

OPTIMIZATION OF PAHS OXIDATION FROM A CONCENTRATE OF SOIL ATTRITION USING POTASSIUM PERMANGANATE

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Abstract

The treatment of soils contaminated with organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), by attrition produced large amounts of highly concentrated attrition sludge (PAH – attrition concentrate – PAC). This paper studied the performance of an oxidation process using potassium permanganate (KMnO₄) to degrade PAHs that were initially present in attrition concentrates. The influence of operating conditions (temperature, concentration of KMnO₄ and reaction time) was studied, and these parameters were optimized using a response surface methodology (RSM). The results showed that the temperature and the reaction time had a significant and positive effect on the degradation of PAHs for the experimental domain studied (temperature between 20 and 60°C and reaction time between 1 and 7 hours). The interaction between the temperature and the concentration of KMnO₄ significantly influenced the degradation of the PAHs. The temperature and the concentration of KMnO₄ were the main parameters that influenced the degradation of both phenanthrene (Phe) and benzo [a] pyrene (BaP). For benzo [a] anthracene (BaA), the temperature was the most influential factor. According to our results, the

optimal conditions were defined as $[\text{KMnO}_4] = 0.4 \text{ M}$ for 5.5 h at 60°C. These optimal conditions led to degradations of 42.9%, 40.8%, 41.0% and 46.0% of the total PAHs, Phe, BaA and BaP, respectively.

Keywords

Box-Behnken; Polycyclic aromatic hydrocarbons (PAHs); Permanganate oxidation; Attrition sludge; Degradation

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that are toxic, carcinogenic, mutagenic and resistant to some biological and/or chemical treatments (USEPA, 2008). PAHs are easily adsorbed onto the organic matter present in soils forming persistent micro-pollutants in the environment. A preliminary inventory of the PAHs present in the United Kingdom's environment showed that the PAHs were mainly deposited on the soil, which led to the contamination of widespread sites across the world (Wild and Jones, 1995). Therefore, the remediation of PAH-contaminated soil is necessary to prevent the exposure of humans or fauna to these toxic contaminants.

Various remediation technologies have been developed to remove organic contaminants, such as PAHs, from soils involving one or a combination of physical, chemical, biological and thermal processes. Among the most promising processes, 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 (Gan et al., 2009). The use of an attrition process is a promising option to concentrate the PAHs present in contaminated soil into a smaller volume of fine particles (attrition sludge). Attrition is a physical process of separation based on the creation of frictions and collisions between the particles and the impeller, the attrition cell walls and the deflectors or between the particles themselves, allowing the removal of films around soil particles and/or the deagglomeration of the fine particles which are contaminated. During the attrition process, the concentration of contaminants present in the treated soil (coarse soil fraction) decreases, while a significant increase in the concentration of contaminants is observed in the fine particles that are generated (attrition sludge) (Stražičar and Sešelj, 1999). The abrasion induced during the attrition by the rotation of the helix allows the detachment of the fine particles onto which the PAHs are adsorbed from the uncontaminated coarse particles. Then, the fine particles containing the PAHs were removed from the coarser ones by sieving (Petavy et al., 2009). Because most of organic contaminants are hydrophobic compounds, it is possible to separate them from the uncontaminated soil particles by attrition in the presence of surfactants. Cationic, anionic and nonionic surfactants or modified cyclodextrin, biosurfactant and saponin can be used to enhance the removal of organic contaminants from the surface of the soil particles (Mulligan et al., 2001). Other methods are used to remove the contamination, like cyclodextrine extraction, solid phase extraction (Tenax), microbial incubations, etc. (Biache et al., 2015).

The removal of PAH compounds adsorbed onto the fine particles from contaminated soil using attrition has been widely studied by several researchers (Mouton et al., 2010; Taillard, 2010; Nielsen, 2011; Bisone et al., 2013). Nielsen (2011) showed that attrition effectively treated soil contaminated by PAHs by removing 86% of the PAHs from the 2 – 5 mm soil fraction and 96% from the 5 – 10 mm soil fraction. However, this attrition process generates a concentrate (sludge) that contains huge amounts of PAHs (PAH – attrition concentrate – PAC). Therefore, these

concentrates must be considered hazardous waste and must be adequately treated or disposed of at specialized landfill sites or in incinerators. The costs related to the management of these hazardous wastes would be high due to the toxicity of the concentrates.

The oxidation processes are promising technologies that could be used for the secondary treatment of highly contaminated residues emerging from the treatment of contaminated soils. Indeed, the oxidation processes convert hazardous contaminants, such as PAHs, into non-hazardous or less toxic compounds. Several researchers highlighted the performance of some oxidizing agents, such as ozone (O'Mahony et al., 2006), hydrogen peroxide or Fenton's reagent (Flotron et al., 2005; Ferrarese et al., 2008) and potassium permanganate (KMnO_4) (Brown et al., 2003), to degrade the PAHs present in a solid matrix. Despite his relatively lower oxidation potential ($E_0 = 1.7 \text{ V}$) compared to the others oxidants (eg. O_3 , H_2O_2 , OH^{\cdot} ...), KMnO_4 is an attractive oxidizing agent because of its effectiveness over a wide range of pH values, its stability and its relative low cost (Kao et al., 2008). Permanganate ions can potentially oxidize aromatic hydrocarbons and carbon-carbon double bonds (Dash et al., 2009). The degradation of phenolic endocrine disrupting compounds (2, 4-dichlorophenol, nonylphenol and bisphenol A) that are present in aqueous solutions using potassium permanganate was evaluated by Abe et al. (2001). These authors observed that the application of KMnO_4 (64 mg/L) effectively decomposed each compound (1 mg/L) after 60 min.

Several authors studied the efficiency of this oxidizing agent to degrade PAHs. For example, Brown et al. (2003) reported significant decreases in the concentrations of benzo [a] pyrene (BaP), pyrene (Pyr), phenanthrene (Phe) and anthracene (Ant) present in contaminated soil in the presence of KMnO_4 , with removal yields reaching 72.1%, 64.2%, 56.2% and 53.8%, respectively. Another study conducted by Lemaire et al. (2013a) compared the performance of several oxidants to degrade the PAHs initially present in aged contaminated soil on a bench scale. Their results demonstrated the effectiveness of potassium permanganate, due to its long persistence, compared to the other oxidizing agents tested (hydrogen peroxide, sodium percarbonate and sodium persulfate). Moreover, these authors showed that the degradation of PAHs was positively correlated to the concentration of the oxidant used in the presence of potassium permanganate, which was not observed for the other oxidizing agents, especially those based on radical mechanisms for the degradation of organic compounds (Lemaire et al., 2013a).

