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Study of degradation intermediates formed during electrochemical oxidation of pesticide residue 2,6-dichlorobenzamide (BAM) in chloride medium at boron doped diamond (BDD) and platinum anodes

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HIGHLIGHTS

- Chloride leads to a more diverse mixture of degradation intermediates.
- Active chlorine oxidation leads to fewer intermediates for Pt anodes.
- BDD leads to lower amounts of intermediates compared to Pt.
- Intermediates from BAM are formed via an amine or a carboxylic acid route.
- Mineralization is possible with both BDD and Pt.

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ABSTRACT

For electrochemical oxidation to become applicable in water treatment outside of laboratories, a number of challenges must be elucidated. One is the formation and fate of degradation intermediates of targeted organics. In this study the degradation of the pesticide residue 2,6-dichlorobenzamide, an important groundwater pollutant, was investigated in a chloride rich solution with the purpose of studying the effect of active chlorine on the degradation pathway. To study the relative importance of the anodic oxidation and active chlorine oxidation in the bulk solution, a non-active BDD and an active Pt anode were compared. Also, the effect of the active chlorine oxidation on the total amount of degradation intermediates was investigated. We found that for 2,6-dichlorobenzamide, active chlorine oxidation was determining for the initial step of the degradation, and therefore yielded a completely different set of degradation intermediates compared to an inert electrolyte. For the Pt anode, the further degradation of the intermediates was also largely dependent on active chlorine oxidation, while for the BDD anode anodic oxidation was most important. It was also found that the presence of active chlorine led to fewer degradation intermediates compared to treatment in an inert electrolyte.

1. Introduction

In numerous studies electrochemical treatment has proven to be an effective method for degradation of pesticides in water through oxidation by anodic generated oxidants as active oxygen species in the so-called electrochemical oxygen transfer process (EOTR) and bulk oxidants as active chlorine (Quiroz et al., 2011). However, most studies have mainly focused on the removal of the pesticide, and have not in detail investigated the formation of degradation intermediates (DIs), which may potentially be more persistent and toxic compared to the original pesticide (Sirtori et al., 2010). For electrochemical oxidation to become an accepted treatment method it is thus necessary to map the entire degradation pathway for a given pesticide, and control of DIs remains a challenge to be solved.

With respect to degradation pathways for pesticides, most knowledge has been gathered for phenoxy acid, triazines and organophosphates, with complete or partial pathways having been mapped for the following compounds: atrazine (Polcaro et al., 2005; Borràs et al., 2010), cyanuric acid, desethyl-desisopropylatrazine (DEIA) (Polcaro et al., 2005), 2,6-dichlorobenzamide (BAM) (Madsen et al., 2014), diuron, dichloroaniline (Polcaro et al., 2004), 4-chloro-2-methylphenoxy acetic acid (MCPA), 2-(4-chloro-2-methylphenoxy)-2-methyl-propionic acid (CPMP) (Boye et al., 2006), 2-(4-chloro-2-methylphenoxy) propionic acid (MCPP)

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(Boye et al., 2006; Flox et al., 2006), malathion, parathion (Muff et al., 2009), methyl-parathion (Vlyssides et al., 2004; Muff et al., 2009), methamidophos (Martínez-Huitle et al., 2008), o-nitrophenol (Rabaaoui et al., 2013), pretilachlor (Wei et al., 2011) and propham (Ozcan et al., 2008). However, in all of the before mentioned studies except one (Vlyssides et al., 2004), an inert supporting electrolyte, predominantly sulfate or perchlorate, has been used. The advantage of applying this type of electrolyte in model solutions is that primarily the EOTR process is occurring, which simplifies the interpretation of overall degradation process, but in relation to real scenarios the presence of only inert ions may be considered unrealistic. In real waters, electroactive ions will most likely be present and these can lead to the formation of strong oxidizing agents (Panizza and Cerisola, 2009). The most typical of these is the formation of $HClO/ClO^-$ (active chlorine), due to the ubiquitous nature of the Cl^- ion. For further information on the mechanisms involved in electrochemical oxidation of organics in water please refer to this reference (Panizza and Cerisola, 2009). The presence of active chlorine leads to a degradation pathway parallel to that mediated by the EOTR process, and may therefore potentially result in the formation of a larger number of and different DIs. The active oxygen species in the EOTR process predominantly result in hydrogen abstraction or hydroxylation, whereas active chlorine can oxidize through different mechanisms and result in chlorination of the chemical structure of the pesticide (Muff and Søgaard, 2011).

