

# **The role of particle size on the conductive diamond electrochemical oxidation of soil-washing effluent polluted with atrazine**

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## **Abstract**

Soil washing using surfactant solutions is a very effective and widely used technique for the remediation of polluted soil. However, it is not a finalistic technology and once the pollutant is transferred to the washing-solution, the resulting aqueous waste has to be treated. In this work, it is studied the feasibility of Conductive - Diamond Electrochemical – Oxidation (CDEO) to treat the effluent of a surfactant-aided soil washing process and it is pointed out some important mechanistic aspects. Atrazine was selected as the model pesticide and sodium dodecyl sulphate (anionic surfactant) was used as washing agent. Besides COD, TOC, and pollutants concentration, the changes of z-potential and particle size were monitored during electrolysis in order to clarify the degradation mechanisms involved in the electrochemical treatment of emulsions. The results show that CDEO enables a complete reduction in the organic load of the waste. However, the process efficiency seems to be influenced by the size of particles present in the reaction media, which decreases continuously during the treatment. Steric hindrance of the large micelles (mean size 1100 um) seems to prevent direct oxidation of micelles on the anodic surface and hence only mediated processes can explain the results obtained. In this case, it may be assumed that peroxocarbonate (from carbonate salts added as supporting electrolyte) and peroxosulphate ions (formed from the oxidation of sulphate ions released from SDS molecule) are the main species expected according to the washing fluid composition.

**Keywords**

Conductive diamond, electrolysis, particle size, surfactant, soil washing

## 1. Introduction

Pesticides may cause serious pollution problems in soils due to its mutagenic and carcinogenic characteristics [1, 2]. Among them, atrazine has been the focus of several researches [3-9] because of its low biodegradability, long half-life and low solubility in water ( $33 \text{ mg dm}^{-3}$  at  $22^\circ\text{C}$ ). Surfactant-aided soil washing (SASW) has become relevant treatment for this type of polluted soil [10-12]. This process remediates the soil and thus converts the problem of soil remediation into a potentially easier wastewater treatment problem [10, 13]. However, this type of effluent is difficult to treat by conventional wastewater treatment methods because of the complexity of the matrix: an emulsified effluent containing pesticide, surfactant (large molecules with complex organic groups) and particles of soil dragged in the washing process[14].

Many works have been published during the recent years about the elimination of atrazine from wastewater [8, 15-21]. In this work, Conductive Diamond Electrochemical Oxidation (CDEO) was selected for the treatment of soil washing effluents from remediated soil polluted with atrazine. This technique has been widely studied in literature to treat numerous types of synthetic and actual wastes [15-20] and it is known for its high efficiency, typically associated to the combination of direct oxidation of the pollutants on the surface of the conductive-diamond with the action of large amounts of  $\bullet\text{OH}$  and other oxidants electrogenerated from the oxidation of electrolyte salts [21].

Electrochemical studies about atrazine removal [22, 23] are mainly focussed on the treatability of synthetic solutions, paying attention to the changes of the typical parameters used for monitoring the oxidation and mineralization rates, but not on the break-up of the emulsion neither the changes in the particle size, what becomes in a real novelty in this work. No attempts have been published regarding on the removal of micelles by CDEO, relating the treatment with the emulsified pollutant and the interaction of these micro-drops of pollutant with the different oxidation mechanisms. Therefore, the objective and main novelty of this work was to investigate the treatment of effluents

generated by soil-washing polluted with atrazine by CDEO, focusing on the effect of the size particle and the oxidation mechanisms of atrazine/surfactant micelles.

