Electro-Fenton treatment of soil washing solution of phenanthrene with cyclodextrin using different kind of anode materials: impacts on toxicity and biodegradability

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Abstract: Electro-Fenton (EF) degradation and mineralization of highly loaded synthetic phenanthrene (PHE) solutions were performed (COD = 11,150 mg O_2 L^{-1} and TOC = 4,500 mg C L^{-1}). Phenanthrene was chosen as a polycyclic aromatic hydrocarbon (PAH) representative and hydroxypropyl-beta-cyclodextrin (HPCD), which is one of the most cost-effective cyclodextrin, was applied as a solubilizing agent. Toxicity and biodegradability of treated solutions were evaluated during the treatment. Different anode materials such as platinum (Pt), dimensional stable anode (DSA; Ti-(RuO_2/IrO_2)) and boron doped diamond (BDD) were employed to carry out the degradation. At optimal catalyst (Fe^{2+}) concentration (i.e., 0.2 mM), the Pt anode was found to be the more efficient one in degradation of PHE. On the other hand, the BDD anode has given the best mineralization performance. PHE and HPCD solutions exhibit high toxicity values vs *Vibrio fischeri* bacteria (about 80-99% inhibition of luminescence) in the beginning of the treatment. This toxicity decreases after 60% of mineralization (end of HPCD degradation) and reach an almost non-toxic value at the end of treatment. Biodegradability results have shown a great enhancement of BOD_5/COD ratio compared to the initial one (0.001). After 40% of mineralization with BDD anode (about 10 h of treatment), the BOD_5/COD ratio was higher than 0.6, which is sufficient when considering a biological step as post-treatment.

Key-Words: AOPs; Electro-Fenton; BDD; Cyclodextrin; HPCD; Phenanthrene; Biodegradability; Toxicity

1 Introduction

Hydrophobic organic compounds (HOCs) like PAHs are well-known to be hazardous contaminant and their potential environmental impact is significant. Among the emerging techniques to treat them, soil washing and soil flushing appear to be cost-efficient techniques [1]. Since PAHs tend to be strongly sorbed to soil, a water-soluble extracting agent is needed. Cyclodextrins, known as host-guest molecules, have been suggested in the last decade as an alternative to the traditional surfactants [2, 3].

As this process only transfers the pollutant from a solid matrix to an aqueous solution, a post-treatment of soil washing solution is required. Advanced oxidation processes (AOPs) [4]), which produce in situ hydroxyl radical ($^\bullet$OH), a highly oxidizing species (E° = 2.80 V/SHE) [5], have been developed as alternative technologies to conventional processes which are inefficient in case of persistents organics pollutants (POPs) like phenanthrene. Among them, electro-Fenton (EF) process has shown promising results especially for industrial wastewaters treatments [6]. In this process, H_2O_2 is generated at the cathode with O_2 or air feeding while an iron catalyst (Fe^{2+}, Fe^{3+}, or iron oxides) is added to the effluent to produce $^\bullet$OH at the bulk solution via Fenton's reaction (Eq. 1). In contrast to the classical Fenton process, the reagents (H_2O_2 and Fe^{2+}) of the Fenton's reaction are electrocatalytically in situ generated in the case of EF process [6, 7].

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

Since chemical oxidation for complete mineralization is usually expensive, combination with biological treatment can reduce the operating costs [8]. Only two studies have reported this possibility [9, 10] and shown that EF is a better option to be combined with a post biological treatment than other treatments like anodic oxidation (AO), AO with H_2O_2 electrogeneration, chemical flocculation and electro-coagulation.

In the present study, we carried out treatment of synthetic soil washing solution by EF process using different anode materials. Degradation and/or mineralization of PHE and HPCD as PAH and cyclodextrin representative respectively, are studied. In both case, the effect of three kinds of anode materials (Pt, Ti-(RuO$_2$/IrO$_2$) and BDD) on the degradation/mineralization efficiency as well as the measure and evolution of the solution toxicity and biodegradability are quantified in order to evaluate the possibility of a combined treatment with a post-biological process.

