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The investigation of fluorene removal with chemical oxidation after soil washing

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ABSTRACT

Soils contaminated by polycyclic aromatic hydrocarbons (PAHs) pose potential risks to human health and the environment. In this study a combined physical-chemical treatment involving soil washing and advanced oxidation was investigated. A fluorene contaminated loamy soil was treated with a washing solution containing a non-ionic surfactant polyoxyethylene 20 cetyl ether (Brij 58). The washing solution containing fluorene (48.5–54.3 mg/L) was afterwards treated with Fenton and electro-Fenton oxidation. The conventional Fenton oxidation results revealed a fast removal of fluorene (>84%) within the first 15 min. COD removal representing the general destruction of washing solution remained at about 10%, but increased to 81% when the reaction time was increased to 480 min using 2% hydrogen peroxide (H_2O_2). The corresponding fluorene removal was about 98%. The pseudo-second order rate constants observed for fluorene (0.0016 L/mg min) and COD (1.5×10^{-6} L/mg min) oxidation supported these results by indicating to a faster oxidation of fluorene. Increase in the H_2O_2 concentration similarly influenced the oxidation of COD rather than fluorene. The COD removal efficiency increased from 43% to 97% when the H_2O_2 concentration was increased from 2% to 10% for a treatment time of 120 min. Electro-Fenton oxidation studies with a current density of 15 mA/cm^2 and an electrolyte conductivity of 2 mS/cm revealed even better results enabling a reduction in reaction time. 60 min of reaction time with 2% H_2O_2 represented removal efficiencies of 98% and 91% for fluorene and COD, respectively.

Keywords: Polycyclic aromatic hydrocarbon (PAH); Soil remediation; Surfactant; Fenton oxidation

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds, generated during the incomplete combustion of solid and liquid fuels or derived from industrial activities. Among the several hundred identified PAHs, 16 PAHs have been recommended by the European Commission (EC) and the US Environmental Protection Agency (U.S. EPA) as priority contaminants [1]. PAHs are of special concern because of their toxic, carcinogenic and mutagenic effects on human health and their persistence in the environment. Due to their hydrophobic nature, PAHs tend to accumulate in soil and sediments [2]. Throughout Europe the number of contaminated sites is estimated to be 250,000 [3]. According to the European Environment Agency [3] about 13% of the contaminants affecting soil and groundwater are PAHs. Therefore, it is important to prevent the transport of these pollutants into the environment by the remediation of source zones, where high concentrations of PAHs exist [4]. Among the many physical, chemical and biological remediation approaches, soil extraction and washing are reported to be potential and economically feasible technologies for the cleanup of contaminated soils [5]. Soil washing is based on the desorption of PAHs from the contaminated soil using organic solvents, surfactants and other complexing agents. The use of such solutions also helps to overcome the limitations related to PAH unavailability in cleanup studies [6,7]. Therefore, the integration of solvents/surfactants into combined treatments like physical-chemical, physical-biological or physical-chemical-biological generally aims to increase the overall PAH removal efficiency [8]. The combination of soil washing and advanced oxidation is used either for

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increasing in-situ PAH removal efficiency of advanced oxidation processes (AOPs) or for further treatment of washing solution containing the eluted PAHs before final disposal. Advanced oxidation processes (AOPs) are accepted as environmentally clean technologies capable of minimizing the generation of degradation products [9]. The oxidation process relies on the formation of non-selective radicals (e.g., hydroxyl (·OH) and sulphate (·SO_4)) using various oxidants like Fenton's reagent, activated persulphate (NaS_4O_8), ozone (O_3), hydrogen peroxide (H_2O_2), etc.[10].

The combination of soil washing with advanced oxidation processes as simultaneous or sequential sequences has been reported in literature [11]. Few of these studies focus on the enhancement of PAH removal from soil using synthetic surfactants followed by ozonation, monosulphate, peroxide, Fenton, electro-Fenton oxidations [5,12]. Saxe et al. [13] used Triton X-100 and Igepal CA-720 surfactant solutions to remove anthracene, phenanthrene and fluoranthene from soil, which were treated with Fenton's reagent to destroy the PAH compounds. It was reported that more than 99% of PAH can be destroyed in the surfactant solution. The results obtained demonstrated that the extent of PAH disappearance from solution for a given dose of Fenton's reagent was inversely proportional to the water solubility of PAH compound. In another study performed by Bendouz et al. [14] the degradation of phenanthrene, fluoranthene and benzo(a) pyrene in cocamidopropyl hydroxysultaine surfactant solution by the Fenton process was investigated under different operating conditions. The results revealed that PAHs were degraded and partially mineralized after 30 min of reaction and that the degradation was proportional to the applied hydrogen peroxide dosage. Mousset et al. [15] combined PAH extraction with electro-Fenton. HPCD and Tween 80 were used to remove six PAHs with different ring numbers from an industrially contaminated soil. Tween 80 presented significantly higher PAH extraction effiencies than HPCD, but complete PAH destruction was achieved twice as quickly with HPCD than with Tween 80.

The aim of this study was to further investigate the oxidative destruction of fluorene that has been removed previously by Brij 58 with a soil washing process. Fluorene was chosen as the model compound of 16 priority PAHs that has not been studied in a combined soil washing and Fenton oxidation process. Fenton oxidation was investigated as chemical and electro-chemical oxidation processes. Optimum treatment conditions were determined by monitoring fluorene and COD removal efficiencies.