In a previous study we have investigated the electrochemical degradation pathways of pesticide residue 2,6-dichlorobenzamide (BAM), an important and persistent groundwater pollutant, at boron-doped diamond (Si/BDD) and platinum-iridium anodes (Ti/Pt-Ir) anodes in a sodium sulfate electrolyte. We found in particular hydroxylation and for BDD dechlorination of the aromatic ring as the main routes towards ring opening and complete mineralization in the EOTR driven process (Madsen et al., 2014). In the present study the aim was to determine the degradation of BAM in a chloride rich medium, with the specific purpose of investigating the influence of the electrochemically formed active chlorine on the formation of DIs both with respect to structure and quantity. This allowed us to make a direct comparison between the two scenarios with and without chloride as a step towards the final aim of predicting the DIs formed in a real groundwater matrix. To investigate the importance of active oxygen species towards active chlorine mediated oxidation in more detail, the performance of an active platinum anode favoring active chlorine formation and a non-active BDD anode favoring EOTR were compared. More specifically, the two anodes were compared with respect to the rates of BAM and TOC removal, the structure and total amount of DIs formed during the degradation process and the evolution in intensity for each detected DI.

2. Materials and methods

2.1. Chemicals

BAM was purchased at Sigma Aldrich with purity >98%. Methanol, (HPLC grade) and ethyl acetate (technical grade) were purchased from VWR. Demineralized water was produced in house with a Silex II ion exchanger from SILHORKO.

2.2. Electrochemical oxidation setup and procedure

The electrochemical oxidation was performed galvanostatically in a batch recirculation setup. The electrolyte solution was pumped from the reservoir in upflow mode through the electrochemical cell (Electrocell, Denmark) and the cooling unit. The electrochemical cell was of plate like design with exchangeable electrodes, an electrode gap of 3 mm operated in one compartment mode. The active electrode area was 10 cm^2 on both electrodes, the cathode was in all experiments stainless steel (AISI 316) and the anodes were platinum coated titanium (Ti/Pt) and boron doped diamond coated niobium substrate (Nb/BDD).

Total electrolyte volume used was 1.0 L and 0.5 L depending on the experiment. Stock solutions of 100 mg L^{-1} BAM were prepared in 0.10 M NaCl solution.

10 mL samples were extracted for analysis, and immediately mixed with 1 mL 1 M Na_2SO_3 for quenching of excess oxidants.

2.3. Analytical procedures

The degradation of BAM and the formation of DIs were analyzed with a HPLC/UV/ESI-MS system (1260 Infinity and 1100 series LC/MSD Trap, ZORBAX Eclipse Plus C18 column, Agilent Technology), and a GC/MS system (Clarius 500, Perkin Elmer).

For the HPLC method, a 20:80 (v/v) mixture of acetonitrile and distilled water was used as eluent, and pumped with a flow rate of 400 $\mu L\ min^{-1}$ at 25 °C. When using the UV detector the absorption wavelength was set at 210 nm, and the injection volume at 5 μL. On the ESI-MS, the nebulizer pressure was set at 2.76 bar, the nebulizer flow at 9 $L\ min^{-1}$, and the dry gas temperature to 350 °C. Nitrogen was used for nebulization and dry gas. The spectra were recorded in negative mode. For quantitative determination of compounds, tandem mass spectroscopy with multiple reaction monitoring (MRM) was applied, and the injection volume was 50 μL.

For the GC/MS method, the temperature was increased from 75 °C to 275 °C in the first 12 min and kept at this level until 15 min. Prior to analysis on the GC/MS, the samples were subjected to solid phase extraction using TELOS ENV 200 mg/6 mL columns. The solid phase extraction procedure was: activation of column with 6 mL methanol, equilibration with 6 mL demineralized water, application of 10 mL sample, elution of interferences with 6 mL demineralized water, vacuum drying of column for 60 min, elution of analytes with 10 mL ethyl acetate, evaporation of ethyl acetate of 80 °C and dissolution in 1 mL ethyl acetate with 1.0 g/L bromobenzene as internal standard.

The HPLC/UV system was used for the quantification of BAM, while the HPLC/ESI-MS system was used for DI identification and quantification. By running the ESI-MS in negative mode, the interferences of BAM and cations, in particular sodium, were avoided. Due to its amide group, BAM is only detectable in positive mode, and ionic interferences are usually always worse for cations relative to anions. The GC/MS was used to aid the identification of the DIs and also to investigate for DIs not detected by the ESI-MS.

The extent of mineralization of organic matter in the samples was investigated by determining total organic carbon (TOC) in the aqueous samples with a multi N/C 2000 analyzer from Analytik Jena, and the total UV absorbance was determined with a Cary 50, Varian.

3. Results and discussion

3.1. Degradation pathway for BAM in chloride medium

Using the analytical tools, the molecular composition of the samples were evaluated and interpreted into an overall scheme showing the proposed degradation pathways in the chloride medium (Fig. 1). In the following, the summarizing proposed degradation pathway is presented with the many arguments underlying the interpretations explained in subsequent paragraphs.

