



PAHs soil decontamination in two steps: Desorption and electrochemical treatment

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ABSTRACT

The presence of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in soils poses a potential threat to human health if exposure levels are too high. Nevertheless, the removal of these contaminants presents a challenge to scientists and engineers. The high hydrophobic nature of PAHs enables their strong sorption onto soil or sediments. Thus, the use of surfactants could favour the release of sorbed hydrophobic organic compounds from contaminated soils. In this work, five surfactants, namely Brij 35, Tergitol NP10, Tween 20, Tween 80 and Tyloxapol, are evaluated on the desorption of PAHs [benzenanthracene (BzA), fluoranthene (FLU), and pyrene (PYR), single and in mixture] from a model sample such as kaolin. In all cases, the best results were obtained when Tween 80 was employed. In order to obtain the global decontamination of PAHs, their electrochemical degradation is investigated. It is concluded that the order of increasing degradation for single compounds is BzA > FLU > PYR when they are subject to the same electrochemical treatment. In addition, there is a direct relationship between the ionization potential and the electrochemical degradation of PAH.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment. PAHs emitted into the atmosphere by natural processes (e.g. forest fires) or industrial sources are largely adsorbed on particulate matter in the atmosphere. Then, adsorbed PAHs can be deposited into aquatic and soil environments by fallout, a process which subsequently leads to water and soil pollution. In a soil environment, the behaviour of PAHs is closely related to their distribution and transportation from soil components such as clay minerals and organic matter [1]. The levels of these compounds in the environment are regulated by government agencies due to the genotoxicity of some high molecular weight PAHs [2]. These PAHs can have detrimental effects on both the flora and fauna of affected habitats through uptake and accumulation in food chains. In some instances, they may also pose serious health problems to humans and/or cause genetic alterations.

Toxic PAHs are persistent, and these molecules are strongly adsorbed on soils, sludges or sediments because of their strong hydrophobicity. This feature makes them less bioavailable, while it simultaneously limits conventional remediation measures. PAHs removal from soils and aquifers by natural attenuation mechanisms or traditional remediation efforts, such as pump-treat, turns out to

be a slow process due to the low solubility of these compounds in water [3].

Therefore, the addition of different water miscible solvents, especially surfactants, is a natural first step to enhance PAH solubility. PAHs are desorbed with surfactants through solid-liquid equilibrium, and the PAHs present in the collected solution could be degraded in a second stage by an adequate treatment.

Surfactants are classified into anionic, cationic and nonionic according to the ionic and hydrophilic characteristics. Surfactants are amphiphilic compounds composed of two portions: a hydrophilic head and one or more hydrophobic tails. Consequently, they could exhibit high solubility in water or in hydrophobic phase, such as PAHs, depends on the balance between both portions. This fact enables surfactants to enhance the solubility of the contaminant through micellar solubilisation. Beyond a certain concentration, referred to as the critical micelle concentration (CMC), aggregations of surfactant monomers form a micelle. Its interior becomes a hydrophobic region suitable for PAH, and, as a result, its solubility is greatly enhanced [4].

Earlier studies were performed in single-surfactant solutions by means of high surfactant concentrations that raised the cost of the treatment. The amount and type of surfactants used could influence the rate of other pollutants in surface water and groundwater [5]. Much of the work on micellar solubilisation of PAHs has focused on individual compounds; however, at contaminated sites, PAHs mostly exist in mixtures of many compounds. Only a limited number of studies have been carried out that examine the effects of

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multiple solutes on micellar solubilisation of an individual component. Chaiko et al. [6] and Nagarajan et al. [7] investigated the solubilisation of binary mixtures of hydrocarbons (benzene and hexane) in anionic and nonionic surfactant systems. They observed selective solubilisation in some mixtures and a synergistic effect on the solubilisation of hexane in the presence of small amounts of benzene [8].

