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Degradation of polycyclic aromatic hydrocarbons in different synthetic solutions by Fenton's oxidation

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Abstract

The Fenton oxidation using phenanthrene (Phe), fluoranthene (Fle) and benzo[a]pyrene (BaP) as representative Polycyclic Aromatic Hydrocarbons (PAHs) contaminants was examined. The effect of the H_2O_2 concentration, the temperature and the competition between PAHs in different solutions (methanol, surfactant and quartz) was investigated. The Fenton oxidation process was performed at pH = 2.5. The best conditions were recorded by adding 15 g H_2O_2 L^{-1} with a molar H_2O_2/Fe^{2+} ratio of 10/1 at T = 60ºC. Phe, Fle, and BaP were efficiently degraded in aqueous solution (Phe = 99%, Fle = 99%, BaP = 90%). The present study demonstrated that Phe, Fle and BaP were degraded to intermediate compounds and also oxidized to carbon dioxide. Among the by-products obtained, phthalic acids and benzoic acid were recorded as the major products.

Keywords

Polycyclic aromatic hydrocarbon, Phenanthrene, Fluoranthene, Benzo[a]pyrene, Fenton oxidation.

Nomenclature

BaP	Benzo [a] pyrene
CAS	Cocamidopropyl hydroxysultaine
Fle	Fluoranthene
MS	Methanol solution (one PAH in methanol solution)
PAHs	Polycyclic aromatic hydrocarbons
Phe	Phenanthrene
POP	Persistant organic pollutant
PSQ	Mix of three PAHs (Phe, Fle, BaP), surfactant and quartz in solution
SQ	Surfactant and quartz with one PAH in solution
TOC	Total organic carbon

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a family of organic compounds consisting of carbon and hydrogen atoms, arranged in the form of two or more benzene rings fused in linear arrays or angular clusters. These compounds can be detected in all environmental matrices (e.g., water, soil and air) and show a strong toxicity for the humans and the fauna due to their carcinogenic effects. [1] PAHs are also a part of the Persistent Organic Pollutants (POPs).

Due to their hydrophobic characteristics, these compounds can be adsorbed on particulate matter. Therefore, the compounds accumulate in sediments, [2,3] in soils [4] and in slag-polluted soils. [5] PAHs present in soil are difficult to remediate, and many remediation technologies have been explored for the removal of PAHs from soils, involving one or a combination of physical, chemical, biological and thermal processes. The thermal technologies can effectively destroy PAHs but entail high costs due to the high temperatures required and the need for the treatment of the gaseous products. [6] In comparison, soil washing using water can be applied easily but is not effective due to the low aqueous solubility of these compounds. Surfactants should therefore be added to enhance the solubility of the PAHs. Among the amphoteric surfactants, cocamidopropyl hydroxysultaine (CAS) has recently been used as a surfactant for PAHs extraction from polluted soils. [4,5] The treatment of these soils generates concentrates containing organic pollutants, including PAHs. Moreover, the CAS used during soil washing could be linked with the particles present in the soil. [7] These concentrates are considered as hazardous waste (exceeding the criteria C and D, which restrict the landfilling) and their management is highly expensive (300 \$ t^{-1}). [8] The degradation of PAHs in these concentrates is a difficult task due to their low solubility, their high initial concentrations and their refractory character. However, degradation of PAHs can be achieved through several treatment methods, such as advanced oxidation processes (AOPs) or biological oxidation. [9]

Background

AOPs are techniques that use different combination of oxidants, energy sources and catalysts to generate $OH^{\bullet}$ in water [10]. AOPs, including O_3/H_2O_2, UV/O_3, UV/H_2O_2, H_2O_2/Fe^{2+} and others, are often used for PAHs degradation. For example, Beltrán et al. [11] concluded that the use of UV/H_2O_2 oxidation yields significant improvement in the rate of PAHs removal from water, and the total oxidation of the initial PAHs was achieved in less than 7 min compared to 20 min for the use of UV radiation or photolysis.

Leadkowicz et al. [12] have also demonstrated that the simultaneous combination of ozone (O_3) with radiation (UV) is an effective and quick method for removal of selected PAHs from the aqueous environment compared to ozonolysis and photolysis separately.

The Fenton oxidation of PAHs has been examined by Saxe et al. [13] in wastewater emerging from soil washing, showed removal yields greather than 99% for the PAHs parent.

Among the AOPs, the Fenton oxidation process represents the most common and simple option. The Fenton process involves the generation of hydroxyl radicals ($OH^{\bullet}$), the strongest oxidant with a redox potential of 2.8 V. These radicals are produced from a mixture of ferrous ion and hydrogen peroxide, as shown in Eq. 1. [14]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \qquad (1)$$

The review article by Bautista et al. [15] described the succesful applications of the Fenton oxidation for the treatment of a wide range of industrial wastewaters.

The efficiency of the Fenton system depends on many parameters, such as the reaction time, the pH, the initial concentrations of ferrous ions and hydrogen peroxide, the H_2O_2 to Fe(II) molar ratio and the temperature. [16] An optimal oxidation of the organic compounds can be obtained in the presence of an excess of hydrogen peroxide. Marti et al. [17] and Kulik et al. [18] have reported that the H_2O_2/Fe^{2+} molar ratio of 10/1 improved the quality of pharmaceutical wastewater by decreasing the chemical oxygen demand (COD).

The hydroxyl radical is capable of oxidizing a wide range of organic compounds (RH or R) either by hydrogen abstraction (Eq. 2) or by hydroxyl addition (Eq. 3):

$$RH + OH^{\bullet} \rightarrow {}^{\bullet}R + H_2O \tag{2}$$

$$R + OH^{\bullet} \rightarrow {}^{\bullet}ROH \tag{3}$$

The presence of an organic substrate, such as a surfactant, changes the predominant reactions present in the Fenton system because the hydroxyl radicals will react with both organic contaminants (PAHs) and the surfactant present in the environment. Indeed, the hydroxyl radicals will react with all organic compounds in a non-selective manner, and the presence of an organic substrate (surfactant) will therefore influence the performance of PAHs degradation. [13]

The present paper will study, on the laboratory scale, the chemical oxidation of phenanthrene (Phe), fluoranthene (Fle) and benzo[a]pyrene (BaP) present in synthetic solutions in the presence or the absence of a surfactant. Phe, Fle and BaP were selected as model compounds of PAHs containing 3, 4 and 5 aromatic rings. The performance of the degradation of PAHs present in synthetic solutions (methanol, surfactant and quartz) containing one PAH (Phe or Fle or BaP) and the three PAHs together (Phe, Fle and BaP) were investigated using Fenton oxidation. The specific issue of the present paper is the study of the effect of the surfactant on the reaction of hydroxyl radicals with both PAHs and the surfactant, which is supposed to be an important inhibitor for the degradation of PAH compounds. The influence of the concentration of hydrogen peroxide, the temperature and the reaction time was investigated followed by the identification of the oxidation by-products. The purpose of this study is to determine if the combination of PAHs with a surfactant or other PAHs in different matrices can influence the performance of the Fenton's oxidation in terms of PAH degradation rates.

