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To cite this article: Milady Renata Apolinário da Silva, Eduardo de Oliveira Rodrigues, Melina Espanhol-Soares, Flavio Soares Silva, Márcia Matiko Kondo & Rossano Gimenes (2018): Application of Fenton process to remove organic matter and PCBs from waste (fuller's earth) contaminated with insulating oil, Environmental Technology, DOI: [10.1080/09593330.2017.1420699](https://doi.org/10.1080/09593330.2017.1420699)

To link to this article: <https://doi.org/10.1080/09593330.2017.1420699>



Accepted author version posted online: 29 Dec 2017.
Published online: 09 Jan 2018.



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Application of Fenton process to remove organic matter and PCBs from waste (fuller's earth) contaminated with insulating oil

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ABSTRACT

Polychlorinated biphenyls (PCBs) are carcinogenic to humans and can be found in fuller's earth used for the treatment of used transformer oil. This work describes an optimization of the Fenton process for the removal of contaminants from fuller's earth. The effects of pH (2.5 and 4.0), [H₂O₂] (1.47 and 2.07 mol L⁻¹), and [Fe²⁺] (1.7 and 40 mmol L⁻¹) were studied. The Fenton process efficiency was monitored using the decreases in the chemical oxygen demand (COD) and the concentrations of oil and grease, total carbon (TC), PCBs, and H₂O₂. The fuller's earth contaminated with insulating oil presented 35% (w/w) of TC, 34% (w/w) of oil and grease, 297.0 g L⁻¹ COD, and 64 mg of PCBs per kg. The material could therefore be considered a dangerous waste. After Fenton treatment, using a slurry mode, there was a removal of 55% of COD, 20% of oil and grease, and 20% of TC, achieved at pH 2.5 using 2.07 mol L⁻¹ of H₂O₂ and 40.0 mmol L⁻¹ of Fe²⁺. No PCBs were detected in the samples after the Fenton treatment, even using smaller amounts of Fenton reagents (1.47 mol L⁻¹ of H₂O₂, 1.7 mmol L⁻¹ of Fe²⁺, pH 2.5). The results indicated that the treated fuller's earth was free from PCB residues and could be disposed of in a simple landfill, in accordance with Brazilian PCB regulations.

ARTICLE HISTORY

Received 1 September 2017
Accepted 17 December 2017

KEYWORDS

Fuller's earth; Fenton reaction; insulating mineral oil; PCBs; factorial experimental design

1. Introduction

Insulation oils are widely used as dielectric fluids in transformers and electrical capacitors. The oils currently used can contain polychlorinated biphenyls (PCBs), which are persistent contaminants in the environment and present potential risks to human health, although in the U.S.A., their use has been banned since 1978 [1].

Synthetic ester fluids have been used as PCB substitutes in compact railroad traction transformers [2]. However, PCBs were not completely eliminated from the transformers and the existing residues must be removed by 2025, with their complete destruction by 2028, according to the Stockholm Convention [3]. Brazilian regulations for the electricity sector consider insulating mineral oil (IMO) to be free of PCBs when it contains less than 3.0 µg mL⁻¹ of PCBs [4].

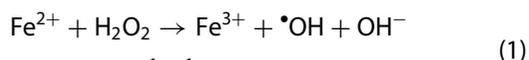
Fuller's earth is an inorganic adsorbent used for the remediation of insulation oil in the electrical industry [5]. It consists of condensed silicate anions (Si₂O₅²⁻) together with magnesium, aluminum, and other metals. In the remediation of insulation oil, fuller's earth shows a high capacity for adsorption of acid molecules generated during degradation of the dielectric

oil. The PCBs present can also be adsorbed by fuller's earth. The resulting material is dangerous to human health and therefore needs special disposal procedures. In general, incineration is the most widely used treatment, but is very expensive and in some cases, if incomplete combustion occurs, can generate toxic byproducts [5]. Nevertheless, in some countries, it is still common to dispose of contaminated fuller's earth in landfills intended for urban solid waste [6].