2. Materials and methods

2.1. Reagents

The fluorene ($C_{13}H_{10}$) was provided by MERCK with a purity of 95%. The surfactant, Brij 58 ($C_{16}H_{33}(OCH_2CH_2)_{20}$-OH), was purchased from Sigma-Aldrich at analytical grade. The number average molecular weight and critical micelle concentration (CMC) is given as 1124 and 7.7×10^{-2} mM (20–25°C), respectively. HPLC grade (>99.9%) acetonitrile (CH_3CN), acetone (CH_3COCH_3) and hexane (C_6H_{12}) were supplied by Sigma-Aldrich. Hydrogen peroxide (H_2O_2) was obtained from MERCK with a purity of 30%. All other chemicals ($FeSO_4 \times 7H_2O$, $K_2Cr_2O_7$, H_2SO_4, $AgSO_4$, $HgSO_4$, Na_2SO_4, NaOH) were ACS reagent grade.

2.2. Characterization and treatment of soil samples

2.2.1. Characterization of soil samples

The soil sample used in this study was collected for an earlier soil survey study from an agricultural area of the Carsamba plain of Samsun Turkey. The topsoil sample (0–20 cm) was air-dried at room temperature and analyzed according to standard procedures. The texture was determined using the ASTM D 422-63 method [16]. Soil pH was measured as described in ASTM D 4972-95a using a Sartorius PB 20 pH meter [17]. The carbonate content was determined using the Scheibler calcimeter [18]. The organic matter analysis was performed as described in TS 8336, which is a Walkey-Black-based method of the Turkish Standards Institute [19]. The cation exchange capacity (CEC) of soil was analyzed according to the method of Rump and Krist [20]. The results revealed that the soil used in this study was a loamy soil (26.9% clay, 46.4% silt and 26.7% sand) with a soil pH of 7.3, a carbonate content of 4.8%, an organic matter content of 2% and a cation exchange capacity of 175 meq/100 g.

2.2.2. Contaminated soil samples

The contaminated soil was artificially prepared by spiking the soil with fluorene which was previously dissolved in hexane to yield an approximate fluorene concentration of 500 mg/kg in soil. This concentration is the typical PAH concentration found near source zones of contaminated sites [21]. The resultant mixture was placed in a ventilation hood at room temperature (20 ± 2°C) for 10 d to allow the complete evaporation of the solvent. After evaporation, the soil was stored in the dark at (+4°C) to avoid biodegradation. A sample was taken to measure the exact concentration of fluorene, as some of the contaminant may volatilize along with the hexane [4].

2.3. Treatments with the washing solution

2.3.1. Soil washing experiments

The washing solution, which was used for the oxidative destruction of fluorene, was obtained at the end of an optimized washing process. Preliminary experiments revealed that a 24 h treatment of fluorene contaminated soil with 1% Brij 58 solution, at a soil to solution ratio of 1/5, were the best process conditions. The Brij 58 solution was simply obtained by dissolving the solid surfactant in distilled water, above its critical micelle concentration (0.0086% or 7.7×10^{-2} mM). The washing process was performed as a series of batch experiments. 250 mL Erlenmeyer flasks containing the soil and surfactant solution were shaken at room temperature at a rate of 150 rpm using a water bath shaker. To avoid cross-contamination before use, all vessels were rinsed with acetone (>99.9%) and then rinsed several times with distilled/deionized water. After these steps the suspension in flasks was centrifuged and supernatant was decanted to determine fluorene concentration.

2.3.2. Oxidation experiments

The destruction of fluorene in the washing solution was investigated with Fenton oxidation and electro-Fenton oxidation processes. The Fenton oxidation experiments were carried out at in a 100 mL continuous stirred batch reactor (CSBR) in the dark [22]. The washing solution and Fenton's reagent were placed into the CSBR yielding a final volume of 50 mL. The reaction in CSBR was initiated by adjusting the pH to about 3.5 by adding 1M H_2SO_4. The mixture was continuously stirred during the oxidation process using a PTFE coated magnetic stir bar on a vortex mixer (Fig. 1). At the end of reaction time, the Fenton process was stopped by decreasing the pH below 1 using 1M H_2SO_4. The kinetic study was carried out with H_2O_2 concentrations of 1 and 2% at a Fe/H_2O_2 molar ratio of 1/50. Reaction times were selected to be 5, 15, 30, 60, 120, 240, 480 min. After the determination of optimum reaction time, the influence of H_2O_2 concentration on fluorene removal was investigated. These experiments were performed at the same Fe/H_2O_2 molar ratio and but different H_2O_2 concentrations which were varying between 0.5 and 10%. After the determination of optimum H_2O_2 concentration, the influence of Fe/H_2O_2 molar ratio (1/15, 1/30, 1/50, 1/100, 1/200) was determined. Most experiments were carried out in triplicate, at room temperature (25±2°C).