Material and Methods

Synthetic solution

Preparation of the PAH solution using methanol

Phe, Fle and BaP analytical grade reagents (99% purity) were obtained from Sigma Aldrich (Oakville, ON, Canada). Due to the low solubility of PAHs in water, the stock solutions (600-800 mg L^{-1}) were prepared in pure methanol (HPLC grade, Fisher, Canada) for each PAH (Phe, Fle and BaP) and kept at -4^{o}C. Each synthetic solution of Phe, Fle or BaP was made by diluting 1 mL of the Phe, Fle or BaP stock solution in 100 mL of distilled water to obtain a final solution containing 1% (w/w) of methanol. The concentration of Phe, Fle and BaP in the final solutions was in the range of 6 to 8 mg L^{-1}.

Preparation of the PAH solution using surfactant and quartz (SQ and PSQ)

In this case, quartz was used as it is a representative matrix of the concentrates that contained the PAHs. The quartz was obtained from a mining site (purity 100 ± 0.2%) and then ground to achieve a diameter similar to the real sample concentration (< 250 µm). For this series of experiments, an exact volume of Phe, Fle or BaP stock solution (1 mL) was added to 15 g of quartz and allowed to evaporate at least one day in a chemical hood (to allow the evaporation of methanol). Then, 100 mL of a solution containing 0.6 g L^{-1} of CAS was added to the quartz containing one of the PAHs (SQ solution). The mixed solution of Phe, Fle and BaP (PSQ solution) was also prepared by keeping the same concentration as in the only one PAH solution (1 mL of each solution of PAH was added to quartz and allowed to evaporate before adding the CAS solution).

Preparation of the CAS solution

The CAS is an amphoteric surfactant that consists of coconut oil radical terminating with the hydroxysultaine group. The CAS was obtained from Chemron, USA. To evaluate the competition between CAS and PAHs, the Fenton’s oxidation was examined on a solution that contained only CAS (0.6 g L^{-1}), prepared with distilled water, and on a solution containing PAHs, quartz and CAS (SQ and PSQ).

Fenton oxidation

In the three series of experiments, the first experiment was carried out in a solution that contained only one PAH (Phe, Fle, or BaP) solubilized in methanol and aqueous solution (MS). The second series was conducted in a solution that contained a surfactant and quartz with one PAH (SQ), and the last series was carried out in a solution that contained a mixture of the three

PAHs (Phe, Fle, BaP), a surfactant and quartz in solution (PSQ). The initial concentration of Phe, Fle and BaP was measured at the beginning of each series of experiments.

Experiments were conducted in a 500-mL Erlenmeyer glass-flask covered with aluminum foil to avoid any photolytic oxidation. All the experiments were carried out in a temperature-controlled bath (Shaker Bath, Cab-line) at 200 rpm. The temperature tested during the different experiments was in the range of 20-60ºC. For all the assays, 100 mL of solution was used. The initial pH of each solution was adjusted to approximately 2.5 using a sulfuric acid solution of 50% (w/w) (Fisher, Canada). The ferrous ions were added from a stock solution of 1 M $FeSO_4 \cdot 7H_2O$ (Laboratoire Mat, Quebec, Canada) prepared at pH = 2. The hydrogen peroxide (Certified ACS, Fisher, Canada) was taken from a commercial bottle ($[H_2O_2] = 31.4\%$). A known amount of $FeSO_4$ and H_2O_2 (5, 10 and 15 g L^{-1}) were added to the 100 mL of solution. The ferrous ions and hydrogen peroxide solutions were added with a $[H_2O_2]/[Fe^{2+}]$ molar ratio fixed at 10/1. The experiments were stopped after different reaction times of 15, 30, 60, 180 and 360 min.

At the end of each experiment, 5.56 g of sodium sulfite (Fisher, Canada) was added to completely stop the oxidation processes. Next, all aliquots were withdrawn before the extraction of the residual PAH content.

Determination of the effect of H_2O_2 concentration

The effect of the H_2O_2 concentration on PAH degradation was examined for three concentrations of H_2O_2 fixed at 5 g L^{-1}, 10 g L^{-1} and 15 g L^{-1} while keeping the molar ratio of $[H_2O_2]/[Fe^{2+}]$ and the temperature constant at 10/1 and 20°C, respectively. The control assay consisted of mixing the Phe, Fle and BaP solution in an Erlenmeyer flask without the addition of H_2O_2 and Fe^{2+}, using the same experimental conditions (agitation, temperature) as for the samples during 360 min.

Determination of the effect of H_2O_2 concentration

The effect of temperature on PAH degradation was examined by controlling the temperature between 20 and 60°C of the solution in a controlled-temperature bath. The assays were carried out for different reaction times: 15, 30, 60 and 180 min at different temperatures (20, 40 and 60°C) by adding 15 g H_2O_2 L^{-1}.

Parameter analysis

General

The pH was determined using a pH meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Canada) equipped with a double junction Cole-Parmer electrode with an Ag/AgCl reference cell.

Total organic carbon (TOC) content was identified using a Shimadzu VCPH according to the NPOC method. [19]

Determination of the surfactant concentration

After application of Fenton's oxidation, the residual CAS contents were analyzed using a Cary Eclipse Fluorescence Spectrophotometer (Varian) set at 600 V after the addition of 1-8-anilino-naphthalene sulfonate (ANS). Emission and excitation wavelengths were set at 370 and 490 nm, respectively. The ANS (Sigma Aldrich, Canada) was weighed and dissolved in distilled water to obtain a stock solution of $1 \cdot 10^{-3}$ M and kept in a light-proof glass bottle prepared 24 h before analysis. Next, 100 µL of the ANS solution was added to 10 mL of each sample, and the mix was allowed to react at room temperature for approximately 10 min before the spectrofluorimetric analysis. As the response varied with reaction time, it was necessary to respect the 10-min reaction time between the preparation of the sample and the analysis. [7]

Determination of the PAHs concentrations

The residual concentrations of PAHs present in methanol solution after the Fenton's oxidation were determined by liquid-liquid extraction and measured by GC/MS (Perkin Elmer, model Clarus 500, column type DB-50, 30 m × 0.25 mm × 0.25 µm). The sample (100 mL) was spiked with recovery standards (pyrene-D10 and benzo[a]pyrene-D12), and the PAHs were twice extracted from aqueous solution using 30 mL dichloromethane (Fisher, Canada). Next, the sample was transferred into a filter containing anhydrous Na_2SO_4 (Fisher, Canada) to remove water. The extracts (approximately 60 mL) were subsequently reduced to 10 mL using a rotary evaporator (Büchi Rotavapor – R, Rico Instrument Co.) at 30°C and kept at - 4°C until analysis.