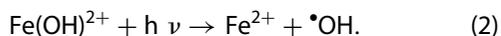
One of the treatments proposed for contaminated fuller's earth is to wash it with water and detergent at 70°C. In this process, a portion of the hydrocarbon is removed, and the washed fuller's earth is submitted to a bioremediation process [6]. Other physico-chemical treatments involve washing with hexane, which can remove around 87% of the dielectric oil, with subsequent biological treatment [7].

Advanced oxidation processes (AOPs) offer a powerful option for the removal of contaminants. Their efficiencies can be monitored by measuring the chemical oxygen demand (COD), biological oxygen demand, or total organic carbon (TOC) content [8–11]. In these processes, the hydroxyl radicals produced can react to destroy

organic compounds. Fenton and photo-Fenton processes use $\text{Fe}^{2+}/\text{Fe}^{3+}$ with H_2O_2 to produce hydroxyl radicals (Equations (1) and (2)) [12].



$$k = 76\text{M}^{-1}\text{s}^{-1},$$



The Fenton and photo-Fenton processes have been shown to be very efficient in removing oil from different matrices [13–18]. The high efficiency of PCB degradation by Fenton reactions has already been reported [19–21]. The photo-Fenton system was found to provide 90% removal of PCBs present in insulation oil [22]. There are several types of treatments proposed for the removal of PCBs from soil [23–25]. Nevertheless, to the best of our knowledge, until now there have been no reports of the use of the Fenton reaction applied to contaminated fuller's earth. In Brazil, large amounts of this material are generated annually, so the need for their treatment constitutes a serious problem. Therefore, considering the efficiency of Fenton processes in treating common contaminants encountered in fuller's earth, this work studied the application of such processes for removal of the organic load and PCBs from contaminated fuller's earth provided by an electricity company in the southern region of Brazil.

2. Materials and methods

2.1. Physico-chemical analysis

The contaminated fuller's earth was donated by an electric power company in southern Brazil and was used as received. The pH value was measured using EPA method 9045D [26]. To quantify the iron, the fuller's earth samples were submitted to acid digestion [27] with sulfuric acid (Synth, Brazil) and hydrochloric acid (Êxodo, Brazil). The final solution was analyzed by atomic absorption spectrometry (Avanta system, GBC) to determine the iron concentration. The oil and grease content was determined using EPA method 9071B [28].

Due to the high concentration of carbon and the viscosity of the sample, it was not possible to determine the TOC content using a TOC analyzer, so the total carbon (TC) concentration was determined using a gravimetric method. In this procedure, 1.00 g of the sample (clean, contaminated, or post-Fenton treatment) was kept in a drying oven at 100°C for 1 h. The sample was cooled in a desiccator until reaching ambient temperature and was then weighed to determine the humidity content. The sample was then placed in a muffle furnace (Model Q318M, Quimis) at 1000°C for 1 h, followed by

weighing. The TC was calculated as the mass difference of the sample before and after the thermal treatment. The COD was determined by EPA method 5220D [29], using a spectrophotometer (SPECORD 600S, Analytik Jena). All the determinations were performed in triplicate.

2.2. Analysis by GC-MS

The GC-MS analyses were carried out using a system (Models 7890A and 5975C, Agilent) equipped with an HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The temperature program was 110°C (held for 1 min), 25°C min⁻¹ to 200°C (held for 1 min), and 2°C min⁻¹ to 260°C. The temperatures of the transfer line, ion source, and quadrupole were 220°C, 230°C, and 150°C, respectively. The mass spectrometer was operated in electron impact mode at 70 eV. Helium (White Martins, Brazil) was used as the carrier gas (0.7 bar, 1 mL min⁻¹). The scanning rate was 0.5 scans s⁻¹, from 50 to 600 (m/z). The samples were diluted in n-hexane (Sigma-Aldrich, pesticide grade) and the injection volume was 1.0 μL (split injection mode, 1:20).

The GC-MS analyses for validation of the methodology were performed in single ion monitoring (SIM) mode, where the PCB ions monitored were: (Group 1) 152, 186, and 222 m/z; (Group 2) 186, 221, and 256 m/z; (Group 3) 220, 256, and 292 m/z; (Group 4) 254, 292, and 326 m/z; (Group 5) 254, 358, and 394 m/z; and (Group 6) 281, 355, and 429 m/z.

