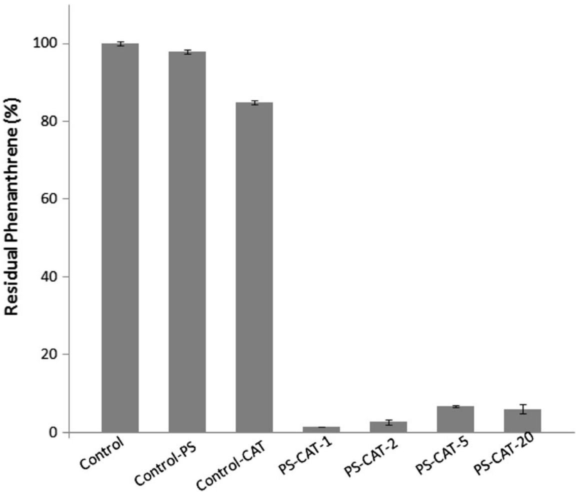


Fig. 2 Residual phenanthrene after remediation with sodium persulfate and different modified diatomites. Control at pH 6; control-PS at pH 4; control-CAT at pH 7; PS-CAT-1 at pH 4; PS-CAT-2 at pH 4; PS-CAT-5 at pH 8; PS-CAT-20 at pH 9. Controls are as follows: control—contaminated soil and water; control CAT—contaminated soil, raw diatomite, and water. [phenanthrene] = 200 mg/kg soil; [$Na_2S_2O_8$] = 45 g/L; amount of catalyst = 1 g; contaminated soil = 10 g; solution volume = 20 mL; temperature = 25 °C; time = 168 h

presented herein. On the other hand, this kind of curve-fitting study would be empirical, while the present approach is an attempt to explain this complex system by representing a model that can be improved and validated with novel experimental data in future studies. There could be greater complexity of this model by including mass transfer resistances and the respective coefficients, which would provide better predictions. Nonetheless, a larger amount of experimental data would be necessary in order to justify the increase in the number of adjustable parameters. Thus, the present simplified kinetic model is robust and provides an initial estimate for rate coefficients (k_1, k_2, and k_3), which can be tested in further studies on this system.

3.4 Experimental Design

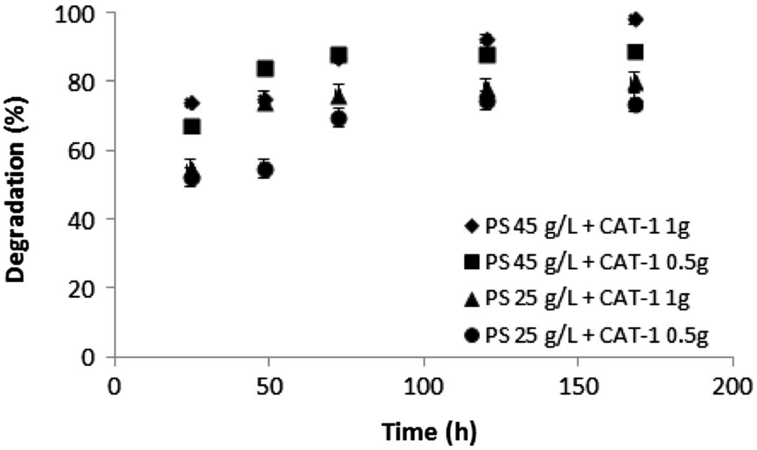
A factorial experimental design was carried out using the following as variables: oxidant concentration and amount of CAT-1, whose results are shown in Table 3 and Fig. 5. According to them, it is observed that the test with 45 g/L of sodium persulfate and 1 g of CAT-1 presented 98% of phenanthrene degradation. Under these conditions, the molar ratio of sodium persulfate to iron content was about 1:1. In this test, residual phenanthrene was approximately 6 mg per kg of soil, which is below the agricultural intervention and industrial waste limits allowed by Brazilian Resolution CONAMA 420/2009 and Dutch Regulation.