After the Fenton's oxidation, the PSQ and SQ solution was allowed to settle, and a solid/liquid separation was performed. The concentration of the PAHs present in the liquid phase was determined using the method mentioned above. For the determination of the PAHs present in the quartz, the solid phase (quartz) was dried at 55°C and then extracted using dichloromethane during 30 min in an ultrasonic bath. A mixture of recovery standards was also added to the solid sample before the solid/liquid extraction to evaluate the effect of the extraction process. The samples were then analyzed using a GC/MS.

Formation of the Fenton oxidation by-products

The by-products were identified only for the experiments carried out on the degradation of Phe, Fle and BaP present in MS solution. The sample after Fenton's oxidation was mixed with dichloromethane for 20 min. The organic phase (dichloromethane) was concentrated and analyzed using a GC/MS (Thermo Scientific, model Trace 1310 Gas Chromatograph coupled with mass spectrometer detector ISQ, column type ZB Semi-volatile, 60 m × 0.25 mm ×

0.25 µm) with a simultaneous Selected Ion and Full Ion scan. Next, a derivatization of the PAHs was carried out by adding 25 µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Sigma, Canada) to the concentrated samples and mixing the solution for 30 min at 65°C before performing the injection into the GC/MS. This step allows the detection of polar compounds that cannot be analyzed directly because of the strong interactions occurring with the stationary phase of the chromatographic column. [20] The GC/MS analysis of the derivatized samples was performed using the same method as the method used for the non-derivatized samples.

Results and Discussion

Effectiveness of Fenton's oxidation processes on the degradation of Phe, Fle and BaP in methanol solution (1% w/w)

Effectiveness of H_2O_2 initial concentration

One of the main factors affecting the efficiency of the Fenton oxidation is the H_2O_2 concentration. [21] Table 1 presents the removal yields obtained from the Phe, Fle and BaP solutions containing methanol (MS) after the Fenton's oxidation was carried out with different H_2O_2 concentrations and reaction times. The pH was adjusted to 2.5 before adding the H_2O_2 and the Fe^{2+} solution at the same time. [22] Initial concentrations of 7.34 mg Phe L^{-1}, 7.23 mg Fle L^{-1} and 6.34 mg BaP L^{-1} were measured in the methanol solutions used to prepare both controls and samples. By comparison, residual concentrations of 6.83 mg Phe L^{-1}, 6.99 mg Fle L^{-1} and 6.18 mg BaP L^{-1} were recorded in the control assay (no addition of H_2O_2 or Fe^{2+}) after 360 min, which corresponded to a decrease in the Phe, Fle and BaP concentrations of 7%, 3% and 2%, respectively. The highest percent of error was recorded for Phe (7%). However, the aqueous solubility of this compound is estimated at 0.95 ± 0.12 mg L^{-1}, [23] so a part of the Phe was probably soluble in the aqueous phase during the liquid/liquid extraction stage. The decrease of Fle (3%) and BaP (2%) concentration during the control assays could be considered as negligible and will not be considered.

As seen from Table 1, the Phe removal yields obtained after 30 min with 5 g H_2O_2 L^{-1} was estimated at 16%, and the Phe removal yields increased to 78% when the concentration of H_2O_2 was increased to 10 g L^{-1}, due to the generation of a larger amount of hydroxyl radicals ($OH^\bullet$). At a higher H_2O_2 dose (15 g L^{-1}), the removal efficiency was approximately 85% after 30 min, and then stabilized at 92% and 93% after a period of 180 min and 360 min, respectively. These results indicated that the H_2O_2 became the limiting parameter for further generation of $OH^\bullet$.

For Fle, when the H_2O_2 dosage was increased from 5 g L^{-1} to 10 g L^{-1}, the removal yield increased from 69% to 83% after only 30 min. At a concentration of 15 g H_2O_2 L^{-1}, the degradation yields obtained were estimated at 85%, 87% and 98% after 30, 180 and 360 min, respectively. For BaP, the maximum degradation was reached after using high concentrations of H_2O_2 (10-15 g L^{-1}) between 70 and 88% degradation. According to these results, it seems that no differences were observed in rate of degradation by applying 10 or 15 g H_2O_2 $L^{-1.}$. Domuic and Haure [24] showed that additional doses of hydrogen peroxide could help to achieve further mineralization. As the Fenton's reaction follows first order kinetics, the increase in the reagent concentration led to an increase in the degradation of organic compounds, such as Phe, Fle and BaP, possibly due to the increase in the number of active sites for H_2O_2 decomposition, which produced more $OH^\bullet$ radicals and enhanced the oxidation rate of the organic pollutants. [25] Therefore, the concentration of H_2O_2 selected for the next experiments was 15 g L^{-1}. The increase in reaction time seemed not to be very important in the range of 180 to 360 min.

Kanel et al. [26] reported that more than 80% of a solution of H_2O_2 (5 M) was consumed within 30 min, and the degradation was almost complete after 180 min of reaction. To establish greater mineralization of PAHs and their by-products, the reaction time was extended to 180 min to ensure the complete chemical consumption. With regard to the kinetics of reaction, the reaction times of 15 min and 60 min were added for the next assays.