2 Material and methods

2.1 Electrochemical system

Electrolysis were carried out in a 0.40 dm^3 undivided glass electrochemical reactor at current controlled conditions. The electrochemical cell was monitored by a power supply HAMEG 7042-5. The cathode was a 150 cm^2 carbon-felt piece (Carbone-Lorraine), and each anode studied (Pt grid, DSA or BDD plates) is centred in the cell and surrounded by cathode covering the inner wall of the cell. Na$_2$SO$_4$ (150 mM) was added to the medium as supporting electrolyte. Prior to each experiment, compressed air was bubbled through the aqueous solutions (10 min) in order to saturate it in O$_2$. The solutions were stirred continuously by a magnetic stirrer. A heat exchanger system was used to keep the solution at constant room temperature by using fresh water. Prior to EF treatment, the pH of initial solutions was set at the optimal value of 3.0 (+/- 0.1). In these experiments FeSO$_4$•7H$_2$O was also added to the solution as catalyst (Fe^{2+}) source. The pH variation was insignificant during the electrolysis and it decreases only to a value of 2.8 at the end of experiment. HPCD (10 g L^{-1}) was used to enhance the PHE solubilization and to mimic future soil extract solutions of washing experiment. Around 17 mg L^{-1} (0.1 mM) of PHE is present in each initial solution containing HPCD.

2.2 Bioassays

2.2.1 Toxicity assays

Toxicity assays were performed by using Microtox$^®$ standard method (ISO 11348-3) with marine bacteria *Vibrio fischeri* from LUMIStock LCK-487 (Hach Lange). A BERTHOLD Autolumat Plus LB 953 equipment was used. 22% of NaCl was added in each sample to insure an osmotic protection for bacteria. Before each toxicity measurement, all the samples were adjusted to circum-neutral pH and samples were filtered with RC filter (0.2 μm) to remove iron precipitates. In each batch test a blank without the compound studied was also measured and used for percentage of inhibition calculation based on 15 min exposure.

2.2.2 Biodegradability tests

The biodegradability is given by the ratio between Biochemical Oxygen Demand at 5 days (BOD$_5$) and the Chemical Oxygen Demand (COD).

BOD$_5$ is determined by respirometric method with the OxiTop$^®$ control system (WTW). An aqueous solution containing a phosphate buffer solution and a saline solution was prepared according to Rodier et al. procedure [11]. This solution was then saturated in oxygen. As this solution and the samples are sterile, bacteria extracted with KCl at 9 g L^{-1} (30 mL with 3 g of soil) and a IKA-MS1 minishaker (1800 rpm during 1 min) from uncontaminated soil are added just before adding the samples. All the samples are adjusted to circum-neutral pH. D(+)-Glucose•H$_2$O is used as a reference and a blank with milli-Q water and the seed solution is prepared for each batch and taken into account for calculation. All the bottles containing the solutions are equipped by a rubber sleeve in which pure NaOH pellets are added to trap the CO$_2$ formed during biodegradation. The samples are incubated at 20 °C during 5 days. The BOD$_5$ measured in each blank is not significant compared to the BOD$_5$ of the samples, which causes no interference.

COD measurements are done by adding 2 mL of samples in COD Cell test (Merck) and by heating at 148 °C during two hours with a Spectroquant$^®$ TR 420 (Merck). COD analyses are accomplished by a photometric method requiring a Spectroquant$^®$ NOVA 60 (Merck) equipment.

2.3 Analytical determinations

The decay of PHE concentration was followed by reversed phase liquid chromatography (HPLC) coupled with a DAD from Dionex. A RP C-18 column placed in an oven and set at 40.0 °C was

used. The mobile phase was a mixture of water/methanol 22:78 (v/v) and the flow rate was set at 0.8 mL min^{-1} (isocratic mode) which allow having a well-defined pic of PHE at 6.9 min retention time. The detection was carried out at 249 nm. To avoid difference of absorbance observed in the presence or absence of HPCD or surfactant during organic analysis, external standards were prepared in the presence of solubilizing agent.