The electro-Fenton oxidation experiments were performed in a undivided 1 L cubic plexi glass cell. Six 4.5 cm × 7.5 cm sized iron plates were placed consecutively into the cell. The electrodes were connected to a digital direct current (DC) power supply (GW GPC-3060D) in a sequence to yield three anode and three cathode electrodes in the cell (Fig. 1). The spacing between each electrode was 0.9 cm. Before each run, the electrodes were washed with acetone to remove surface grease, and the impurities on the electrode surfaces were removed by dipping for 5 min in a solution freshly prepared by mixing 100 mL HCl solution (35%) and 200 mL of hexamethylenetetramine aqueous solution (2.80%) [23]. During electro-Fenton oxidation experiments, 900 mL of washing solution was placed into the electrolytic cell and solid $NaSO_4$was added to improve the solutions conductivity. After the adjustment of current density and addition of H_2O_2, the operation was started similarly by decreasing the pH to about 3.5. The mixture was continuously stirred at 200 rpm during the oxidation process using a PTFE coated magnetic stir bar on a vortex mixer. At the end of reaction time, the oxidation process was stopped by decreasing the pH below 1 using 1 M H_2SO_4. To keep the temperature at about 25°C cooling was applied. After treatment, the solution was left for precipitation, and then the solid phase and liquid phase were separated by centrifugation at 2000 rpm.

2.4. Analytical procedures

2.4.1. Determination of fluorene in soil

The fluorene (FLU) concentration in the contaminated soil before and after treatments were determined by performing Soxhlet extractions with a mixture of hexane and acetone (50:50 v:v) as described in U.S. EPA test method 354°C [24]. The soil samples that were dried with anhydrous Na_2SO_4 were transferred into Whatman cellulose extraction thimbles (43 × 123 mm) dipped in solvent at least for 24 h before use. The extraction was carried out for 24 h at a rate of 4–6 cycle/h. The extracts were allowed to cool to room temperature and were subjected to solid phase extraction process before HPLC analyses.

2.4.2. Determination of fluorene in washing solution

Fluorene was determined using HPLC (Shimadzu LC-20A Prominence) coupled with a ultraviolet diode array detector (UV-DAD) and a Pinnacle® II reverse-phase column (250 mm × 4.6 mm i.d. 4 µm) at the Department of Pharmacology and Toxicology of Veterinary Faculty at the Ondokuz Mayıs University. The injection volume was set at 5 µL, and the isocratic eluent (60:40 acetonitrile:water) was

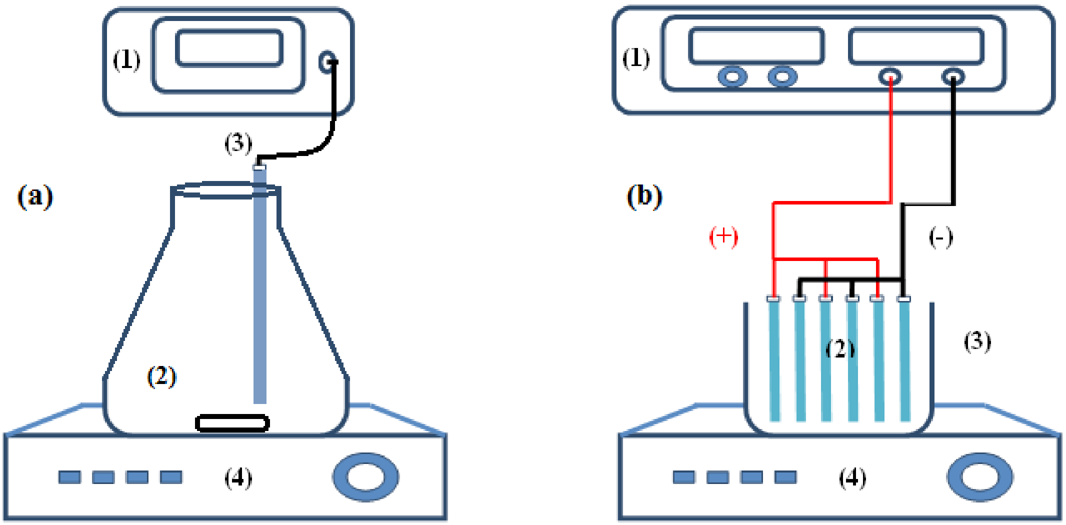

Fig. 1. Experimental setup: (a)(1) pH meter, (2) glass flask, (3) pH electrode and (4) magnetic stirrer; (b) (1) DC power supply, (2) electrode pair, (3) electrolytic cell and (4) magnetic stirrer.

pumped at a rate of 0.5 mL/min for 35 min [25]. During the detection, the column temperature was maintained constant at 20°C and the effluent flux was set at a constant rate of 1.5 mL/min. After fluorene injection at HPLC, retention time, limit of detection (LOD) and limit of quantification (LOQ) of fluorene were determined as 15.205 min, 0.296 ng/mL and 0.896 ng/mL, respectively.

2.4.3. Determination of the chemical oxygen demand in washing solution

COD measurements were carried out to represent changes in the overall organic matter content of washing solutions (e.g., soil organic matter, fluorene and surfactant). COD measurements were performed as recommended in the closed reflux method [26]. 2 mL of samples were added to COD cells that were containing 1.5 mL of digestion solution K_2CrO_7 and 2.5 mL of acid reagent solution. The COD samples were heated at 148°C for 2 h in a thermoreactor (MERCK TR 620) and analyzed at 600 nm using a photometer (Spectroquant NOVA 60).

2.5. Data analysis

The studies were performed in series of batch experiments. The fluorene and COD removal efficiencies were calculated according to Eq. (1), where C_0 represents the initial concentration (mg/L) at the beginning of each oxidation process and C_t the residual concentration at reaction time t (min). The results are presented as average of three independent measurements.

$$\text{Removal efficiency } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

The kinetics of Fenton process is very complex as it involves various catalytic chain reactions [27,28]. Generally, the pseudo-first order rate model was employed in most studies, however, papers presenting high correlations with the pseudo-second order rate model also exist [14,28,29]. Therefore, the kinetic data was evaluated with both models.