However, the degradation of PAHs from environmental samples is a difficult task due to their hydrophobic and refractory characteristics. They can be adsorbed onto the intrinsic components of the soils or diffused into the organic matter. Several studies have reported that the use of a pretreatment enhanced the oxidation efficiency of PAHs from a solid matrix (Lee and Hosomi, 2001; Lundstedt et al., 2006; Usman et al., 2012; Biache et al., 2015). Different methods can be used to desorb the PAHs and therefore increase their availability. Biache et al. (2015) preheated the soil to 100°C for one week before chemical oxidation to increase the availability of the PAHs. This pretreatment was proven to enhance the degradation of PAHs when using chemical oxidation. However, this pretreatment might be very expensive due to the heating costs, limiting the potential application of this treatment at a larger scale.

Another study conducted by Usman et al. (2012) revealed that a pretreatment using a solvent significantly increases the degradation of PAHs from contaminated soil during the oxidation process. These authors found that the most critical factors related to the oxidation efficiency of PAHs from a solid matrix are their unavailability (Usman et al., 2012).

Nowadays, the researches carried out on the PAHs oxidation are mainly achieved using batch experiments in duplicate or triplicate to find the optimal conditions (one parameter at a time) of the oxidation parameters, leading to a large number of experiments. Response surface methodology (RSM) is a statistical method that is useful to study the effects of several factors influencing the responses of interest while performing a limited number of experiments (Ranc et al., 2016). The RSM is a collection of mathematical and statistical methods that can be used to evaluate the influence of several variables in response to interest and to predict this response in the experimental domain (ED) studied (Zaviska et al., 2011). Among the different RSM designs, the Box-Behnken (BB) experimental design has been widely used to optimize various processes including biological and/or chemical remediation technologies (Körbahti et al., 2007; Dong et al., 2009; Sakkas et al., 2010; Yetilmezsoy et al., 2009; Li et al., 2010; Zaviska et al., 2011; Coudert et al., 2012; Mocellin et al., 2016).

The present study focused on the development and the optimization of an oxidation process in the presence of KMnO_4 to degrade the PAHs (total PAHs and/or each PAH molecule) present at high concentrations in a sludge concentrate using an experimental design methodology. The BB experimental design methodology has been successively applied in order to point out the main and interaction effects of the factors on oxidant performance to degrade PAHs from a concentrate.

2 Materials and methods

2.1 Characterization of PAH-attrition concentrate

The PAH-attrition concentrate (PAC) was obtained at the end of an attrition process (Fig. 1) conducted in the presence of a surfactant on a contaminated soil collected from an industrial area. The history of the contamination and the location of the site cannot be provided. Before our experiments, the PAC was dried at 60°C for 24 h and then ground with a porcelain mortar and pestle to provide a homogenous medium, crucial for the application of a RSM. This pretreatment of the PAC will be not required for the application of the oxidation process at a larger scale.

2.2 Experimental set-up and KMnO_4 oxidation assays

The experiments of KMnO_4 oxidation were conducted in 250 mL opaque glass flasks that were hermetically sealed. For the different experiments, the temperature was controlled using a water-bath and checked using a thermometer (Cole-Parmer, Model Thermo Scientific Ertco). The oxidation was conducted without any adjustment of the pH of the solution. The PAC and the oxidation solution were mixed at 250 rpm to obtain good contact between the oxidant and the PAHs. The experiments were

stopped after the desired retention time by filtration through a G6-filter (porosity = 1.5 μm) and soil washing. The solid phase was then dried at 60°C before extracting the residual PAHs.

2.3 Preliminary assays

The preliminary experiments consisted of determining the reasonable solid/liquid ratio that should be used to optimize the operating conditions of the KMnO_4 oxidation process. During these experiments, the same quantity of KMnO_4 was added to the different amounts of PAC (5, 10, 20 and 30 g) to obtain different solid/liquid ratios varying from 5 to 30% (w/v) with a final volume fixed at 100 mL. The concentration of KMnO_4 (required oxidant quantities) was determined based on the stoichiometric amount of permanganate ion required to oxidize each PAH compound initially present in the PAC as reported in the Equation 1 (De Souza e Silva et al., 2009; Simonnot and Croze, 2012). In this equation, the oxidation of PAHs led to the production of manganese dioxide (MnO_2) and CO_2 or organic intermediates (PAH-OX).



Based on the concentration of each PAH compound, the stoichiometric oxidant demand (SOD) was calculated using Equation 2:

$$\text{SOD} = \text{MM}_{\text{oxidant}} * \sum([\text{PAH}_i] * S_i / \text{MM}_{\text{PAHi}}) \quad (2)$$

Where

SOD: Stoichiometric oxidant demand (mg/kg dry soil);

MM_{oxidant}: Molar mass of the oxidant (g/mol);

MM_{PAHi}: Molar mass of each PAH (g/mol);

[PAH_i]: Initial concentration of each PAH (mg/kg);

S_i: Stoichiometric coefficient of PAH in the reaction between the oxidant and PAH.

2.4 Box-Behnken experimental design

In the present study, a BB experimental design was used to determine the optimal conditions for the degradation of PAHs from PAC using KMnO_4 oxidation. Three variables were investigated: (A) temperature, (B) concentration of KMnO_4 and (C) retention time. Due to the semi-volatile characteristics of the PAHs, the influence of the temperature was studied between 20 and 60°C, and the effect of the retention time was evaluated between 1 and 7 h. The low, middle and high levels of each variable, designated as -1, 0, +1, respectively, are presented in Table 1. In a system involving three independent variables, A, B and C, the mathematical relationship between the responses can be defined using a

quadratic (second degree) polynomial equation (Equation 3). A multiple regression analysis was then used to determine the coefficients:

$$Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \quad (3)$$

where

Y :	<i>Process response (dependent variable);</i>
b_0 :	<i>Average value of the different experiments;</i>
b_1, b_2 and b_3 :	<i>Linear coefficients;</i>
b_{12}, b_{13} and b_{23} :	<i>Interaction coefficients between the three factors;</i>
b_{11}, b_{22} and b_{33} :	<i>Quadratic coefficients.</i>

For this series of assays, the experiments were performed with a solid/liquid ratio fixed at 30% (w/v). Therefore, a mass of 30 g of dried PAC was mixed with 100 mL of a KMnO_4 solution with a concentration ranging from 0.1 to 0.4 M. In the present study, the experimental results were analyzed using Design–Expert 8.0 software.