Remediation of PAHs in soil systems strongly depends on their desorption rates from the soil surface and on their subsequent treatment in aqueous phase. The use of an electrochemical treatment represents an environmentally friendly approach for PAHs degradation in aqueous solution.

Liquid electrochemical oxidation has the potential to replace existing processes for PAHs degradation [9–12]. In fact, it is receiving increasing attention due to its convenience and simplicity. The electric current induces redox reactions upon the surface of the electrodes and results in the destruction of the organic compound. It makes the treatment of liquids, gases, and solids possible; it is compatible with the environment because the main reagent, the electron, is considered as a clean agent [13]. Electric current is an environmentally friendly and cost-competitive alternative. A generalised scheme of the electrochemical degradation of organic compounds on metal oxide anodes was proposed by Comminellis [9]. Furthermore, the electrochemical oxidation of p-substituted phenols on Pt anodes by employing sodium sulphate as supporting electrolyte was studied by Torres et al. [12].

The aim of this study is to evaluate the potential of a combined treatment in two stages: desorption of PAHs from contaminated samples followed by degradation of the extracted solution by electrochemical treatment.

2. Experimental methods

2.1. Materials

2.1.1. Contaminants

In this study, benzantracene (BzA), fluoranthene (FLU), and pyrene (PYR) were used as model PAHs to contaminate soil. They were purchased from Aldrich. Their characteristics are shown in Table 1.

2.1.2. Surfactants

The surfactants utilised were Brij 35 (Fluka), Tergitol NP10 (Sigma), Tween 20 (Sigma), Tween 80 (Panreac), and Tyloxapol (Sigma). Their characteristics are shown in Table 1. The types and concentrations selected were based on previous studies [14–22].

2.1.3. Soil

Kaolin is a dense, low permeable soil, with low buffer and cation exchange capacity, non-reactive character, and a consistent and uni-

form mineralogy. The kaolin used had an average particle size of 3 μm and a specific surface of 13.5 $\text{m}^2 \text{g}^{-1}$. The mineralogy analysis by X-ray diffraction indicated the presence of kaolin clay 85%, mica 14%, and quartz 1% [23].

2.2. Soil preparation

The soil was spiked with seven different PAHs solutions: individuals (BzA, FLU, and PYR), two-PAHs mixtures (BzA–FLU, BzA–PYR, and FLU–PYR), and three-PAHs mixtures (BzA–FLU–PYR). 0.1 grams of each PAH were added to 200 grams of soil to yield 500 mg PAH per kg soil, which is the typical PAH concentration at contaminated sites [24]. The different PAHs were dissolved in 100 ml of hexane before addition to the soil. The soil–hexane–contaminant mixture could be easily stirred and blended homogeneously. Afterwards, the mixture was placed beneath a ventilation hood for a week and was stirred every day until the hexane was completely evaporated and the contaminated soil was dry. All mixing operations were performed in glass beakers with stainless steel spoons. A sample of each mixture was taken for the initial analysis of PAHs concentration, as portions of the contaminant might volatilise. Initial PAHs weights are given in Table 2.

2.3. Desorption with surfactants

In all of the experiments carried out, the extractions were performed in 250 mL Erlenmeyer flasks containing 2.5 g of polluted kaolin and 50 mL of the surfactant solution with a concentration of 10 g L^{-1} . The Erlenmeyer flasks were maintained in an orbital shaker (Gallenkamp) at 150 rpm and 30 °C during the treatment, which lasted two days. Samples were taken every day and the PAHs concentration was assayed. Experiments were carried out in duplicate. The results shown in each figure correspond to mean values.

2.4. PAHs liquid concentration

PAHs were separated by HPLC (Agilent 1100) equipped with a XDB-C8 reverse-phase column (150 mm \times 4.6 mm i.d., 5 μm). Previous to injection, samples were filtered by using a 0.45 μm Teflon filter. The injection volume was set at 5 μL , and the isocratic eluent (70:30, acetonitrile:water) was pumped at a rate of 1 mL min^{-1} . A diode array detector operating from 200 to 400 nm was used to monitor the eluate. The column temperature was maintained at 30 °C. Sample analyses were carried out in triplicate, with a standard deviation lower than 15%.

