Conductive-diamond electrochemical-oxidation of surfactant-aided soil-washing effluents

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Abstract

Washing of soils polluted with polycyclic aromatic hydrocarbons (PAHs) using surfactant is a technique used widely. Once the pollutant is transferred to the washing-solution, the polluted wastewater has to be treated. In this work, it is studied the feasibility of Conductive-Diamond Electrochemical-Oxidation (CDEO) to treat wastewater polluted with phenanthrene (selected as model PAHs) and three different surfactants (anionic, cationic and non-ionic) which were tested as the washing-solution. The results show that CDEO enables a significant reduction in the organic load of the wastes regardless of the surfactant present. However, the process efficiency is largely influenced by the type of surfactant employed. Thus, aliphatic linear-chain species seem to lead to the formation of oxidation-refractory compounds, whereas molecules with an aromatic structure favour the formation of insoluble species. The observed changes in pH and conductivity seem to confirm this assumption. On contrary, Dimensionally Stable Anode (DSA) technology is ineffective in the treatment of these effluents.

Keywords: surfactant, wastewater, diamond, electrochemical-oxidation.

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1 **1. Introduction**

2 Numerous compounds are now known to cause serious pollution problems in
3 soils. Polycyclic aromatic hydrocarbons (PAHs) have become an important group of
4 pollutants because some of these compounds have been identified as carcinogenic,
5 mutagenic and teratogenic¹⁻⁴. These compounds are present in the environment due to
6 incomplete combustion of fossil fuels; therefore, they generally exist in locations
7 associated with gas production plants, oil refining and wood manufacturing. PAHs are
8 characterized by their low solubility in water and their apolarity⁵⁻⁷. These characteristics
9 hinder the removal of this type of compound from soils. However, the use of surfactants
10 in soil treatment can enhance the solubility of PAHs by partitioning them into the
11 hydrophobic cores of surfactant micelles⁸⁻¹¹. For example, technologies such as
12 surfactant-aided soil washing (SASW) and electrochemical surfactant-aided soil-
13 washing (ESASW) have become relevant treatments for these types of soils, as they
14 allow transfer of the pollutants from the soil to the washing fluid. This process
15 remediates the soil and thus converts the problem of soil remediation into a potentially
16 easier wastewater treatment problem.

17 However, this type of effluent is difficult to treat by conventional wastewater
18 treatment methods because the PAHs are recalcitrant and unreactive in water and the
19 surfactants are large molecules with complex organic groups. For this reason several
20 researchers have focused on developing methods to treat these effluents and these
21 include advanced oxidation¹²⁻¹⁴, coagulation technologies^{15, 16}, electrochemical
22 oxidation¹⁷⁻¹⁹ and even combinations of biological treatments²⁰⁻²² with some of the
23 previously mentioned technologies.

24 In the work described here, conductive diamond electrochemical oxidation
25 (CDEO) was selected for the treatment of effluent from remediated soil polluted with a

PAH. This approach was chosen due to the significant advantages associated with it²³, which include environmental compatibility, versatility, energy efficiency, safety, amenability to automation and cost effectiveness. CDEO has become a very promising technology for the electrochemical treatment of wastewater polluted with organic compounds²⁴⁻³⁰. This approach was used successfully to treat numerous types of synthetic and actual wastes and in all cases the complete mineralization of the wastes was achieved with very high efficiency, which was only limited by mass transfer. This technology combines the production of large amounts of hydroxyl radicals with the direct electrooxidation of the pollutants on the surface of the conductive-diamond. In this process mediated oxidation also occurs by other oxidants electrogenerated on the surface from the oxidation of electrolyte salts.

The goal of this research was to evaluate the treatment by Conductive Diamond Electrochemical Oxidation (CDEO) and the comparison with the DSA Electrochemical Oxidation (DSA-EO) of three effluents generated in a soil-washing process. The effluents were contaminated with phenanthrene and three surfactants with different molecular structures: anionic, cationic and non-ionic.