The total organic carbon (TOC) values were determined by catalytic oxidation using a Shimadzu V$_{CSH}$ TOC analyser.

The HPCD concentration was determined by a fluorimetric technique based on enhancement of fluorescence intensity of 2-(P-toluidino)naphthalene-6-sulfonic acid sodium (TNS), when they are complexed with the cyclodextrin. This method allows quantifying HPCD and slightly modified HPCD (hydroxylated) in the same time, since the non-polar HPCD cavity brings about a TNS fluorescence intensity enhancement until the CD cavity is cleaved by the degradation technique. A Kontron SFM 25 spectrofluorimeter was set out at 318 nm for excitation and 428 nm for emission. Each sample is diluted in TNS (3 x 10^{-6} M) with a dilution factor of 200. The fluorescence intensity of phenanthrene is not significant in this range of wavelength and concentration (data not shown).

3 Results and discussion

3.1 Electro-Fenton degradation of phenanthrene in the presence of HPCD

3.1.1 Determination of optimal iron(II) concentration

As iron(II) is required at a catalytic amount in EF process, it is important to know its optimal value. In order to evaluate optimal concentration of ferrous iron (catalyst) a large range of iron(II) concentration (from 0.05 mM to 10 mM) was studied and results obtained are shown in Figure 1. The optimal concentration is obviously 0.2 mM, which is often given in literature [6]. All the experiments are then operated with this optimal value. At lower concentration there is a lack of iron(II) to produce $^{\bullet}$OH by reacting with H$_2$O$_2$ via Fenton's reaction. In contrast, at concentration higher than this value, the process efficiency is progressively inhibited due to the enhancement of the waste reaction (2) [6]:
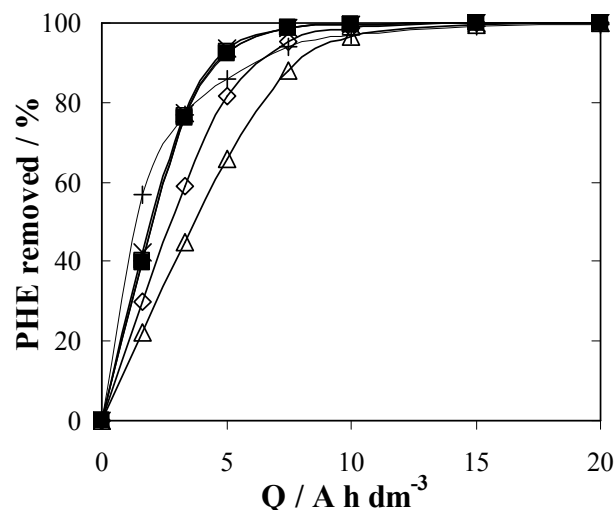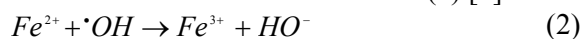
$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + HO^{-} \qquad (2)$$

Fig. 1. Effect of catalyst (Fe^{2+}) on EF degradation of PHE (0.1 mM) in presence of HPCD (10 g L^{-1}): 0.05 mM ($\triangle$), 0.1 mM ($\lozenge$), 0.2 mM ($\blacksquare$), 0.5 mM ($\square$), 1 mM (x) and 10 mM (+). J = 13.3 mA cm^{-2} and Pt anode.

3.1.2 Effect of current density and anode material on oxidative degradation of PHE

Figure 2 depicts the effect of current density with the three anodes. By comparing the apparent rate constants values from Table 1, we can conclude that Pt anode exhibits significantly better degradation efficiency compared to DSA and BDD anodes. The complete oxidation of PHE needs only 75 min with Pt anode at 13.3 mA cm^{-2} applied current density whereas complete oxidation was not reached even after 240 min treatment in the case of DSA and BDD anodes.