2.5 Influence of a pretreatment using solvent extraction on PAHs oxidized from PAC

To improve the performances of PAHs degradation, additional tests were performed, including the pretreatment of PAC using two different solvents to increase the availability of PAHs initially present in the PAC. As the solubility of PAHs, which are highly hydrophobic compounds, is higher in solvents than in aqueous solutions, hexane and methanol were used to enhance the desorption and the solubilization of the contaminants to improve the degradation of PAH compounds by rendering them more available to oxidant attack. The solvents, hexane and methanol (Fisher, Canada), were tested at different concentrations fixed at 5% and 20% (v/v). Homogenous slurry (30%, w/v) was obtained by mixing the PAC with the solvent at 250 rpm for 1 h at room temperature. Then, the KMnO_4 oxidation of PAHs was conducted using the optimal conditions defined and presented in Section 3.3.

2.6 Analytical methods

2.6.1 Operating parameters

Total carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) were analyzed by a CHNS Leco Analyzer. The particle size distribution was measured using a Laser Particle Size Analyzer (Particle Laser Scattering

LA-950V2, Japan). The physical and chemical characteristics of the sample were determined by the Agri-Direct laboratory (Quebec, Canada).

2.6.2 Extraction and analysis of PAHs

The residual concentration of PAHs present in the PAC was determined from GC-MS analysis after extraction performed on 5 g of dry soil in the presence of 25 mL of dichloromethane for 30 min in an ultrasonic bath. Two recovery standards, pyrene-D₁₀ and chrysene-D₁₂, were added to the PAC sample to confirm the adequacy of the solid/liquid extraction process. The extraction solution was purified using silica and stored in hermetically sealed vials at -4°C.

The residual concentrations of the PAHs were measured by GC-MS (Perkin Elmer, model Clarus 500) that was equipped with a DB-50 (30 m × 0.25 mm × 0.25 µm) column. External calibrations were performed at the beginning of each series of measurements with standard solutions containing a mix of 27 PAHs.

3 RESULTS AND DISCUSSION

3.1 PAC characterization

Table 2 summarized the main physico-chemical characteristics of the PAC, and Table 3 presented the initial concentrations of the 27 PAHs listed by the Minister of Sustainable Development, Environment and the Fight against Climate Change (MDDELCC). Conforming to these results, the PAC initially contained 12.3% C, 0.22% N, 0.13% S and 2,975 mg.kg⁻¹ of PAHs. The particle size distribution of the PAC revealed that approximately 90% of the particles had a size below 250 µm. Among the PAHs present in the PAC, 11 molecules of PAHs were individually followed in the present study due to their high concentrations. As reported in the results presented in Table 3, PAH compounds with 3- to 5-rings, such as Fle (511 mg.kg⁻¹), Pyr (351 mg.kg⁻¹), Phe (340 mg.kg⁻¹), Chry (219 mg.kg⁻¹), BaA (218 mg.kg⁻¹), BbF (207 mg.kg⁻¹) and BaP (202 mg.kg⁻¹), were present in higher concentrations than the compounds having 6-rings, such as Ind[1,2,3cd]P (119 mg.kg⁻¹), B[g,h,i]P (143 mg.kg⁻¹), Dib[a,l]P (69.8 mg.kg⁻¹) and Dib[a,i]P (101 mg.kg⁻¹).

3.2 Preliminary experiments

Preliminary experiments were conducted to determine the reasonable solid/liquid ratio that should be used to optimize the operating conditions of the KMnO₄ oxidation process (5%, 10%, 20% and 30%). Table 4 presented the total degradation yields obtained and the amount of PAHs removed from the PAC depending on the solid/liquid ratio used. The results showed that the highest PAH degradation yields (49.2%) were recorded for the experiments conducted with 5% solids. However, when combining the consumption of KMnO₄ and the amount of PAHs removed from the PAC, the increase in the solid/liquid

ratio led to an increase in the amount of the PAHs that degraded from the PAC. The highest degradation of PAHs (22.8 mg) was obtained for the experiment conducted with 30% solids. Therefore, the solid/liquid ratio chosen for the following assays was 30%.

3.3 Evaluation of experimental parameters on oxidant performances

The degradation percentages of total PAHs (27 PAHs) and of 11 individual PAH compounds obtained during the different experiments were presented in Supplementary Table 1. According to our results, the degradation of PAHs varied from 21 – 47% for total PAH degradation (for 27 PAHs), 11 – 50% for Phe, 5 – 50% for Fle, 1 – 54% for Pyr, 14 – 51% for BaA, 15 – 65% for Chry, 15 – 43% for BbF, 7 – 47% for BaP, 21 – 65% for Ind[1,2,3cd]P, 4 – 54% for B[g,h,i]P, 3 – 78% for Dib[a,l]P and 11 – 63% for Dib[a,i]P. The large variations observed in the PAH degradation yields indicated that the ED studied in the present study was well-defined. Despite the differences in the chemical structures of the different PAH compounds studied, the performances of degradation were similar for some compounds with different structures. Brown et al. (2003) observed that the oxidation of PAHs in the presence of permanganate potassium is closely dependent of the chemical reactivity of the targeted compound. The reactivity order for a mixture of six PAH towards permanganate ion was defined as follows BaP > Pyr > Phe > Ant > Fle > Chry. In our study, similar results were obtained for some operating conditions (Supplementary Table 1 – Runs 3; 4; 7; 8 and 9) with average degradation performances following the same order: BaP (45%) > Pyr (32%) > Chry (23%) > Fle (22%). However, the literature mentioned that the oxidation of PAHs increased with an increase in the number of polycyclic rings. As reported by these authors, this might be because the energy required to overcome the aromatic character of a polycyclic ring was lower than for benzene (Brown et al., 2003; Forsey et al., 2010; Wang et al., 2015). Forsey et al. (2010) also reported that other factors such as steric interactions, oxidation conditions and the connectivity of aromatic rings can affect the reaction rate of PAHs under certain conditions. On the other hand, De Souza e Silva et al. (2009) highlighted that the oxidation of Phe from contaminated soils in the presence of KMnO_4 was much easier than the oxidation of Pyr, even though the Pyr has a higher number of polycyclic rings than Phe.

As reported by our results, it appeared that the highest degradation yields were obtained when the temperature was fixed at 60°C for the total PAHs, Phe, Fle, Chry, BaA, Ind[1,2,3cd]P and B[g,h,i]P and at 40°C for Pyr, Dib[a,l]P and Dib[a,i]P.

The results obtained were analyzed using the Expert Design software 8.0 to determine the relationship between the response and the different factors. The statistical significance of these models was evaluated using ANOVA. Table 5 presented the F values and $\text{Pr}>F$ values obtained for the mathematical models established to predict the degradation of total PAHs, Phe, BaA and BaP because the models defined for the other PAH compounds were not significant. If the “ $\text{Pr}>F$ ” value is lower than 0.05, the model and/or the factor is significant.