Effect of the temperature and the reaction time

The temperature is also an important factor that could affect the performances of the Fenton's oxidation. The reaction order and the rate constant of the degradation of Phe, Fle and BaP can be determined by plotting ln (C_t/C_0) against reaction time, as defined in Eq. 4.

$$\mathbf{k\ t = -\ln (C_t/C_0)} \tag{4}$$

where:

C_0 is the initial concentration of PAHs (mg L^{-1})

C_t is the residual concentration of PAHs at time t (min)

k is the first-order kinetic constant (min^{-1})

t is time (min)

Fig. 1 presents the relationship between $\ln(C_t/C_0)$ and the reaction time for the degradation of Phe, Fle and BaP. The results obtained (not shown) showed that residual concentrations of Phe, Fle and BaP after 60 min and 180 min were not different. Therefore, the first 60 min of reaction seemed to be the limit to calculate the kinetic constant. Fig. 1a showed the Phe decomposition profiles obtained for different temperatures. According to the results, the Phe degradation occurred in a pseudo-first-order reaction with a rate coefficient (k) of 0.048, 0.068 and 0.097 min^{-1}, corresponding to the experiments carried out at 20, 40 and 60^oC, respectively. The experimental data obtained for Phe degradation at 20^oC and 40^oC fitted well to the first-order kinetics ($R^2 = 0.90$ and 0.96, respectively). At 60^oC, the Phe degradation remained stable after 30 min, which explained why the decomposition of this compound did not fit well to first-order kinetics ($R^2 = 0.72$). In this case, the increase of reaction time did not improve the degradation of Phe. This phenomenon is in agreement with the observations made by Neyens and Baeyens [27] to enhance the sludge dewaterability using Fenton reagent. According to these authors, the reaction time and the amount of H_2O_2 required for the reaction could be reduced by increasing the temperature. The degradation of Fle showed the same behavior, the time and the degradation rate constants obtained showed the following order: $k_{60^oC} > k_{40^oC} > k_{20^oC}$. However, the correlation coefficients highlighted that the degradation of this compounds did not fit well to the first-order kinetics ($R^2 = 0.73$, 0.79 and 0.73 for experiments carried out at 20, 40 and 60^oC, respectively). In Fig. 1b, all the points obtained after 60 min of reaction are below their trend lines, possibly due to the completion of the Fenton's reaction before 60 min, meaning that the formation of $OH^{\bullet}$ radicals was limited, which restricted the degradation of Fle. An enhancement of the degradation of Fle was also observed with an increase of the temperature. The same conclusion was reached by Detomaso et al. [28], who revealed the advantage of performing the process at a temperature higher than 70^oC. However, the literature mentioned that the removal performance declines at high temperatures due to the decomposition of hydrogen peroxide, resulting in a decrease in the production of hydroxyl radicals. [29,25,30] Indeed, Jacobs and

Testa [31] mentioned that the peroxide becomes more volatile and produces a wispy white vapor at temperatures higher than 57°C.

For BaP, high degradation rate constants were observed with the same order: $k_{60^oC} > k_{40^oC} > k_{20^oC}$ (0.048; 0.036; 0.033 min^{-1}, respectively) (Fig. 1c). The correlation coefficients obtained were approximately 0.8. These results were in accordance with the observation made by Homem et al. [32] who showed that an increase in the temperature from 30 to 70°C improved the degradation kinetics of BaP present in aqueous solutions. For the three PAHs tested, the temperature had a positive effect on the performance of PAH degradation using the Fenton's process. Therefore, the temperature was fixed at 60°C for the next assays.

Fenton oxidation of Phe, Fle and BaP in CAS solution with quartz (SQ, and PSQ)

This experiment enables the comparison of the degradation rate of 3 PAHs mixture under the same conditions by adding 15 g H_2O_2 L^{-1}, $[H_2O_2]/[Fe^{2+}]$ at a molar ratio of 10/1 during 180 min at 60°C to demonstrate the potential competition effects of PAHs and CAS present in solutions with quartz (support).

The Fenton oxidation of a solution containing only CAS was also studied. After one minute of reaction, all CAS was degraded (data not show). Fig. 2 shows the degradation performance of Phe, Fle and BaP present in the same solution of CAS in the presence of quartz. The Fenton reagent seemed to be more efficient for the degradation of Fle (4 aromatic rings) contrary to the BaP that was more recalcitrant (5 aromatic rings). In addition, the results showed that the degradation of Phe (3 rings) exhibited intermediate performance. According to these results, it seemed that there was no difference between the rates of degradation of Fle and Phe. Due to the non-specificity of action of the hydroxyl radicals generated, they are distributed in a random manner in the solution. The free PAHs present in the solution were more accessible than the molecules adsorbed on the particles of quartz. Watts et al. [33] have shown that the proximity of hydroxyl radicals to PAHs is important to allow an efficient degradation. Lemaire et al. [34,35] reported that the progressive addition of reagent is more effective than a single addition because the progressive addition minimizes the competing reactions and the rapid consumption of hydrogen peroxide.

The effect of the mixture (MeOH, quartz and quartz + CAS) on the oxidation of each PAH was also studied. Fig. 3a shows the effect of the Fenton’s oxidation on the degradation of Phe in different solutions (MS, SQ and PSQ). The degradation of the Phe present alone in the MeOH solution was important during the first 30 minutes and started to stabilize at a percentage of 99% after 60 min of reaction. Its degradation decreased to 96% and 88% in the SQ and PSQ, respectively. The degradation of Fle was complete in the three mixtures studied (Fig. 3b).These results were in opposition to the study of Sanches et al. [36], who showed that differences in the composition of the different water matrices (laboratory grade, ground and surface waters) can influence the degradation of PAHs. The degradation of BaP, presented in Fig. 3c, exhibits the same behavior, showing high degradation rates between 90% (MS) and 82% (SQ and PSQ). Despite the high hydrophobicity of BaP and the presence of suspended solids that can limit the availability of hydroxyl radicals to the PAHs, the matrix effect on the Fenton’s oxidation of the PAHs was not observed. The presence of CAS did not influence the degradation of PAHs in comparison to the results obtained during the experiments carried out in MeOH solutions (MS). Flotron et al. [37] studied the degradation of three PAHs (BaP, Fle and benzo[b]fluorenthene) in the presence of an anionic surfactant (Brij-35). Their results showed that there was a little competition between the PAHs and the Brij-35 for $OH^{\bullet}$ radicals, at low concentrations of surfactant. The use of methanol also consumed some of the hydroxyl radicals. The constant rate of oxidation of an alcohol with $OH^{\bullet}$ radicals in water increased with the length of the carbon chain. [38]

According to our results, the presence of surfactant and methanol at low concentrations did not have an influence on the consumption of hydroxyl radicals, whereas the presence of other PAHs at high concentrations seemed to influence the rate of degradation of Phe, Fle and BaP. Although the structure of each PAH is expected to influence their degradation, the high degradation of Phe, Fle and BaP present in the three solutions (MS, SQ and PSQ) can be explained by the high temperature and the addition of H_2O_2 in excess compared to the initial concentrations of PAHs.

