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# Direct electrochemical oxidation of a pesticide, 2,4-dichlorophenoxyacetic acid, at the surface of a graphite felt electrode: Biodegradability improvement



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## ARTICLE INFO

## Article history:

Received 25 February 2014

Accepted after revision 15 May 2014

Available online 2 July 2014

## Keywords:

2,4-D

Combined process

Electrochemical process

Biological treatment

Carbon felt electrode

## ABSTRACT

Pesticides' biorecalcitrance can be related to the presence of a complex aromatic chains or of specific bonds, such as halogenated bonds, which are the most widespread. In order to treat this pollution at its source, namely in the case of highly concentrated solutions, selective processes, such as electrochemical processes, can appear especially relevant to avoid the possible generation of toxic degradation products and to improve biodegradability in view of a subsequent biological mineralization. 2,4-D was found to be electroactive in oxidation, but not in reduction, and the absence of hydroxyl radicals formation during the electrochemical step was demonstrated, showing that the pretreatment can be considered as a "direct" electrochemical process instead of an advanced electrochemical oxidation process. The presence of several degradation products in the oxidized effluent showed that the pretreatment was not as selective as expected. However, the relevance of the proposed combined process was confirmed since the overall mineralization yield was close to 93%.

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## 1. Introduction

The large accumulation of endocrine disruptors, in continental and marine natural waters are the consequence of the worldwide general application of intensive agricultural methods, the large-scale development of the agrochemical and food industry and the high levels found in some specific effluents (textile, pharmaceutical, hospital waste. . .). For instance, in the Brittany region (France), the

Regional Direction of the Environment (DIREN) observes river contamination by phytosanitary products, including pesticides, which can interfere with hormone systems of living beings (endocrine disruptors) [1]. Partly responsible for this pollution, low volumes containing high concentrations of persistent organic pollutants, in the range of concentrations found in some specific industrial and agricultural effluents (unused treatment solution, spray, machine and container washing. . .) [2], can result in large polluted volumes that are difficult to treat owing to their low pollutant concentrations. One solution would be therefore to treat pollution at its source, as intended in this study.

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Pesticides' impact on the environment is complex and varied according to various factors, such as toxicity and ecotoxicity of the parent molecule or by-product metabolites, synergistic effects with other pollutants, length of the half-life, exposure time and dose, etc. Various acute or chronic poisoning effects on human health have been described [3–6]. There is therefore an urgent need for efficient processes for their removal and, owing to the possible toxicity of the by-product metabolites, total mineralization is mainly targeted.

For this purpose, biological processes, the most cost-effective for wastewater treatment, which are destructive and have been extensively studied [7–11], do not always appear relevant for the removal of recalcitrant compounds, owing to their low biodegradability.

Contrarily, physicochemical techniques have proved their efficiency for such removal. Among them, advanced oxidation processes constitute the most important and widely documented group [2,12,13], owing to the high reactivity of the free  $\cdot\text{OH}$  radicals produced. However, and due to the lack of selectivity of the free radicals, possible toxic by-products can be generated, which in some cases can appear more toxic than the parent compounds [14,15]. Consequently, the mineralization time is of major importance; a too low processing time can result in toxic by-products, while a long processing time to ensure total mineralization can induce high-energy costs.

It is noteworthy that pesticides biorecalcitrance can be related to the presence of a complex aromatic chain or to the presence of specific bonds, such as nitro- or halogenated bonds. For instance, among the most used pesticides, a three-quarter of them contain halogenated bonds, and the presence of chlorine atoms on phenyl ring is a factor that favors the toxicity of aryl compounds [16]. From this, the development of processes targeting a selective attack of specific functional groups to improve the biodegradability of a given effluent can constitute another approach to treat pesticide-containing effluents.

Indeed, if agricultural effluents are for instance considered, pesticides levels can reach  $500\text{ mg}\cdot\text{L}^{-1}$  [2], as it is the case in farm bottom tanks. Hence, a selective attack of specific functional groups can constitute a relevant solution to relieve AOPs drawbacks. The generation of possible toxic by-products could thus be avoided owing to the expected control of the resulting by-products as well as the high-energy costs, since total mineralization is not the objective, due to the expected improvement of biodegradability.

For this purpose and in the case of an electroactive target compound, its electrochemical oxidation or reduction can be carried out for its degradation. Total mineralization can be subsequently completed during biological treatment, since the potential advantages of the strategy of combining physicochemical and biological processes to treat contaminants in wastewater were previously underlined [17–20]. However, the literature dealing with the use of direct electrochemical oxidation/reduction for effluent pretreatment remains scarce. Doan et al. [21] and Ghafari et al. [22] coupled an electrochemical process and a biological treatment for the removal of heavy metals and nitrate, respectively, while regarding organic pollutants,

up to now our work seems to be the only one available dealing with the combination of a direct electrochemical process and a biological treatment. It was investigated for the removal of phosmet, an organophosphorous insecticide [23], some antibiotics, tetracycline [24], sulfamethazine [25], and a chlorinated phenoxy herbicide, 2,4-dichlorophenoxyacetic acid [26,27].

The promising results obtained regarding 2,4-D should be underlined [28,29], since halogenated pesticides are the most widespread pesticides. Indeed, it was shown that mild oxidation of the target compound can be sufficient to improve biodegradability [28], allowing subsequent biological treatment [29]. However in view of the targeted selectivity, the nature of the electrochemical process should be clearly elucidated, namely the involvement or not of free hydroxyl radicals in pesticide oxidation; it is discussed in this study.

However, the production of this highly reactive species is closely linked to the electrode material used and to some operating parameters such as oxygen overvoltage. If some electrodes (boron-doped diamond electrodes for instance) are well-known as powerful candidates for  $\cdot\text{OH}$  generation, it is not at all obvious for some other materials, such as graphite felt, the material used in the laboratory [23,25–27]. Indeed, the use of a graphite felt working electrode with a high specific area in a flow electrochemical cell [30] allows the electrochemical reaction of the electroactive species at macroscale level with low electrolysis times. Even if mechanisms involving  $\cdot\text{OH}$  have been previously suggested for studies based on the use of graphite felt [31], to our knowledge such production at the surface of such electrode material has never been demonstrated up to now. However, this question appears to be of major importance to understand the electrochemical oxidation phenomena occurring when using such material and to confirm the specificity and selectivity of the considered processes, namely a direct reaction at the electrode surface. For this purpose, three points have to be considered, the nature of the working electrode, the experimental conditions and the indirect determination of the hydroxyl radicals; these points are investigated in this study.

In addition and to complete the mechanism's knowledge, the electrochemical reaction of 2,4-D at the electrode was also examined.

Biological treatment involving activated sludge was then considered to examine the efficiency of the electrochemical pretreatment.

## 2. Materials and methods

### 2.1. Chemicals

2,4-Dichlorophenoxyacetic acid (2,4-D) (98%) was purchased from Alfa Aesar (Schiltigheim, France). Chlorohydroquinone (85%) was purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France). Acetonitrile (ACN) and formic acid were LC/MS grade from JT Baker (Deventer, Netherlands). All standards were prepared with ultra-pure water (PurelabOptions-Q7/15, Elga,  $18.2\text{ M}\Omega\cdot\text{cm}$ ).

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