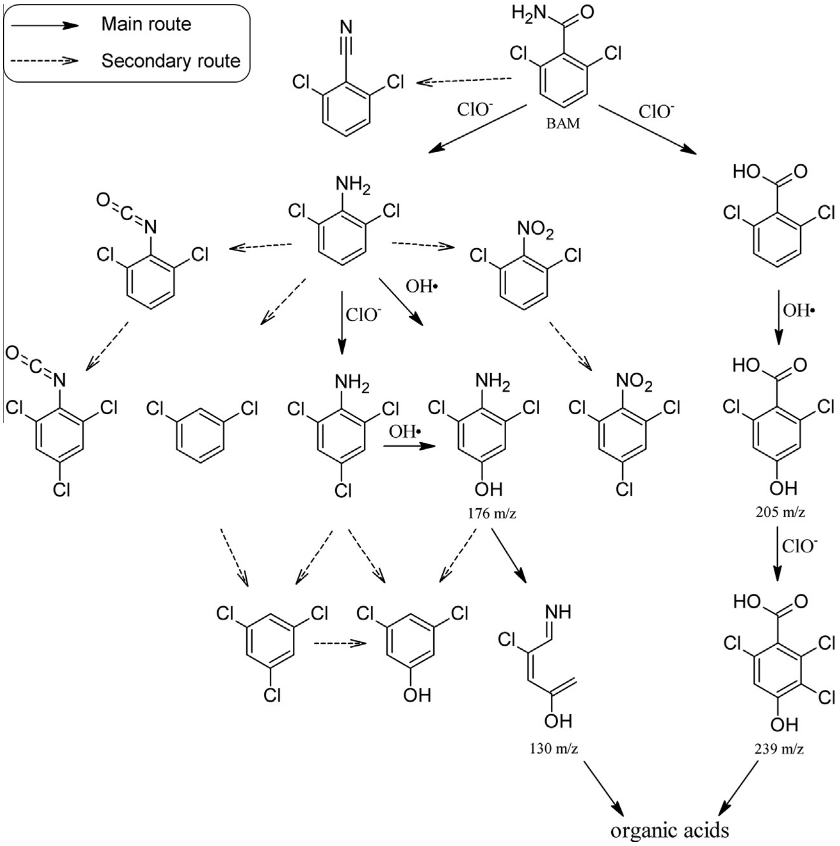


Fig. 1. Proposed degradation pathway for BAM in chloride medium. The scheme distinguishes between main and secondary routes. The compounds formed in the secondary routes were only detected with GC/MS after increasing the concentration 100× with SPE and in intensities much lower than the compounds of the main routes. The possible formation of condensate products is not shown.

When compared to our previous studies, the electrochemical degradation of BAM in a chloride medium was found to lead to a more complex mixture of degradation intermediates compared to when an inert sulfate electrolyte was used (Madsen et al., 2014). The initial step in the chloride electrolyte was an oxidation of the amide group, either to an amine or a carboxylic acid. In the amine route, BAM was first oxidized to 2,6-dichloroaniline (DCA), which was then further chlorinated to 2,4,6-trichloroaniline (TCA). In both of these reactions, the oxidizing agent was active chlorine (likely hypochlorite), which was verified in a standard hypochlorination experiment where sodium hypochlorite was used to oxidize BAM. At the anode, these compounds were hydroxylated to 2,6-dichloro-4-hydroxy-aniline (DCHA), which was further degraded to a small amine compound with a nominal mass of 131 Da. In the carboxylic acid route, BAM was oxidized to 2,6-dichlorobenzoic acid, which was hydroxylated (205 m/z) and then chlorinated (239 m/z). 2,6-Dichlorobenzoic acid itself was not detected, but this was due to very low sensitivity for this compound with both the HPLC and the GC method.

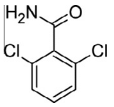
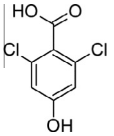
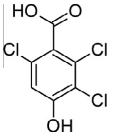
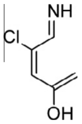
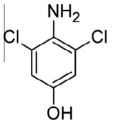
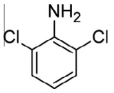
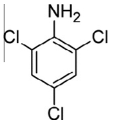
Next to these main routes of degradation, a number of secondary routes were observed. In the initial step, BAM may be converted to 2,6-dichlorobenzonitrile, and in the amine reaction path, the amine group may be oxidized to a nitro or an isocyanato-group, or may be completely removed. The compounds in the secondary routes were however formed in significantly smaller amounts with intensities around 1–5% of that of the compounds in the main route.

Oxidation of chloroanilines or pesticides such as dichlofenac and diuron that readily convert to chloroanilines have been investigated in a number of studies (Arias and Brillas, 1986; Brillas et al., 2010, 2004; Hadasch and Meunier, 1999; Mihály et al., 2001; Polcaro et al., 2004; Carrier et al., 2009; Homlok et al., 2012; Hussain et al., 2012), and it was interesting to compare degradation pathways across studies. In these studies, some of the same DIs as in this study have been found, showing similar reaction trends. There were however also notable differences. In some of the studies, where the oxidation was mediated by hydroxyl radicals, the amine group was found to be substituted for a hydroxy group (Arias and Brillas, 1986; Brillas et al., 2010), which was not the case in this study. Here the amine group was found to be intact through the entire main degradation path from DCA to the 131 Da compound, while the loss of the amine group represented a secondary route. In another study where the hydroxyl radicals were formed via ionizing radiation (Homlok et al., 2012), the amine group was found to intact through ring opening, which is more in line with the observations made in this study. The exact reason for the difference is unknown, but it is possible that the combination of EOTR and hypochlorite mediated oxidation in this study allows for ring opening prior to oxidation of the amine group. Another interesting finding from the other studies on chloroaniline oxidation is the formation of polyaniline condensate products (Hadasch and Meunier, 1999; Mihály et al., 2001; Carrier et al., 2009; Hussain et al., 2012). In this study an unidentified peak with a mass charge ratio of 288 m/z was observed in negative ESI-MS mode, and given its high molecular weight, it might be such a condensate product although its m/z value did not match with any of the previously reported compounds.