To assess the adequacy of the models, it is important to evaluate if there is a lack of fit to the models. A significant lack of fit to a mathematical model is explained by the fact that, for few experimental values, the differences observed between the experimental and predicted values are slightly higher than the variations measured between the five replicates conducted at the center of the ED (Coudert et al., 2012). Therefore, a non-significant lack of fit is preferable because this indicates that the mathematical models fit well with the experimental values. Conforming to our results, the lack of fit was not significant for the different models established. Fig. 2 presents the variations between the actual (experimental) values and the predicted values obtained for the degradation of total PAHs, Phe, BaA and BaP. The adequacy of the proposed models was confirmed by the satisfactory correlations that were observed between the experimental and predicted values.

The correlation coefficients (R-Squared, Adj R-Squared and Pred R-Squared), as presented in Table 6, ranged from 0.81 to 0.96 for the model defined for the degradation of total PAHs and ranged from 0.70 to 0.94 for the models established for the degradation of Phe, BaA and BaP. These R^2 values indicated that 4 to 30% of the experimental values could not be explained by the empirical models. As reported by Joglekar and May (1987), the R-squared values should be higher than 0.80 for a good fit between the mathematical models and the experimental values. The values of Adequation precision (Adeq precision), which evaluates the signal to noise ratio, were equal to 22.0, 15.0, 11.7 and 17.1 for the models defined to predict the degradation of total PAHs, Phe, BaA and BaP, respectively. A ratio greater than 4 is desirable (Kumar et al., 2008). The values obtained in the present study supported the suitability of the models established to predict the degradation of total PAHs, Phe, BaA and BaP.

The mathematical models, in terms of coded factors, obtained to predict the degradation of total PAHs, Phe, BaA and BaP were presented in Equations 4 to 7.

$$\text{Total PAHs}(\%) = 29.9 + 6.05A + 1.30B + 2.75C + 5.91AB + 4.19A^2 - 1.72C^2 \quad (4)$$

$$\text{Phe}(\%) = 20.33 + 10.28A + 3.87B + 2.24C + 5.16AC + 5.86BC + 10.89A^2 \quad (5)$$

$$\text{BaA}(\%) = 41.61 + 4.15A + 2.70B + 2.62C + 6.44AB + 6.96A^2 - 10.62B^2 - 8.03C^2 \quad (6)$$

$$\text{BaP}(\%) = 45.10 + 6.14A + 5.38B + 7.36C - 12.99B^2 - 16.18C^2 \quad (7)$$

Where *A* represents the Temperature, *B* represents the concentration of KMnO_4 and *C* represents the reaction time.

From Equations 4 to 7 and the results presented in Table 6, it can be seen that the temperature had a significant and positive influence on the different responses studied for the experimental domain studied. The positive influence of the temperature between 20 and 60°C indicated that an increase in the temperature led to an increase in the degradation yields for the total PAHs, Phe, BaA and BaP. According to our results, the concentration of KMnO_4 had a significant and positive effect on the degradation of Phe and BaP, whereas the influence of reaction time was only significant for the degradation of total PAHs

and BaP. These results were in accordance with the observations made by Xu et al. (2005) and Aleboye, et al. (2009) on the decolorization of dye. Indeed, Xu et al. (2005) reported that the concentration of potassium permanganate and the temperature had significant effects on the decolorization efficiency. Most of dye solutions can be decolorized effectively within 30 min. However, Aleboye, et al. (2009) reported that the effect of temperature on the performances of dyes decolorization was not significant and that the color removal was enhanced by increasing the amount of potassium permanganate. The difference between the results could be explained by the different chemical structures of the targeted organic compounds and the degradation of the double bonded dye molecules which does not require significant activation energy. Hence, the degradation rates of this group of dyes when using potassium permanganate were quite faster than those of other organic compounds.

The value of each coefficient present in the mathematical equation (defined in terms of the coded factor) indicated the importance of each factor on the response. Equations 4 to 7 showed that the degradation of total PAHs, Phe and BaA was mainly influenced by the temperature, whereas the degradation of BaP was mainly and positively impacted by the reaction time.

Figure 3 presented the three-dimensional response surface of the degradation Total PAHs (Fig. 3a.), Phe (Fig. 3b.), BaA (Fig. 3c.) and BaP (Fig. 3d.) depending on the temperature (factor A) and the concentration of KMnO_4 (factor B) to have a better understanding of the effects of experimental parameters on PAH degradation. Figure 4 illustrated the significant influence of the interaction AC (temperature and retention time) and BC (concentration of KMnO_4 and retention time) on the degradation of Phe.

3.4 Optimization of the operating conditions for the oxidation of PAHs

To identify the optimal conditions, only the response for which significant mathematical models were obtained can be considered. The optimal operating conditions were determined based on maximizing the degradation of the total PAHs, Phe, BaA and BaP. Thus, the Expert Design 8.0 proposed numerous solutions (not shown) classified by the order of desirability. The optimal conditions selected were as $[\text{KMnO}_4] = 0.4 \text{ M}$ for 5.5 h at 60°C . Additional assays were conducted in triplicate with the optimized conditions to validate the results. Supplementary Table 2 presented a comparison between the predicted values and the experimental results. According to our experiments, the degradation efficiencies of the total PAHs, Phe, BaA and BaP obtained under the optimal conditions were estimated to be 42.9%, 40.8%, 41.0% and 46.0%, respectively. It seemed that the oxidation process efficiency was slightly over-estimated by the mathematical equations for the degradation of total PAHs, Phe and BaA under the optimal conditions. The variations between the experimental and predicted values obtained for the degradation of total PAHs, Phe and BaA were approximately 9.3%, 10% and 20%, respectively. This may be due to the heterogeneity and complexity of the matrix (attrition sludge) or to the lower R-squared values, especially for the degradation of Phe and BaA. However, these error values were close to the coefficient of variation obtained for the different models (data not shown). For the degradation of BaP,

the experimental and predicted values were similar (error = 5.5%). Generally, the variations between the predicted and experimental PAH degradation yields for the four significant models were close or similar to the CV values of the mathematical models, allowing us to validate the optimal conditions.