2.5. PAHs soil concentration

The concentration of PAHs in the spiked soil was determined through the extraction process from kaolin by using a Soxhlet appa-

Table 1
Physicochemical properties of PAHs and surfactants used in this study.

Compound	Molecular formula	CMC (g L^{-1})	MW	Density (g mL^{-1})	Solubility in water ^a (mg L^{-1})
Benzantracene	$\text{C}_{18}\text{H}_{12}$	–	228.29 ^a	1.274	0.010 ^b
Fluoranthene	$\text{C}_{16}\text{H}_{10}$	–	202.26	No data	0.20–0.26 ^c
Pyrene	$\text{C}_{16}\text{H}_{10}$ ^c	–	202.3 ^d	1.271	0.077 ^b
Brij 35	$(\text{C}_2\text{H}_4\text{O})_n\text{C}_{12}\text{H}_{26}\text{O}$	0.1	1198 ^e	1.030	40,000
Tergitol NP10	$(\text{C}_2\text{H}_4\text{O})_n\text{C}_{15}\text{H}_{24}\text{O}$	0.04	Not applicable	1.06	>1,000
Tyloxapol	$\text{C}_8\text{H}_{11}\text{NO}$	0.0025	137.181	1.77	>1,000
Tween 20	$\text{C}_{58}\text{H}_{113}\text{O}_{26}$	0.06	1228 ^e	1.105	10,000
Tween 80	$\text{C}_{64}\text{H}_{124}\text{O}_{26}$	0.016	1310 ^e	1.073	50,000

^a Eller [42].

^b Yalkowsky and Pinal [43].

^c IARC [44].

^d IARC [45].

^e Average.

Table 2
Mass balances of PAHs in soil in the presence of Tween 80 and their soil removal (%) for the batch desorption experiments with binary and ternary mixtures of PAHs.

		BzA		FLU		PYR		Global PAHs Removal (%)
		mg	Removal (%)	mg	Removal (%)	mg	Removal (%)	
BzA–FLU	Initial	0.629		0.538		–		
	Final	0.139	76.995	0.058	88.862	–	–	82.519
	Solution ^a	0.485		0.478		–		
BzA–PYR	Initial	0.618		–		0.501		
	Final	0.117	80.587	–	–	0.051	88.990	84.361
	Solution ^a	0.498		–		0.446		
FLU–PYR	Initial	–		0.547		0.524		
	Final	–	–	0.075	85.052	0.050	89.563	87.301
	Solution ^a	–		0.465		0.470		
BzA–FLU–PYR	Initial	0.391		0.375		0.382		
	Final	0.046	86.536	0.036	89.778	0.068	80.160	85.453
	Solution ^a	0.338		0.337		0.306		

^a Amount of PAH recovery on the Tween 80 solution.

ratus. Dry soil (2.5 g) was thoroughly mixed with approximately 2.5 g of Na₂SO₄ and placed into a Whatman cellulose extraction thimble. The solution used in the Soxhlet extraction process was 100 mL of a 1:1 mixture of hexane and acetone, both purchased from Panreac. The process was operated at 5 cycles h⁻¹ for 24 h. The procedure is outlined in USEPA Test Method 3540 C [25]. Concentrations were determined by the use of the analytical technique previously described. The PAHs extraction process was carried out in duplicate, and samples were analysed in triplicate, with a standard deviation lower than 15%.

2.6. Electrochemical treatment

The electrochemical degradation of PAHs solutions was carried out in a Cubic Plexiglass electrochemical cell with a working volume of 0.4 L, graphite electrodes with an immersed area of 52 cm², and an electrode gap of 8 cm [26]. For every experiment, neat mixtures of contaminant (100 μM), surfactant (1%), and electrolyte (0.1 M Na₂SO₄) were prepared.