3.2. Identification of degradation intermediates

For the compounds detected with GC/MS, identification was primarily made from comparison with fragmentation spectra in a

Table 1
Identification of main degradation intermediates. The table displays the different parameters used in the identification process. nd Indicates for ESI-MS and GC/MS that the compound was not detected in this particular mode.

ESI-MS positive $m/z = M + 1$	ESI-MS negative $m/z = M - 1$	HPLC t_{ret} (min)	GC/MS $m/z = M$	Cl atoms	N atoms	Suggested structure
190 (BAM)	nd	3.2	189	2	1	
nd	205	1.7	nd	2	0	
nd	239	2.3	nd	3	0	
nd	130	10.1	nd	1	1	
nd (DCHA)	176	9.2	177	2	1	
nd (DCA)	nd	nd	161	2	1	
nd (TCA)	nd	nd	195	2	1	
nd	288	2.2	nd	2	1	? (Condensate)

NIST library. Not all compounds could however be detected on the GC/MS, and the structure of the peaks only observed with HPLC/ESI-MS therefore had be deduced from other parameters. These are listed in Table 1. To determine the number of nitrogen atoms the nitrogen rule was used, with an odd molecular mass charge ratio inferring the presence of an odd number of nitrogen atoms and an even number inferring the presence of zero or an even number of nitrogen atoms. In this study, this was taken as either one or zero nitrogen atoms since the occurrence of more than one nitrogen atom per molecule was deemed unlikely, except for condensate products. The number of chlorine atoms was determined from the relative intensity of the +2 isotope peak to the main peak. Also, since the ESI-MS was run in negative mode, detection here could be used to infer the presence of functional groups capable of deprotonating (–OH, –COOH). The retention time of the compounds on the HPLC was used to investigate their relative polarity, which could be used to distinguish amide from amine compounds.

For the 205 and 239 m/z peaks, their even molecular mass charge ratio showed that they had lost their nitrogen atom, and from the relative isotope peak intensity they were found to contain two and three chlorine atoms respectively. Also, from their HPLC retention times, they were found to have similar polarities as BAM. Together these observations suggested the two structures shown in Table 1.

The odd molecular mass charge ratio of the 130 m/z peak showed that it still contained a nitrogen atom and by comparing with the 176 m/z that showed similar HPLC retention, this was taken as strong indications for the presence of an amine rather than an amide group. The isotope ratio showed the compound to contain one chlorine atom, and since it was seen in negative ESI-MS it also contained a deprotonizable group. From these facts, two molecular formulas could be combined to give a molecular mass of 131 Da: $C_4H_2O_2NCl$ and C_5H_6ONCl. Due to the low hydrogen number of the first structure, the second was taken as the most likely. Finally, as seen in Fig. 6, the intensity of the 130 m/z peak was found to follow that of DCHA, which indicated that it was formed from DCHA. With these observations in mind, a proposed scheme for this conversion was made, see Fig. 2, where one of the chlorine atoms was substituted for a hydroxy group and the

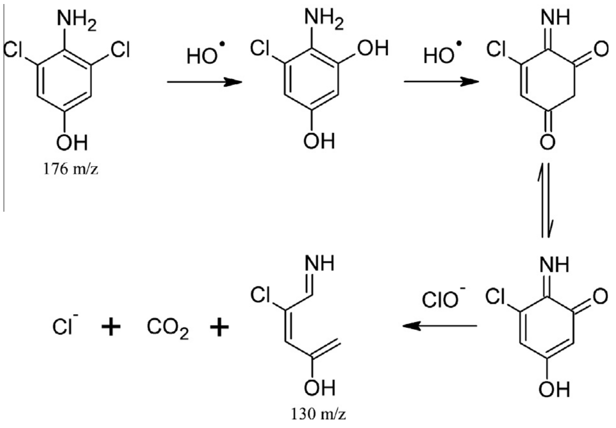


Fig. 2. Proposed scheme for formation of the 131 Da compound.