Application of currents intensity higher than 2 A (leading to a current density of 13.3 mA cm^{-2}) increases the extent of waste reactions, decreasing the process efficiency [6]. Finally, the kinetic of oxidative degradation efficiency follows the rank: Pt >> DSA > BDD.

Table 1. Apparent rate constants values (expressed in min^{-1}) obtained for PHE oxidation with Pt, DSA and BDD anodes at different current density, assuming pseudo-first order kinetics model.

J \ Anodes	Pt	DSA	BDD
3.3 mA cm^{-2}	0.028	0.013	0.012
6.7 mA cm^{-2}	0.031	0.015	0.012
13.3 mA cm^{-2}	0.043	0.014	0.011

3.2 Mineralization of phenanthrene in presence of HPCD by electro-Fenton process

EF mineralization of PHE and HPCD (4 h of treatment) was performed with EF process using Pt, DSA and BDD anodes and results obtained are represented in Figure 3.
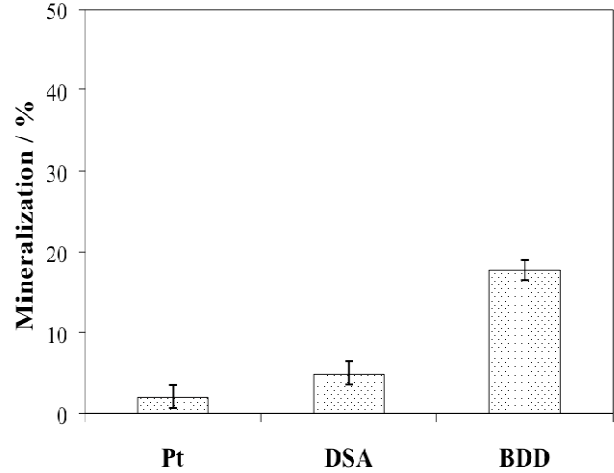

Fig. 3. TOC removed after 4 hours EF treatment of PHE (0.1 mM) in aqueous solution containing 10 g L^{-1} HPCD at 6.6 mA cm^{-2} current density and $[Fe^{2+}]$ = 0.2 mM.

The kinetic of mineralization after 4 hours of treatment followed the sequence: BDD (18%) >> DSA (5%) > Pt (2%). The high mineralization power of BDD compared to other anodes was already reported several times [6, 12]. It is due to the higher O_2 evolution overpotential leading to generation of heterogeneous BDD($^{\cdot}$OH) at the electrode surface (Eq. (3)) in addition of those produced in bulk from Fenton reaction.

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + e^- \qquad (3)$$
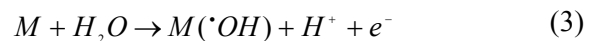
Consequently, during EF treatment with BDD anode, both degradation and mineralization mechanisms take place at the same time. It makes the degradation slower (as shown in section 3.1.2) but the mineralization quicker.

Figure 4 illustrates the complete EF mineralization using BDD anode. Knowing that initial experimental TOC value is about 4,500 mg C L^{-1}, 24 hours is required to mineralize completely the solution by following an inverted "S" shape.
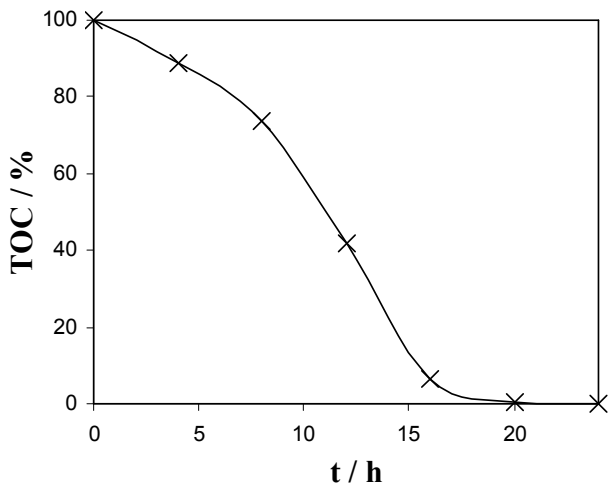
Fig. 2. Effect of applied current density (3.3 mA cm^{-2} (x), 6.7 mA cm^{-2} (Δ) and 13.3 mA cm^{-2} ($\Diamond$)) on the degradation kinetics of PHE (0.1 mM) in the presence of 10 g L^{-1} HPCD with various anode materials: Pt (a), DSA (b) and BDD (c). $[Fe^{2+}]$ = 0.2 mM.