A constant potential difference (5 V) was applied with a power supply (HP model 3662), and the process was monitored with a multimeter (Fluke 175). Samples of reaction mixtures were taken every hour from the electrochemical cell to be analysed for pH and PAHs concentration. pH was measured with a Sentron pH meter (model 1001), and PAHs concentration was analytically determined.

3. Results and discussion

3.1. Desorption with surfactants

Previous studies by our research group [27] permit to conclude that the desorption of PAHs from soil is affected by the type of PAHs, their concentration, and the type of surfactant employed in the desorption process. Thus, it is determined that the most adequate surfactants for anthracene, benzo[a]pyrene, and phenanthrene removal were Tyloxapol, Brij 35, and Tween 80, respectively. In addition, to our knowledge there are other PAHs such as benzoanthracene, fluoranthene, and pyrene that have not been examined in similar processes although they are widely distributed in the environment. For this reason, the desorption process of individuals (BzA, FLU, and PYR), two-PAHs mixtures (BzA–FLU, BzA–PYR, and FLU–PYR), and three-PAHs mixture (BzA–FLU–PYR) was examined as the first stage of a sequential PAHs degradation process.

Nonionic surfactants were chosen due to their higher solubilisation capacities and due to their lower cost if compared to cationic and anionic ones. As pointed out in the Introduction section, the most used surfactants are Tween 80, Brij 35, and Tergitol NP10.

In this work, the screening of surfactants was extended to some analogous nonionic surfactants such as Tween 20 and Tyloxapol.

As shown in Fig. 1, significant differences in the levels of PAHs removal are perceived depending on which surfactants and PAHs are selected. Thus, it was determined that Tergitol NP10 did not extract any of the PAHs tested. The results obtained clearly show the convenience of employing Tween 20 and Tween 80. With Tween 80, the total removal was the highest, attaining a value of almost 85%. On the other hand, where Tween 20 was present the total removal achieved came close to 82%.

It is fairly difficult to compare technologies from different papers because the operational conditions (surfactant type and concentration, soil preparation, experimental procedure...) as well as the environmental problems (PAHs type and concentration, soil type and structure, pH...) are often based on different assumptions. Consequently, they can lead to fairly different results. However, several authors have pointed out the efficiency of these surfactants for other PAHs. Cheng and Wong [28,29] found that Tween 80 would be the most suitable candidate among four surfactants (Tween 80, Brij 35, Triton X-100, and sodium dodecyl sulphate) for improving solubilisation and extraction of PAHs in a soil–water system. Chang et al. [14] and Khodadoust et al. [17] determined that around 50% of phenanthrene might be removed with Tergitol NP10 and Tween 80, respectively.

The effects of the surfactant concentration on the removal levels were tested in order to improve the desorption process. The surfactants employed were Tween 20 and Tween 80, and the range of

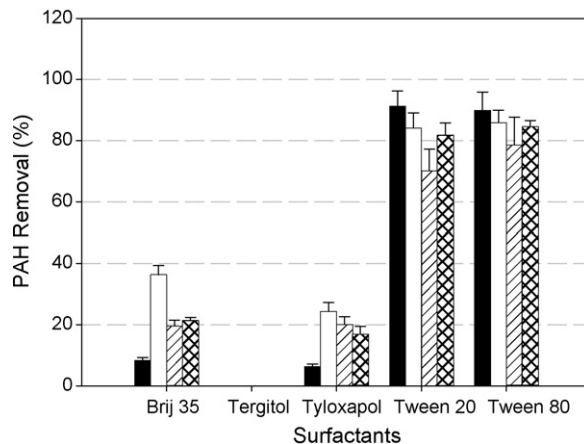


Fig. 1. Effect of surfactants addition during desorption of BzA (solid bar), FLU (void bar), PYR (lined bar) and total PAHs (checkerboard bar). Error bars represent standard deviation.