2.3. GC-MS method validation

Aroclors 1242, 1254, and 1260 (99.9% purity; Supelco, Bellefonte, PA, U.S.A.) were used as standards for validation of the analytical methodology. The number 12 refers to PCBs, as they have 12 carbon atoms, and the last two digits indicate the amount of chlorine in the mixture. Hence, the mixture denoted Aroclor 1242 contains PCBs (12) with 42% chlorine by mass [2]. A mixture of congeners (reported as the sum of the 1242, 1254, and 1260 Aroclors that are most commonly encountered in mineral oil, here termed PCBs) was used as the analytical standard. Accuracy and precision were evaluated using spiked fuller's earth samples containing three concentrations of Aroclors ranging from 0.12 to 17.20 mg kg⁻¹.

The PCBs were extracted from the fuller's earth by Soxhlet extraction (EPA method 9071B [30]), with clean-up using Florisil (100–200 mesh) and elution with n-hexane:acetone (9:1), according to the procedure previously evaluated by the California Department of Food and Agriculture, followed by GC-MS analysis (ASTM

method D4059 [31]). Control samples (fuller's earth free of PCBs) were also analyzed in order to evaluate the selectivity of the method. The spiked samples were analyzed in triplicate and the fuller's earth samples were analyzed using seven replicates. Recoveries were calculated from the differences between the spiked and unspiked samples. The repeatability of the method was evaluated from the coefficient of variation for replicates. The method was validated according to the guidelines established by IUPAC [32].

The limits of detection and quantification were 0.19 and 0.64 $\mu\text{g mL}^{-1}$, respectively, calculated according to the IUPAC recommendations [33,34].

2.4. Degradation experiments

For the Fenton degradation process, factorial experiment design was employed, with 2 levels and 3 variables. The H_2O_2 (Synth) and Fe^{2+} (as FeSO_4 , Isofar) concentrations used were 1.47 and 2.07 mol L^{-1} , and 1.7 and 40.0 mmol L^{-1} , respectively. The choice of these values was based on the best results reported previously for PCB removal from soil [21,35]. The pH was adjusted to 2.5 using sulfuric acid (Synth, Brazil) at the beginning of the experiment, since this is the best pH for the Fenton reaction in soil [36]. Experiments were also performed without pH adjustment, where the initial pH value was 4.0.

The Fenton process was performed in slurry mode, mixing the Fenton reagents with 5 g of the contaminated fuller's earth. The slurry was maintained under constant mixing using an orbital shaker (Model 7570, Thoth). The experiments were carried out for 24 h at room temperature (maximum of 28°C). Chemical analyses of the solid material were performed in order to determine the organic load remaining in the fuller's earth. Control experiments were also performed to evaluate the influence of each parameter of the Fenton reagents. The efficiency of the Fenton process was analyzed by monitoring COD [29] and the concentrations of oil and grease [28], TC, PCBs, and H_2O_2 [37]. All the experiments were carried out in triplicate and the results shown in this paper are the averages of the data.

2.5. Full factorial design

A full factorial design (24 experiments, $n = 3$) was applied to evaluate the effects on PCBs degradation of variations in the iron, hydrogen ion (pH), and hydrogen peroxide concentrations. The levels of each factor (shown in Table 1) were selected based on the values most frequently reported in the literature [35]. The experiments were randomized and the applied design fitted the following first-order polynomial equation [38]:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i, \quad (3)$$

where Y is the value of the PCBs degradation (response), β_0 is the constant coefficient, n is the number of variables, β_i is the coefficient of the linear parameters, and X_i is the coefficient of the interaction of the parameters [38].

3. Results and discussion

3.1. Chemical characterization of the contaminated fuller's earth

Table 1 shows the characterization results for the fuller's earth before the Fenton treatment. The pH value is very important in the Fenton reaction, because it determines the iron species that will be present in the solution [39]. Nogueira and Guimarães [40] reported that the best pH for the Fenton reaction is between 2.5 and 2.8. The pH of the fuller's earth without oil was 6.83 (± 0.02). This was in agreement with the manufacturer's report, which stated that the pH value for this material was between 5.0 and 7.5, and was very close to the pH of 6.12 reported by Agudelo and Gallo [7] for clean fuller's earth.