The second-order rate equation becomes pseudo-first order, when the principle radical of Fenton process $[OH^{\bullet}]$ is in excess in solution [Eq. (2)]. By integration, the Eq. (2) becomes Eq. (3), which enables a linearized plot of ln (C_t/C_0) vs. time.

$$\frac{d[C]}{d[t]} = -k_1[C]\left[OH^{\bullet}\right] \rightarrow \frac{d[C]}{d[t]} = -k_1[C] \qquad (2)$$

$$\ln[C_t] = \ln[C_0] - k_1 t \qquad (3)$$

Similarly, the below given third order rate equation becomes pseudo-second order. By integration, Eq. (4) becomes Eq. (5), which enables a linearized plot of $[(1/C_t) - (1/C_0)]$ vs. time.

$$\frac{d[C]}{d[t]} = -k_2[C]^2\left[OH^{\bullet}\right] \rightarrow \frac{d[C]}{d[t]} = -k_2[C]^2 \qquad (4)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \qquad (5)$$

For both models the rate constants were determined from the slopes of plots of corresponding data vs. time. Half lives were calculated from Eqs. (6) and (7), which can be obtained when Eqs. (3) and (5) are rearranged after substituting the values $t = t_{½}$ and $C_t = C_0/2$.

$$\text{First order reaction} \rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{k_1} \qquad (6)$$

$$\text{Second order reaction} \rightarrow t_{\frac{1}{2}} = \frac{1}{k_2 C_0} \qquad (7)$$

3. Results and discussion

3.1. Fluorene concentration in the contaminated soil and washing solutions

The studies were performed in series of batch experiments. Therefore, spiking the soil with fluorene and washing the contaminated soil with Brij 58 was performed separately for each oxidation process. The fluorene concentration determined in the contaminated soil samples was ranging between 308.9 mg/kg and 368.8 mg/kg. The fluorene concentrations measured in the contaminated soils were always lower, due to fluorene volatilization during solvent evaporation and fluorene adsorption onto glassware during contamination [4,13]. The fluorene concentration found in the washing solutions was between 48.5–54.3 mg/L. The COD of 1% Brij 58 solutions, after the washing processes, was measured between 11850–15875 mg/L.

3.2. Fluorene removal with Fenton process

The conventional Fenton process relies on catalytic chain reactions of ferrous iron and hydrogen peroxide under low pH conditions to generate hydroxyl radical [Eq. (8)] and some other additional radicals (e.g. superoxide $(O_2^{\bullet-})$ and perhydroxyl radical $(OOH^{\cdot})$, Eqs. (9) and (10). The oxidation reactions are known to be very complex [27,28].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad (8)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\bullet}/O_2^{\bullet-} + H^{+} \qquad (9)$$

$$H_2O_2 + OH^{\bullet} \rightarrow OOH^{\bullet}/O_2^{\bullet-} + H_2O \qquad (10)$$

The highly reactive but nonselective hydroxyl radical $(OH^{\bullet})$ is accepted as the principle radical (E_0 = 2.8 V) in the Fenton process [27]. Free hydroxyl radicals are capable of oxidizing a variety of organic compounds to carbon dioxide (CO_2) and water (H_2O) if the oxidation is carried out until completion [Eq. (11)].

$$\text{Organics}_{\text{oxidisable}} + OH^{\bullet} \rightarrow CO_2 + H_2O \qquad (11)$$

Factors like reaction time, oxidant concentration and catalyst/oxidant ratio are known to play a crucial role in the removal efficiency. Within the scope of this study, the influence of these factors was investigated to determine the optimum operating conditions.

3.2.1. The influence of reaction time on fluorene removal with Fenton oxidation

The influence of reaction time on fluorene removal was investigated with 1% and 2% H_2O_2 at a Fe/H_2O_2 ratio of 1/50. The results, presented in Fig. 2, reflect different trends for fluorene and COD removals. For both hydrogen peroxide concentrations, about 84% of fluorene was removed within the first 15 min, while the COD removals remained at about 10%. A significant increase in fluorene removal after 120 min was especially not observed for 2% H_2O_2 and only an additional increase of 10% for 1% H_2O_2. COD removals increased with time and reached efficiencies of about 38% and 81% at the end of 480 min using 1 and 2% H_2O_2 concentrations, respectively. The corresponding fluorene removals were 93.6 and 97.6%, respectively. These results imply that reaction time had little influence on fluorene removal, but a significant impact on COD removals. Similarly, H_2O_2 concentration had little effect on the destruction of fluorene, but reflected more than two fold increase in the oxidation of COD. Saxe et al. [13] similarly reported Fenton oxidations of phenanthrene, anthracene and fluoranthene with 1% H_2O_2 to occur in minutes; however removal efficiencies were influenced by the type of surfactant and the organic matter content of washed soil. Much higher PAH removal efficiencies were observed for the surfactant Triton X-100 than for Igepal CA-720, which was related to the structural difference in the length of ethoxylate unit of surfactants. Thus, the results of present study reflect that the structure of Brij 58 is not inhibiting a fast oxidation of fluorene at higher levels.