Fig. 4. Evolution of TOC of 0.1 mM PHE aqueous solution including 10 g L^{-1} HPCD during EF process with BDD anode. J = 6.6 mA cm^{-2}, [Fe^{2+}] = 0.2 mM.

3.3 Impact of electro-Fenton process on toxicity and biodegradability

Evolution of toxicity feature during EF degradation of PHE with Pt, DSA and BDD anodes was given in Figure 5 (a). It demonstrates that the solution toxicity became 40% higher than the initial toxicity during 10 h treatment (between 85-99% of inhibition), whatever the anodes employed. That is probably due to the formation of highly toxic oxidation by-products during electrolysis [8]. However, the toxicity during the first 4 hours of treatment (time to degrade PHE) is higher (99%) with BDD than with DSA and Pt (85-90%) anodes. That means that different oxidation/mineralization kinetics were involved according to the anode used, and the quicker formation of toxic intermediates observed with BDD anode can be explained by the paired electrocatalysis process (see section 3.2.) involved with this anode. Biodegradability experiments shown in Figure 5 (b) highlight also different behaviors between the anodes. During the first 6 hours of treatment, very low BOD$_5$/COD ratios are obtained by using BDD anode. However, this ratio increases until 65% after 10 hours of treatment, knowing that the initial ratio (before treatment) was about 0.001 with an initial COD of 11,150 mg O$_2$ L^{-1}. Since an effluent with a ratio higher than 0.33 is considered as biodegradable in wastewater treatment [11], a biological post-treatment of PHE solution would be reliable after 10 h of treatment (equivalent to 40% of mineralization). Regarding the DSA and Pt biodegradability experiments, similar behaviors are noted. BOD$_5$/COD ratio increases until a plateau at 2 hours of treatment (equivalent to 98% of increase

from initial ratio). Then it increases from 4 to 10 hours of treatment reaching a ratio of 0.31, which is slightly biodegradable. Biodegradability with Pt and DSA are higher than with BDD during the first 6 hours of treatment. In the meantime the toxicity is higher and BOD$_5$ is lower with BDD and the TOC (related to COD) is still too high. After 6 hours of treatment the biodegradability with BDD increases very quickly even if the toxicity is still high and BOD$_5$ lower than with Pt and DSA, because the quick TOC decreases in the meanwhile.
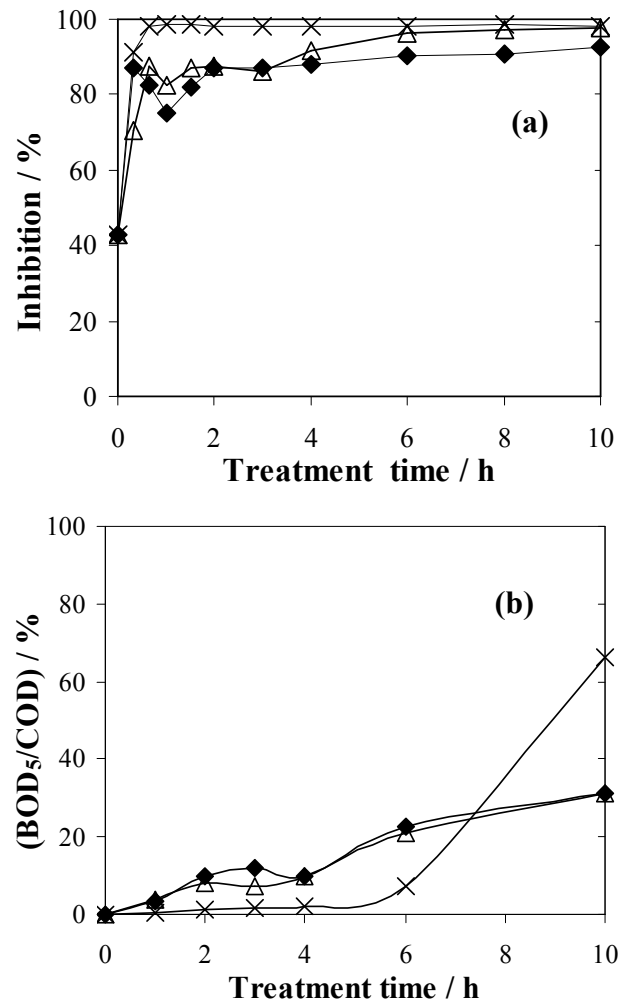