For the fuller's earth contaminated with IMO, no significant change was observed in the pH, with a value of 6.34 (± 0.03). Agudelo and Gallo [7] also reported a small shift of the pH value to 5.61 for contaminated fuller's earth, compared to the clean material.

However, when the Fenton reagents were added to the contaminated fuller's earth, the pH decreased to 4.06 (± 0.03). This could be attributed to the addition of ferrous sulfate as the iron source, which exhibits acid characteristics. Although the optimum pH is around 2.8 [41], good efficiency of the Fenton reaction has been reported at different pH values [42]. The success of the

Table 1. Characterization of the fuller's earth contaminated with insulating oil.

Parameter	Value
pH	6.83 (± 0.02)
Total iron concentration	93.35 \pm 3.30 mg kg^{-1}
Total oil and grease	34 \pm 1% (w/w)
Total carbon	35 \pm 1% (w/w)
Chemical oxygen demand	297.0 \pm 8.3 g of oxygen per kg of contaminated fuller's earth
PCB determination	64 mg of PCB per kg of contaminated fuller's earth

Fenton reaction at high pH can be explained by the formation of compounds by reaction between the iron and the target compound, or the presence of degradation intermediates, which are active in the Fenton process [41,43]. Therefore, in this work, experiments were also performed without pH adjustment.

The fuller's earth manufacturer's report indicated that the material contained approximately 5.34% (w/w) of iron oxide (~37.4 g of iron per kg of sample). The presence of iron in this matrix could contribute to the Fenton reaction. Therefore, it was necessary to investigate the amount of iron that was available to participate in the reaction. For this test, clean fuller's earth was immersed in an acid solution [44] for 24 h (the same time period as used for the Fenton process), and the desorbed iron in solution was determined by Atomic Absorption Spectroscopy (AAS). The total iron concentration observed was $93.35 \pm 3.30 \text{ mg kg}^{-1}$ of fuller's earth. Despite the fact that the fuller's earth contained a considerable quantity of iron oxides, a very small amount of iron was released to the acid solution and could participate in the Fenton reaction. The results, therefore, showed that it was necessary to add more iron in order to optimize the Fenton process. It was not possible to determine the iron concentration in the contaminated fuller's earth, because the presence of the mineral oil rendered the material unsuitable for the acidic extraction process in aqueous solution.

The contaminated fuller's earth contained $34 \pm 1\%$ (w/w) of total oil and grease per kg (Table 1), reflecting the good adsorbent characteristics of the material. No significant amount of oil and grease was observed in the clean fuller's earth sample.

The contaminated fuller's earth presented $350.0 \pm 10.0 \text{ g}$ of carbon per kg (Table 1), in agreement with the oil and grease determination. In the absence of contamination, the fuller's earth contained $15.0 \pm 2.0 \text{ g}$ of carbon per kg, probably due to the presence of residues of organic matter or adsorbed CO_2 .

The COD value (Table 1) was $297.0 \pm 8.3 \text{ g}$ of oxygen per kg of contaminated fuller's earth. Insignificant COD ($0.3 \pm 0.1 \text{ g kg}^{-1}$) was found for the fuller's earth without contamination.

The contaminated fuller's earth contained 64 mg of PCBs per kg (Table 1). This was higher than the maximum concentration permitted according to Brazilian regulations ($<3.0 \mu\text{g kg}^{-1}$) [45], so this material could not be disposed of in an ordinary landfill.

3.2. Control experiments

Control Fenton reaction experiments were performed to evaluate the influence of each parameter. The COD was chosen to evaluate the efficiency of the reaction, since

this parameter is regulated by Brazilian law. All the experiments were studied at pH 2.5 and 4.0, 1.47 and 2.07 mol L^{-1} of H_2O_2 , and 1.7 and 40 mmol L^{-1} of Fe^{2+} , using a fractional factorial design chemometric approach, implemented using Statistica v. 7.0 software.