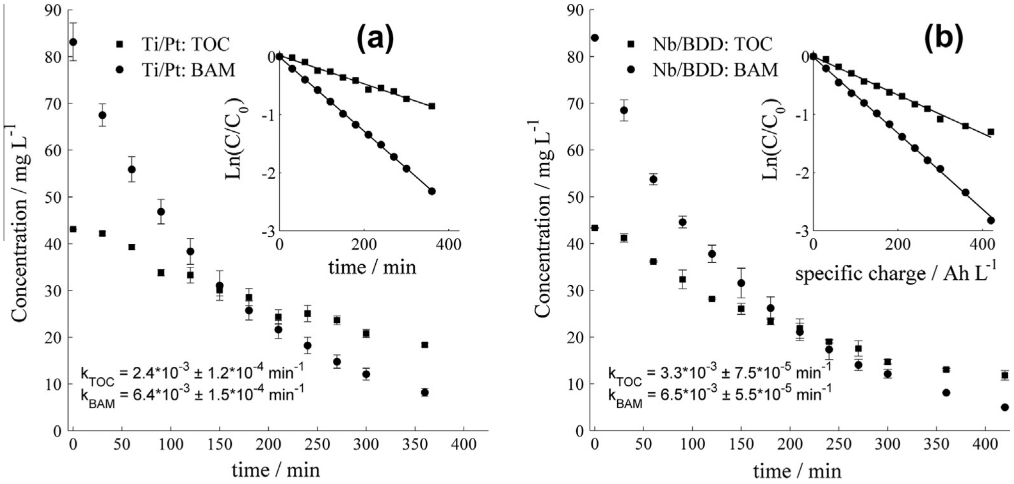


Fig. 3. Degradation plots and kinetics for removal of BAM and TOC with Ti/Pt (a) and Nb/BDD (b) anode. The main plots show the actual data with error bars, representing the standard deviation determined from a double determination. The inset plots show the pseudo first order fits from which the rate constants, lower left corner of plots, have been determined.

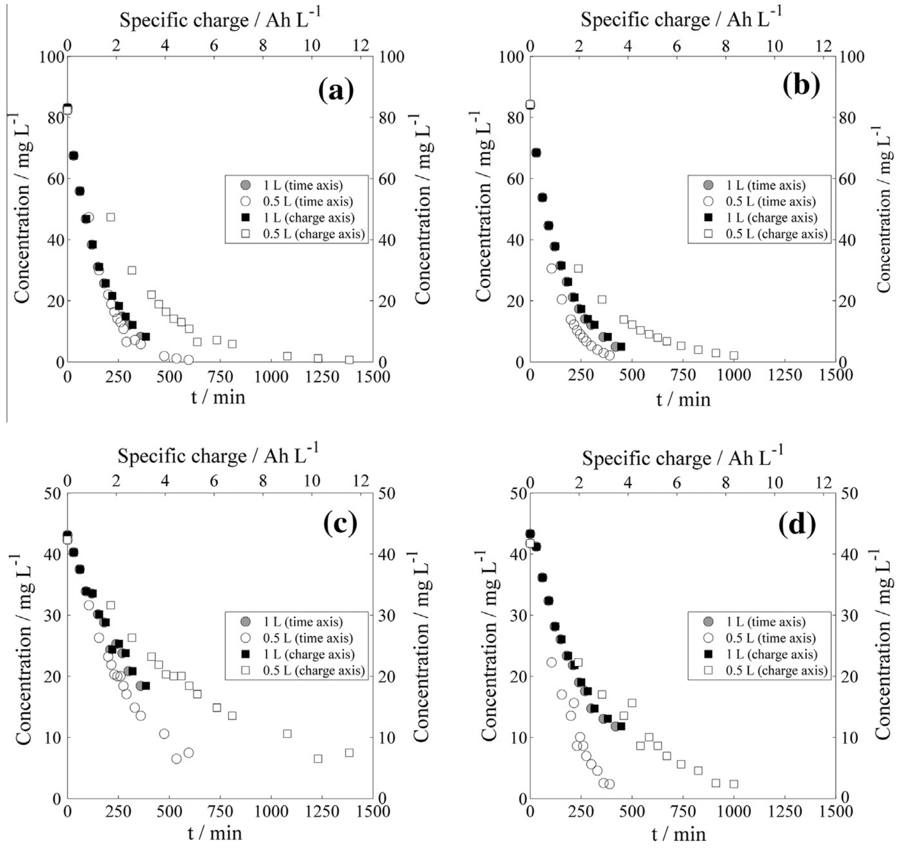


Fig. 4. Plot of BAM and TOC degradation in solutions with starting volumes of 0.5 L and 1.0 L. (a) Pt anode, BAM, (b) BDD anode, BAM, (c) Pt anode, TOC, and (d) BDD anode, TOC.

two hydroxy groups were then oxidized to carbonyl groups. Although neither of the two suggested compounds were detected, both of these processes are commonly suggested for EOTR oxidation of aromatics (Vlyssides et al., 2004; Boye et al., 2006; Ozcan et al., 2008), and the compounds may either have been too short lived or present in too low amounts to allow detection. Quinone can exist in equilibrium with an isomer, which can then react with active chlorine via the same reaction mechanism as seen for the conversion of BAM to DCA.