In another study by Bendouz et al. [14] on Fenton oxidation of phenanthrene and fluoranthene present in amphoteric surfactant (cocamidopropyl hydroxysultaine) and quartz solution, removal efficiencies of above 80% were achieved within 30 min with 15 g/L H_2O_2. The reaction time was extended to 180 min to observe higher mineralization of PAHs and their by-products. In this study on Fenton oxidation of fluorene present in Brij 58 washing solution, the optimum time was selected to be 120 min.

The oxidation of fluorene and other organic compounds (COD) was also evaluated using rate constants and half lives. The reaction that will ultimately determine the overall rate in the Fenton oxidation process is the reaction with hydroxyl radical [OH•] [30], which is assumed to be the principle radical of Fenton process. Therefore, pseudo-first order and pseudo-second order rate models involving the reaction of fluorene with the hydroxyl radical was evaluated by plotting ln C_t/C_0 or $1/C_t - 1/C_0$ with respect to time and calculating rate constants and half lives as described in Section 2.5 (Fig. 3). As can be seen from Table 1, fluorene oxidation by the conventional Fenton process can be a little better described by pseudo-second order kinetics. Bendouz et al. [14] also reported that oxidation of phenanthrene, fluoranthene did not fit well to the first order kinetic model. COD oxidation seems to be describable by both kinetic models, pseudo-second order kinetics presenting slightly higher correlation coefficients. It was interesting to observe that almost two times higher correlation coefficients were observed when the first order kinetic data of fluorene was split into two kinetic stages; 0–30 min and 30–480 min. These two kinetic stages were also noticeable from the rate constants which presented a sharp drop in the oxidation rate for the second stage. Burbano et al. [28] similarly reported an initially fast phase (approximately 3–5 min) and a subsequent phase with negligible contribution to the overall degradation of MTBE by the Fenton reagent. Splitting the second order kinetic data of fluorene into the same two kinetic stages supports the presence of two different oxidation stages. This might be related to the rapid oxidation of fluorene, which is about 90% within the first 30 min. Another interesting observation was to determine higher rate constants

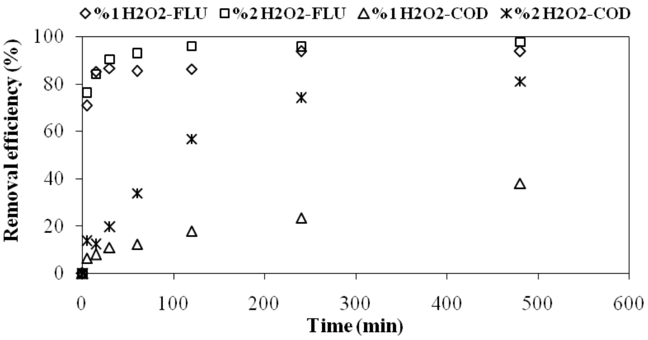

Fig. 2. Influence of reaction time on fluorene (FLU) and COD removal with Fenton oxidation using 1% and 2% H_2O_2 (Fe/H_2O_2: 1/50).

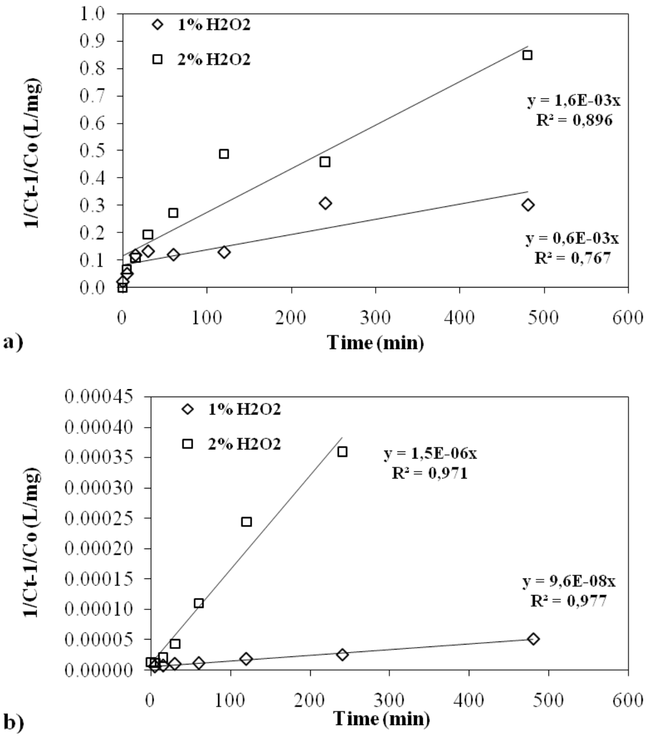

Fig. 3. The pseudo-second order kinetic plots for (a) fluorene and (b) COD oxidation.

