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Combined process for 2,4-Dichlorophenoxyacetic acid treatment—Coupling of an electrochemical system with a biological treatment

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ABSTRACT

A coupled process was studied for the removal of a chlorinated pesticide: 2,4-Dichlorophenoxyacetic acid (2,4-D). A home-made electrochemical flow cell was used for the pre-treatment and a biological treatment was then carried out using activated sludge supplied by a local wastewater treatment plant. 2,4-D was used as a target compound for the study. Several parameters were monitored during the biological treatment, like dissolved organic carbon (DOC), the target compound and the major by-product. Pretreatment led to a quick decrease of DOC during the biological process, since a 66% mineralization yield was measured after the second day, and 79% after the seventh day of culture. After two days of treatment, HPLC results revealed a total degradation of Chlorohydroquinone, the major by-product. The electrochemical pretreatment shortened the length of the biological treatment, since DOC measurements showed that in the case of non-pretreated 2,4-D, no mineralization was observed before day 7. These promising results should be subsequently confirmed on commercial 2,4-D-containing solutions and then on real effluents.

1. Introduction

The usage of pesticides in intensive agricultural practice has brought out environmental and health concerns since it negatively impacts water and soil quality. Removing pesticides to protect water resources has thus become a great challenge in current research [1]. Wastewater from agricultural industries like pesticides formulating plants or bottom farm tanks can contain high levels of pesticides (up to 500 mg L^{-1}) [2]. Theses effluents need therefore to be treated by specific physical, chemical or biological processes.

2,4-Dichlorophenoxyacetic acid (2,4-D, Fig. 1) is one of the most used phenoxyalkanoic herbicides in the world [3,4], and more than 1500 pesticides contain 2,4-D as the main active substance [5]. Phenoxyalkanoic herbicides are considered as serious contaminants of streams, lakes and rivers [6], especially because of their high solubility in water and low tendency to accumulate in organic matter [7]. As a matter of fact, 2,4-D has frequently been detected in surface and ground waters in Europe and North America [8,9]. Moreover, 2,4-D is known to present serious ecological impact, like toxic effects on birds, beneficial insects, non-target plants but also on algae, small invertebrates, amphibians, fishes and more generally on aquatic life [10,11].

Over the past few decades, the literature has disclosed a plethora of studies focusing on 2,4-D degradation. Many bacterial strains capable of degrading 2,4-D have been isolated, such as several strains of *Pseudomonas*, *Arthrobacter* and *Alcaligenes* [12–16]. However, in many cases, the mineralization yield was low or even not measured [17]. The feasibility of a biological treatment based on pure strains of bacteria remains therefore limited, and 2,4-D removal was thus also studied with consortium of bacteria, isolated from soil samples or activated sludge from wastewater treatment plant. A 250 mg L^{-1} 2,4-D concentration as a sole carbon source was degraded in 8 days using different enrichment cultures based on soil samples from a fertilizer manufacturing plant site [18]. Activated sludge from municipal wastewater treatment plant has also shown the ability to partially degrade a waste stream containing 10 mg L^{-1} of the herbicide [19]. Experiments carried out in Sequencing Batch Reactors (SBRs) led to the removal of a 100 mg L^{-1} 2,4-D concentration. However, a 4 months acclimation period of the activated sludge was necessary [8]. More recently, this acclimation period was reduced to 30 days to degrade up to 500 mg L^{-1} of 2,4-D, but this results were obtained with a biomass that was previously exposed to the pesticide [20]. Despite the economical advantage of

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Nomenclature

2,4-D	2,4-Dichlorophenoxyacetic acid
SBRs	sequencing batch reactors
AOPs	advanced oxidation processes
SCE	saturated calomel electrode
HPLC	high pressure liquid chromatography
LC/MS/MS	liquid chromatography/mass spectroscopy/mass spectroscopy
GC/MS	gas chromatography/mass spectroscopy
DOC	dissolved organic carbon
NPOC	non purgeable organic carbon
COD	chemical oxygen demand
BOD_5	biological oxygen demand after 5 days

the activated sludge, the efficiency of the biological treatment can be limited with recalcitrant compound and also be time-consuming when a long acclimation period is necessary.