By-product formation

In addition to Phe, Fle and BaP measurements, the effectiveness of the Fenton's oxidation was also evaluated by measuring the Total Organic Carbon (TOC) content in the initial and oxidized solutions. The initial TOC concentration in the Phe, Fle and BaP solutions was approximately 2 900 mg L^{-1}. After 30 min, TOC removals of 73%, 67% and 66% were obtained for the solution containing Phe, Fle and BaP, respectively. The reduction of the TOC content was related to the complete mineralization of PAHs into carbon dioxide and water. Therefore, only a small fraction of PAHs was partially degraded into intermediate molecules. The identification of by-products was carried out by comparing the obtained product mass spectra with those from the library mass spectra. The main problem of the identification of by-products after the oxidation of PAHs by hydroxyl radicals is the absence of standard solutions. It was evident that an oxidation of intermediate can occur because of the increase in the pH after the addition of sodium sulfite.

The by-products, identified by GC/MS in the synthetic solutions of PAHs in methanol (MS) after 30 min, are listed in Table 2. These compounds show that the two main by-products (phthalic anhydride and phthalic acid) were produced during the degradation of Phe, Fle and BaP. Both phthalic anhydride and phthalic acid were reported by some other researchers when using AOPs. Zeng et al. [39] showed the presence of phthalic anhydride, phthalic acid and benzoic acid during the degradation of BaP by ozonation in the aqueous phase. Similarly, another study showed that phthalic anhydride was formed after the Fenton's oxidation of Phe. [40]

When using BSTFA for derivatization, the hydroxyl and carboxyl compounds were detected. The derivatization rendered the by-products more volatile, favoring their detection by GC. Indeed, all free -OH and -COOH groups were converted into their volatile $–O-Si(CH_3)_3$ and $–COO-Si(CH_3)_3$, respectively. The results of silylation used to identify -OH and -COOH groups are shown in Table 2b.

According to the intermediates found during the oxidation of Phe, Fle and BaP, reaction pathways of Phe, Fle and BaP degradation can be proposed.

Lee et al. [41] studied the Fenton oxidation position for five PAHs including BaP. The quinones formed were identified as by-products. The authors reported that the positions of oxidation of quinones corresponded with predicted positions in which the frontier electron density was high. Fig. 4 presents proposed pathways of degradation of Phe, Fle and BaP by Fenton oxidation in methanol (1%). The main degradation processes involved the formation of quinone compounds. Subsequently, these quinone compounds were oxidized, and phthalic acid was formed, which was rapidly transformed into phthalic anhydride when applying high temperatures. Similarly, the phthalic anhydride can be transformed into phthalic acid by attacks of hydroxyl radicals. The continued oxidation leads to the formation of benzoic acid.

Conclusions

The Fenton process was investigated under different operating conditions (oxidant concentration, temperature, reaction time) in the presence of Phe, Fle, and BaP, which are representative compounds for PAHs. The degradation of Phe, Fle, and BaP present in MS, SQ or PSQ systems was proportional to the applied hydrogen peroxide dosage. Within the range of conditions studied, PAHs were degraded and partially mineralized after 30 min of the reaction. The temperature was a key parameter to enhance the mineralization, provided the oxidant concentration used was higher than the stoichiometric dose. However, at higher temperature, the oxidant could be less efficiently used, and a short reaction time is required. The main reaction products produced by Fenton’s oxidation of Phe, Fle and BaP were phthalic acid, phthalic anhydride and benzoic acid.

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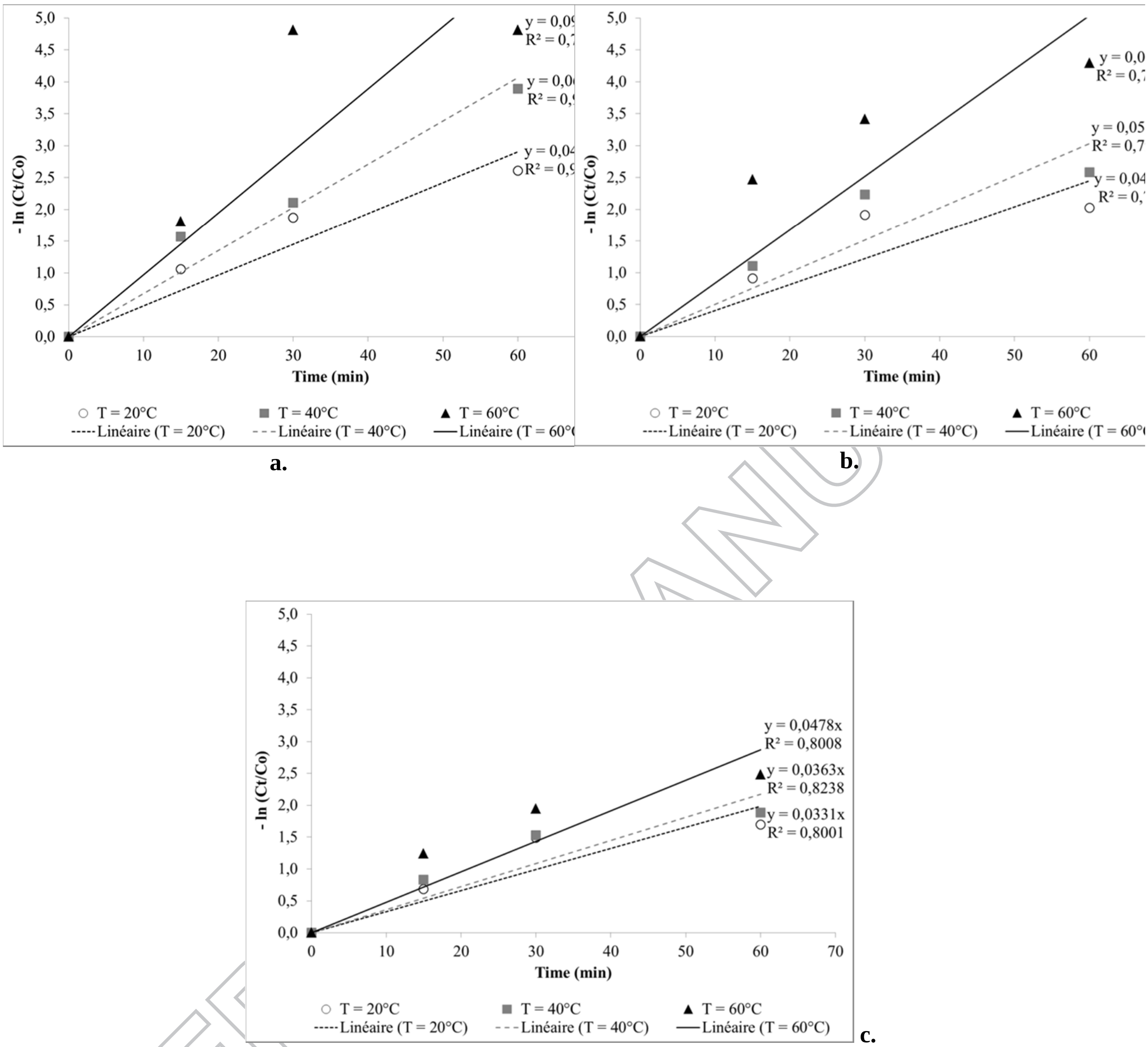
Figure Caption