## **2. Materials and methods**

**Chemicals.** Kaolinite was selected as a model clay soil and atrazine (Fluka) as model of organic compound. Sodium dodecyl sulphate (SDS) (Panreac) was used as solubilizing agent and NaHCO<sub>3</sub> (96 %, Panreac) as supporting electrolyte. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

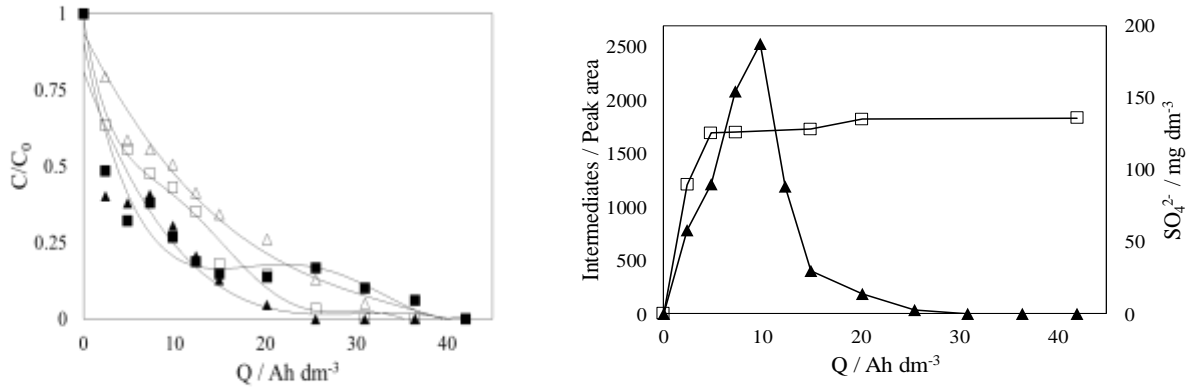
**Analytic techniques.** All samples extracted from electrolyzed solution were filtered with 0.45 µm nylon filters (Whatman) before analysis. The atrazine was extracted using ethyl acetate/hexane as solvent and quantified by HPLC (Agilent 1100 series) using analytical column Phenomenex Gemini 5 µm C18 at 223 nm and 25°C, with acetonitrile/water (45:55 v/v) at 0.3 cm<sup>3</sup> min<sup>-1</sup> as mobile phase. TOC was monitored using a Multi N/C 3100 Analytik Jena analyser. COD was measured using a HACH DR2000 analyzer. SDS was measured colorimetrically [24]. Z-potential was measured using a Zetasizer Nano ZS (Malvern, UK) and particle size with a Mastersizer Hydro 2000SM (Malvern, UK). Measurements of pH were carried out with an InoLab WTW pH-meter.

**Preparation of spiked soil.** The polluted soil sample was made by dissolving atrazine in hexane and then mixing this atrazine/hexane solution with the kaolinite. The spiked clay was aerated during one day to promote evaporation of the hexane. In this way the atrazine was homogeneously distributed on the clay surface. The resulting atrazine concentration in the soil was around 100 mg kg<sup>-1</sup> of soil.

**Experimental procedure.** Surfactant-aided soil washing tests were carried out in a stirred bench-scale tank operated in discontinuous mode. The tank volume was 1000 cm<sup>3</sup>. Low-permeability soil (1000 g) polluted with 100 mg atrazine kg<sup>-1</sup> of soil and 800 cm<sup>3</sup> of washing solution (containing deionised water, 500 mg dm<sup>-3</sup> of NaHCO<sub>3</sub> and 100 mg dm<sup>-3</sup> of surfactant) were mixed in the tank for 6 h at a stirring rate of 120 rpm. Then, the same tank acts as a settler (during 24 h) to separate the soil from the effluent generated during the soil-washing process. Electrochemical experiments were carried out in a setup described elsewhere [25].

## Results and Discussion

A synthetic soil-washing solution obtained according to the procedure described in the experimental section was separated from the tank and filtered prior to electrochemical experiments to remove particles of soil dragged in during the washing process. It consists of an emulsion of atrazine in water stabilized by the surfactant (particle size distribution <100 μm=0.09%; <500 μm=6.3%; <1000 μm=47.7%; <1500 μm=77.5%; <1750 μm=90.1% and <2000 μm=100%; COD=276 mg dm<sup>-3</sup>; TOC=40.9 mg dm<sup>-3</sup>; Conductivity=0.272 mS cm<sup>-1</sup>; pH=8.48; z-potential=-22.7 mV and mean particle size=1121 μm) with two main organic pollutants (the pesticide and the surfactant) and several species from the viewpoint of reactivity, because the dissolved pesticide, dissolved surfactant and the micro-drops are expected to behave in a different way during the treatment. Mean particle size is around 1100 μm and most of the particles (80%) are within the range 500-1750 μm. The extremely high mean size of micelles does not promote but even prevent by steric hindrance the direct oxidation of micelles on the electrode surface. The changes in COD, TOC, atrazine and surfactant concentrations with the electrical charge passed during the galvanostatic CDEO of the soil washing effluent are shown in Figure 1a.