2. Materials and methods

2.1. Materials

Kaolinite was selected as a model clay soil in this work. This material is not reactive and it has low hydraulic conductivity, low cation exchange capacity and no organic content. The physico-chemical properties of this soil are shown in Table 1. Phenanthrene (97%) was selected as a model PAH and it was obtained from Merck. Three types of surfactant were used in the washing solutions: sodium dodecyl sulphate (SDS) as a model anionic surfactant, alkylbenzyltrimethylammonium chloride

1 (ABDMA) as a model cationic surfactant and polyoxyethylene sorbitan monooleate
2 (Tween 80) as a model non-ionic surfactant. These compounds were obtained from
3 Panreac. The properties of these compounds are shown in Table 2.

4 **2.2. Preparation of simulated soil**

5 The polluted soil sample was made by dissolving phenanthrene in acetone and
6 then mixing this phenanthrene/acetone solution with the kaolinite. The spiked clay was
7 aerated during one day to promote evaporation of the acetone and in this way the
8 phenanthrene was homogeneously distributed on the clay surface. This method has been
9 described in the literature ^{19,31,32}.

10 **2.3. Model solution samples**

11 Soil-washing experiments were carried out in a laboratory-scale plant in a batch
12 reactor. The tank volume was 2000 cm³. Low-permeability soil (135 g) polluted with
13 500 mg phenanthrene kg⁻¹ of soil and 1800 cm³ of washing solution (containing
14 deionised water and 10 g dm⁻³ of surfactant) were mixed in the reactor for 6 hours at a
15 stirring speed of 120 rpm. The same tank then acts as a settler to separate the soil from
16 the effluent generated during the soil-washing process. These effluents consisted of
17 aqueous mixtures of phenanthrene and surfactants with a very high COD.

18 **2.4. Experimental setup**

19 CDEO and DSA-EO assays were carried out in a single-compartment
20 electrochemical flow-cell under a batch operation mode. Electrolyses were carried out
21 in galvanostatic conditions, controlling the current density (30 mA cm⁻²) and
22 monitoring the cell potential. A diamond-based material and DSA were used as the
23 anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100
24 mm diameter), with a geometric area of 78 cm² and an electrode gap of 9 mm. The
25 model solution was stored in a glass tank (600 cm³) and circulated through the

electrolytic cell by means of a centrifugal pump (flow rate $2.5 \text{ dm}^3 \text{ min}^{-1}$). In this case of DSA-EO, 3000 mg dm^{-3} of Na_2SO_4 was added to the solution to diminish the cell potential. A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point. The experimental setup also contained a cyclone for gas-liquid separation and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide. Boron-doped diamond films were provided by CSEM (Switzerland) and were synthesized by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si (100) wafers ($0.1 \Omega \text{ cm}$, Siltronix). Commercial DSA- O_2 electrodes were supplied by ElectroCell AB (Sweden). Prior to use in galvanostatic electrolysis assays, all electrodes were anodically polarized for 0.5 h in $1 \text{ M H}_2\text{SO}_4$ and 0.5 h in 1 M NaOH at 70 mA cm^{-2} to remove any kind of impurity from their surfaces. Electrolyses were carried out in galvanostatic mode with a fixed current density of 30 mA cm^{-2} . The pH was not controlled.

2.5. Efficiency

The Chemical Oxygen Demand (COD) method was used to determine the average current efficiency (ACE) in CDEO experiments and this was calculated using Eq. 1, where COD_0 and COD_t are the COD (in $\text{g O}_2 \text{ dm}^{-3}$) at times 0 and t (in seconds), respectively, I is the current intensity (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistence ($32 \text{ g O}_2 \text{ mol}^{-1} / 4 \text{ mol e}^{-1} \text{ mol}^{-1} \text{ O}_2$)³³.

$$\text{ACE} = \frac{[\text{COD}_0 - \text{COD}_t] F V}{8 I t} \quad [1]$$

2.6. Analyses

The degradation of washing effluents was evaluated by chemical oxygen demand analyses (HACH DR2000 analyzer), with the organic load contained in the

1 washing effluents determined. Prior to analysis, samples taken during electrolyses
2 assays were filtered using 45 μm syringe filters.