Response surface showed in Fig. 5 was obtained from Eq. 16. The normalized variables are represented by x (catalyst amount), y (oxidant concentration), and Z (phenanthrene degradation). Equation 16, obtained through Statistica v.13 software, shows the proposed statistical approach for phenanthrene degradation.

$$Z = +\ 85.2 + 4.75x + 7.25y + 1.75xy \tag{16}$$

Studies suggest that, for an acceptable fit, the correlation coefficient (R^2) should be at least 0.8

Fig. 3 Phenanthrene degradation (200 mg/kg) promoted by sodium persulfate and modified diatomite in diferent experimental conditions. pH = 4; contaminated soil = 10 g; solution volume = 20 mL; temperature = 25 °C



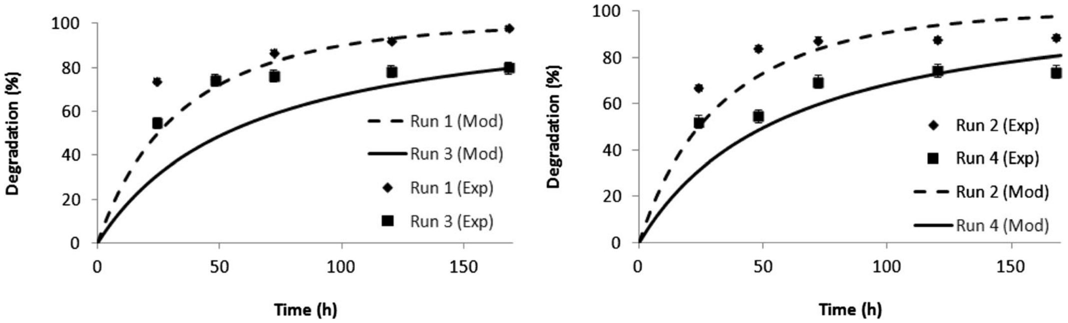


Fig. 4 Results obtained with the kinetic model for CAT-1. Experimental conditions: pH = 4; [phenanthrene] = 200 mg/kg soil; contaminated soil = 10 g; solution volume = 20 mL; temperature = 25 °C. ($k_1 = 500$, $k_2 = 800$, $k_3 = 110$ L mol^{-1} h^{-1} and $K_{PP} = 1.62$ g/L)

(Fu et al. 2007; Joglekar and May 1987; Silva et al. 2015). The R^2 value for response variables shown in Table 3 was 0.96, thus indicating that Eq. 16 satisfactorily represents the process.

After calculating the effect of experimental variables (Eqs. 17 and 18), it can be verified that the effect of both the catalyst and the oxidant showed positive values. A value of 8 was obtained for catalyst effect, which indicates that an increase in the amount of catalyst improves the efficiency by 8% on average, when CAT-1 amount varies from lower level (0.5 g) to higher level (1.0). The effect of varying oxidant concentration revealed a positive value (+16), which shows that degradation efficiency increases by 16% on average when sodium persulfate concentration varies from lower level (25 g/L) to higher level (45 g/L). The interaction effect between CAT-1 and oxidant concentration revealed a value of 2. Thereby, oxidant concentration is the most significant variable in the system.

Table 3 Factorial experimental design 2^2 results

Trials	Catalyst (g) (x)	Persulfate (g/L) (y)	Observed degradation (%) (Z)	Calculated degradation (%)
1	0.5	45	88	82
2	1	45	98	99
3	0.5	25	74	76
4	1	25	80	88
5	0.75	35	87	86
6	0.75	35	86	86
7	0.75	35	87	86

$$Oxidant = \frac{1}{2}(z_1 - z_2) + \frac{1}{2}(z_3 - z_4) \tag{17}$$

$$\text{CAT-1} = \frac{1}{2}(z_2 - z_4) + \frac{1}{2}(z_1 - z_3) \tag{18}$$

A comparison between statistical and kinetic approaches is depicted in Fig. 6. The most

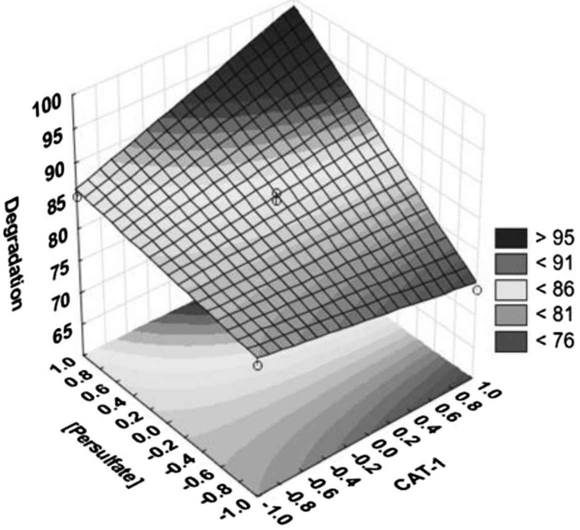


Fig. 5 Response surface of factorial experimental design 2^2 for phenanthrene degradation (200 mg/kg). Sodium persulfate concentration ranging from 25 to 45 g/L and amount of CAT-1 ranging from 0.5 to 1.0 g. Exerimental conditions: pH = 4; contaminated soil = 10 g; solution volume = 20 mL; temperature = 25 °C; time = 168 h