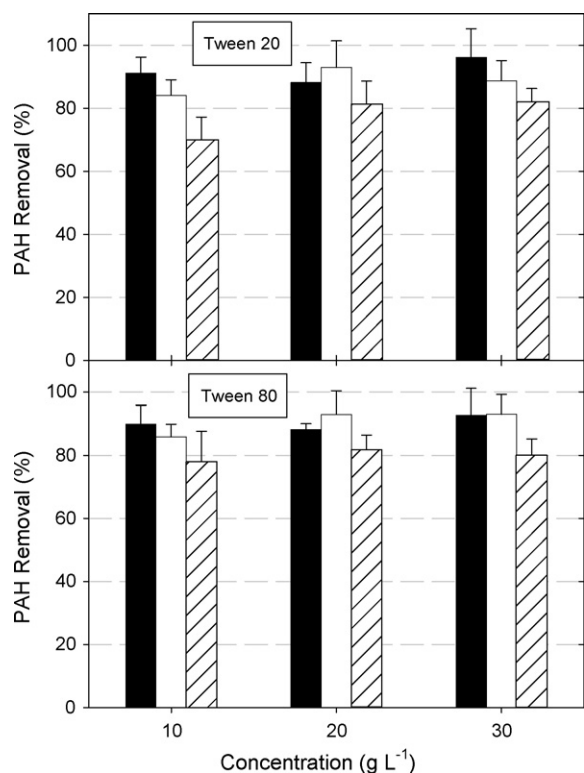


Fig. 2. Final PAH removal yields in the spiked kaolin after treatments at different surfactant concentrations of Tween 80 and Tween 20. BzA (solid bar), FLU (void bar), PYR (lined bar). Error bars represent standard deviation.

concentrations was 10, 20 and 30 g L⁻¹ (Fig. 2). The increase in surfactant concentration did not lead to a significant increase in the level of removal; hence, the following experiments were carried out with the smallest concentration (10 g L⁻¹).

Recently, several papers [3,5] have reported on the applicability of the surfactants mixtures on the solubilisation of organic compounds. Therefore, knowledge of the solubility enhancement of organic pollutants by means of mixed surfactants could extend the scope of contaminant remediation. Thus, a consideration of this fact and previous results (Fig. 2) led to an experiment performed with Tween 20 and Tween 80 with a final concentration of 10 g L⁻¹. The level of PAHs removal attained in presence of the combination of surfactants was similar to those obtained with just one surfactant. For the BzA, the level of removal attained by the researchers operating in this condition was analogous to the one obtained in presence of Tween 80 (around 88%); for FLU and PYR, the maximum level of removal was achieved when the combination of surfactants was used, namely, more than 90% for FLU and 80% for PYR. These results are in accordance with the results obtained by Zhu and Feng [5], who suggest that larger quantities of PYR move into mixed micelles than into single micelles. According to Zhu and Feng [5], the level of desorption is synergistically enhanced by mixed-surfactant micelles and sodium dodecyl sulphate (SDS)-Brij 35.

3.2. Experiments for mixtures of PAHs

As shown in Fig. 1, the highest capacity for the global desorption of the three PAHs evaluated was found when Tween 80 was used. Thus, this surfactant was chosen to test the desorption process in samples spiked with a mixture of PAHs: BzA-FLU; BzA-PYR; FLU-PYR; BzA-FLU-PYR. The total initial amount is shown in Table 2. The percentage of removal for all the combinations was higher than 80%; the highest removal was achieved for the FLU-PYR