Fig. 1. Kinetic degradation of Phe(a), Fle(b) and BaP(c) in 1% methanol at different temperatures (20, 40 and 60°C) by Fenton oxidation (H_2O_2 = 15 g L^{-1}, pH = 2.5, $[H_2O_2]/[Fe] = 10$)

Fig. 2. Effect of Fenton's oxidation on the degradation of Phe, Fle and BaP in PSQ solution at 60^{o}C (H_2O_2 = 15 g L^{-1}, pH = 2.5, $[H_2O_2]/[Fe] = 10$, $[Phe]_i$ = 7.23 mg L^{-1}, $[Fle]_i$ = 7.63 mg L^{-1} and $[BaP]_i$ = 7.30 mg L^{-1})

Fig. 3. Degradation of Phe(a), Fle(b) and BaP(c) in different solutions (methanol, SQ and PSQ) (H_2O_2 = 15g L^{-1}, pH = 2.5, $[H_2O_2]/[Fe] = 10$, T = 60°C, $[Phe]_i$ = 7.23 mg L^{-1}, $[Fle]_i$ = 7.63 mg L^{-1} and $[BaP]_i$ = 7.30 mg L^{-1})

Fig. 4. Proposed pathways of Phe, Fle and BaP degradation by Fenton oxidation


- ln (Ct/Co)
Time (min)
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0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0
0
10
20
30
40
50
60
70
y = 0,09
R² = 0,7
y = 0,06
R² = 0,9
y = 0,04
R² = 0,9
y = 0,0
R² = 0,7
y = 0,05
R² = 0,7
y = 0,04
R² = 0,
y = 0,0478x
R² = 0,8008
y = 0,0363x
R² = 0,8238
y = 0,0331x
R² = 0,8001
○ T = 20°C
■ T = 40°C
▲ T = 60°C
Linéaire (T = 20°C)
Linéaire (T = 40°C)
Linéaire (T = 60°C)

a.

b.

c.

Fig. 1

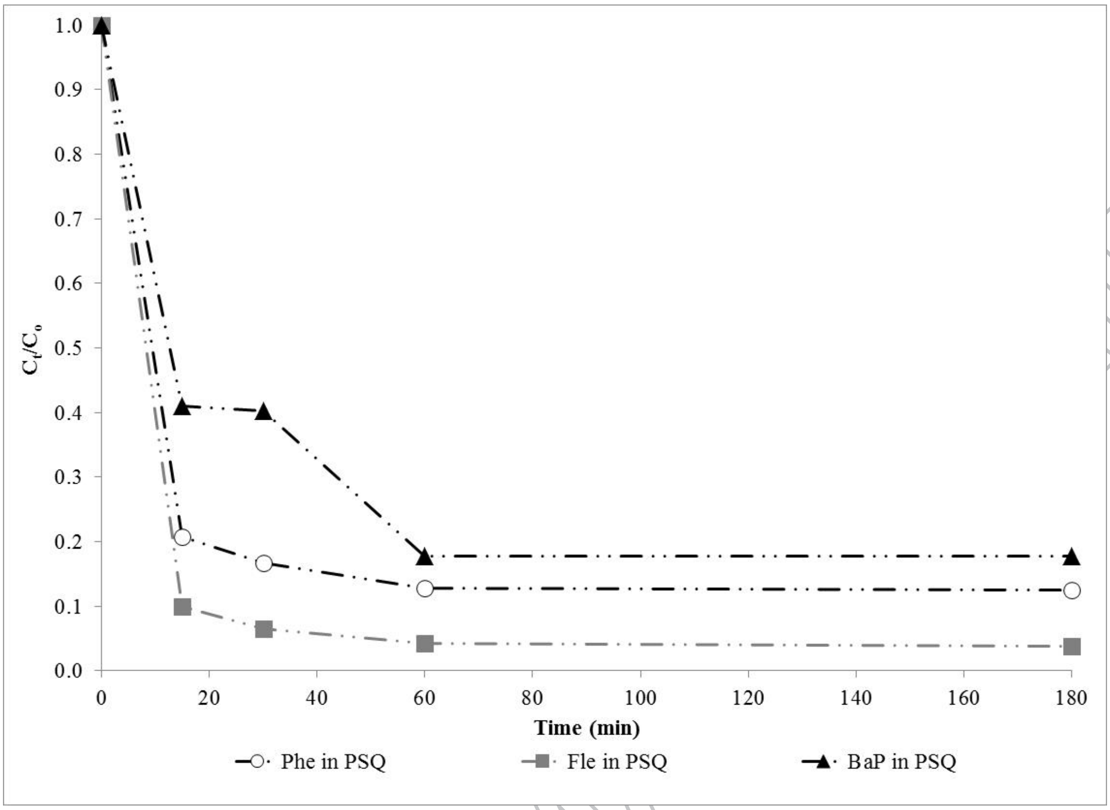
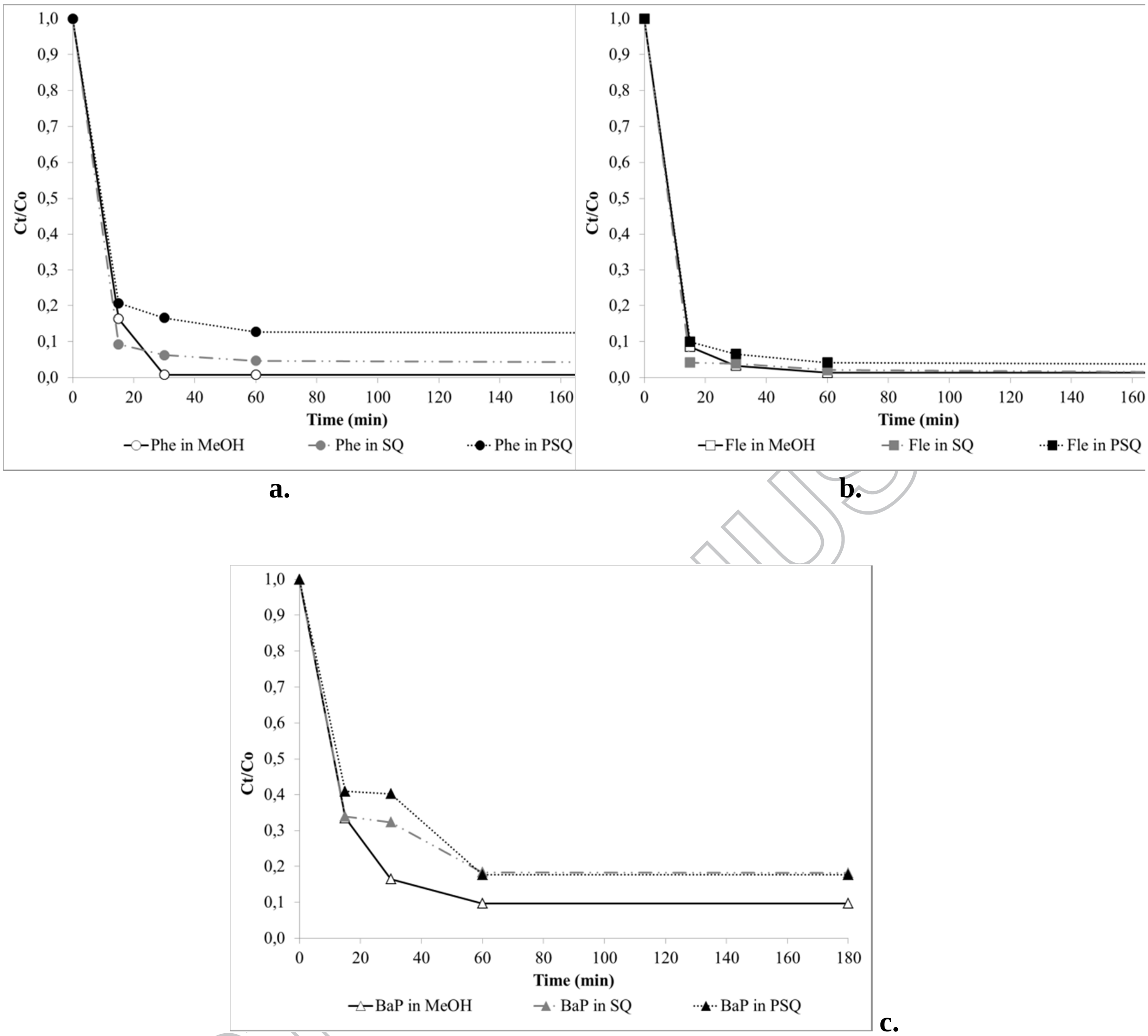