Table 1
Fenton oxidation rate constants and half lives calculated for fluorene and COD for different H_2O_2 concentrations

	Pseudo-first order			Pseudo-second order		
	k (1/min)	$t_{1/2}$ (min)	R^2	k (L/mg min)	$t_{1/2}$ (min)	R^2
%1 H_2O_2						
Fluorene	3.6×10^{-3}	1.9×10^{2}	0.46	0.6×10^{-3}	3.4×10^{1}	0.77
COD	0.9×10^{-3}	7.7×10^{2}	0.96	9.6×10^{-8}	8.8×10^{2}	0.98
%2 H_2O_2						
Fluorene	5.2×10^{-3}	1.3×10^{2}	0.54	1.6×10^{-3}	1.3×10^{1}	0.90
COD	3.6×10^{-3}	1.9×10^{2}	0.90	1.5×10^{-6}	5.6×10^{1}	0.97

for the second stage of COD oxidation rather than the first stage for both kinetic models. Overall, the rate constants determined for fluorene oxidation were several orders of magnitude higher than the constants calculated for COD. This supports the higher reactivity of fluorene with the hydroxyl radical. Additionally, constants were all much higher for oxidations with 2% H_2O_2 reflecting the importance of oxidant dosage during the treatment of contaminated sites. Regarding the half life values for both fluorene and COD, it can be seen that for both kinetic models the difference is very much higher when 1% H_2O_2 was used. Half lives calculated for fluorene and COD were 192.5 and 770 min and 34.4 and 879 min for pseudo-first and second order kinetics, respectively. These results certainly imply that the surfactant Brij 58 in the washing solution did not influence the oxidation of fluorene, reflecting little competition for [$OH^•$], despite its high concentration [14].

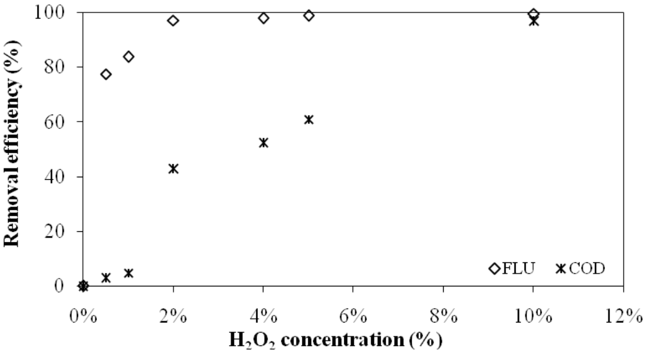

Fig. 4. Influence of H_2O_2 concentration on fluorene (FLU) and COD removal with Fenton oxidation (reaction time: 120 min, Fe/H_2O_2: 1/50).

3.2.2. The influence of H_2O_2 concentration on fluorene removal with Fenton oxidation

In the Fenton reaction, the hydroxyl radical is generated from the reduction of hydrogen peroxide. The influence of H_2O_2 concentration on fluorene removal was investigated with H_2O_2 concentrations varying between 0.5% and 10% for 120 min at a Fe/H_2O_2 ratio of 1/50. As can be observed from Fig. 4, the lowest H_2O_2 concentration (0.5% H_2O_2) resulted in a fluorene oxidation of 80%. The corresponding COD oxidation was found to be only 3% indicating that Fenton oxidation was more selective towards fluorene rather than other organic molecules in washing solution (e.g., soil organic matter and Brij 58). A linear increase in fluorene removal (97%) was observed with an increase in H_2O_2concentration to 2%, but higher concentrations did only lead to additional fluorene oxidations (≤2.5%). On the contrary, COD removals steadily increased with H_2O_2 concentration, about 43% was removed with 2% H_2O_2 and about 97% with 10% H_2O_2. It is known that high hydrogen peroxide concentrations can have adverse effects on oxidation resulting from the scavenging reaction of H_2O_2 with the generated [$OH^•$] radical [Eqs. (12) and (13)] [10,12,31]. In this study the consumption of hydroxyl radical by H_2O_2 was avoided by the high COD levels of washing solution. Especially in treatments with 10% H_2O_2, the generated hydroxyl radical was immediately consumed by the organic constituents (e.g., Brij 58, soil organic matter) present in the washing solution [Eq. (14)], resulting in higher COD removal efficiencies.

$$H_2O_2 + OH^• \rightarrow OOH^• + H_2O \tag{12}$$

$$OH^• + OOH^• \rightarrow O_2 + H_2O \tag{13}$$

$$\text{Surfactant/soil organic matter}_{\text{washing sol}} + OH^• \rightarrow CO_2 + H_2O \tag{14}$$

Thus, higher H_2O_2 concentrations lead to almost total destruction of organic compounds (99.63% fluorene and 97% COD removals) and fluorene concentration dropped below 0.1 mg/L. However, temperature rise and foaming were observed in high H_2O_2 concentration treatments. In 2% H_2O_2 treatments the fluorene concentrations measured were below 1 mg/L yielding removal efficiencies of about 97%. Low COD removals can be seen as beneficial as it enables the reuse of Brij 58 surfactant solution [32]. Therefore, a treatment with Fenton's reagent at a Fe/H_2O_2 ratio of 1/50 for 120 min and a H_2O_2 concentration of 2% was found most suitable.

3.2.3. Effect of Fe/H_2O_2 ratio on fluorene removal

Ferrous iron plays a crucial role in the activation of H_2O_2 conversion to hydroxyl radicals. Therefore, the influence of Fe/H_2O_2 ratio on fluorene removal was investigated with ratios of 1/15, 1/30, 1/50, 1/100, 1/200. From Fig. 5, similar removal trends were observed for fluorene and COD. The lowest ratio (1/200) yielded the lowest removal efficiencies

