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Abstract

The electrocatalytic activity of bismuth considered as a low cost and green electrode material was studied in reductive dechlorination processes. Cyclic voltammetry analyses showed that the Bi electrode exhibited a high catalytic activity to reduce alachlor, a chlorinated herbicide, in aqueous medium at different pH. Bulk electrolyses were performed at different potentials and pH. Alachlor was reduced in deschloroalachlor, its dechlorinated derivative, with a high selectivity (96%) and with a current efficiency of 48%. The reductive dechlorination of other chlorinated compounds with an activated carbon atom was then studied, showing that the bismuth electrode catalyzed the electroreduction of chloroacetamides, α-halocarbonyl and α-haloallyl pollutants. Cyclic voltammetry experiments allowed us to propose a mechanism explaining the high catalytic activity of bismuth to reduce these families of compounds.

Keywords. dechlorination, chloroacetamide, chloracetanilide, bismuth, electroreduction, pollutants

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1. INTRODUCTION

Bismuth is a white-pink brittle metal well-known as an environmentally benign element obtained at a relatively low cost and for its intrinsic properties such as its high hydrogen evolution overpotential, its high diamagnetic susceptibility and low thermal conductivity. Owing to the increasing emphasis on greener catalysts, bismuth metal and its oxidation state Bi(III) have been widely studied in the last fifteen years for their catalytic ability.[1-3] Bi(III) catalyzes many essential reactions in organic synthesis as for example oxidation, alkylation, allylation, cycloaddition and etherification. A few reactions involving Bi(0) catalyst have been also described as for example a Reformatsky-type reaction occurring in the presence of $BiCl_3$ and Al(0)[4] and the selective reduction of α,β-unsaturated esters with the $NaBH_4$-$BiCl_3$ system.[5] Whereas bismuth metal was not active, its generation *in situ* by a reductive agent allowed the reactions to occur. Bi(0) activated by fluoride salts has also shown a high catalytic ability toward the dehalogenation of α-halocarbonyl compounds.[6]

Bismuth metal has been also studied as electrocatalyst material to achieve electrochemical reductions. Thus, the reduction of nitro derivatives on a platinum electrode modified by underpotentially-deposited monolayers of bismuth has been investigated.[7-9] The presence of Bi adatoms on Pt allowed the extension of the potential window and catalysed the four-electron reduction of the nitroaromatic group *via* an electron-transfer mechanism and not by a hydrogenation mechanism as on Pt. Interesting catalytic properties toward the reduction of O_2 and H_2O_2 have been also observed with electrodes prepared by underpotential deposition of Bi on Au(111) surfaces.[10,11] Although dioxygen reduction occurs *via* a four-electron pathway, the formation of superoxide on the surface after the transfer of one electron suggested a serial mechanism.[12] More recently, bismuth metal has shown interesting catalytic properties for the selective hydrogenation of biomass chemicals such as 5-hydroxymethylfurfural[13-14] and

glucose[15] and for the electroreduction of CO_2 toward the formation of formate or carbon monoxide depending on the nature of the electrolytic medium.[16-19]

Contamination of soil, groundwater and surface water by synthetic halogenated organic chemicals has resulted in an increasing interest for reductive dehalogenation reactions since it often rendering them less offensive environmentally. Many metals such as silver,[20-21] palladium,[22] gold,[23] copper[24-25] and nickel[26] have shown good catalytic activity toward the electroreduction of chlorinated compounds. However, to our knowledge, bismuth metal has never been described as catalyst for the electroreduction of chlorinated compounds. In the course of our study to perform the dehalogenation of chloroacetanilide herbicides by electrochemical reduction processes,[26-29] we observed that bismuth metal has a high electrocatalytic activity toward the reduction of alachlor. In this work, the electrocatalytic behavior of bismuth toward the reductive dechlorination of several chloroacetamide pollutants was therefore investigated. Its ability to reduce other compounds containing an activated carbon atom was highlighted. Mechanistic investigations were performed to understand the high reactivity of bismuth metal toward chloroacetamide compounds.

2. 2. EXPERIMENTAL SECTION

2.1. Chemical and materials. Alachlor (2-Chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) and dimethenamid (2-Chloro-*N*-(2,4-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl)acetamide) were supplied by Sigma-Aldrich, USA, and trichloroacetamide (2,2,2-trichloroacetamide) and allyl chloride (3-Chloroprop-1-ene) from Acros Organics, Belgium. Dichloroacetamide (2,2-dichloroacetamide) was obtained from Merck KGaA, USA and chloroacetamide (2-chloracetamide) was provided by Alfa Aesar, USA. Pretilachlor (2-Chloro-2',6'-diethyl-N-(2-propoxyethyl)acetanilide) was bought from

TCL, Japan and trichloroacetic acid and chloroacetic acid from Janssen Chimica, Belgium. The preparation and main characterizations of bismuth modified graphite felt has been previously reported.[30] The material has a specific surface area of 0.40 ± 0.03 m^2 g^{-1} and a bulk density of 0.181 ± 0.007 g cm^{-3}, corresponding to a Bi loading of 1.7 mg cm^{-2} and a thickness for the Bi layer from 0.5 to 1 μm.

2.2. Electrochemical analysis. Cyclic and linear voltammetry analyses were carried out using a VersaSTAT3 AMETEK Model (Princeton Applied Research) potentiostat/galvanostat. A bismuth electrode (1.77 mm^2) prepared by electrodeposition of bismuth on a copper electrode (disk of 1 mm diameter) (in 1 mol L^{-1} Bi_2O_3 with 1.1 equivalents of 2,2-Bis(hydroxymethyl)-2,2',2'-nitrilotriethanol at pH 14 for 30 min, 1 mA) or a glassy carbon electrode (0.78 mm^2), a platinum plate auxiliary electrode, and a reference electrode (Mercury-mercurous sulfate – MSE) were used in a standard three-electrode configuration. The working electrodes were carefully polished before use and an electroreduction in the studied electrolyte medium at -2 V_{MSE} for 10s was performed on the bismuth electrode before each analysis.

2.3. Flow electroreduction of chlorinated compounds. The electrochemical reduction of chlorinated compounds was performed in a home-made flow cell (Figure 1).