**Figure 1.** Changes during the CDEO of surfactant-soil-washing effluent (a) (▲) TOC: (■) COD (Δ) Atrazine: (□) SDS concentration. (b) total amount of intermediates (▲) quantified as total chromatographic area and (■) concentration of SO<sub>4</sub><sup>2-</sup>.

As it can be observed, organic load of the washing fluid is completely depleted during the electrolysis, pointing out the effectiveness of the CDEO in the treatment of complex wastewater, in spite pollution of this effluent lies outside the recommended target for the applicability of CDEO [26]. Trends observed in the decay of the four parameters are slightly different, being this fact indicative of the complexity of the system. In comparing the changes in the globalized pollution parameters (TOC and COD) with those of the surfactant and pesticide, it can be observed a plateau zone for applied electric charges in the range 5-10 Ah dm<sup>-3</sup>, which is not consistent with the exponential decay of the two raw pollutants. This type of change was previously observed in the treatment of other species with low water solubility such as chlorophenols [27-29] and it was explained in terms of the formation of reaction intermediates with high oxidizability, which consumes more efficiently the oxidants electrogenerated on the anode surface during the electrolysis (mediated electrolysis) and also may react faster on the anode surface (direct electrolysis). Differences observed between TOC and COD pointed out the uncertainty of the globalized parameters in the monitoring of the treatment of complex effluents consisting in heterogeneous mixtures, like the soil washing fluid studied in this work. Another important point to

be considered is the formation of oxidant species in the reaction media. In electrolytes with carbonates/bicarbonates is known to be produced peroxocarbonates [30] according to equations 1 - 3.

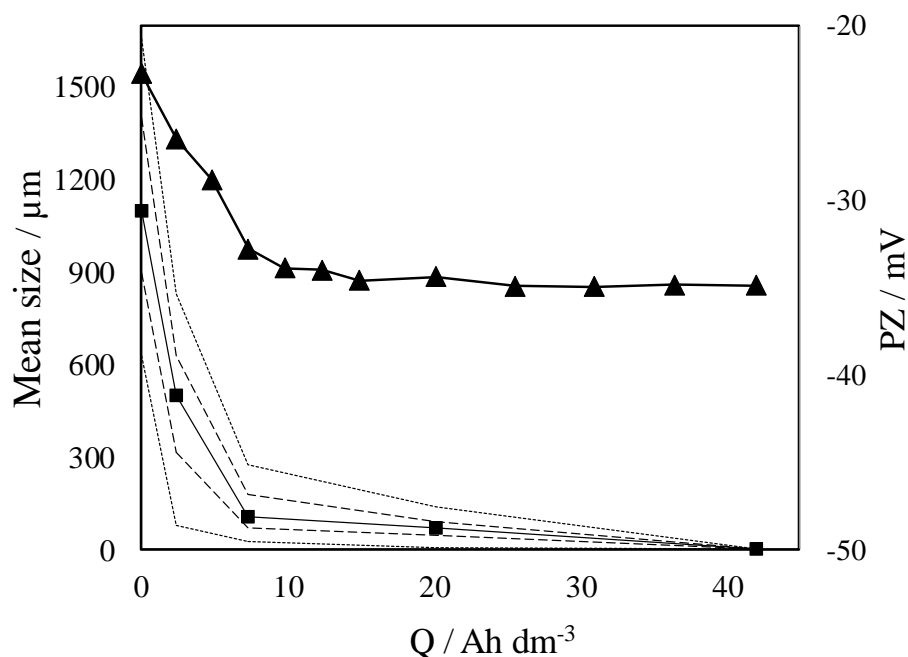


Likewise, during the degradation of SDS, the release of sulphate ions contained in the surfactant molecule takes place. This release can be clearly observed in Figure 1b, where the concentration of sulphate is shown during the electrolysis. It is well-known [26-29] that peroxodisulphates can be produced by direct (eqs. 3) or hydroxyl-radical mediated (eqs. 4 and 5) oxidation during CDEO.