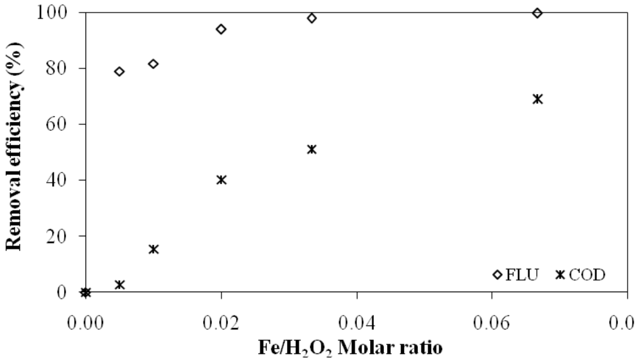

Fig. 5. Influence of Fe/H_2O_2 ratio on fluorene (FLU) and COD removal with Fenton oxidation (reaction time: 120 min, 2% H_2O_2).

of about 79% and 3% for fluorene and COD, respectively. These efficiencies increased to approximately 94% and 40% when the iron concentration increased 4 fold (Fe/H_2O_2; 1/50), respectively. Fluorene removals became stable reaching an efficiency of 99.6% when the Fe/H_2O_2 ratio increased to 1/15. The COD removal efficiency increased to about 69%, respectively. In a similar study by Saxe et al. [13], on PAH destruction present in a washing solution (Triton X-100 and Igepal CA-720) through Fenton process, high PAH removals reaching 90% were found with high H_2O_2 and Fe^{+2} levels. Regarding the trend in fluorene removal efficiencies from Brij 58, the optimum Fe/H_2O_2 ratio was chosen to be 1/50 or 1/30.

When the results from Fenton oxidation experiments for the removal of fluorene from the washing solution are evaluated in general, it can be concluded that fluorene removals were found to reach 90% easily. Optimized Fenton process variables can be summarized as: oxidant concentration, 2% H_2O_2; Fe/H_2O_2 ratio, 1/50; and reaction time, 120 min. Under these operating conditions about 94% of fluorene and about 40% of Brij 58 and other organic molecules were removed from the washing solution by Fenton oxidation.

3.2.4. General consideration about the surfactant-fluorene relation and fate of surfactant during oxidation

The exact reaction mechanisms are complicated and not clear, especially considering the complexity of washing solution and the simultaneous formation of various radicals in solution. It is well known that the concentration of surfactants used in soil washing processes are higher than their CMC [33], as it was in this study with Brij 58. Thus, fluorene and Brij 58, including the soil organic matter, were present as micelles in the washing solution. PAHs have been reported to have the tendency to remain inside the micelle [29]. Some earlier investigations reported that the degradation of target pollutant was inhibited because of this micelle structure acting like a protection at lower oxidant doses [34,35]. Under such conditions the micelle has to be destructed by the radical before contacting the pollutant [33,36]. Other studies emphasized the consumption of hydroxyl radicals by the surfactant and/or soil organic matter resulting in lower PAH removal efficiencies [33,37]. In general, the type and concentration of surfactant and PAH compound, together with oxidant dosage seem to influence the overall oxidation mechanism. Regarding the results observed in this study, it can be stated that the presence of Brij 58 and other organic compounds at relatively higher levels (11850–15875 mg/L COD) did not inhibit the oxidation of fluorene (48.5–54.3 mg/L). Comparison of the trends for fluorene oxidation with the trend of COD of the washing solution, definitely reveals that fluorene oxidation occurs faster. Even at lower reaction times and H_2O_2 concentrations, the destruction of fluorene seems to be preferred as also indicated by the kinetic data. The 3 aromatic ring structure and the relatively lower octanol water coefficient of fluorene (log K_{ow} ~4.2) might be the reasons. Flotron et al. [29] reported that the ring structure of PAHs has an influence on the oxidation level. Higher number ring PAHs are supposed to be more recalcitrant than the lower 2 or 3 ring PAHs. Bendouz et al. [14], on the other hand, found no correlation between the rates of degradation of phenanthene (3 ring), fluoranthene (4 ring) and benzo[a]pyrene (5 ring). Trellu et al. [35] stated that compounds with lower octanol water coefficients (less hydrophobic) are located closer to the external shape of micelle, rather than the middle of micelle, making them easier accessible. The structure of Brij 58 might also influence the consumption of hydroxyl radicals. In a study by Flotron et al. [29] Brij 35 was not found to rapidly attack with [$OH^\bullet$]. In another study by Bogan et al. [38] on the pre-treatment with vegetable oils prior to the treatment with Fenton's reagent, it was stated that contaminants within micelles may be preferentially attacked, relative to those outside the lipid phase, as the peroxidative "cascade" sweeps through the micelle. Cheng et al. [33] reported that due to the difference in reaction rates with [$OH^\bullet$], pollutants can be selectivity degraded and the surfactant can be regenerated. Thus, it appears that the hydroxyl radical reaches fluorene within the micelle and reacts more easily and faster than with the Brij 58 (Fig. 6), yielding a 44 mg/L fluorene removal (~84%). Even though Brij 58 seems to have a lower reactivity for [$OH^\cdot$], the non-selective nature of hydroxyl radical enables the oxidation of surfactant and soil organic matter in washing solution simultaneously. The low appearing COD removal efficiencies (~10%) corresponded to a destruction of 1200 mg/L COD within the first 15 min with 1% H_2O_2. Increasing the H_2O_2 concentration (10% H_2O_2) and time (120 min), yielded even higher COD degradation efficiencies (~97% COD) corresponding to an oxidation of 13,000 mg/L COD. These results generally emphasize that more hydrophilic and more biodegradable by-products can be expected from Fenton oxidation of washing solution, which still requires a comprehensive work to fully understand the fate of Brij 58 in solution.