3

4 **3. Results and discussion**

5 The changes in COD during the electrolyses with conductive-diamond anodes
6 are shown in Figure 1 for the three different types of washed soil fluids. It can be clearly
7 observed that CDEO is able to reduce significantly the organic load of the wastes
8 regardless of the surfactant agent used in the soil-washing process. However, it can also
9 be observed that the efficiency of the process is largely influenced by the type of
10 surfactant, with a more efficient treatment of the solution produced by washing the soils
11 with the cationic surfactant and a less efficient process in the case of the anionic
12 reagent. It should also be noted that the former case corresponds to a molecule with an
13 aromatic structure while the anionic surfactant is an aliphatic linear-chain species. One
14 very important point is that treatment of this last wastewater seems to lead to the
15 formation of oxidation-refractory compounds, since the COD decreases to a value at
16 which the process becomes inefficient. This finding is interesting as it is the first
17 observation of refractory-COD formation during a CDEO process. In previous studies
18 ^{34,35} it has always been shown that complete removal of pollutants is possible. It is
19 feasible that in these cases the linear structure of the surfactant molecule and the
20 absence of functional groups that can be attacked by the oxidants produced during
21 CDEO, or by direct electrolysis of these molecules on the conductive-diamond surface,
22 can explain this observation.

23 The influence of COD on the efficiency of the electrolytic process is represented
24 in Figure 2 along with the changes in the efficiency expected according to a well-known
25 CDEO model, which was validated with a significant number of wastewaters^{36, 37}. This

1 model assumes maximum efficiencies in COD removal for COD values higher than a
2 specific value called the COD limit (which can be related to the average mass transfer
3 coefficient of the pollutants in the electrochemical cell). Below this particular value the
4 efficiency decreases in a linear manner with COD down to zero. In the experimental
5 system used in this work (cell and electrochemical and fluid dynamic conditions) the
6 COD limit³⁷ is around 1750 mg dm⁻³.

7 It is important to mention that the model (solid line) does not fit any of the three
8 electrolysis experiments carried out here, suggesting a complex type of treatment in all
9 three cases. The very high values obtained in the treatment of the wastewater produced
10 with the cationic surfactant, with efficiencies over 100%, are especially curious. This
11 behaviour can only be explained by the electropolymerization of the species contained
12 in the molecule and the formation of insoluble species that are removed by filtration.

13 It is also important to note that within a broad range of COD concentrations the
14 electrolysis efficiency in the treatment of the other two model solutions remains
15 constant at a value around 65%, and that this value is only diminished in the COD-range
16 in which the formation of refractory compounds is observed in the case of the
17 wastewater produced with the anionic surfactant. Once again, unexpected behaviour
18 was observed, which in this case suggests an important role for mediated oxidation,
19 especially bearing in mind the complex structure and large size of the surfactant-
20 phenanthrene pollutants (which hinder direct electrolysis) and the significant proportion
21 of the current that is not used for COD removal.

22 The pH and conductivity changes during the electrolyses of the three model
23 solutions are represented in Figure 3. A significant pH decrease is observed and this can
24 be related to the formation of carboxylic acid intermediates during the treatment. The
25 formation of such intermediates can also explain the conductivity increase observed

1 during the three electrolysis processes. The initial decrease in the conductivity observed
2 in the CDEO of the wastewater produced with the cationic surfactant is consistent with
3 the electropolymerization proposed above and this indicates that the
4 electropolymerization is combined with the oxidation processes of the organic
5 pollutants.

6 The results obtained in the electrolyses of the three model solutions with
7 conductive-diamond anodes and with DSA are represented in Figure 4. In contrast to
8 CDEO, DSA technology is completely inefficient in the treatment of the wastes
9 produced by washing soils with anionic and non-ionic surfactants and unusual
10 behaviour is observed for the cationic waste: initially there is no appreciable change in
11 the COD and then it suddenly decreases down to a new constant value.

12 These observations are consistent with those shown in Figure 5, where it can be
13 observed that conductivity in the electrolytic media remains unchanged in the DSA
14 electrolyses of the wastes containing anionic and non-ionic surfactants. Indeed, the
15 conductivity does not increase but decreases in the case of the wastewater containing
16 cationic surfactant, suggesting some sort of polymerization rather than any type of
17 oxidation, which would be expected to lead to the formation of carboxylic acids and
18 thus to an increase in the conductivity.