Figure 5 compared the concentration of the 11 PAH compounds present in high concentrations in the PAC before and after KMnO_4 oxidation under optimal conditions. The application of KMnO_4 treatment decreased the concentrations of Fle, Pyr, Chry and BbF from 511 to $316 \pm 25 \text{ mg.kg}^{-1}$, from 351 to $215 \pm 22 \text{ mg.kg}^{-1}$, from 218 to $141 \pm 10 \text{ mg.kg}^{-1}$ and from 207 to $106 \pm 16 \text{ mg.kg}^{-1}$, respectively. This oxidation process allowed for the degradation of 38, 39, 36 and 49% of Fle, Pyr, Chry and BbF, respectively. The residual concentrations of PAHs initially present in lower concentrations were as follows: $77.7 \pm 4.6 \text{ mg Ind}[1,2,3\text{cd}]\text{P.kg}^{-1}$, $85.1 \pm 6.3 \text{ mg B}[g,h,i]\text{P.kg}^{-1}$, $27.9 \pm 1.7 \text{ mg Dib}[a,l]\text{P.kg}^{-1}$ and $49.1 \pm 7.32 \text{ mg Dib}[a,i]\text{P.kg}^{-1}$. For these compounds, the oxidation process allowed for the degradation of 35, 41, 60 and 51% of Ind[1,2,3cd]P, B[g,h,i]P, Dib[a,l]P and Dib[a,i]P, respectively. According to these results, the degradation yields obtained for the different PAH compounds ranged from 35 to 60% under the optimal conditions. These low percentages of PAH degradation could be because the amount of oxidant added to the matrix corresponded to 4*SOD based on the concentrations of the 27 PAHs listed by MDDELCC. This value did not include the presence of other organic compounds that could react with the KMnO_4 . High contents of organic matter in the soil and therefore in the attrition sludge (12.3%) can consume significant amounts of oxidant during the oxidation process. Chen et al. (2009) found that a strong adsorption of PAHs and the competition with organic matter limited the degradation rate. However, the amount of KMnO_4 added was limited to 4*SOD to ensure the economic feasibility of the process. Another explanation could be the low availability of the PAHs present in the PAC. Lemaire et al. (2013b) showed that the degradation of PAHs was limited due to their low availabilities. The highest PAH degradation rate obtained from spiked soil was 55%, but it reached only 30% in aged soils. Therefore, the addition of a solvent to improve the availability of PAHs may be of interest.

3.5 *Effects of solvents on PAH oxidation from PAC*

Figure 5 presented the effects of different solvents on PAH oxidation. For the majority of the molecules (Phe, Fle, Pyr, BaA, Chry, BbF and Dib[a,i]P), the use of a solvent improved the degradation compared to the use of KMnO_4 alone. In the presence of hexane (5%), the degradation yields increased from 41 to 59% for Phe, from 38 to 50% for Fle, from 39 to 55% for Pyr, from 41 to 50% for BaA, from 36 to 40% for Chry and from 51 to 71% for Dib[a,i]P. In contrast, the degradation yields of BaP, Ind[1,2,3cd]P, B[g,h,i]P and Dib[a,l]P decreased from 46 to 44%, 35 to 32%, 41 to 32% and 60 to 52%, respectively, when using 5% hexane. According to these results, the addition of a solvent slightly increased the availability and therefore the degradation of some PAH compounds. The previous study of Wang et al. (2015) showed

that the extraction technology by using hexane as solvent to enhance the removal of light PAHs was very effective. Conforming to their results, huge amounts of light PAHs have been extracted, especially for Phe with removal yields beyond 90%. However, a part of the methanol or hexane might be degraded by KMnO_4 , increasing the amount of oxidant required. Therefore, the addition of a solvent to enhance the availability of PAHs was not efficient enough to compensate for the increase in KMnO_4 required and the decrease in the performance observed for some PAH compounds.

4 Conclusion

The efficiency of PAH chemical oxidation from PAC in the presence of KMnO_4 was studied using an experimental design methodology. The treatment of data by the software produced non-significant models for most of the molecules (Fle, Pyr, Chry, BbF, Ind[1,2,3cd]P, B[g,h,i]P, Dib[a,l]P and Dib[a,i]P), and significant for only the degradation of total PAHs, Phe, BaA and BaP.

The BB design highlighted that temperature had a positive effect on the degradation of total PAHs, Phe, BaA and BaP. The concentration of KMnO_4 had a positive effect on the degradation of Phe and BaP, whereas the reaction time impacted the oxidation of total PAHs and BaP. The temperature was the main parameter that influenced the degradation of the total PAHs, Phe and BaA, whereas the degradation of BaP was mainly influenced by the reaction time.

The optimal conditions were defined as $[\text{KMnO}_4] = 0.4 \text{ M}$ for 5.5 h at 60°C . The optimal conditions yielded degradations of 42.9%, 40.8%, 41.0% and 46.0% of the total PAHs, Phe, BaA and BaP, respectively. The oxidation performance of some PAH compounds could be improved by adding a solvent, but this improvement was not efficient enough to compensate for the increased amount of KMnO_4 required and the reduction in the performance observed for some PAH compounds. According to our results, the optimal oxidation conditions allowed the diminution of the concentration of only two molecules of PAHs among the eleven PAHs compounds followed; indicating that the concentrate could not be considered as non-hazardous after oxidation treatment even if toxicity was reduced. The results of the bench scale studies demonstrated that chemical oxidation of PAHs initially present in highly contaminated samples using permanganate can occur. Our results highlighted that this treatment significantly enhanced the degradation of PAHs and mainly the degradation of high-molecular weight PAHs (with five or six aromatic rings), which were proven to be more recalcitrant to biological degradation. Besides its lower reactivity, the performances of KMnO_4 to degrade PAHs from PAC were better which can be due to its high persistence compared to hydroxyl radicals (very short life) and its lower sensitivity to pH. The application of chemical pre-oxidation can be a promising technique for the remediation of environmental matrices contaminated by recalcitrant PAHs to overcome the recalcitrance of PAHs to biodegradation. However, the performances of the process developed should be enhanced to meet the regulations established by the MDDELCC. The combination of KMnO_4 oxidation with another

oxidation process (Fenton) might be of interest to reach the limit concentration established by MDDELCC. Further experiments should be performed to identify the by-products obtained from permanganate oxidation of PAHs and to compare the toxicity of these degradation products to original PAHs.