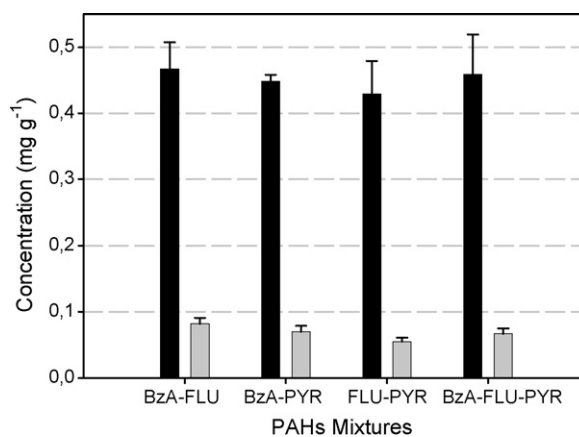


Fig. 3. Effect of PAHs mixtures during extraction in presence of Tween 80. Total initial (black bar) and final (gray bar) concentration in soil. Error bars represent standard deviation.

mixture, while a smaller removal was obtained for the BzA-FLU combination (Fig. 3).

According to the results obtained on screening the surfactants, the order of increasing desorption is BzA > FLU > PYR (Fig. 1). Thus, it can be postulated that working with a combination of PAHs, the highest level of removal will be achieved by the combination BzA-FLU, and so on. Nevertheless, according to the results, the real order of increasing desorption was unexpected (Fig. 3).

Several authors studied other PAHs mixtures with different results. Bernal-Martínez et al. [20] studied the desorption of a PAHs mixture (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, di benzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3,cd]pyrene) by using Tyloxapol, Tergitol NP10 and Brij 35 as surfactants. They found that the level of removal was similar for all surfactants: 60% for Brij 35, 60% for Tergitol NP10, and 65% for Tyloxapol. However, Fabbri et al. [30] treated a PAHs mixture (2-naphtol, 2,4-dichloroaniline, 3,4-dichloroaniline, chlorobenzene, 1,4-dichlorobenzene, tetra-chlorobenzenes, 9,10-anthraquinone, benzantrone) with Brij 35 and attained a level of recovery ranging from 14% to 69% depending on the PAH analysed.

Dhenain et al. [31] reported that Tween 80 is the best surfactant for the treatment of a PAHs mixture of fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene, with PAHs removal levels ranging from 35% to 50% for several PAHs.

According to our results, the single-component level of desorption cannot be used to predict the binary or ternary mixture level of removal. This is likely due to the increasing solubility of the more hydrophobic solutes in presence of less hydrophobic ones [8,32].

3.3. Electrochemical treatment

In order to obtain the total PAHs degradation, the polluted effluent must be treated; therefore, in this work electrochemical oxidation was proposed as a suitable treatment. In the electrochemical treatment, the electric current induces redox reactions upon the surface of the electrodes and the oxidation reaction results in the destruction of the organic compound [27,33]. Thus, several studies [34–37] have demonstrated that this technology allows the almost complete mineralisation of the organics contained in the waste with very high current efficiencies. The oxidation mechanisms involved in this technology have also been characterised and include direct electrooxidation, hydroxyl radical-mediated oxidation, and oxida-