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
C_t/C_o
0
20
40
60
80
100
120
140
160
180
Time (min)
Phe in PSQ
Fle in PSQ
BaP in PSQ

Fig. 2

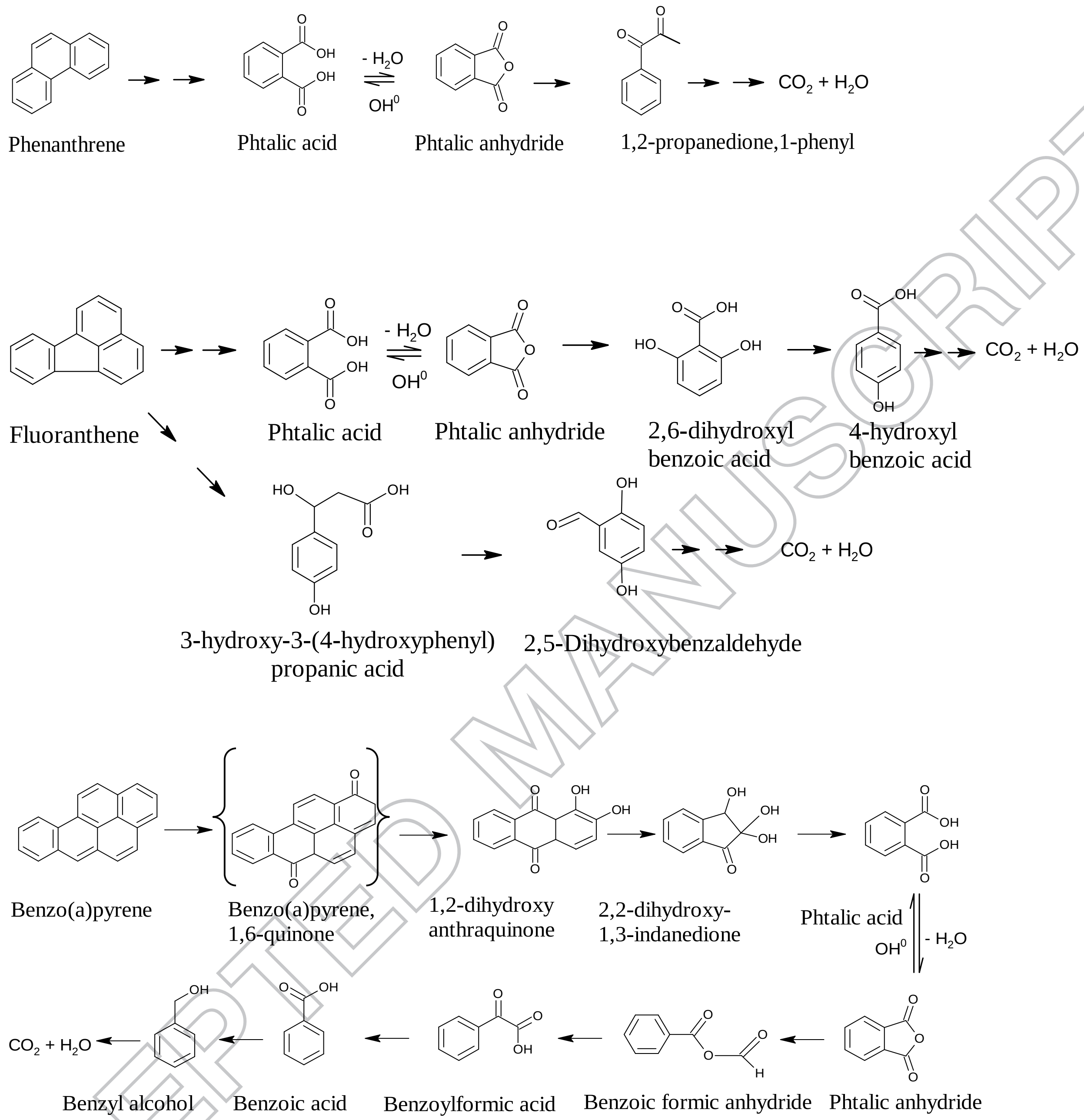

Ct/Co
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
20
40
60
80
100
120
140
160
180
Time (min)
Phe in MeOH
Phe in SQ
Phe in PSQ
Fle in MeOH
Fle in SQ
Fle in PSQ
BaP in MeOH
BaP in SQ
BaP in PSQ

a.

b.

c.