NOMENCLATURE

ANOVA	Analysis of variance
BaA	Benzo [a] anthracene
BaP	Benzo [a] pyrene
BBD	Box-Behnken
BbF	Benzo [b] fluoranthene
B[ghi]P	Benzo [g,h,i] perylene
Chry	Chrysene
Dib[a,i]P	Dibenzo [a,i] pyrene
Dib[a,l]P	Dibenzo [a,l] pyrene
ED	Experimental Domain
Fle	Fluoranthene
Ind[1,2,3cd]p	Indeno [1,2,3-cd] pyrene
PAC	PAHs-attrition concentrate
PAHs	Polycyclic aromatic hydrocarbons
Phe	Phenanthrene
Pyr	Pyrene
RSM	Response surface methodology
SOD	Stoichiometric oxidant demand

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Table 1 *Experimental domain studied for the optimization of PAHs degradation from PAC using RSM*

Factor	Unit	Experimental domain		
		Minimum value	Maximum value	Middle value
		(-1)	(+1)	(0)
A: Temperature	°C	20.0	60.0	40.0
B: [KMnO ₄]	M	0.10	0.40	0.25
C: Reaction time	hours	1.00	7.00	4.00

Table 2 Physical and chemical characteristics of the PAC

Parameters	Value
pH	7.50
Organic matter (%)	5.20
Carbon (%)	12.3
Hydrogen (%)	0.60
Azote (%)	0.22
Sulfur (%)	0.13
Aluminium (Al) (ppm)	694
Cation Exchange Capacity (CEC) (meq/100g)	60.7

Table 3 Concentrations of PAHs (mg/kg) in PAC

Name	Abbreviation	Concentration (mg/kg)	Compound Followed
Naphtalene	Nap	9.40	
2-Methyl Naphtalene	2-MNap	3.88	
1-Methyl Naphtalene	1-MNap	4.46	
1,3-Dimethylnaphtalene	1,3-MNap	6.22	
Acenaphthylene	Acyl	4.06	
Acenaphtene	Ace	33.6	
2,3,5-Trimethyl Naphthalene	2,3,5-MNap	0.90	
Fluorene	Flu	35.3	
Phenanthrene	Phe	340	√
Anthracene	Ant	69.9	
Fluoranthene	Fle	511	√
Pyrene	Pyr	351	√
Benzo [c] phenanthrene	BcP	29.5	
Benzo [a] anthracene	BaA	218	√
Chrysene	Chry	219	√
Benzo [b] fluoranthene	BbF	207	√
Benzo [j] fluoranthene	BjF	98.8	
Benzo [k] fluoranthene	BkF	114	
7,12-Dimethylbenzo[a]anthracene	DMBA	1.63	
Benzo [a] pyrene	BaP	202	√
3-Methylcholanthrene	3-MC	13.8	
Indeno [1,2,3-cd] pyrene	Ind[1,2,3cd]P	119	√
Dibenzo [a,h] anthracene	Dib[a,h]A	47.1	
Benzo [g,h,i] perylene	B[g,h,i]P	143	√
Dibenzo [a,l] pyrene	Dib[a,l]P	69.8	√
Dibenzo [a,i] pyrene	Dib[a,i]P	101	√
Dibenzo [a,h] pyrene	Dib[a,h]P	21.2	
Total		2 975	

Table 4 Influence of the solid/liquid ratio on the degradation of total PAHs by KMnO_4 oxidation
($T = 20^\circ\text{C}$, $[\text{KMnO}_4] = 0.2 \text{ M}$, $t = 3 \text{ h}$)

Solid/liquid ratio (% w/v)	5.0	10	20	30
Degradation yields (%)	49.2 ± 2.4	30.3 ± 1.0	39.2 ± 7.3	38.9 ± 7.9
Quantity of PAHs removed (mg)	4.83 ± 0.24	5.87 ± 0.22	15.4 ± 2.9	22.8 ± 4.7

Table 5 Results from ANOVA for Response Surface Quadratic Model for the degradation of total PAHs, Phe, BaA and BaP from PAC

Reponse	Source	Sum of square	df*	Mean square	F value	Pr>F	Conclusion
Total PAHs	Model	587	6	97.7	36.3	<0.0001	Significant
	Residual	24.2	9	2.69			
	Lack of fit	14.2	5	2.84	1.14	0.46	Not Significant
	Pure error	10.0	4	2.50			
Phe	Model	1750	6	292	20.9	< 0.0001	Significant
	Residual	140	10	14.0			
	Lack of fit	103	6	17.2	1.88	0.2818	Not Significant
	Pure error	36.7	4	9.16			
BaA	Model	1350	7	193	11.1	0.0009	Significant
	Residual	157	9	17.4			
	Lack of fit	65.8	5	13.2	0.58	0.7211	Not Significant
	Pure error	91.2	4	22.8			
BaP	Model	2889	5	578	34.1	< 0.0001	Significant
	Residual	187	11	17.0			
	Lack of fit	163	7	23.3	3.97	0.1003	Not Significant
	Pure error	23.5	4	5.87			

Fle, Pyr, Chry, BbF, Ind(1.2.3 cd)P, B(g.h.i)P, Dib(a.l)P, Dib(a.i)P: Mathematical models Not Significant

* *df: degree of freedom*

Table 6 Significance of mathematical models and influencing factors for the degradation of total PAHs, Phe, BaA and BaP from PAC according to experimental design

Reponses	Model – Conclusion	Influencing factors	R ² Values			
			R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
Total PAHs	Significant	A, C, AB, A ²	0.96	0.93	0.81	22.0
Phe	Significant	A, B, AC, BC, A ²	0.93	0.88	0.74	15.0
BaA	Significant	A, AB, A ² , B ² , C ²	0.90	0.82	0.70	11.7
BaP	Significant	A, B, C, B ² , C ²	0.94	0.91	0.82	17.1

A: Temperature

B: [KMnO₄]