The results showed that there was up to 5% COD removal when H_2O_2 alone was employed. This removal could be explained by the fact that H_2O_2 itself is a strong oxidant [35] and/or that the iron present in the fuller's earth could have reacted with the added H_2O_2 , improving the degradation of the organic matter [46]. Nevertheless, this low rate of COD removal also indicated that the iron present in the fuller's earth or in the adsorbed oil did not participate effectively in the Fenton reactions.

No removal of COD was observed when only iron was added to the contaminated fuller's earth.

3.3. COD removal

The removal of COD by the Fenton process after 24 h of reaction was in the range of 43–55% (Table 2).

Analysis of the influence of pH (experiments A and G), using the same $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio, showed that a similar COD removal was obtained in the pH range from 2.5 to 4.0. In other words, the system was not dependent on the pH value and no initial pH adjustment was necessary. Nogueira et al. [39] also reported that Fenton processes can occur above the optimum pH of 2.8. At the end of the treatments, the observed pH values were 3.13 ± 0.03 and 4.30 ± 0.10 for initial pH values of 2.5 and 4.0, respectively. These increases were probably due to the OH^- generated in the Fenton reaction (Equation (1)).

Change in the iron concentration from 1.7 to 40.0 mmol L^{-1} , at pH 4.0 and 2.07 mol L^{-1} of H_2O_2 (experiments A and C), resulted in a similar percentage COD removal, indicating that at pH 4.0, the iron concentration did not affect the Fenton process. A small improvement was observed using the higher concentrations of Fe^{2+} and H_2O_2 and lower pH (experiment H), which was the optimum pH for the Fenton reaction [12]. In this

Table 2. COD and oil and grease removal (%) from the fuller's earth contaminated with insulating mineral oil, using different Fenton reagent concentrations, after 24 h of reaction.

Experiment	$[\text{H}_2\text{O}_2]$ (mol L^{-1})	$[\text{Fe}^{2+}]$ (mmol L^{-1})	pH value	COD removal (%)	Removal of oil and grease (%)
A	2.07	1.7	4.0	45	18
B	1.47	40.0	4.0	45	10
C	2.07	40.0	4.0	43	11
D	1.47	1.7	2.5	45	15
E	1.47	1.7	4.0	48	19
F	1.47	40.0	2.5	46	18
G	2.07	1.7	2.5	45	14
H	2.07	40	2.5	55	20

Note: Initial COD: 297.0 g of O_2 per kg. Initial oil and grease: 340.0 g kg^{-1} .

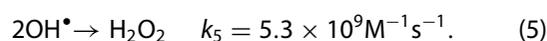
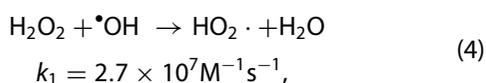
Table 3. Concentration of H₂O₂ after 24 h of Fenton reaction applied to the contaminated fuller's earth.

Experiment	[H ₂ O ₂] (mol L ⁻¹)	[Fe ²⁺] (mmol L ⁻¹)	pH value	Final [H ₂ O ₂] (mol L ⁻¹)	H ₂ O ₂ removal (%)
A	2.07	1.7	4.0	0.62	70
B	1.47	40	4.0	0.13	91
C	2.07	40	4.0	0.10	95
D	1.47	1.7	2.5	0.61	58
E	1.47	1.7	4.0	0.59	60
F	1.47	40	2.5	0.055	97
G	2.07	1.7	2.5	0.51	75
H	2.07	40	2.5	0.055	98

Note: Initial COD: 297.0 g kg⁻¹.

experiment, the H₂O₂ removal was the highest among all the conditions tested (Table 3). This was a good result, because in excess, H₂O₂ could act as a scavenger of [•]OH, hence decreasing the efficiency of the Fenton process.

It has been reported previously that the use of a high concentration of H₂O₂ is required to oxidize oil or other contaminants adsorbed on soil [47]. However, in some cases, an excess of H₂O₂ can act to scavenge [•]OH radicals, generating a less oxidizing radical (Equation 4), and [•]OH recombination can also occur (Equation 5) [39,46]. Therefore, it is important to establish the best ratio between the concentrations of iron and H₂O₂. Dincer et al. [48] also reported a decrease in the efficiency of COD removal during treatment of the wastewater from an oil recovery industry, when the H₂O₂ concentration in the Fenton system was increased.