Fig. 5. Evolution of toxicity (a) and biodegradability (b) during EF degradation of PHE (0.1 mM) and HPCD (10 g L^{-1}) at J = 6.6 mA cm^{-2} and different anode materials: Pt (♦), DSA (△) and BDD (x).

During this period of time, the solution treated with Pt anode was less toxic but the mineralization rate was too low whereas with DSA the mineralization rate was slightly higher but the toxicity is also higher. These results are in agreement with those obtained in section 3.1 and 3.2.

Figure 6 shows the relation between the toxicity, the HPCD degradation and the mineralization rate. After reaching 60% of mineralization (at 12 h treatment with BDD anode), all the cyclodextrin was degraded and the solution toxicity started to decrease until the end of mineralization (24 h).
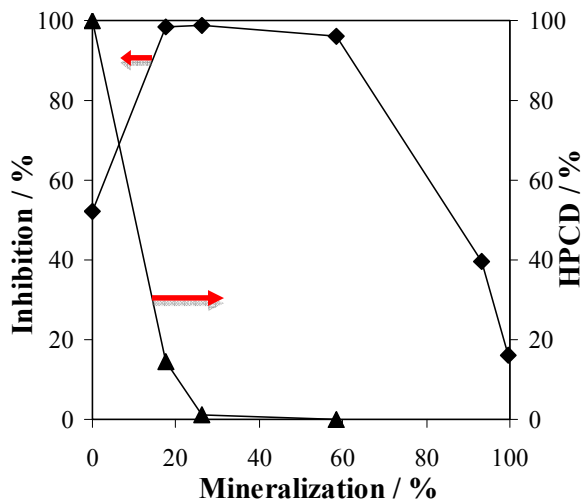

Fig. 6. Toxicity measurement (♦) and HPCD degradation percentage (▲) as a function of TOC removal during EF mineralization (with BDD anode) of PHE (0.1 mM) and HPCD (10 g L^{-1}) at J = 6.6 mA cm^{-2} and [Fe^{2+}] = 0.2 mM.

4 Conclusion

Oxidative degradation of PHE was investigated by EF process using 3 different anodes: Pt, DSA and BDD. Although the PHE degradation efficiency followed the sequence Pt >> DSA > BDD, the last one exhibited significantly better performances in TOC removal (mineralization efficiency) and toxicity removal. The superiority of BDD anode is directly related to its higher O_2 evolution overvoltage leading to the formation of highly reactive BDD($^•$OH) in addition of those generated by Fenton's reaction in the bulk solution. Toxicity and biodegradability data confirmed these trends. Solution toxicity decreased after 60% of mineralization and after the HPCD is totally degraded, and it became very low at the end of mineralization. Regarding the biodegradability, the BOD$_5$/COD ratio reached value higher than 0.6 after 40% of mineralization, indicating the interest of EF pre-treatment combined to a biological post-treatment.

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