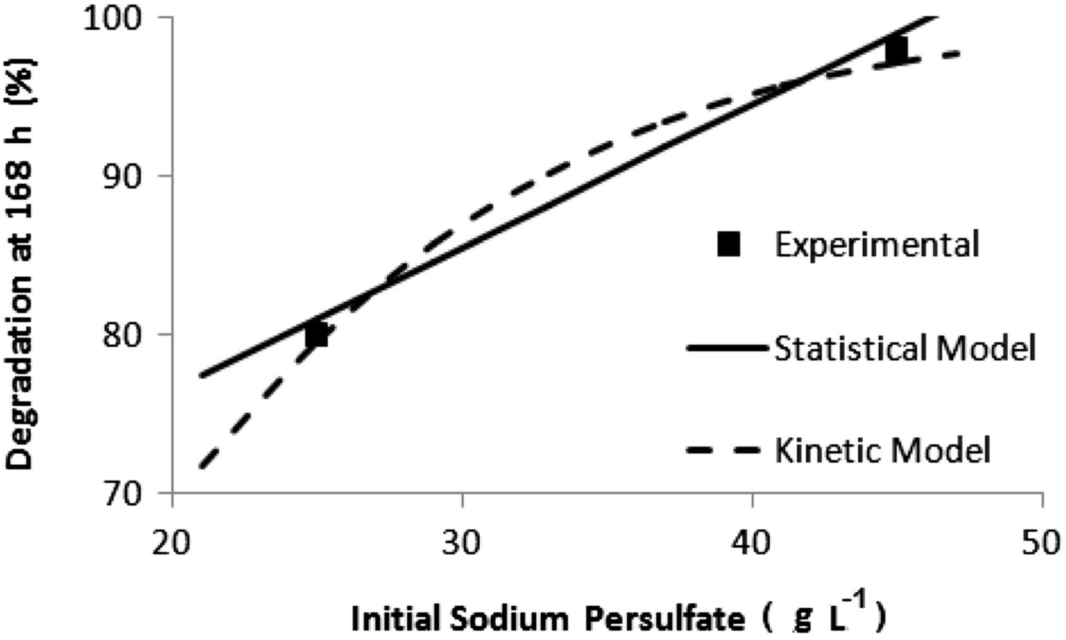


Fig. 6 Comparison of kinetic and statistical approaches. m = 1 g of CAT-1

significant difference observed among the approaches is the obtained trends. Generally speaking, statistical approaches provide satisfactory predictions within the range of initial experimental conditions. On the other hand, kinetic models provide a trend regarding phenomena that occur along the process. In Fig. 6, the kinetic model indicates that there is a very small increase in degradation for sodium persulfate concentrations of over 45 g/L.

4 Conclusions

A set of different diatomite-supported catalysts have been prepared and tested on phenanthrene-contaminated soil remediation in the presence of sodium persulfate. The results showed that CAT-1 was the most efficient catalyst under all studied conditions. It might be associated with a lower amount of undesirable by-products formed during preparation, which is caused by NaOH addition. Thus, a lower concentration of sodium hydroxide produced a more reactive material (CAT-1), which may result in lower production cost without compromising efficiency in comparison with other catalysts studied herein. The experimental design has revealed that maximum phenanthrene degradation (98%) was obtained with 45 g/L of sodium persulfate and 1.0 g of CAT-1 and a molar ratio of persulfate to iron content of 1:1. Statistical and kinetic approaches provided satisfactory predictions for the presently conducted experiments.

Acknowledgements Acknowledgements to the National Institute of Science and Technology for Environmental Studies (INCT-EMA), Brazilian Research Council (CNPq), State of São Paulo Research Foundation (FAPESP—Project No. 2014/22080-9), Coordination for the Improvement of Higher Education Personnel (CAPES—Project PROCAD-CAPES No. 88881.068433/2014-01) for the financial support.

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