3.3. Fluorene removal with electro-Fenton oxidation

Recently, electrochemical oxidation has also been combined with soil washing to observe better removal efficiencies in the treatment of PAH contaminated soils. The electro-chemically assisted Fenton oxidation applied in this study relies on the electro-generation of ferrous iron from the anode. The combination of Fenton's reagents occurred in the electrolytic cell after addition of 2% H_2O_2. Conditions

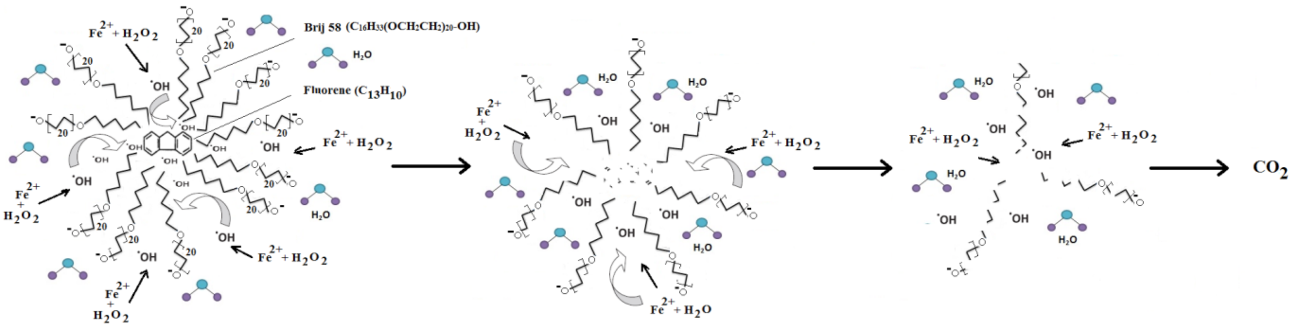

Fig. 6. Schematic of Fenton oxidation of fluorene containing washing solution.

Table 2
Electro-Fenton oxidation rate constants and half lives calculated for fluorene and COD

	Pseudo-first order			Pseudo-second order		
	k (1/min)	$t_{1/2}$ (min)	R^2	k (L/mg min)	$t_{1/2}$ (min)	R^2
%2 H_2O_2						
Fluorene	1.6×10^{-2}	4.3×10^{1}	0.59	1.1×10^{-3}	1.2×10^{1}	0.86
COD	1.8×10^{-2}	3.8×10^{1}	0.99	3.7×10^{-6}	1.6×10^{1}	0.92

used were previously optimized as; current density, 15 mA/cm^2; reaction time, 60 min; and electrolyte conductivity, 2 mS/cm. The fluorene and COD removal efficiencies were found as approximately 98% and 91%, respectively. These results are in line with similar studies in literature. In a study by Tran et al. [39] on the removal of 16 PAH compounds from an amphoteric surfactant solution, a PAH degradation efficiency of about 46% was found in 60 min with a Fe/H_2O_2 of 1/11 at pH 4. The efficiency increased to about 80–82% through electro-chemical oxidation in 90 min with a current density of 9.23 mA/cm^2 at pH 4.

When these results are compared with the results of conventional Fenton oxidation performed with the same washing solution, it can be stated that electro-Fenton oxidation revealed removal efficiencies above 90% in only 60 min. In the conventional Fenton oxidation experiments conducted with 2% H_2O_2 for 120 min, fluorene removal efficiencies were 93.9 and 97.9% for Fe/H_2O_2 ratios of 1/50 and 1/30, respectively. The fluorene removal efficiency observed within 60 min in the electro-Fenton oxidation experiments was 98%. COD removal efficiencies obtained with conventional Fenton oxidation were only about 42.9% and 51.2%, which are quite lower than that (91.3%) observed with the electro-Fenton. Alcántara et al. [40] stated that in electrochemical treatment, the electric current induces redox reactions upon the electrode surface. As can be seen from Table 2, the pseudo-first and second order rate constants and half lives of this electro-Fenton study support the results of Alcántara et al. [40]. The second order rate constant (3.7×10^{-6} L/mg min) and half life (16.1 min) calculated for COD oxidation is higher than those determined for the conventional Fenton process (Table 1). On the other side, the oxidation of fluorene by electro-Fenton process did not reveal a significant change in the kinetic data. Additionally, half lives determined for fluorene and COD did not present a significant difference as was observed for the conventional Fenton process.

4. Conclusions

The combination of soil washing followed by Fenton and electro-Fenton oxidation was found most promising. Brij 58 was capable of removing most of the fluorene from soil and did not inhibit the destruction of fluorene in the washing solution. Fluorene was generally very rapidly oxidized, which was also presented by the pseudo-first and second order kinetic models. Therefore, the influence of operational parameters like reaction time, peroxide concentration and Fe/H_2O_2 molar ratio were more apparent for the COD of washing solution. These parameters were optimized as 120 min, 2% H_2O_2 and 1/50, respectively. The electro-Fenton oxidation helped to decrease the reaction time to 60 min. Optimized operational parameters were a current density of 15 mA/cm^2, an electrolyte conductivity of 2 mS/cm and a peroxide concentration of 2%. The results indicate that the micelle structure formed by Brij 58 is not inhibiting the oxidation of fluorene and that fluorene in the washing solution is destructed relatively faster than the Brij 58 surfactant. A more comprehensive work is still required to fully understand the Fenton oxidation and by-products of washing solution.

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