19 Finally, the influence of the COD on the current efficiency of the process is
20 represented in Figure 6. The continuous line shows the expected behaviour for an ideal
21 electrochemical process according to the model mentioned previously^{36,37}. It can be
22 observed that the COD concentration does not influence the efficiency of the
23 electrolyses with DSA, even in the case where the electrolytic system is able to diminish
24 the COD.

25

1 **4. Conclusions**

2 Conductive-diamond electrochemical oxidation can be successfully used to treat
3 soil-washing model solutions polluted with phenanthrene and with three different
4 surfactant solutions used as washing fluids. However, the efficiency of the process
5 seems to be largely influenced by the type of surfactant: the treatment of model
6 solutions containing a cationic surfactant proved more efficient than those with the
7 anionic reagent. In the former case, electropolymerization processes contribute to
8 enhance the efficiency, while in the case of the anionic surfactant the generation of
9 oxidation-refractory compounds takes place. These results can be explained in terms of
10 the molecular structure: the cationic surfactant corresponds to a molecule with an
11 important aromatic structure while the anionic surfactant is an aliphatic linear-chain
12 species. Changes in pH and conductivity seem to confirm this assumption. In contrast to
13 CDEO, DSA technology is completely inefficient in the treatment of the wastes
14 produced in the soil-washing process.

15

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- 3

Table 1. Physico-chemical properties of kaolinite.

Mineralogy		Particle size distribution (%)	
Kaolinite	100.00%	Gravel	0
Fe ₂ O ₃	0.58%	Sand	4
TiO ₂	0.27%	Silt	18
CaO	0.10%	Clay	78
K ₂ O	0.75%	Specific gravity	2.6
SiO ₂	52.35%	Hydraulic conductivity (cm/s)	1 x 10 ⁻⁸
Al ₂ O ₃	34.50%	Organic content (%)	0
Others	11.42%	pH	4.9

1

Table 2. Properties of surfactants.

Surfactant	Type	Formula	MW	Density	Molecular structure
Tween 80	Non-ionic	$C_{64}H_{124}O_{26}$	1309.63	1.064
Sodium dodecyl sulfate	Anionic	$C_{12}H_{25}NaO_4S$	288.38	-
Alkylbenzyltrimethylammonium chloride	Cationic	$C_{21}H_{38}ClN$	339.99	0.98

2

3

1 **Figure captions**

2 **Figure 1.** Changes in the COD during the electrolyses with conductive-diamond anodes
3 of three different types of washing soil fluids (Current density (j): 30 mA cm⁻²). ■
4 Anionic surfactant, ◆ Non-ionic Surfactant, ▲ Cationic surfactant.

5

6 **Figure 2.** Changes in the Average current efficiency (ACE) with the COD during the
7 electrolyses with conductive-diamond anodes of three different types of washing soil
8 fluids (j: 30 mA cm⁻²). ■ Anionic surfactant, ◆ Non-ionic Surfactant, ▲ Cationic
9 surfactant. Solid line: CDEO model³⁷.

10

11 **Figure 3.** Changes in the pH (a) and conductivity (b) during the electrolyses with
12 conductive-diamond anodes of three different types of washing soil fluids (j: 30 mA
13 cm⁻²). ■ Anionic surfactant, ◆ Non-ionic Surfactant, ▲ Cationic surfactant.

14

15 **Figure 4.** Changes in the COD during the electrolyses with boron doped diamond (■)
16 and DSA (◆) electrodes of three different types of washing soil fluids (j: 30 mA cm⁻²).
17 (a) Anionic surfactant, (b) Non-ionic Surfactant, (c) Cationic surfactant.

18

19 **Figure 5.** Changes in the pH (a) and conductivity (b) during the electrolyses with DSA
20 electrodes of three different types of washing soil fluids (j: 30 mA cm⁻²). ■ Anionic
21 surfactant, ◆ Non-ionic Surfactant, ▲ Cationic surfactant.

22

23 **Figure 6.** Changes in the Average current efficiency (ACE) with the COD during the
24 electrolyses with DSA electrodes of three different types of washing soil fluids (j: 30

- 1 mA cm⁻²). ■ Anionic surfactant, ◆ Non-ionic Surfactant, ▲ Cationic surfactant. Solid
- 2 line: CDEO model³⁷.
- 3

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6