3.3. Influence of the nature of active oxygen species

As is typical in AOP studies, the kinetics for both TOC and BAM removal were found to be pseudo first order as seen in Fig. 3. More interestingly was that only TOC removal was found to be dependent on the applied anode. Similar rate constants were found for BAM for both Ti/Pt and Nb/BDD indicating that active chlorine oxidation was determining the initial oxidation of BAM. This was in accordance with the identified DIs, which were different from the

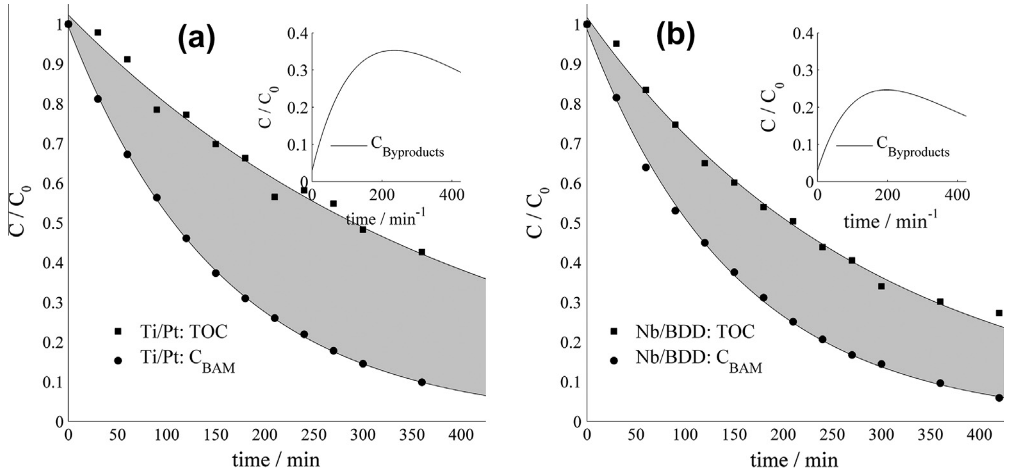


Fig. 5. Total amount of carbon originating from DIs formed during oxidation at Ti/Pt (a) and Nb/BDD (b) anodes. The grey area between the TOC and BAM curves represents the carbon bound in DIs. The subplots show the change in amount of DIs as a function of time.

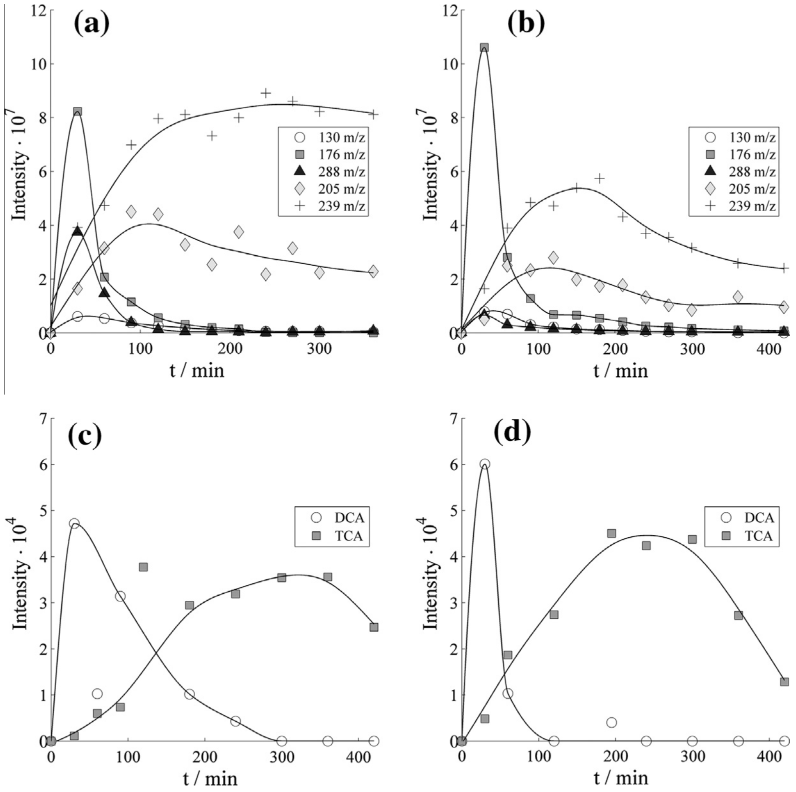


Fig. 6. Evolution in intensities of DIs. (a) Ti/Pt anode, HPLC/ESI-MS, (b) Nb/BDD anode, HPLC/ESI-MS, (c) Ti/Pt anode GC/MS and (d) Nb/BDD anode GC/MS. 2,6-dichloro-4-hydroxy-aniline (176 *m*/*z*) was detected with both HPLC-ESI/MS and GC/MS. It has not been plotted in the GC/MS plots (c and d), but was found to give similar intensities as DCA and TCA. From this it could be inferred that the two main degradation routes were of comparable importance. The chemical structure of the compounds can be found in Table 1.

ones seen for the EOTR oxidation of BAM in inert electrolyte (Madsen et al., 2014), as would be expected with a different initial step in the degradation scheme.