2,4-D removal has been thoroughly studied using ozonation processes [21–23] or advanced oxidation processes (AOPs) like anodic oxidation, Fenton and Fenton-like processes [24–27], photocatalysis [28,29]. Despite their efficiency, the total mineralization of the effluent to treat can be time and energy-consuming, thus increasing operational costs. Moreover, these processes showed other drawbacks such as the disposal of iron waste in case of Fenton and Fenton-like processes. The combination of AOP with biological treatments can therefore appear as a good alternative to reduce operating costs. The aim of the pre-treatment step is to increase the biodegradability of the initial biorecalcitrant solution; the intermediates formed should therefore be more biodegradable than the target compound, while the mineralization yield should remain limited to ensure significant residual organic carbon content for the subsequent biological treatment and to limit the energy costs. The literature reports numerous studies dealing with AOPs as pre-treatment steps prior to biological processes. For example, isoproturon was mineralized by combining heterogeneous photocatalysis with a bioreactor containing bacteria supported on biolite [30]. The herbicides diurion and linuron treated by photo-Fenton led to non-toxic and biodegradable intermediates that were degraded in a biological Sequencing Batch Reactor [31].

As an alternative to Advanced Oxidative Processes, electrochemical systems can also be considered. Electrochemical systems were already combined with biological processes to remove heavy metals or nitrates from different wastewaters [32,33]. Regarding organic recalcitrant compounds, the biodegradability of a 100 mg L^{-1} tetracycline solution was found to increase after electrolysis in a home-made flow cell involving a carbon felt electrode [34], as well as the biodegradability of a 1000 mg L^{-1} acetamipirid solution after pretreatment using a boron-doped diamond electrode [35]. In both cases, the Biological Oxygen Demand after 5 days (BOD_5) on Chemical Oxygen Demand (COD) ratio (BOD_5/COD) increased from negligible values for the target compounds to above 0.4, namely the limit of biodegradability, after the electrochemical pretreatment, showing that the produced intermediates can be most likely biodegraded during biological treatment. However and to our knowledge, the implementation of an electrochemical pretreatment and a biological process seems to be only performed for the treatment of an herbicide, phosmet, leading to 97% of mineralization [36].

The feasibility of the electrochemical pre-treatment to increase the biodegradability of 2,4-D was previously shown in the laboratory [37]. The electrochemical step was based on a home-made flow cell using bare graphite felt as a working electrode. The graphite felt presents several advantages, like its moderate cost and its high specific area. The electrochemical behavior of the target compound was investigated and major intermediates were detected and quantified. To complete this previous work, the relevance of the combined process for 2,4-D treatment should be assessed. This task was the main purpose of this work. The aerobic biological treatment was carried out using activated sludge purchased from a local wastewater treatment plant. Assessment of the efficiency of the combined process was based on the monitoring of specific parameters namely the target compound and the major by-products (HPLC measurements) on the one hand, and global parameters namely mineralization and oxidation through the determination of DOC and COD values on the other hand.

2. Experimental

2.1. Chemicals

2,4-Dichlorophenoxyacetic acid (98%) was purchased from Alfa Aesar (Schiltigheim, 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 MΩ cm).

2.2. Materials for the electrochemical pre-treatment

The electrochemical pre-treatment has been carried out as previously described [37]. This electrochemical step was based on a home-made flow cell using a graphite felt as a working electrode supplied by Mersen (RVG 4000-Mersen, Paris La Défense, France). The dimensions of the graphite felt were 48 mm diameter and 12 mm width.

A potential of 1.6 V/SCE was applied using a VersaSTAT 3 potentiostat from Ametek/Princeton Applied (Elancourt, France). The cell was thoroughly rinsed with distilled water before and after each experiment. The electrolyte solution (500 mg L^{-1} 2,4-D in 0.1 M Na_2SO_4) percolated the porous electrode at a constant flow rate of 1 mL min^{-1} monitored by a Gilson minipuls 2 peristaltic pump (Middleton, WI, USA).

2.3. Biological treatment

After only one pass through the electrochemical flow-cell, the effluent was collected for the subsequent biological treatment,

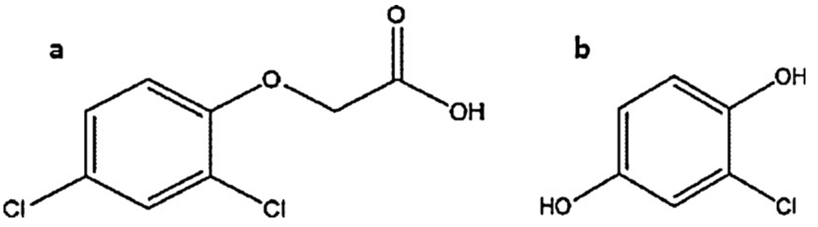

Fig. 1. Chemical structures of 2,4-Dichlorophenoxyacetic acid and Chlorohydroquinone.