

Electro-Fenton and anodic oxidation treatments of phenanthrene in the presence of hydroxypropyl-beta-cyclodextrin: biodegradability and toxicity data

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Introduction

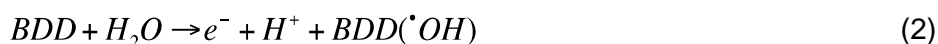
The removal of polycyclic aromatic hydrocarbons (PAHs), which are highly sorbed into soil, is a part of challenges of the coming years. As an alternative to pump and treat application, which turns out to be a slow process due to the low solubility of these compounds in water, soil washing (SW) and soil flushing (SF) appear to be more effective processes, especially with surfactants and co-solvents. However, thanks to their specific properties cyclodextrins (CDs) are also becoming very interesting as an extracting agent. Hydroxypropyl-beta-cyclodextrin (HPCD) proved to be one on of the most cost-effective CDs derivative.

Since the enhanced SW or SF processes only permit to extract the pollutant but not to destroy it, a post-treatment is needed. Advanced oxidation processes (AOPs, (Glaze et al., 1987)), which involve the *in-situ* generation of a very powerful oxidizing agent such as hydroxyl radical ($\cdot\text{OH}$) ($E^\circ = 2.80 \text{ V/SHE}$), have shown promising and environmentally friendly methods. One of them is based on the Fenton's reagent (a mixture of H_2O_2 and Fe^{2+} ion) to produce hydroxyl radical $\cdot\text{OH}$ according to equation (1) (Brillas et al., 2009; Pignatello et al., 2006).



Electro-Fenton (EF) process, a modified Fenton treatment, was applied for treating synthesized soil washed solution. It consists of H_2O_2 generation 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 oxidant $\cdot\text{OH}$ at the bulk solution via Fenton's reaction (Oturan, 2000; Brillas et al., 2009). Compared to chemical Fenton process, the electro-Fenton process permits to minimize the use of reagent since the production of H_2O_2 is *in-situ* and a catalytic amount of soluble iron is enough because it is continuously electro-regenerated at the cathode. Thanks to these enhancements, higher degradation rate and mineralization degree of organic pollutants and no sludge production are observed.

An alternative technique coupling electrochemistry and AOP is the anodic oxidation (AO) process. With a high O_2 -overvoltage electrode (such as boron doped diamond (BDD)) it offers the possibility to run experiment without adding iron and operate at natural pH without a decreased in the removal efficiency, by producing hydroxyl radical at the anode (equation (2)).



Methods

Experiments were carried out with phenanthrene (PHE) as a PAH representative and HPCD at 10 g L^{-1} in ultrapure water. The initial PHE apparent concentration is around 18 mg L^{-1} . Three ways are considered to run experiment. The first way is to study the possibility to reuse the CD in a SW process after the EF or OA degradation of the pollutant. This could be possible since a ternary complex formation (Fe^{2+} -HPCD-PHE) was characterized with UV/VIS spectrometric analysis. By increasing the iron (II) concentration from 0.05 to 1 mM, in the

presence of HPCD (10 g L^{-1}) and PHE (1 mg L^{-1}), the absorbance peaks increase and shift slightly to the left ($\Delta\lambda = 1 \text{ nm}$) (hypsochromic shift). This confirms Lindsey et al. (2003) theory of the ternary complex formation and Hanna et al. (2005) results about similar UV/VIS experiments with ferrous ions, HPCD and PCP.

The second way is to study the possibility to combine a biological process after EF or OA treatment of soil washed solution.

The third way is to study the complete mineralization of the soil washed solution by EF or OA treatment.

Toxicity (Microtox® with *Vibrio fischeri*) and biodegradability (BOD by respirometric method with OxiTop® and COD by colorimetric method with COD tube tests) experiments were conducted during EF treatments using different natures of anode materials (Pt, Dimensional Stable Anode (DSA) with Ti ($\text{RuO}_2\text{-IrO}_2$) materials, BDD) at optimal current intensity and ferrous ion concentration determined in a previous study. They were also determined during OA treatment with BDD at optimal current intensity.

Main results

The optimal ferrous ion concentrations in EF treatment were 0.2 mM in degradation or mineralization experiments and 0.05 mM in order to degrade PHE by keeping HPCD after treatment. The optimal current intensity in EF and AO treatment was 2 A with Pt anode and 1 A with DSA and BDD anodes.

In EF degradation experiment, pseudo-first order kinetic model show that PHE degradation with DSA is similar to BDD ($k_{\text{app}} = 0.010 \text{ min}^{-1}$) which is much slower than with Pt ($k_{\text{app}} = 0.031 \text{ min}^{-1}$) experiments. In EF mineralization experiment, the percentages of TOC removal with DSA are similar to Pt ($95\% \pm 1.40\%$ at 4 h), which is higher than with BDD ($82\% \pm 1.22\%$ at 4 h) experiments (in the same conditions). OA mineralization experiment with BDD is a little bit less efficient ($86\% \pm 1.11\%$ at 4h).

About degradation in toxicity studies, the percentages of inhibition are still high (between 90% and 100%) even after 10 hours of EF and AO treatments, whatever the anode materials. About mineralization, percentages of inhibition start to decrease from 16 hours until 24 hours (end of mineralization) of EF or AO treatment.

In biodegradability studies, the more the treatment time increases, the more biodegradability increases to reach around 50% (BOD/COD) after 10 hours of EF or AO process.

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