A response surface plot (Figure 1) was used to show the interaction of the variables and to determine the optimum levels that provided the maximum response. Azuma and Mino [22] studied the removal of PCBs from IMO employing a photo-Fenton process and found no clear relationship between the Fenton reagent and PCBs removal. In this work, the parabolic nature of the contours (Figure 1) indicated that the interactions among the variables were significant. Higher concentrations of both Fe²⁺ and H₂O₂ led to increased COD removal efficiency. However, increasing the pH resulted in lower removal efficiency (Table 2). In summary, the optimized values for the removal of COD by the proposed Fenton process were 2.07 mol L⁻¹ of H₂O₂, 40 mmol L⁻¹ of Fe²⁺, and pH 2.5.

3.4. Oil and grease removal

The oil and grease content of the contaminated fuller's earth was 34% (w/w). After treatment using the Fenton process, the average removal was 16% (53 g of oil per kg of contaminated fuller's earth), with the maximum removal of 20% (Table 2) using the optimized Fenton reagent values. Millilioli et al. [17] also observed the removal of oil and grease when the Fenton process was used to treat a petroleum spill on beach sand.

When smaller amounts of the Fenton reagents were used, with 1.47 mol L⁻¹ of H₂O₂ and 1.7 mmol L⁻¹ of

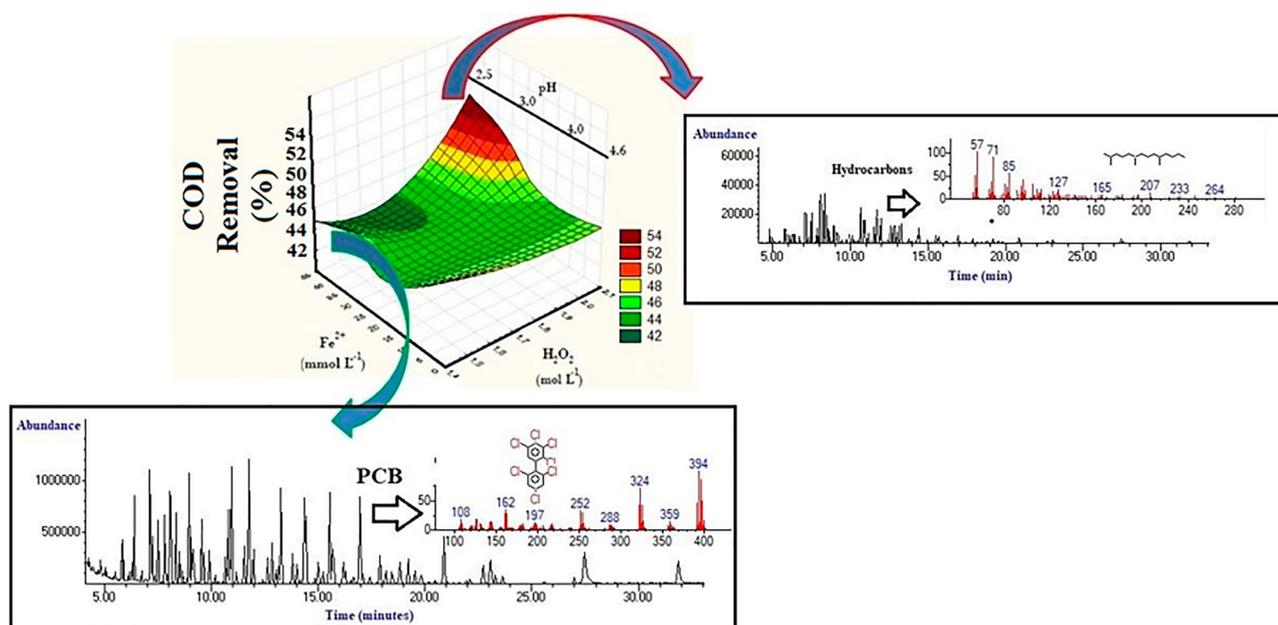


Figure 1. Response surface plot and chromatograms for the interactions among the Fe²⁺ and H₂O₂ concentrations and pH values for the Fenton process applied in treatment of the oil-contaminated fuller's earth (considering COD removal).

