



## Reductive dechlorination of a chloroacetanilide herbicide in water by a Co complex-supported catalyst



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### ABSTRACT

Chloroacetanilide herbicides are widely used pesticides in agriculture, resulting in contamination of ground and surface waters. Among the methods studied to enhance their degradation rate, reductive dechlorination is proposed. A  $[\text{Co}(\text{bpy}(\text{CH}_2\text{OH})_2)_2]^{2+}$  complex allowing electrocatalytic reduction of chloroacetanilide herbicides is covalently immobilized on a 3D porous electrode previously functionalized by electrografting methods. Bulk electrolyses performed on alachlor in a flow electrochemical cell show the high catalytic activity of the Co complex, leading to a total reduction of the substrate and a good selectivity toward the formation of the dechlorinated derivative. Interestingly, when it is immobilized, the catalyst is more stable than in solution as shown by the turnover number of more than 360 compared with a value of 4 in solution. Biodegradability on 5 days did not show any improvement compared with the starting material, highlighting that even if chlorine atoms that are often responsible for the toxicity of a molecule are removed, the substrate can still have a biorecalcitrant behaviour. The main by-product, deschloralachlor, was identified and was found to be not biodegradable accounting for this recalcitrance.

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### 1. Introduction

Pesticides belong to emerging contaminants and have been largely detected in ground and surface waters [1–5]. The large accumulation of pesticides in continental and marine natural waters [4] is the consequence of the worldwide general application of intensive agricultural methods. In 2001 in the United States, the use of conventional pesticides exceeded 500,000 t, for a worldwide usage of 2 million tons [6]. France is the first European consumer of pesticides and the third globally, with 80,000–100,000 tons/year for the last thirty years [7].

The chloroacetanilide herbicides such as alachlor, metolachlor and metazachlor belong to one of the most widespread classes of herbicides used for control of annual grasses and broadleaf weeds in agricultural crops. They have moderate to high chronic toxicity and have been characterized as probable human carcinogen. They also persist for a long time in soil and their residues and degradation metabolites have been frequently detected in ground and surface waters [8–10].

The degradation of chloroacetanilide herbicides is difficult in conventional activated sludge systems and requires specific microorganisms [11,12]. Thus, advanced oxidation processes (AOPs) have been studied for enhancement of their biodegradability. For example, direct photolysis and ozonation of alachlor have proven to be insignificant and slow processes, which nevertheless can be improved by addition of  $\text{TiO}_2$  [13–15]. Photo-Fenton and  $\text{Fe(III)/H}_2\text{O}_2$  Fenton system have proved their efficiency for the degradation of chloroacetanilide herbicides [16–18]. However, the partial degradation of the biorecalcitrant compound can be accompanied by an increase of toxicity, as it has been noticed with alachlor [19]. The enhancement of biodegradability of alachlor has also been achieved by gamma irradiation in the presence of hydrogen peroxide [20].

Oxidation treatments are usually efficient to degrade organic compounds due to the formation of very active hydroxyl radicals but can present some drawbacks for the treatment of chlorinated compounds. Thus, the formation of harmful and hazardous by-products such as inorganic and organic chloramines and perchlorate has been reported during electrooxidation and ozonation processes of chloro-species [21,22]. An inhibitory effect of chloride ions on the Fenton process has also been noticed and attributed to

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the complexation of Fe(III) in competition with hydrogen peroxide [23–25].

The enhancement of the degradation rate of alachlor by reduction processes has also been reported, especially dechlorination processes, since the presence of chloro groups in the structure of a molecule is known to increase its biorecalcitrance [26].

Thus zero valent iron ( $\text{Fe}^0$ ) can promote reductive dechlorination of chloroacetanilide herbicides, to accelerate the remediation of pesticide-contaminated soil [27–29]. Further studies have also shown that  $\text{Fe}^{\text{II}}$  sites are also capable of reducing chloroacetanilide herbicides [30–32]. Dechlorination has also been achieved by nucleophile substitution by bisulfite and dithionite, leading to sulfonic acids and thiosulfates, respectively [33–35]. Another approach consists in the hydrodechlorination of alachlor with hydrogen in aqueous phase under relatively mild conditions of temperature and pressure with the use of different carbon supported copper, nickel and palladium catalysts [36]. Although palladium was found as the most active, copper and nickel based catalysts have also shown a reasonably good activity, leading to conversion values in the 80–93% range.

Dechlorination involving catalysts has been the subject of numerous studies [37–43]. Whereas molecular catalysts have shown their high catalytic activity for dechlorination processes in organic [10,44–49] as well as aqueous media [50–53], their use in heterogeneous catalysis has not been largely explored [49,51,54] as it is the case with supported metal catalysts [37,39,41–43].

We have recently reported the high catalytic activity of a new bipyridyl cobalt complex containing two bipyridine ligands toward the dechlorination of chloroacetanilide herbicides in aqueous medium, giving rise to a total and selective reduction of alachlor into its dehalogenated derivative, deschloroalachlor (Scheme 1) [55].