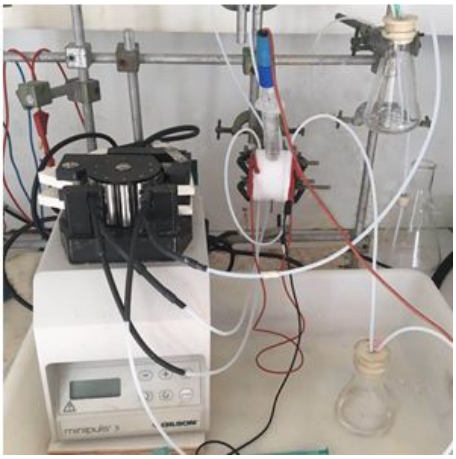


Figure 1. Home-made electrochemical flow cell

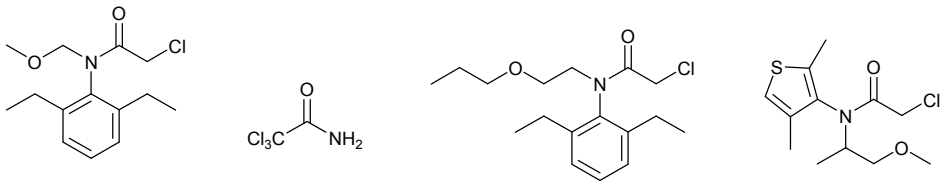
To ensure a good homogeneity of the potential distribution in the three dimensional working electrodes, the bismuth modified graphite felt electrode was located between two interconnected DSA counter-electrodes (dimensionally stable anodes, AC-2004, supplied by ECS International Electro Chemical Services, France).[31] The compartments were separated by cationic exchange membranes (Nafion^{TM} 417 membrane, France) and the reference electrode (Mercury-mercurous sulfate – MSE) was positioned in the middle of the working electrode (10 mm diameter and 1.7 mm thickness). The solution percolated the porous electrode using a Gilson minipuls 3 peristaltic pump (Middleton, WI, USA).

2.4. Analytical chromatography. The concentration of chloride ions (diluted four times) before and after electrolysis was determined using DIONEX DX120 ion chromatography equipped with a conductivity detector and a DIONEX AS19 (4 × 250 mm) ion-exclusion column. The sample was eluted with potassium hydroxide at a flow rate of 1 mL min^{-1}. The detection was carried out by conductivity with a Self-Regenerating Suppressor (SRS).

The concentration of alachlor and deschloroalachlor were determined using a Waters 996 High Performance Liquid Chromatography (HPLC) system equipped with a Waters 996 PDA (Photodiode Array Detector) and a Waters 600 LCD Pump. The separation was achieved on a Waters C-18 (5 μm; 4.6 × 250 mm) reversed-phase and the mobile phase consisted in a mixture of acetonitrile/ultra-pure water (70/30, v/v). The flow rate was set at 0.4 mL min^{-1} and 50 μL injection was considered. Detection was carried out at 195 nm.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH on the electroreduction of alachlor. Alachlor **1** (Scheme 1), a common chloroacetanilide herbicide, was first analyzed on Bi electrode by cyclic voltammetry in different pH media (Figure 2).



Scheme 1. Structure of chloroacetamide derivatives

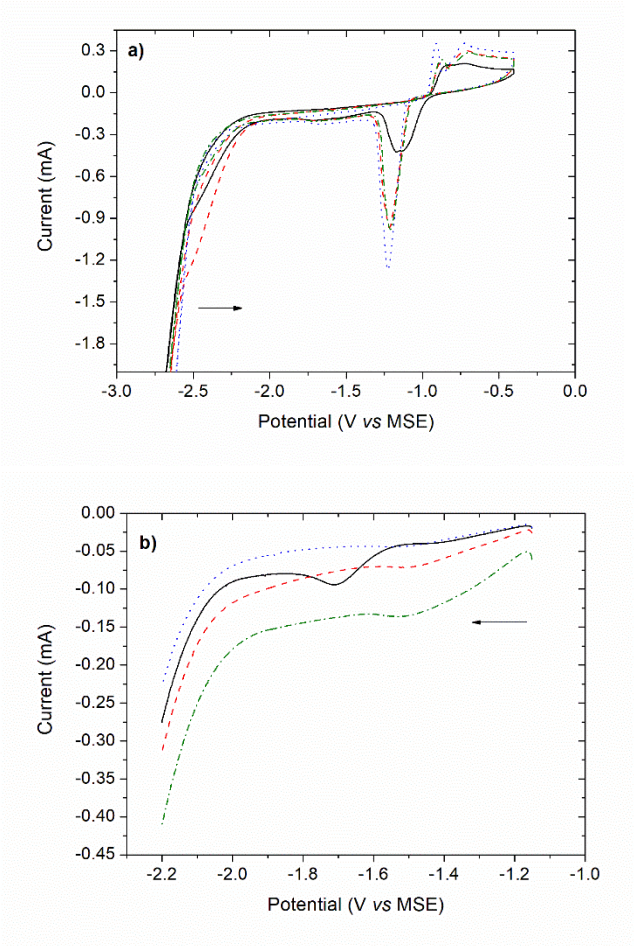


Figure 2. Cyclic voltammetry analysis on a bismuth disk electrode (1.5 mm diameter) of a solution of 0.1 mol L^{-1} Na_2SO_4 at pH 3 (—), pH 7 (-----), pH 10 (-.-.-.), pH 13 (.....) (pH

123 adjusted with H_2SO_4 or NaOH) without (a) and with (b) alachlor (200 ppm, 0.74 mmol L^{-1}).
124 Scan rate: 0.1 V s^{-1}.

125

126 A blank was first performed at different pH (Figure 2a). Oxidation peaks were observed around
127 -0.8- -0.4 V_{MSE} on all cyclic voltammograms with a reduction peak at -1- -1.2 V_{MSE} depending
128 on the pH. It corresponds to the formation of a layer of Bi salts on the electrode surface at
129 potentials less negative than -0.8 V_{MSE} and their subsequent reduction.[32-34] In the presence of
130 alachlor, a peak can be observed for the four studied pH in the potential range from -1.5 to -1.7
131 V_{MSE}, corresponding to the reduction of alachlor on bismuth. Compared with the reduction peak
132 of alachlor observed on glassy carbon electrode (Figure S1), the potentials are positively shifted
133 for all studied pH (Table 1). Interestingly, the difference of potential increased with the pH of
134 the solution from 270 to 510 mV, suggesting a more efficient catalysis for pH ≥ 7.