Fig. 3



{ } Hypothesized intermediate (Zeng *et al.* 2000)

→ → Double arrows represent two or more steps

⇄

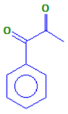
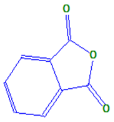
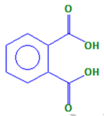
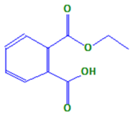
Fig. 4

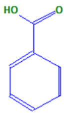
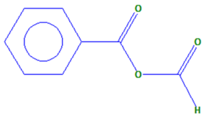
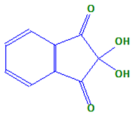
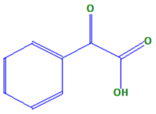
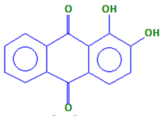
Table 1 Phe, Fle and BaP removal yields (%) obtained after Fenton's oxidation using different H_2O_2 concentrations and reaction time ($[Phe]_i = 7.34$ mg L^{-1}; $[Fle]_i = 7.23$ mg L^{-1} and $[BaP]_i = 6.34$ mg L^{-1})

PAHs molecule	H_2O_2 (g L^{-1})	Oxidation time (min)		
		30	**180**	**360**
1.1.1 Phe (%)	Control	-	-	7
	5.0	16	86	86
	10	78	87	87
	15	**1.1.2** 85	92	93
1.1.3 Fle (%)	Control	-	-	3
	5.0	69	78	98
	10	83	85	98
	15	85	87	98
1.1.4 BaP (%)	Control	-	-	2
	5.0	49	60	61
	10	70	71	88
	15	74	**1.1.5** 79	**1.1.6** 88

Table 2 By products identified and their corresponding parent PAHs, after Fenton oxidation of Phe, Fle and BaP in 1% methanol ($[H_2O_2] = 15$ g L^{-1}, pH = 2.5, $[H_2O_2]/[Fe] = 10/1$, a: products found without derivatization; b: products identified with derivatization)

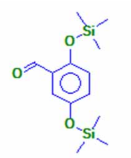
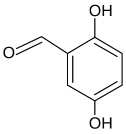
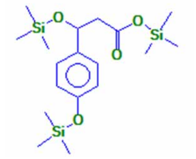
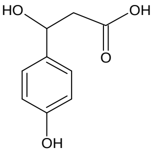
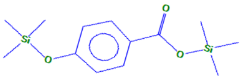
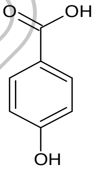
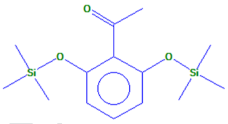
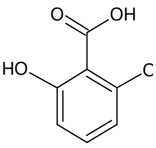
a): Product found without derivatization

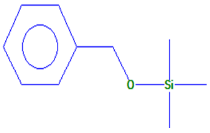
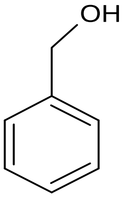
Identified Products	Synonyms	Formula and MW	CAS	PAH parent	N°
	Acetylbenzoyl; 1,2-Propanedione 1-phenyl;	$C_9H_8O_2$ 148	579-07-7	Phe	1
	Phtalic anhydride; 1,3-Isobenzofurandione;	$C_8H_4O_3$ 148	85-44-9	Phe, Fle, BaP	2
	Phtalic acid ; 1,2-Benzenedicarboxylic acid;	$C_8H_6O_4$ 166	88-99-3	Phe, Fle, BaP	3
	Phtalic acid,monoethyl ester; 1,2-Benzenedicarboxylic acid, monoethyl ester;	$C_{10}H_{10}O_4$ 194	2306-33-4	Fle, BaP	4

	Benzoic acid ; Benzenecarboxylic acid;	$C_7H_6O_2$ 122	65-85-0	BaP	5
	Methanol,oxo-,benzoate; Formyl benzoate; Benzoic formic anhydride;	$C_8H_6O_3$ 150	78823-32-2	BaP	6
	Ninhydrin; 1,2,3-Indantrione monohydrate; 2,2-Dihydroxy-1,3-indanedione; Trioxohydrindene monohydrate;	$C_9H_6O_4$ 178	485-47-2	BaP	7
	Phenylglyoxylic acid; Benzoylformic acid;	$C_8H_6O_3$ 150	611-73-4	BaP	8
	Alizarin; 1,2 Dihydroxyanthraquinone; Mordant Red 11;	$C_{14}H_8O_4$ 240	72-48-0	BaP	9

b): Products identified with derivatization

Derived Products	**Corresponding products**

Molecule	**Synonyms**	**Molecule**	**Synonyms**	**Formula and MW**	**CAS**	**PAH parent**	**N°**
	2,5-bis ((trimethylsily)oxy) Benzaldehyde		2,5 Dihydroxybenzaldehyde;	$C_7H_6O_3$ 138	1194-98-5	Fle	10
	Trimethylsilyl 3-((trimethylsilyl)oxy) -3-(4-(trimethylsilyl)oxy) phenyl)propanoate;		3-hydroxy-3-(4-hydroxyphenyl) propanoic acid;	$C_9H_{10}O_4$ 182	76833-34-6	Fle	11
	Benzoic acid,p-(trimethylsiloxy)-,trimethylsilyl ester		4-hydroxylbenzoic acid;	$C_7H_6O_3$ 138	99-96-7	Fle	12
	2',6'-Dihydroxyacetophenone,bis(trimethylsilyl)ether		2,6-dihydroxyl benzoic acid;	$C_7H_6O_4$ 154	303-07-1	Fle, BaP	13

	Silane,(benzyloxy)trimethyl		Benzyl alcohol; Benzenemethanol;	C_7H_8O 108	100-51-6	BaP	14