Fe^{2+} , at pH 4.0 (experiment E, Table 2), approximately 19% oil and grease removal (65.6 g of oil per kg of contaminated earth) was observed after 24 h of reaction. Under the same conditions, 48% COD removal was obtained (Table 2). This result was interesting, since the use of smaller amounts of reagents can decrease the cost of treatment. It also indicated that the Fenton process provided an efficient removal of oil and grease from the fuller's earth using a low concentration of reagents.

The % removal of oil and grease (20%) was similar to the % removal of TC, indicating that the Fenton process mainly promoted the removal of oil and grease, leading to complete mineralization.

3.5. PCBs removal

The results (Figure 1) showed that the optimum Fenton reagent concentrations and pH for treatment of the samples were 2.07 mol L^{-1} of H_2O_2 , 40.0 mmol L^{-1} of Fe^{2+} , and pH 2.5. Nevertheless, use of 1.47 mol L^{-1} of H_2O_2 , 1.7 mmol L^{-1} of Fe^{2+} , and pH 4.0 also resulted in high COD removal efficiency of 48%. Therefore, these two process conditions were investigated in the study of PCB removal by the Fenton process. The contaminated fuller's earth contained 64 mg of PCB per kg. After treatment using the Fenton process under the two different conditions, no PCBs were detected in the extracts.

It has been reported previously that the efficiency of PCBs removal by the Fenton process can be as high as 100% [18–21,49]. However, the matrices studied did not contain as high a load of carbon as in the present study.

Some intermediates of PCBs destruction were detected, such as 7-heptadecene-17-chloro, octadecane-1-chloro, and 1-chloroeicosane. Similar results were reported by Manzano et al. [21] and Przado et al. [20]. Manzano et al. [21] obtained high removal of PCBs present in sand and discussed the formation of open-ring chloro intermediates. Przado et al. [20] did not detect aromatic intermediate products in the hexane solution extract from the degradation of PCBs using a Fenton system. The Fenton process is so aggressive that intermediates with higher degrees of oxidation are formed.

According to Brazilian law, the maximum permissible PCB concentration in solid residues is $<3.0 \mu\text{g kg}^{-1}$. Therefore, in the present case, the residues generated could be considered free from PCBs and could be deposited in urban landfills. Although increased biodegradability and decreased toxicity have been observed for soil or solution treated using the Fenton reaction [7], further studies are required of the intermediates generated, considering their biodegradability and toxicity, prior to allowing the disposal of these residues. Economic

viability studies are also needed in order to confirm the feasibility of using the Fenton process as an alternative treatment for contaminated fuller's earth. Nevertheless, the findings of this preliminary study suggest that the Fenton process offers an alternative for the efficient treatment of this type of waste.

4. Conclusions

Fuller's earth contaminated with IMO initially presented 35% (w/w) of TC, 34% (w/w) of oil and grease, 297.0 g L^{-1} COD, and 64 mg of PCBs per kg. It could, therefore, be considered a dangerous and toxic residue. After treatment using the Fenton process in slurry mode, removal of up to 55% of COD, 20% of oil and grease, and 20% of TC was observed, using 2.07 mol L^{-1} of H_2O_2 , 40.0 mmol L^{-1} of Fe^{2+} , and pH 2.5. No PCBs were detected in the sample after the Fenton treatment, even employing smaller amounts of Fenton reagents and no pH adjustment (1.47 mol L^{-1} of H_2O_2 , 1.7 mmol L^{-1} of Fe^{2+} , and pH 4.0). These results indicated that according to Brazilian law, the treated material could be disposed of in an urban landfill.

Acknowledgements

The authors would like to thank the Federal Institute of Education, Science and Technology of South of Minas Gerais (IF-Sul de Minas, Inconfidentes campus) for collaboration and Dr. Andrew G. Allen for revising the manuscript.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by Fundação de Amparo a Pesquisa do Estado de Minas Gerais – FAPEMIG [Grant Number APQ02459-12], CAPES, CNPq, Rede Mineira de Química (RQ-MG), and PROAP-UNIFEI and Federal Institute of Education, Science and Technology of South of Minas Gerais (IF-Sul de Minas, Inconfidentes campus).

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