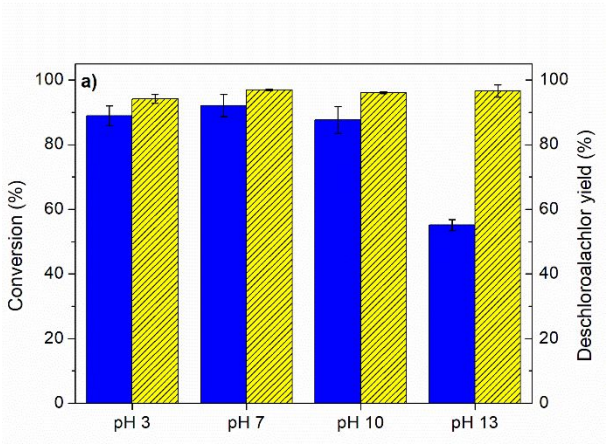
135

136 **Table 1.** Peak potential of studied compounds in 0.1 M Na_2SO_4 on Bi and GC electrodes and
137 electron transfer coefficient calculated from cyclic voltammetry experiments

Chlorinated compounds		Peak potential (V_{MSE}) GC	Bi	$\Delta E_{(Bi-GC)}$ (V_{MSE})	α
Alachlor	pH 3	-1.98	-1.71	0.27	0.34
	pH 7	-1.91	-1.50	0.41	0.18
	pH 10.5	-2.01	-1.52	0.49	0.08
	pH 13	-2.04	-1.53	0.51	0.18
Chloroacetamide		-2.22	-1.89	0.33	--
Dichloroacetamide		-2.16	-1.88	0.28	--
		-1.83	-1.41	0.42	--
Trichloroacetamide		-2.16	-1.91	0.25	0.32
		-1.87	-1.49	0.38	0.16
		-1.39	-1.12	0.27	0.50
Pretilachlor		-1.84	-1.62	0.22	0.21
Dimethenamid		-1.95	-1.68	0.27	0.25
Trichloroacetic acid		--	-2.02	--	--
		-2.02	-1.29	0.73	0.31
Allyl chloride		-1.96	-1.64	0.32	0.32
Chloroacetic acid		--	--	--	--

138

Electroreduction of a solution of 50 ppm (0.18 mol L^{-1}) alachlor in 0.05 mol L^{-1} Na_2SO_4 were performed at different pH at a potential of -1.8 V_{MSE} (Figure 3a). The reaction was very efficient in all media with a conversion of alachlor around 96%. The yield of its dechlorinated derivative, deschloroalachlor, was estimated by UPLC-MS/MS to be around 90% for electrolyses performed at pH 3, 7 and 10, showing the high selectivity of the dehalogenation process. Indeed, previous reductive dehalogenation of alachlor performed on Ni-coated graphite felt modified by silver nanoparticles led to the formation of descholoralachlor with a yield around 76%, underlining the high selectivity of bismuth.[35]



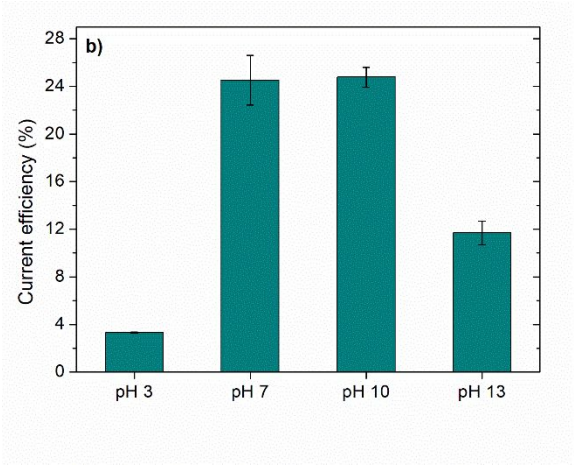


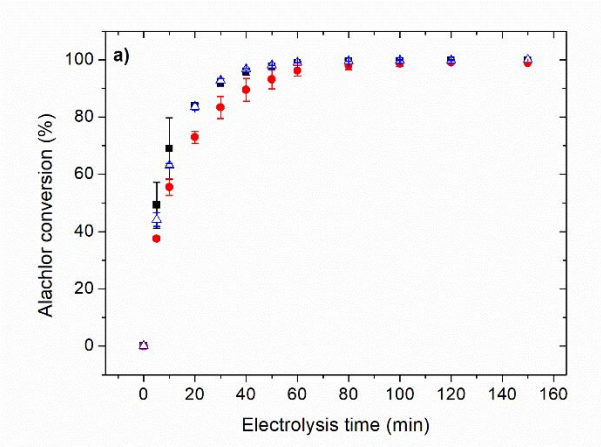
Figure 3. a) conversion yield of alachlor (hatched yellow area) and yield of deschloroalachlor (blue area) after 1 h of electrolysis at -1.8 $V/_{MSE}$ of 50 ppm (0.18 mol L^{-1}) alachlor in 0.05 mol L^{-1} Na_2SO_4 (pH adjusted with H_2SO_4 or NaOH) for 1 h b) current efficiency after electrolysis. Error bars are based on two experiments.

153

154 The low yield of deschloroalachlor at pH 13 showed that alachlor underwent other reduction
155 processes than dechlorination and that the reaction was less selective, even if no other peak than
156 those of deschloroalachlor was observed in HPLC even after 5h of electrolysis. The current
157 efficiency was calculated according to the amount of chloride ions measured by ion
158 chromatography (Figure 3b). The highest current efficiencies were obtained at pH 7 and 10.
159 The low value obtained at pH 3 is probably due to the competition with hydrogen evolution
160 since the reduction of alachlor occurred at a potential (-1.7 V_{MSE}) closed to the reduction of
161 water. The lower current efficiency observed at pH 13 is in accordance with the presence of
162 side reactions that led to the formation of chlorinated by-products.

163

164 **3.2. Effect of the applied potential on the electroreduction of alachlor.** Since alachlor
165 dechlorination was very effective and selective at pH 7, this medium was considered thereafter.
166 Reductive dechlorination of alachlor was then tested at three different applied potentials to
167 check the effect on the selectivity of the reaction and on its current efficiency (Figure 4).
168 Alachlor conversion was almost total for all applied potentials after 80 min of electrolysis,
169 although the kinetic was slightly slower at -1.4 V_{MSE}.



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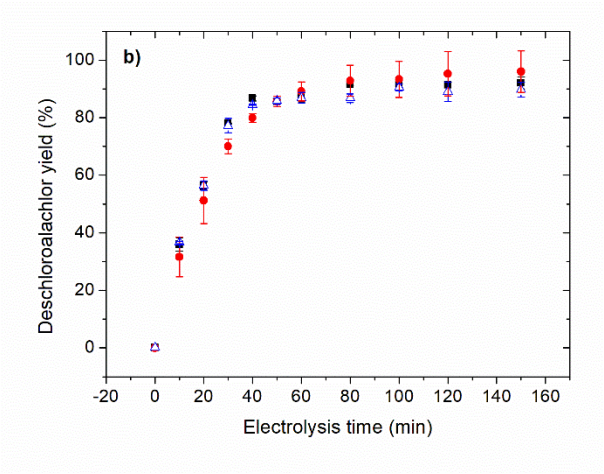