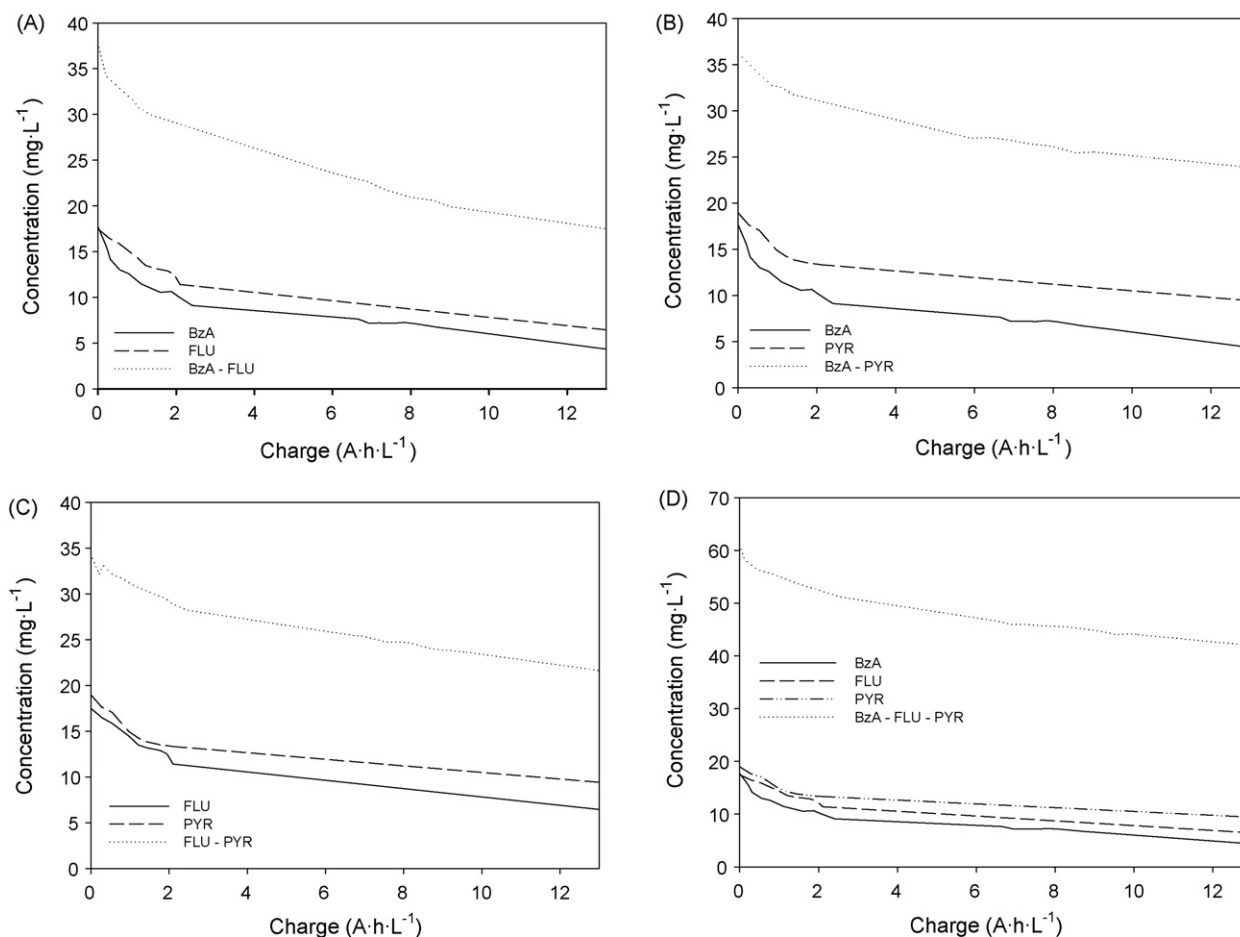


Fig. 4. PAHs concentration profiles versus current charge of electrochemical treatment of individual and their mixtures (dotted) in solutions of Tween 80. Initial individual PAHs concentration of $100 \mu\text{M}$. (A) BzA (solid), FLU (medium dash), (B) BzA (solid) and PYR (medium dash), (C) FLU (solid) and PYR (medium dash) and (D) BzA (solid), FLU (long dash), and PYR (dash-dot-dot).

tion mediated by oxidants generated during the treatment of the salts contained in the waste [38].

Initially, the degradation of individual BzA, FLU, and PYR, as well as the degradation of their mixtures, was carried out in this work. Fig. 4A–D shows the concentration profiles versus current charge.

According to Tran et al. [39], the anodic oxidation of pollutants occurs heterogeneously. First, organic pollutants must be transported toward the anode electrode surface to be oxidised. Thus, two different regions can be distinguished (Fig. 4A–D). When the charge loading is below 2 A h L^{-1} , the yield of PAH removal decreases linearly. Beyond 2 A h L^{-1} , the rate of PAH degradation remains quite stable.