To elucidate the respective importance of the amount of active chlorine and the EOTR in the process the initial electrolyte volume was changed to 0.5 L, based on the hypothesis that due to the high flow rate (34.4 L h^{-1}) relative to the total volume, the bulk active chlorine concentration could be maintained at a constant high level independent of the solution volume. This would apply since the net production of active chlorine in the cell would be far larger than the consumption due to bulk reactions. Degradation mediated by active chlorine oxidation should therefore occur at the same rate for both an initial volume of 1.0 L and 0.5 L. Removal rate through EOTR was on the other hand inverse dependent on the electrolyte volume due to the dependency on recirculation frequency. On average from a macroscopic viewpoint, the BAM molecules were brought in anodic surface contact twice as frequently in the same time span when the solution volume was 0.5 L compared to 1.0 L.

The effect was investigated by plotting the degradation for both 0.5 L and 1.0 L in the same plot as a function of time (min) and specific charge passed through the electrolyte (A h L^{-1}), respectively

(Fig. 4). If active chlorine oxidation was dominant, the degradation curves would be overlapping in the time plot while the 0.5 L experiment would be less efficient in the specific charge plot. If EOTR oxidation was dominant, the specific charge plot would be overlapping while the rate of reaction was faster in the time plot of the 0.5 L experiment due to the doubled recirculation frequency.

For the Ti/Pt anode, the degradation curves for BAM in both 0.5 L and 1.0 L were almost completely overlapping when plotted as a function of time (Fig. 4a), while for the Nb/BDD anode the degradation was faster in the 0.5 L setup compared to the 1.0 L (Fig. 4b). These results showed that for the Ti/Pt anode, the initial step of the degradation of BAM was almost completely due to active chlorine oxidation, while both active chlorine and EOTR oxidation contributed to the degradation at the Nb/BDD anode. However, active chlorine oxidation was still dominating compared to EOTR at the Nb/BDD as seen from both the rate constants and the close resemblance of the 0.5 L and 1.0 L time plot.

As with BAM, the comparison between the two setups showed that TOC removal was largely determined by active chlorine oxidation for the Ti/Pt anode (Fig. 4c), while it was dominated by EOTR at the Nb/BDD anode. The dominance of the EOTR could even be seen for specific degradation intermediates, like the recalcitrant 239 *m*/*z* peak (supporting Fig. S1). Here, the peak intensities of the two experiments completely overlapped when plotted as a function of the applied specific charge.

Since TOC was less efficiently removed by active chlorine oxidation, the use of the active Ti/Pt anode led to a larger amount of total DIs as shown in Fig. 5a. In Fig. 5, the evolution with time of relative carbon originating from DIs is shown in subplots. However, it should be noted that since the active chlorine oxidation was more efficient compared to the EOTR at Ti/Pt with respect to TOC removal, the presence of chloride ions resulted in relatively fewer DIs compared to the degradation operated in inert electrolytes (Madsen et al., 2014). Electroactive ions may therefore both improve the rate of removal and result in fewer DIs for a primarily active anode as Ti/Pt. Since the TOC removal was predominantly determined by EOTR at the Nb/BDD anode, the amount of DIs (Fig. 5b) were similar to that determined previously for the single EOTR process (Madsen et al., 2014).

In Fig. 6, the evolutions in intensity of the individual DIs are shown for a representative experiment. It was mainly the chlorinated species (239 *m*/*z* and TCA) and the acid species that resulted in the difference in TOC removal by the two anodes. These compounds were more resistant to active chlorine oxidation which resulted in stable levels of these when using the Ti/Pt anode. When using the Nb/BDD anode all DIs were found to be oxidized, observations in accordance with the general comprehension of the preference of partial oxidation by active anodes and total mineralization by the increased amount of hydroxyl radicals at non-active anodes.

4. Conclusions

In the present study it was found that the presence of chloride ions in the electrochemical oxidation of BAM leads to a more diverse mixture of degradation intermediates (DIs) different from the ones formed in a single electrochemical oxygen transfer reaction (EOTR) process. This was primarily due to the initial oxidation being largely due to active chlorine (hypochlorous acid/hypochlorite) independent of the anode material. The degradation mainly occurred through two pathways. One in which the amide group at BAM was oxidized to an amine group and another in which it was oxidized to a carboxylic acid. The DIs then underwent both chlorination and hydroxylation until ring cleavage occurred.

When using the non-active Nb/BDD anode, the total amount of DIs was lower compared to the more active Ti/Pt anode, and the chlorinated DIs were removed more effectively. The reason for the difference was that for the Nb/BDD anode, TOC and DI removal were dominated by EOTR, whereas for the Ti/Pt anode TOC and DI removal were dominated by the less effective active chlorine oxidation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.10.058.

References

Arias, A., Brillas, E., 1986. Electrochemical oxidation of 2,4-dichloroaniline in aqueous sulphuric acid medium at a platinum electrode. J. Electroanal. Chem. Interfacial Electrochem. 198, 303–318.

Borràs, N., Oliver, R., Arias, C., Brillas, E., 2010. Degradation of atrazine by electrochemical advanced oxidation processes using a boron-doped diamond anode. J. Phys. Chem. A 114, 6613–6621.