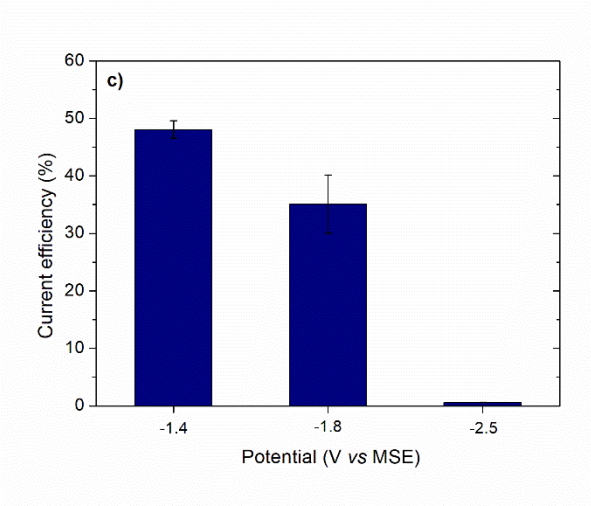
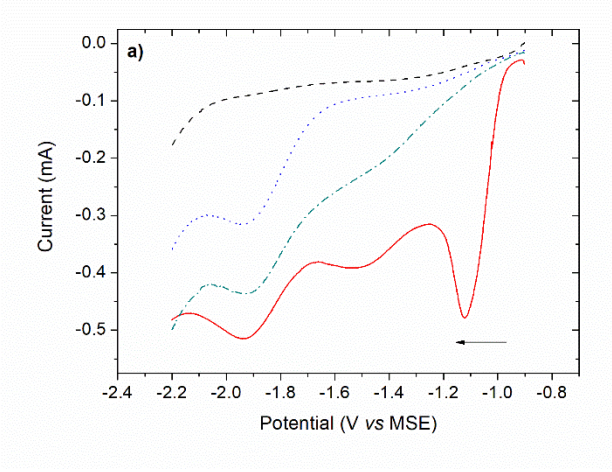


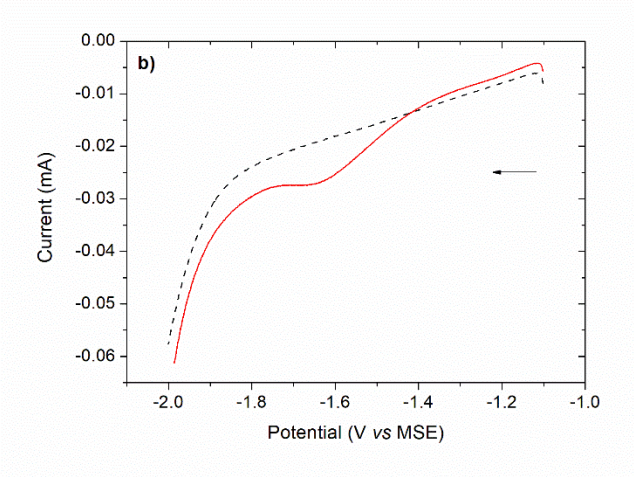
Figure 4. a) alachlor conversion, b) yield of deschloroalachlor c) current efficiency after the electrolysis of 50 ppm alachlor in 0.05 mol L^{-1} Na_2SO_4 (pH 7) at potentials of -1.4 V_{MSE} (●), -1.8 V_{MSE} (■) and -2.5 V_{MSE} (Δ). Error bars are based on two experiments.

The selectivity toward the formation of deschloroalachlor was also very high for all studied potentials, leading to a yield of 89-96% (Figure 4b). The effect of the applied potential on the current efficiency was significant. It decreased for more negative potentials, owing to the competition with hydrogen evolution, and reached a value of 48 ± 2% for electroreduction performed at -1.4 V_{MSE}.

Comparison with results previously reported for the reductive dechlorination of alachlor on Ni-coated graphite felt modified with silver nanoparticles (96% conversion for 100 min electrolysis with a current efficiency up to 33%[35]) underlines the high catalytic efficiency of bismuth. Furthermore, the high selectivity of the reaction on bismuth is noteworthy. Deschloroalachlor yield reached 96%, against 76% on Ni-coated graphite felt modified with silver nanoparticles[35] and 86% with a Co catalyst.[27-28]

3.3. Electroreduction of other chloroacetamides. To confirm the high catalytic activity of bismuth toward the electroreduction of chloroacetamide pollutants, the reductive dechlorinations of trichloroacetamide, a disinfection by-product, and, pretilachlor and dimethenamid, two herbicides, were investigated. The electrocatalytic activity of bismuth was first studied by cyclic voltammetry (Figure 5).





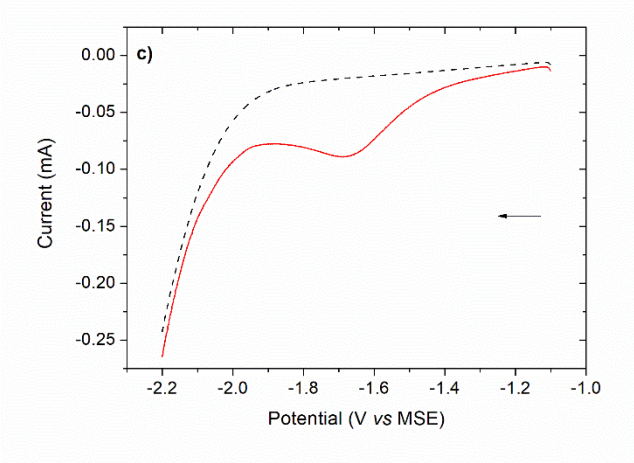
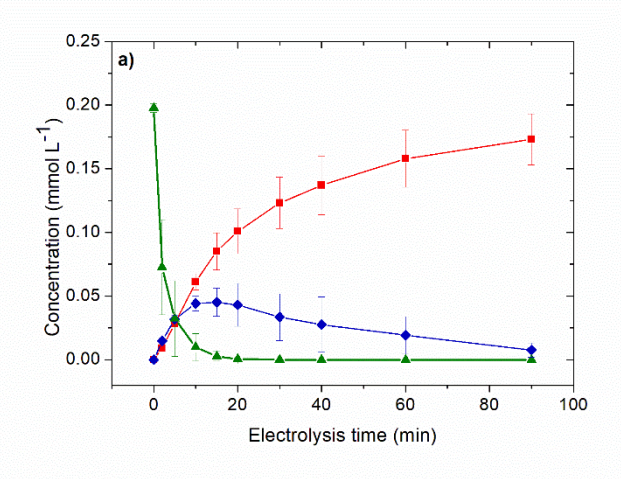