Decomposition of peroxocarbonates and peroxosulphates yields hydrogen peroxide, which in addition to contribute to the complex mixture of oxidants produced in the electrolysis, may affect the value of COD measured. Due to the high size of the micelles, their direct oxidation on the surface of the diamond is not alike to happen. This fact means that mediated oxidation is playing an important role in this treatment. Regarding mechanisms, Figure 1b also informs about intermediates produced in the reaction media because it shows the total chromatographic area of the three intermediates detected by HPLC. As it can be observed, total concentration is low and complete removal is obtained for electric charges as low as 25 Ah dm<sup>-3</sup>.

In this point, it is important to check the behaviour of the emulsion of atrazine/surfactant during the electrolysis, because the break-up of the emulsion is not expected to be instantaneous and no previous information is found in the literature about the way in which micelles are depleted in an electrochemical oxidation process. To assess this point, particle size and zeta potential were also monitored during the electrolysis and results are shown in Figure 2.



**Figure 2.** Changes in z-potential (▲) and mean particle size (■) during the CDEO of surfactant-soil-washing effluent. Size limits including (---) 50% of the particles; size limits including 80% of the particles (.....).

As it can be observed, the particle size decreases rapidly during the initial stages of the electrolysis from 1100 down to 100  $\mu\text{m}$  (for electric applied charges around 7  $\text{Ah dm}^{-3}$ ) as well as the range of particle sizes. This trend is consistent with the changes obtained in the z-potential, which decreases rapidly until attaining a constant value around -35 mV for similar electrical charge passed. This indicates that the atrazine/surfactant micelles are drastically attacked during the first stages to form smaller particles with more negative surface charge. In this point, it is important to take in mind that



it is used an anionic surfactant and thus, the expected superficial charge of micelles is negative. The smaller the particles, the higher is the surface of micro-drops which has to be covered with surfactants and hence the more negative is the resulting zeta potential. After this initial rapid reduction in size of the micro-drops, size continues decreasing till the end of the test although at a lower rate, while the z-potential value kept almost constant (in fact a small trend towards more negative values is observed).

Regarding oxidation performance, in reducing the size of the particles, the readily available surface of surfactant and pesticide to be attacked in the micelles becomes higher. Hence, oxidation rate may become promoted, either by the attack of oxidants or even by the direct oxidation on the surface of the electrode once the micelles are reduced to a very low size (as the steric hindrance of micelles is minimized). This can help to explain the increase observed in the oxidation rate of pollutant for electrical charges higher than  $10 \text{ Ah dm}^{-3}$  (Figure 1) and in particular the plateau observed in the COD and TOC decay. In comparing the decay of surfactant and pesticide, it is observed a faster depletion of the surfactant which is consistent with the attack to the surface of the micro-drops in which this SDS is protecting the pesticide. Likewise, the continuous decrease in the TOC, COD, surfactants and pesticide indicates that these species are mineralized from the beginning of the experiment and that micelles reduction is accompanied by mineralization of the organic species.

## **Conclusions**

Surfactant aided soil washing fluid can be efficiently treated by CDEO. This oxidation is very complex from the mechanistic point of view and involves the reduction in size of the micro-drops of pesticide-surfactant formed during the soil washing treatment and the simultaneous mineralization of the organic content. Large size of the micelles prevents their direct oxidation on the diamond surface, indicating that electrolytic process should be controlled by mediated oxidation, being peroxocarbonates the main species expected according to the composition of the soil washing fluid.

Release of sulphate during the oxidation of the surfactant and production of persulphates helps to keep a significant organic degradation rate during the process. In comparing the degradation of the two raw organic species, surfactant is depleted faster because it is more easily accessible to oxidants in the surface of the microdrops.

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