In all cases, the degradation rate of BzA alone was higher than the one obtained for the other PAHs. The average BzA removal after 13 A h L^{-1} charge input was around 80%. At the same charge input, similar profiles are shown for the degradation of FLU and PYR, achieving a value around 70% and 55%, respectively (Fig. 4A–D). As might be expected, the degradation rate of the PAHs mixture was lower than the one corresponding to each PAH separately. Furthermore, the PAHs degradation order in mixtures was as follows: $\text{BzA} > \text{FLU} > \text{PYR}$.

Based on these results, it is estimated that total PAHs degradation could be reached at high current charge. However, the energy consumption during the electrochemical treatment increased; for this reason, this variable is a key parameter for the optimisation of this process. These results are in accordance with Rajkumar et al. [40]. They studied the electrochemical degradation of mixed phenolic compounds in wastewater with chloride as support-

ing electrolyte. They concluded that all aromatic fractions were removed after the passage of a current charge higher than 18 A h L^{-1} . Moreover, the energy consumption increased around 20% when the current charge used was 32 A h L^{-1} .

Finally, a first-order reaction became evident. The data were well fitted to each PAH, and the rate constant was calculated by using the Sigma Plot 8.00 software. As shown in Table 3, an obvious relationship between the ionization potential of a PAH and its rate constant for oxidation can be highlighted.

In addition, the ability of the electrochemical process to oxidise PAHs mixtures in solutions of Tween 80 in an electrochemical cell was examined. Interactions of the PAHs present in the solutions and their effect on degradation processes were investigated. The total hydrocarbon level of degradation decreased when the PAHs were combined. Moreover, the presence of PYR in a two-PAHs mixture decreased the level of degradation of the PAHs mixture. In the mixture of BzA and FLU, the level of degradation attained

Table 3

Constant coefficients obtained in the fitting of experimental data from electrochemical treatment of individual PAHs to first-order kinetic and their ionization potential.

Compound	Ionization potential (eV)	First-order constant (h^{-1})
Fluoranthene	7.76 ^a	0.0497
Benzenanthracene	7.46 ^b	0.0198
Pyrene	7.41 ^c	0.0119

^a Pickard et al. [46].

^b Simonsick and Hites [47].

^c Valentín et al. [48].

amounted to around 55%. An important degradation reduction was verified: around 31% and 21% lower than those reported for BzA and FLU, respectively. Moreover, for a three-PAHs mixture, the level of degradation reached was around 34%, which is the smallest level of degradation achieved for all the PAHs mixtures tested. These results are in agreement with our previous investigations [41] in which dyes, single and in mixtures, were treated by electrochemical technology. It was found that the decolourisation rate corresponding to each dye clearly changed when the technique was applied to the mixture of dyes. This fact may be explained by the interactions among the different initial compounds and the reaction products present in the reaction mixtures during the electrochemical treatment.

4. Conclusions

Observations of desorption for three PAHs by means of five different surfactants indicated that the efficiency of surfactants in enhancing PAHs removal strongly depended on the structure of the surfactant and on PAHs properties. It was determined that for the three PAHs studied, namely BzA, FLU, and PYR, the best yields of global PAHs removal were obtained by Tween 20 and Tween 80, with more than 80% of global removal after two days of treatment. Moreover, the negligible synergistic solubilisation of PAHs was determined by mixing Tween 20 and Tween 80 on the desorption process. On the other hand, markedly different tendencies are shown in PAHs mixtures, depending on the hydrophobic content of the PAHs tested.

Regarding electrochemical degradation, the results obtained show the enormous potential of this treatment in PAHs degradation. In view of these encouraging results, more studies are underway in our laboratory in order to determine the optimal operation conditions (electrolyte concentration, current charge, scale-up, etc.).

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