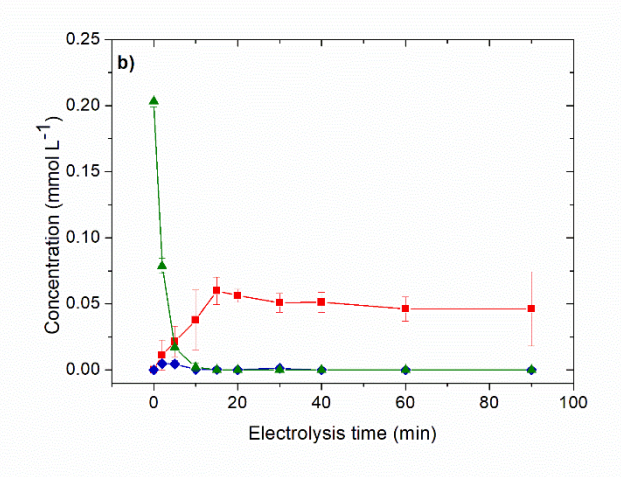
Figure 5. Cyclic voltammogram of a solution of 0.1 mol L^{-1} Na_2SO_4 at pH 7 on a bismuth disk electrode (Ø 5mm) (-----) a) 20 mmol L^{-1} trichloroacetamide (——), dichloroacetamide (-.-.-), chloroacetamide (.....) b) 1 mmol L^{-1} pretilachlor c) 3.6 mmol L^{-1} dimethenamid. Scan rate: 0.1 V s^{-1}.

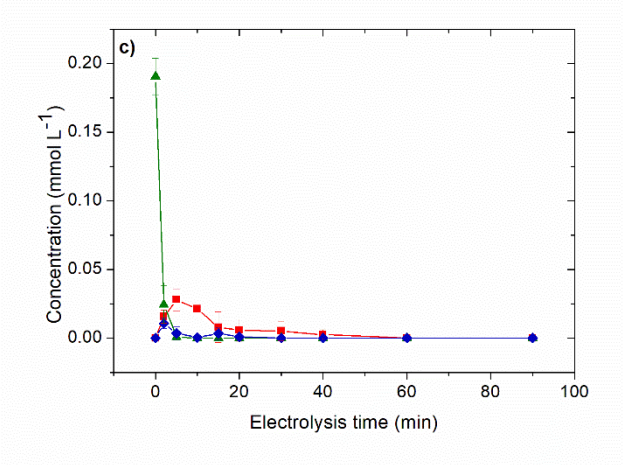
Trichloroacetamide exhibited three reduction peaks at -1.1, -1.5 and -1.9 V_{MSE}. Comparison with the voltammograms of di and chloroacetamides showed that they correspond to the reduction of each C-Cl bond, the first one being the easiest to reduce. The reduction of the two first C-Cl bonds happened on glassy carbon electrode with a negative shift of potential of 0.25 to 0.38 V (Figure S2, Table 1). This difference of potential underlines the high catalytic activity

of bismuth toward the reduction of these chloroacetamide compounds compared with glassy carbon. Pretilachlor and dimethenamid were also reduced at -1.6 and -1.7 V_{MSE}, respectively (Figure 5b and c). Their reduction on glassy carbon electrode occurred at more negative potentials with a shift of 0.22 and 0.27 V, respectively (Figure S3, Table 1), highlighting the high catalytic activity of bismuth for these species.

Bulk electrolyses of trichloroacetamide were performed at -1.2, -1.6 and -2 V_{MSE} in 0.05 mol L^{-1} Na_2SO_4 at pH 7 (Figure 6).







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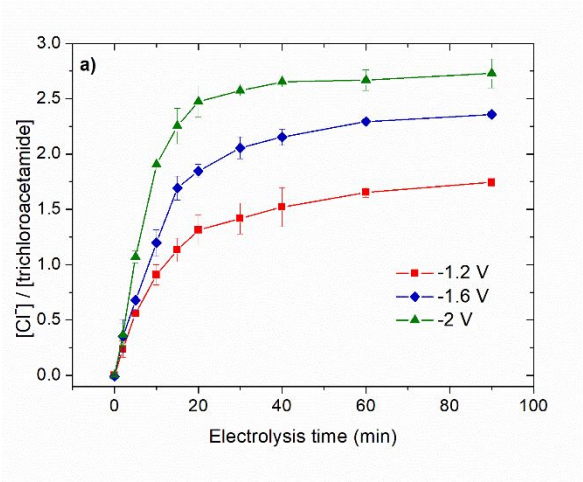
220 **Figure 6.** Concentrations of trichloroacetamide (-▲-), dichloroacetamide (-♦-) and
221 chloroacetamide (-■-) during electrolysis of 0.2 mmol L^{-1} trichloroacetamide in 0.05 mol L^{-1}
222 Na_2SO_4 at potential of a) -1.2 V_{MSE}, b) -1.6 V_{MSE} and c) -2.0 V_{MSE} with initial pH 7. Error bars
223 are based on at least two experiments.

224 The concentration of chloride ions was measured by ion chromatography (Figure 7a).



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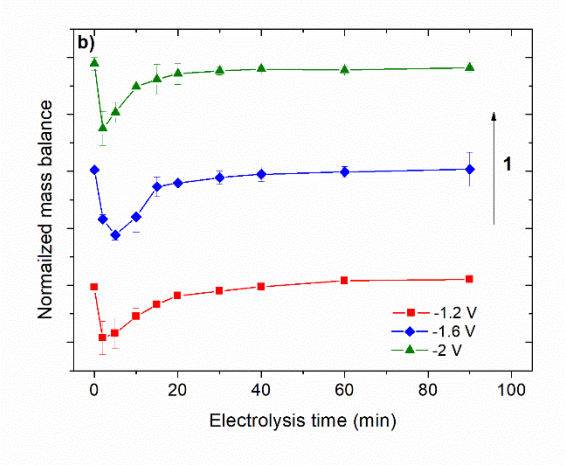


Figure 7. a) Chloride ions concentration and b) Mass balance of chlorinated species based on trichloroacetamide, dichloroacetamide, chloroacetamide and chloride ions normalized by the initial concentration of trichloroacetamide for electrolyses performed at -1.2, -1.6 and -2 V_{MSE} in 0.05 mol L^{-1} Na_2SO_4 at pH 7. Error bars are based on at least two experiments.