C: reaction time

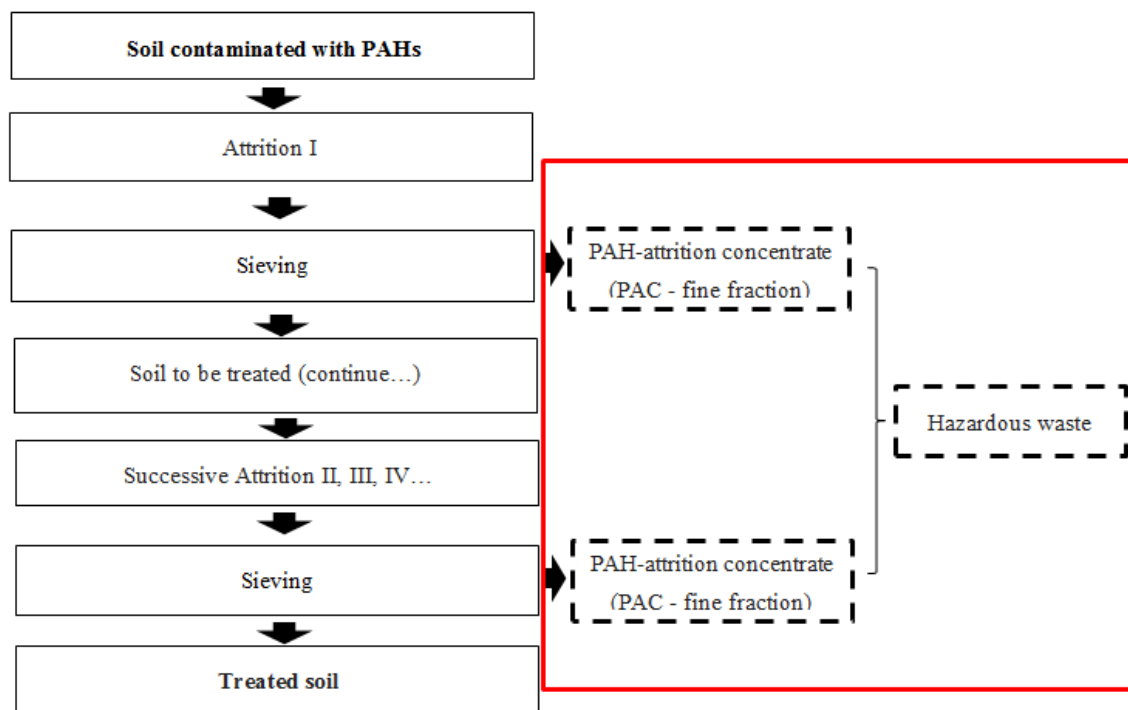


Figure 1 Schema of successive attrition process (Nielsen, 2011)

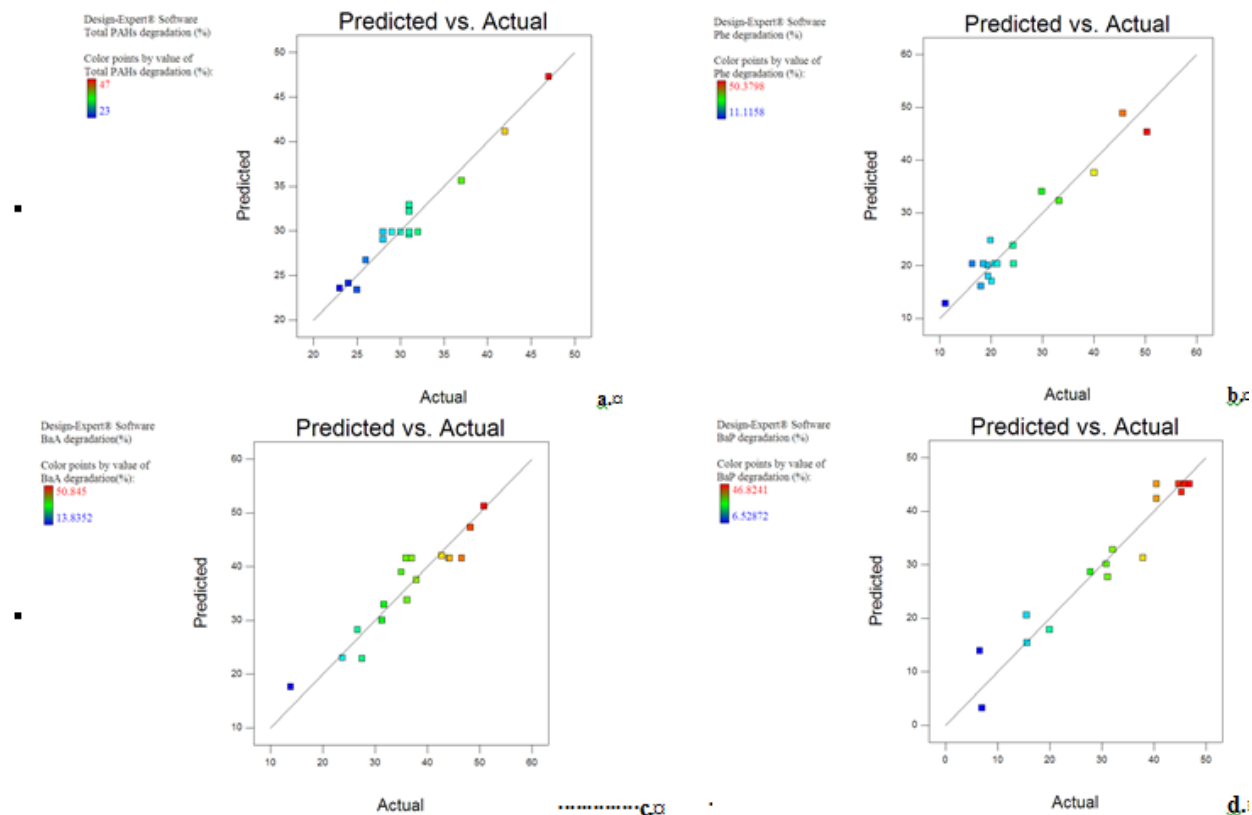


Figure 2 Comparison of actual and predicted values defined for the degradation of total PAHs (a.), Phe (b.), BaA (c.) and BaP (d.) from PAC