We took advantage of the high selectivity and efficiency of the catalyst to achieve a flow system for dechlorination of chloroacetanilide herbicides. The Co complex was first covalently immobilized on a porous 3D electrode functionalized by an electro-grafting method and the performances of the flow cell were tested for dehalogenation of alachlor. Since combined methods have proved their efficiency to mineralize biorecalcitrant compounds [56–59], the feasibility of the combination of this dechlorination process with a further biological treatment was evaluated through biodegradability measurements.

## 2. Experimental

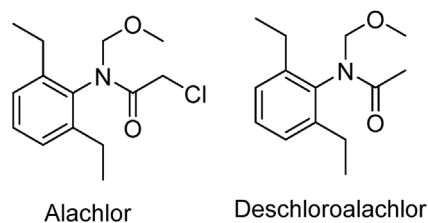
### 2.1. Chemicals and materials

Alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) and sodium nitrite were purchased from Sigma-Aldrich and deschloroalachlor (*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) from Alpha Chimica (France). Graphite felt (Recycled Vein Graphite RVG 4000) was supplied by Mersen (France). Its specific area measured by the BET (Brunauer, Emmett and Teller) method, its volume density and its carbon content were  $0.7 \text{ m}^2 \text{ g}^{-1}$ ,  $0.088 \text{ g cm}^{-3}$  and 99.9%, respectively. The synthesis of  $[\text{Co}(\text{bpy}(\text{CH}_2\text{OH})_2)_2](\text{BF}_4)_2$  has been already reported [55].

### 2.2. Preparation of the modified electrode

#### 2.2.1. Electrochemical functionalization of the graphite felt

100 mg ( $6.6 \times 10^{-4} \text{ mol}$ ) of 2-(4-aminophenyl)acetic acid were dissolved in 100 mL of degassed 0.5 M HCl. 288 mg ( $4.17 \times 10^{-3} \text{ mol}$ ) of sodium nitrite were added at  $0^\circ\text{C}$  and the solution was stirred for 20 min. Cathodic reduction of the



Scheme 1. Chemical structure of alachlor and deschloroalachlor.

diazonium salts prepared *in situ* was performed at  $-0.3 \text{ V}_{\text{SCE}}$  for 10 min under nitrogen at room temperature, with a graphite felt (48 mm diameter, 12 mm thickness) as working-electrode in a flow electrochemical cell [60] (flow rate:  $3 \text{ mL min}^{-1}$ ). Then the derivatized graphite felt was ultrasonicated 3 times in deionized water for 10 min and dried under vacuum.

#### 2.2.2. Esterification reaction

The functionalized graphite felt was placed in 50 mL anhydrous dichloromethane in a reactor under argon at  $0^\circ\text{C}$ . 1 mL of oxalyl chloride was added and the solution was stirred at room temperature for 18 h to prepare the acyl chloride. The felts were rinsed in anhydrous dichloromethane and then dried under vacuum. Then, the electrode was placed in a solution containing 50 mL of anhydrous dichloromethane, 1 mL of triethylamine and 50 mg of  $[\text{Co}(\text{bpy}(\text{CH}_2\text{OH})_2)_2](\text{BF}_4)_2$ . The solution was stirred at room temperature for 6 days. The modified electrode was ultrasonicated three times in dichloromethane and once with acetonitrile for 10 min.

### 2.3. Dechlorination conditions

The dechlorination reaction was performed in a home-made flow cell [54]. To ensure a good homogeneity of the potential distribution in the three dimensional working electrode [61], the felt was located between two interconnected DSA counter electrodes (dimensionally stable anodes, AC-2004, supplied by ECS International Electro Chemical Services, France). The compartments were separated by cationic exchange membranes (Ionac 3470–Lanxess SAS, Courbevoie, France). The reference electrode (Mercury-mercurous sulfate – MSE) was positioned in the middle of the modified graphite felt (10 mm diameter and 12 mm width) and a potential of  $-1.65 \text{ V/MSE}$  was applied with a VersaSTAT 3 potentiostat from Ametek/Princeton Applied (Elancourt, France). The solution ( $10\text{--}100 \text{ mg L}^{-1}$  pesticide in 25 mL of a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution) percolated the porous electrode at a flow rate of  $1 \text{ mL min}^{-1}$  monitored by a Gilson minipuls 3 peristaltic pump (Middleton, WI, USA).

### 2.4. Analytical procedures

#### 2.4.1. Electrochemical measurements

The electrochemical analysis was performed at room temperature under a dinitrogen atmosphere with a versaSTAT3 AMETEK Model (Princeton Applied Research) potentiostat/galvanostat. A glassy carbon electrode, a platinum plate auxiliary electrode, and a saturated calomel reference electrode were used in a standard three-electrode configuration. Cyclic voltammetry was carried out in acetonitrile with  $0.1 \text{ M Bu}_4\text{NBF}_4$  at  $20 \text{ mV s}^{-1}$ . The analysis of a modified graphite felt sample ( $\sim 1 \text{ cm}^3$ ) was performed by fixing it to a platinum wire. The error on volume concentrations is based on three reproducibility measurements.

High Performance Liquid Chromatography (HPLC) and UPLC-MS/MS analysis conditions have been previously reported [55].

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