Boye, B., Brillas, E., Marselli, B., Michaud, P., Comninellis, C., Farnia, G., Sandonà, G., 2006. Electrochemical incineration of chloromethylphenoxy herbicides in acid medium by anodic oxidation with boron-doped diamond electrode. Electrochim. Acta 51, 2872–2880.

Brillas, E., Boye, B., Sirés, I., Garrido, J.A., Rodríguez, R.M., Arias, C., Cabot, P.-L., Comninellis, C., 2004. Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode. Electrochim. Acta 49, 4487–4496.

Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., 2010. Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes. Chemosphere 79, 605–612.

Carrier, M., Besson, M., Guillard, C., Gonze, E., 2009. Removal of herbicide diuron and thermal degradation products under Catalytic Wet Air Oxidation conditions. Appl. Catal., B 91, 275–283.

Flox, C., Cabot, P.L., Centellas, F., Garrido, J.A., Rodríguez, R.M., Arias, C., Brillas, E., 2006. Electrochemical combustion of herbicide mecoprop in aqueous medium using a flow reactor with a boron-doped diamond anode. Chemosphere 64, 892–902.

Hadasch, A., Meunier, B., 1999. Oxidation of dichloroanilines and related anilides catalyzed by iron(III) tetrasulfonatophthalocyanine. Eur. J. Inorg. Chem. 1999, 2319–2325.

Homlok, R., Takács, E., Wojnárovits, L., 2012. Ionizing radiation induced reactions of 2,6-dichloroaniline in dilute aqueous solution. Radiat. Phys. Chem. 81, 1499–1502.

Hussain, I., Zhang, Y., Huang, S., Du, X., 2012. Degradation of p-chloroaniline by persulfate activated with zero-valent iron. Chem. Eng. J. 203, 269–276.

Madsen, H.T., Søgaard, E.G., Muff, J., 2014. Study of degradation intermediates formed during electrochemical oxidation of pesticide residue 2,6-dichlorobenzamide (BAM) at boron doped diamond (BDD) and platinum–iridium anodes. Chemosphere 109, 84–91.

Martínez-Huitle, C.A., De Battisti, A., Ferro, S., Reyna, S., Cerro-Lopez, M., Quiro, M.A., 2008. Removal of the pesticide methamidophos from aqueous solutions by electrooxidation using Pb/PbO$_2$, TiSnO$_2$ and Si/BDD electrodes. Environ. Sci. Technol. 42, 6929–6935.

Mihály, K., Zoltán, N., Tamás, K., Farsang, G., 2001. The electrochemical oxidation of 4-chloroaniline, 2,4-dichloroaniline and 2,4,6-trichloroaniline in acetonitrile solution. Electrochim. Acta 46, 1297–1306.

Muff, J., Søgaard, E.G., 2011. Identification and fate of halogenated PAHs formed during electrochemical treatment of saline aqueous solutions. J. Hazard. Mater. 186, 1993–2000.

Muff, J., Andersen, C.D., Erichsen, R., Soegaard, E.G., 2009. Electrochemical treatment of drainage water from toxic dump of pesticides and degradation products. Electrochim. Acta 54, 2062–2068.

Ozcan, A., Sahin, Y., Koparal, A.S., Oturan, M.A., 2008. Propham mineralization in aqueous medium by anodic oxidation using boron-doped diamond anode: influence of experimental parameters on degradation kinetics and mineralization efficiency. Water Res. 42, 2889–2898.

Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic pollutants. Chem. Rev. 109, 6541–6569.

Polcaro, A.M., Mascia, M., Palmas, S., Vacca, A., 2004. Electrochemical degradation of diuron and dichloroaniline at BDD electrode. Electrochim. Acta 49, 649–656.

Polcaro, A.M., Vacca, A., Mascia, M., Palmas, S., 2005. Oxidation at boron doped diamond electrodes: an effective method to mineralise triazines. Electrochim. Acta 50, 1841–1847.

Quiroz, M.A., Bandala, E.R., Martínez-huitle, C.A., 2011. Advanced oxidation processes (AOPs) for removal of pesticides from aqueous media. In: Stoytcheva, M. (Ed.), Pesticides – Formulations, Effects, Fate, one ed. InTech, pp. 685–730.

Rabaaoui, N., Saad, M.E.K., Moussaoui, Y., Allagui, M.S., Bedoui, A., Elaloui, E., 2013. Anodic oxidation of o-nitrophenol on BDD electrode: variable effects and mechanisms of degradation. J. Hazard. Mater. 250–251, 447–453.

Sirtori, C., Agüera, A., Gernjak, W., Malato, S., 2010. Effect of water–matrix composition on trimethoprim solar photodegradation kinetics and pathways. Water Res. 44, 2735–2744.

Vlyssides, A., Barampouti, E.M., Mai, S., Arapoglou, D., Kotronarou, A., 2004. Degradation of methylparathion in aqueous solution by electrochemical oxidation. Environ. Sci. Technol. 38, 6125–6131.

Wei, J., Feng, Y., Sun, X., Liu, J., Zhu, L., 2011. Effectiveness and pathways of electrochemical degradation of pretilachlor herbicides. J. Hazard. Mater. 189, 84–91.