When the electrolysis was performed at -1.2 V_{MSE}, the formation of dichloroacetamide was not selective and the presence of chloroacetamide was also observed. The concentration of chloride ions was 1.5 times the initial concentration of trichloroacetamide (Figure 7a) after 90 min electrolysis whereas the total reduction of trichloroacetamide and dichloroacetamide as observed in Figure 6a should lead to a ratio of 2. This result shows that the reduction of trichloroacetamide and dichloroacetamide led to other by-products than their dechlorinated derivatives. This was confirmed by the presence of new peaks in HPLC analyses (Figure S4). Mass balance of chloride atoms calculated from the amount of chloride ions and remaining dichloroacetamide and chloroacetamide also indicated the formation of other chlorinated by-products in the first 20 min of electrolysis (Figure 7b). After 90 min electrolysis, the ratio reached a value of 1 for electrolyses performed at -1.2 and -1.6 V, showing that a total dechlorination of these by-products occurred. Thus the only chlorinated compounds remaining in solution after electrolyses performed at -1.2 and -1.6 V were chloroacetamide and chloride

ions. For reduction performed at -2 V, a ratio of 0.9 was reached indicating the presence of a few unidentified chlorinated by-products after 90 min electrolysis. This was confirmed by the results highlighted in Figure 6c showing that trichloroacetamide, dichloroacetamide and monochloroacetamide were totally reduced after 90 min electrolysis although the ratio of chloride ions was only 2.7 (Figure 7a). Current efficiencies after 30 min of bulk electrolysis are given in Table 2. The dechlorination yield increased when a more negative potential was used. However, potentials more negative than -1.6 V also led to a decrease of the current efficiency owing to competition with hydrogen evolution.

Table 2. Dechlorination yield and current efficiency of 0.2 mmol L^{-1} chloroacetamide electroreduction on the Bi modified electrode after 30 min electrolysis in 0.05 mol L^{-1} Na_2SO_4 at pH 7.

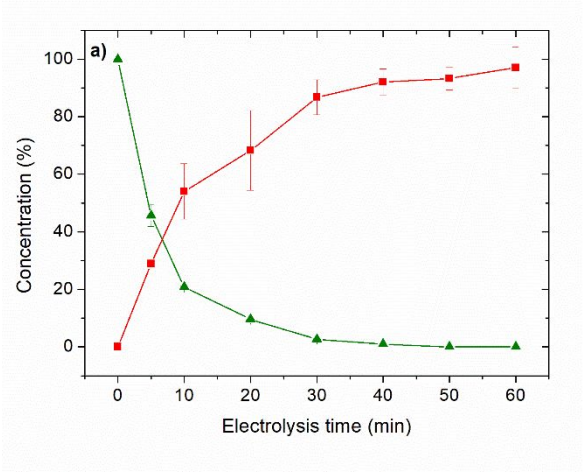
Pollutant	Applied potential (V_{MSE})	Cl^- yield (%)[a]	Current efficiency (%)
Trichloroacetamide	-1.2	47 ± 5	50 ± 4
	-1.6	69 ± 3	58 ± 7
	-1.8	72 ± 5	28.84 ± 0.04
	-2.0	85.7 ± 0.1	14 ± 4
Dichloroacetamide	-1.2	26 ± 1	20 ± 4
	-1.6	60 ± 7	47 ± 12
	-1.8	72 ± 1	21.6 ± 0.1
	-2.0	89 ± 3	11 ± 2
Chloroacetamide	-1.6	32 ± 2	15.4 ± 0.8
	-1.8	76.4 ± 0.5	12.0 ± 0.1
	-2.0	95.1 ± 7	6.2 ± 0.6

[a] The Cl^- yield is calculated from the initial amount of pollutant

The same experiments were carried out with dichloroacetamide and chloroacetamide for comparison (Figure S5 to S8). Electrolyses performed at less negative potentials led to higher current efficiency since the competition with hydrogen evolution decreased. However, higher electrolysis time would be required to obtain good dechlorination yields. Mass balance of chloride ions showed the formation of chlorinated by-products at the beginning of the

263 electrolyses, especially for electrolyses performed at -2 V (Figure S6 and S8). However, the
264 variation of the mass balance is less important than for the reduction of trichloroacetamide,
265 showing that the reduction is more selective toward the formation of acetamide.

266 Bulk electrolyses of 0.2 mmol L^{-1} pretilachlor and dimethenamid were performed at -1.8 V_{MSE}
267 in 0.05 mol L^{-1} Na_2SO_4 at pH 7. The pollutants were totally reduced after 60 min of electrolysis
268 (Figure 8a and b).



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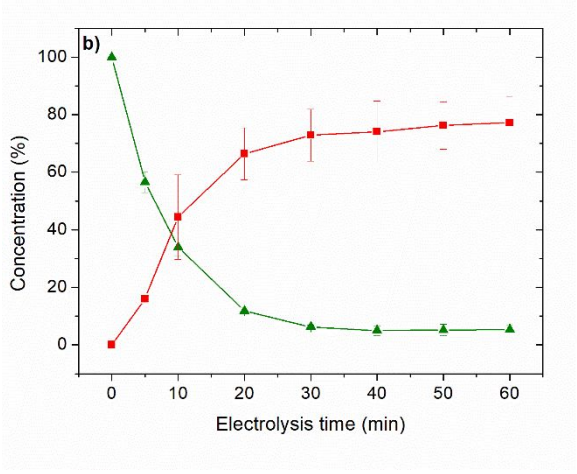


270

271 **Figure 8.** Concentration of chlorinated starting material (-▲-) and dechlorination yield (-■-)
272 during electroreduction of 0.2 mmol L^{-1} a) pretilachlor and b) dimethenamid in 0.05 mol L^{-1}
273 Na_2SO_4 at potential of -1.8 V_{MSE} with initial pH 7. Error bars are based on at least two
274 experiments.

275

276 The dechlorination yields estimated by measuring the concentration of chloride ions by ion
277 chromatography were 97% and 77% for pretilachlor and dimethenamid, respectively,
278 underlining the good efficiency of the dechlorination process.

279 A comparison of the dechlorination yields and current efficiencies after 30 min electrolysis for
280 the studied chloroacetamide compounds is given in Table 3.

281

282 **Table 3**. Dechlorination yield and current efficiency after 30 min of electroreduction at -1.8
283 V_{MSE} of 0.2 mmol L^{-1} chlorinated compounds on the Bi modified electrode in 0.05 mol L^{-1}
284 Na_2SO_4 at pH 7.