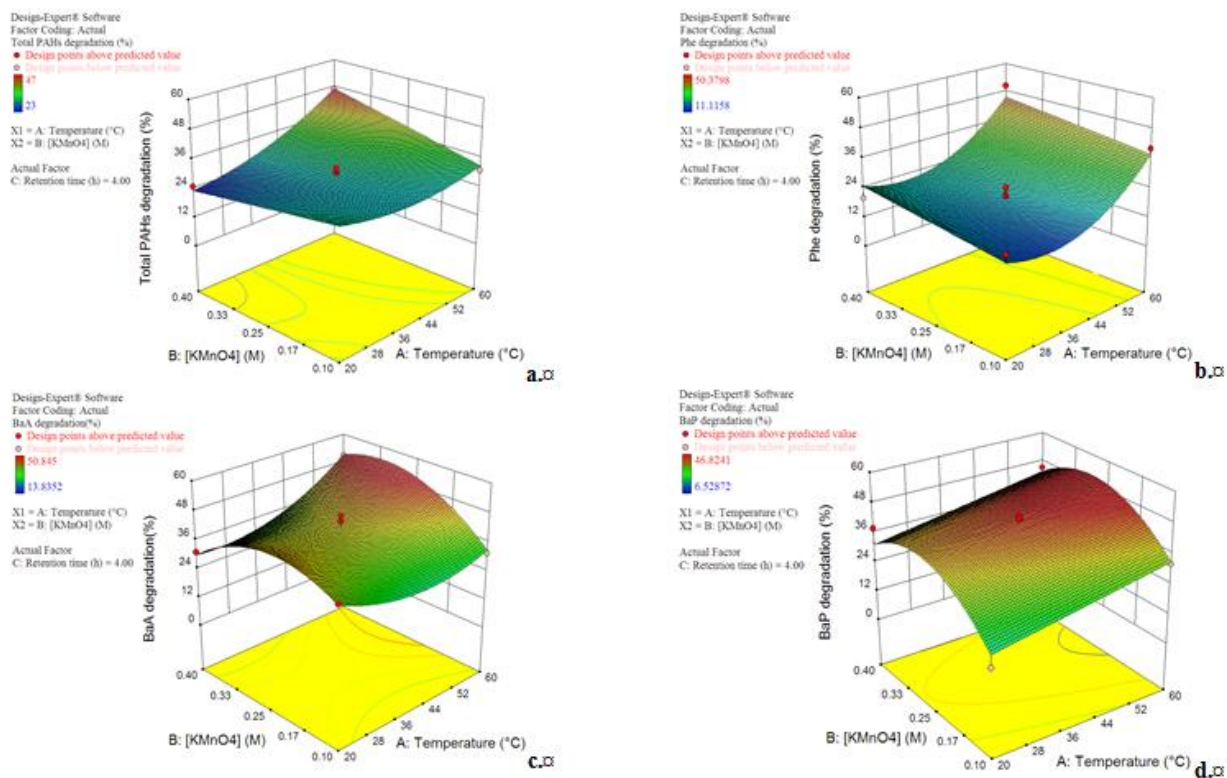


Figure 3 Effect of temperature and KMnO_4 concentration onto the degradation of total PAHs (a.), Phe (b.), BaA (c.) and BaP (d.) using a 3D response surface after 4 h of reaction

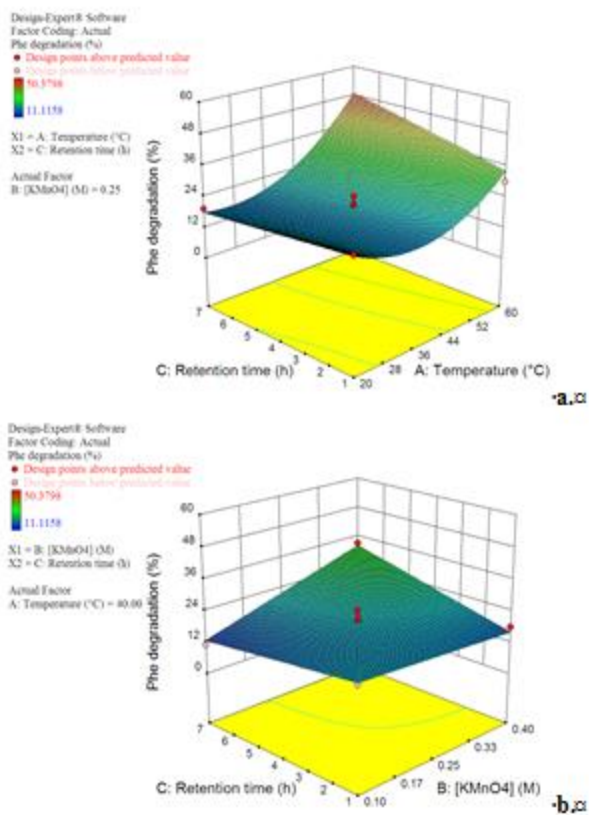


Figure 4 Phe degradation as a function of temperature and retention time with concentration of KMnO_4 fixed at 0.25 M (a.) and as a function of KMnO_4 concentration and retention for a temperature of 40°C (b.)

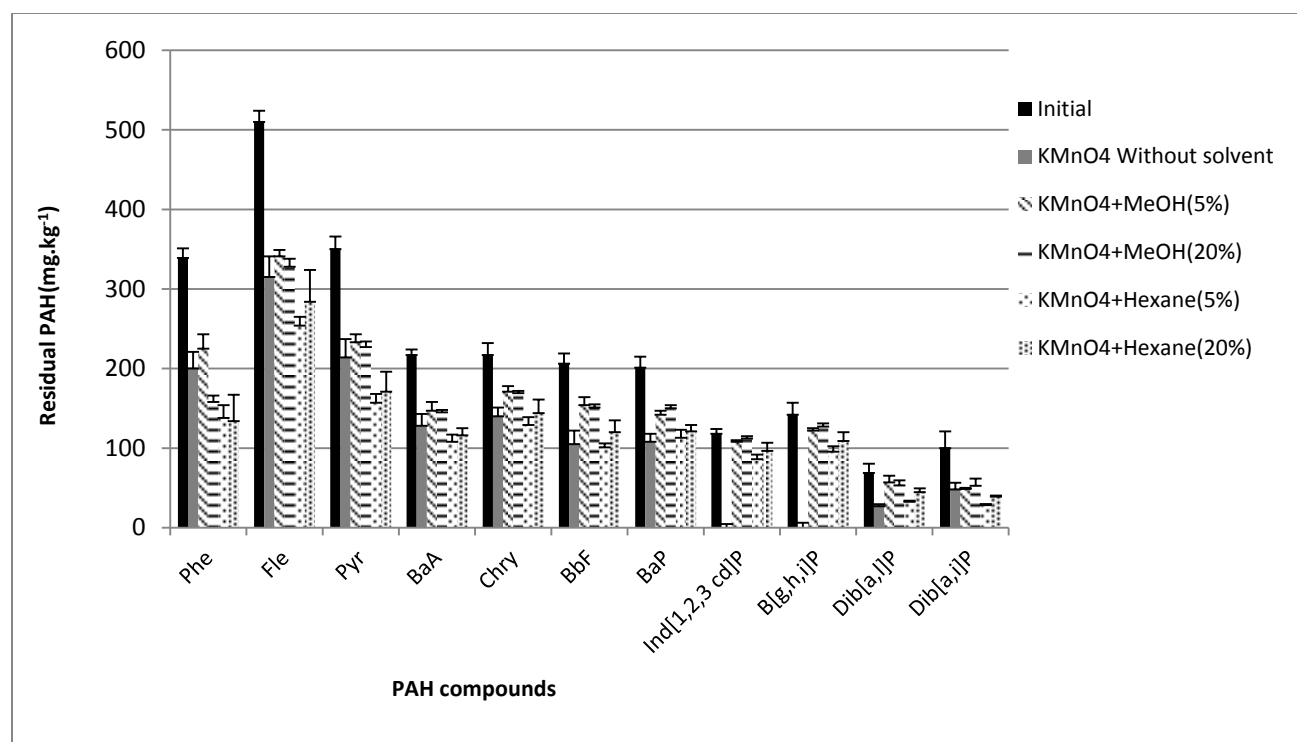


Figure 5 Effect of solvent on the efficiency of PAHs oxidation