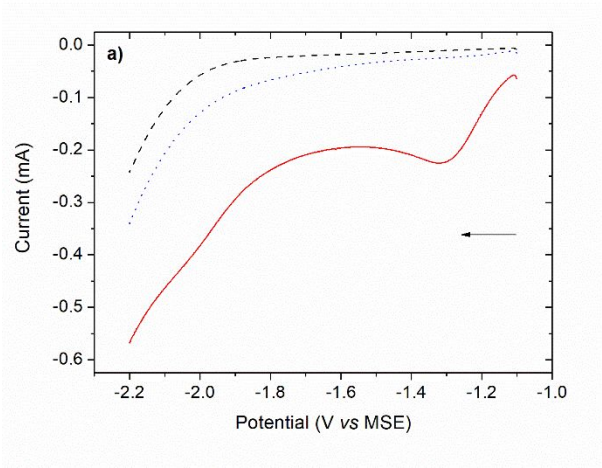
Pollutant	Cl^- Yield (%)	Current efficiency (%)
Pretilachlor	97 ± 7	20 ± 2
Alachlor	85.2 ± 0.3	26 ± 3
Dimethenamid	77 ± 9	11.8 ± 0.4
Chloroacetamide	76.4 ± 0.5	12.0 ± 0.1
Dichloroacetamide	72 ± 1	21.6 ± 0.1
Trichloroacetamide	72 ± 5	28.84 ± 0.04
Trichloroacetic acid	35.5 ± 2	19.0 ± 0.1
Allyl chloride	39.3 ± 0.6	5.61 ± 0.06
Chloroacetic acid	0	--

285

286 The kinetic of the reaction clearly depends on the chemical structure of the pollutants with
287 higher dechlorination yields for chloroacetanilide derivatives (pretilachlor and alachlor).
288 Current efficiencies were around 10-20% owing to competition with hydrogen evolution at -
289 1.8 V_{MSE}. The electroreduction on bismuth of chloroacetamides is so very efficient with a total
290 reduction of the targeted compounds and high dechlorination yields (between 72 and 97%) after
291 30 min electrolysis.

292

3.4. Electroreduction of other compounds with activated carbon atoms. The ability of bismuth to reduce other compounds with activated carbon atoms was also tested with trichloroacetic acid, chloroacetic acid and allyl chloride. Cyclic voltammetry analyses (Figure 9a) revealed two reduction peaks at -1.29 and -2.02 V_{MSE} for trichloroacetic acid. Whereas the first reduction occurred at a potential close to those of trichloroacetamide, the second one was at a more negative potential and the analysis of chloroacetic acid did not reveal the presence of a peak.



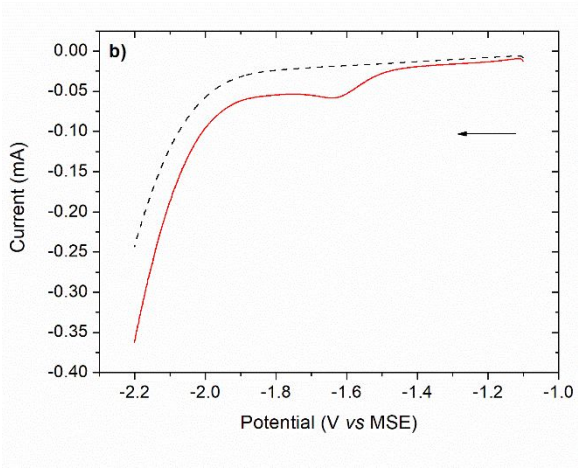
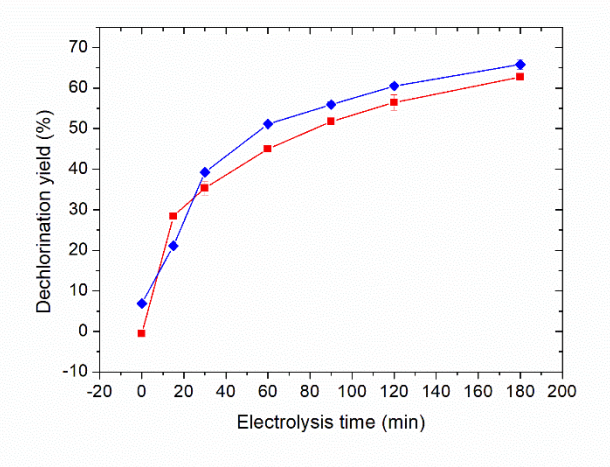


Figure 9. Cyclic voltammogram of a solution of 0.1 mol L^{-1} Na_2SO_4 at pH 7 on a bismuth disk electrode (Ø 5mm) (-----) of a) 20 mmol L^{-1} trichloroacetic acid (——), 20 mmol L^{-1} chloroacetic acid (…….) b) 20 mmol L^{-1} allyl chloride. Scan rate: 0.1 V s^{-1}.

306 However, compared with the reduction peak of trichloroacetic acid observed on glassy carbon
307 electrode (Table 1, Figure S9), the first reduction peak was positively shifted by 0.73 V and the
308 second reduction was not observed on glassy carbon, underlining the high catalytic ability of
309 bismuth to reduce trichloroacetic acid. As seen in Figure 9b, the reduction of allyl chloride
310 occurred at -1.64 V, i.e. 0.32 V earlier than on glassy carbon (Table 1, Figure S9), confirming
311 also the catalytic effect of bismuth.

312 Bulk electrolyses of 0.2 mmol L^{-1} trichloroacetic acid, chloroacetic acid and allyl chloride were
313 then carried out at -1.8 V_{MSE} in 0.05 mol L^{-1} Na_2SO_4 at pH 7.

314 The reduction of trichloroacetic acid led to a dechlorination yield of 63% after 180 min
315 electrolysis (Figure 10).



316

317 **Figure 10.** Dechlorination yield during electroreduction of 0.2 mmol L^{-1} trichloroacetic acid (-
318 ■-) and allyl chloride (-♦-) in 0.05 mol L^{-1} Na_2SO_4 at potential of -1.8 V_{MSE} with initial pH 7.
319 Error bars are based on two ion chromatography analyses.

320

321 The same experiment performed at -2 V_{MSE} gave a dechlorination yield of 66% after 4h,
322 showing that only two chloride atoms can be removed from trichloroacetic acid in these
323 conditions. Thus these results confirmed cyclic voltammetry analyses that showed the presence

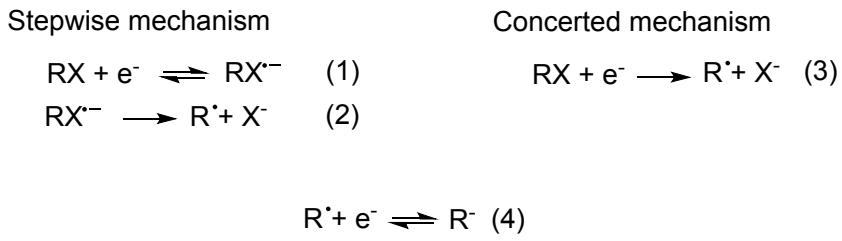
of only two reduction waves. Moreover, the electroreduction of chloroacetic acid performed at -1.8 V_{MSE} failed in these conditions. The lowest reactivity of trichloroacetic acid compared with trichloroacetamide can be explained by the presence of a carboxylate group at pH 7 instead of an electron withdrawing amide group.

Allyl chloride was dechlorinated with a yield of 66% after 180 min electrolysis. The reaction was clearly slower than with α-halocarbonyl compounds.

A comparison of electroreductions performed at -1.8 V_{MSE} for 30 min on bismuth electrode is made in Table 3. The highest dechlorination yields were obtained for chloroacetamide compounds, especially choroacetanilides. The reductions of other studied chlorinated compounds containing an activated carbon atom were slower even if the difference in peak potentials between bismuth and glassy carbon electrodes observed in cyclic voltammetry (Table 1) was in the same order of magnitude. The reduction of chlorinated compounds on Bi appears to be specific to species with an activated carbon atom since our attempts to reduce other derivatives such as chloroaromatic compounds failed.

3.5. Mechanism. Additional insights about the mechanism were derived from the cyclic voltammetry studies notably the variations of the peak potential E_p as a function of the scan rates. These variations have been demonstrated to be a good criterion to distinguish between different mechanisms.[36] E_p was found to linearly vary with *log (v)* with slopes in the range of -43 - -380 mV/*log(v)* (Figure S9 to S13). Such large slopes are indicative of a control of the electrochemical process by the electron transfer that could (or not) be associated with a chemical step. A control by the electron transfer is indicative of large reorganisation energy upon the electron transfer. As discussed previously, the electrochemical reduction of a carbon-halogen bond could be described as involving a chemical step with the electron transfer that

348 globally could occur *via* a dissociative electron transfer, according to a stepwise or a concerted
349 mechanism (Scheme 2):



350

351 **Scheme 2.** Stepwise and concerted mechanisms for the reduction of a carbon-halogen bond

352 For a concerted mechanism, the heterogeneous electron transfer contains the additional
353 contribution of the dissociative energy of the halogen-bond, which is not the case for a stepwise
354 mechanism. Thus, a control by the electron transfer falls in line with a concerted mechanism.
355 The slope of the variation of E_p with *log(v)* is equal to *1.151 RT/αF*[37-38] where α is the charge
356 transfer coefficient, *T* the temperature, *R* the gas constant, *F* the Faraday constant. Using this
357 relation, the charge transfer coefficient α was calculated for all studied molecules (Table 1). In
358 the framework of the Marcus-Hush model, α depends on the free energy $\Delta G°$ of the reaction
359 *i.e.* the difference between E_p and the thermodynamic potential (Equation 5).[39]

360

361 $$\alpha = \frac{\partial \Delta G_f^{\neq}}{\partial \Delta G°} = 0.5\left(1 + \frac{\Delta G°}{4\Delta G_0^{\neq}}\right) \quad (5)$$

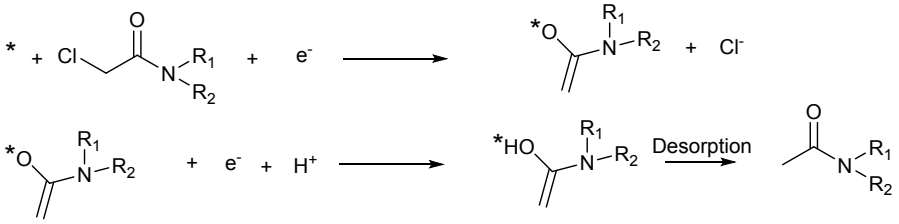
362 with $\Delta G_f^{\neq}$ the forward activation free energy, $\Delta G°$ the standard free energy of reaction, $\Delta G_0^{\neq}$
363 the standard activation free energy (intrinsic barrier).

364

365 A small value of α is thus indicative of a large overpotential and likely of concerted mechanism
366 as found for the electroreduction of alkyl halide.[36] For all considered molecules, α was found

to be much smaller than ≤ 0.5 that indeed supports the occurrence of a concerted electron transfer with the chemical steps.

In the case of α-halocarbonyl derivatives, it was shown that adsorbates with O−Bi bonds are systematically more stable than those with C−Bi bonds.[40-41] For example, *OCHO is −0.87 eV more stable than *COOH. The high affinity of bismuth for the oxygen atom could explain the observed high catalytic activity toward the reduction of chloroacetamide compounds and trichloroacetic acid. Based on these considerations, we could propose the following mechanism (Scheme 3) for the electroreduction of chloroacetamide on Bi :



Scheme 3. Electroreduction of chloroacetamide compounds on bismuth.

For α-haloallyl derivatives such as allyl chloride, it can be deduced that the Bi ability to catalyse their reduction is due to an interaction between bismuth and the double bond although this interaction is probably lower as suggested by the slower kinetic observed for the dechlorination process.

In conclusion, this work demonstrates for the first time the electrocatalytic activity of bismuth to break the carbon-halogen bond. Chloroacetanilide herbicides such as alachlor and pretilachlor can be totally reduced with a high selectivity, leading to dechlorination yields higher than 96%. The high catalytic activity of bismuth toward the reduction of other chloroacetamides pollutants has also been shown. Interestingly, the electroreduction process is efficient on all compounds containing an activated carbon atom as it has been demonstrated in

this work with α-halocarbonyl and α-haloallyl derivatives. Cyclic voltammetry experiments show that the electrochemical reduction of the carbon-halogen bond implies a dissociative electron transfer *via* a concerted mechanism. Therefore, the high affinity of bismuth for oxygen atoms is probably responsible for its high catalytic ability toward the reduction of α-halocarbonyl compounds. This cost-effective and green porous bismuth electrode incorporated in a flow electrochemical system would be particularly interesting for the water treatment of biorecalcitrant pollutants. A coupling with a biological treatment is possible if the dechlorinated compounds are biodegradable. If the by-products are still persistent, a coupling process with electro-Fenton can be advantageously envisaged as it has been previously demonstrated with alachlor.[42]

ACKNOWLEDGEMENTS

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Supporting Information.

Comparison of electroreduction on Bi and glassy carbon electrodes by linear sweep voltammetry analysis (Figures S1 to S3 and S9), HPLC analysis during electroreduction of trichloroacetamide (Figure S4), electroreduction of dichloroacetamide and chloroacetamide (Figures S5 to S8), linear sweep voltammetry analyses for mechanistic investigations (Figure S10 to S13).

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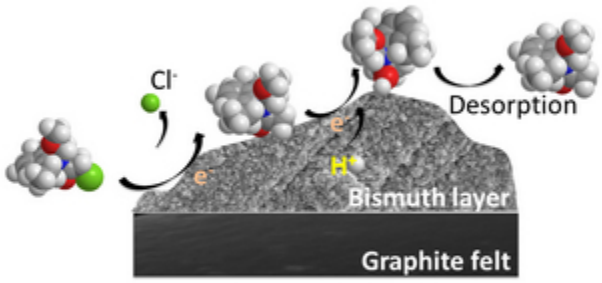

Graphical abstract

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