Avoidance of Chlorine Formation during Electrolysis at Boron-Doped Diamond Anodes in Highly Sodium Chloride Containing and Organic-Polluted Wastewater

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In the present contribution, the behavior of sodium chloride containing electrolytes at boron-doped diamond anodes is investigated. The study is focusing on industrial process water treatment and is based on half-cell measurements (active area of the working electrode: 3.14 cm²) and technical laboratory electrolysis measurements (active area: 100 cm²). It was found that the diamond electrode has a considerable overvoltage for chlorine formation (approx. 740 mV vs. RHE), regrettably not sufficient for hydroxyl radical formation before chlorine formation, regarding the electrochemical potential. Nevertheless, an operating point was identified through process parameter variation, which leads to wastewater purification at the diamond electrode without generating chlorine emissions. The application of the identified operating point is shown at the purification of real diaminodiphenylmethane-production wastewater (10 wt% sodium chloride) and artificial process water contaminated with N-(chloromethyl)-N-ethylpiperidinium chloride organic. Valuable component of both wastewaters are the high salt loads, which are reusable if the organic substances are successfully treated. The observations are confirmed by ultratrace analysis of organic products and do not show any chlorinated products at the desired operating point.

Nowadays many processes in the chemical industry can only be further improved regarding their cost-effectiveness by recycling energy and material flows between different chemical plants. This integration and recycling of alleged waste streams also reduces energy and raw material consumption. This does not only increase the economic efficiency but also the environmental compatibility and sustainability of a process or a closed process with a full recycle chain at best.

The electrochemical treatment of wastewater could be a promising process chain addition. In particular, advanced oxidation processes (AOP) based on boron-doped diamond electrodes (BDD) enable a high purification performance for almost all organic impurities by generating especially highly reactive hydroxyl radicals ([OH]) and could make wastewater containing organic compounds usable.

Such unused process flows are the waste streams of the poly carbonate (PC) production and the diamine diphenylmethane (MDA) production, which is a preprocess in the polyurethane production chain. For reusing the sodium chloride (NaCl) and the deionized wastewater (10 wt% sodium chloride) and artificial process water contaminated with N-(chloromethyl)-N-ethylpiperidinium chloride organic. Valuable component of both wastewaters are the high salt loads, which are reusable if the organic substances are successfully treated. The observations are confirmed by ultratrace analysis of organic products and do not show any chlorinated products at the desired operating point.

Due to the lower standard potential of chlorine formation (Equation 1) on the anode side (E = 1.36 V vs. SHE), 3 compared to the standard potential of hydroxyl radical formation (E = 2.8 V vs. SHE, Equation 2), 4 the formation of chlorine is a major factor that could significantly decrease the electrochemical yield of hydroxyl radicals. It should be avoided at best. In addition, a BDD anode enables the formation of other oxidizing agents, such as ozone (Equation 3) from direct water oxidation (E = 1.51 V vs. NHE). 5 Its standard potential is also greater compared to chlorine development.

\[
2 \text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2e^- \quad [1]
\]

\[
\text{H}_2\text{O} + M \rightleftharpoons M(\cdot\text{OH})_{\text{ads}} + \text{H}^+ + e^- \quad [2]
\]

\[
3 \text{H}_2\text{O} \rightleftharpoons \text{O}_3 + 6\text{H}^+ + 6e^- \quad [3]
\]

To avoid the formation of chlorinated hydrocarbons, the formation of chlorine gas (Cl₂), hypochlorous acid (HClO) and hypochlorite ions (ClO⁻) must be avoided. The proportions of the dissolved chlorine species (Cl₂, HClO acid and ClO⁻) depend on the pH value. The equilibrium is entirely on the side of the ClO⁻ at a pH value greater than 5.9. 6,9

Furthermore, in consequence of the radical formation at the BDD electrode, secondary reactions and reaction chains correspondingly

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vary and strongly depend on the organic and inorganic compounds in the investigated wastewater. Several publications have investigated the influence of chloride ions on BDD electrodes, the evolution of chlorine and the consecutive chlorination of organic matter. Chloride systems without any additional organic compound were investigated by Chen and Hubler. Chen et al. investigated the overvoltage of chlorine development in the acid media (pH 1) and observed an increasing overvoltage of the chlorine evolution over time, traced back to BDD surface changes measured by Raman spectra. However, self-made BDDs were investigated and results may not be representative for commercial state of the art BDDs.

Further understanding of the electrochemical behavior of chloride ions at the BDD electrode is provided by Hubler’s investigation, which studies the formation of chloride and chlorate at the BDD anode. Batch experiments showed that the complete oxidation of chlorides to perchlorate is possible, but a high electrolysis time is required. Perchlorate formation at the BDD takes place through progressive oxidation of higher oxychlorides, but the perchlorate formation can be minimized or even avoided by low current densities and high chloride concentrations. Thus, the high salt load of the considered MDA wastewater and the artificial wastewater (aiming PC wastewater) form the prerequisites for a minimal progressive oxidation to oxychlorides. Further publications study the electrochemical behavior of chloride ions regarding the degradation performance in the presence of organic substances.

The influence of the chloride content at varying current densities (255 A/m², 1273 A/m²) and sodium chloride concentrations (3 g/l, 30 g/l) during BDD electrolysis of simulated ballast water (Batch process, pH 8–9) was studied by Lacasa et al. Both an increase in the chloride concentration, as well as an increase in current density led to an increased chlorine formation. A similar observation was made by Panizza et al., who showed a decreasing chlorine concentration over electrolysis time and thus also a formation of chlorine. Degaki et al. investigated the influence of NaCl in aqueous solution on organic degradation (dye Reactive Blue 19 solution) and determined a significant acceleration in degradation due to small amounts of NaCl. In addition, the lower the pH value (pH 1, pH 6, pH 10) and the lower the temperature (10 °C, 25 °C, 40 °C), the faster the total organic carbon (TOC) was degraded. Such a correlation was also published by Sires et al.

Due to the diverse reaction network between in-situ generated oxidizing agents and organic impurities, recent publications focus more on the possible reaction products and partially identify them. Chen et al. evaluated the electrochemical treatment of phenol at two different chloride concentrations (5 mM and 50 mM). The presence of chloride caused the formation of chlorinated oligomers, which are next to phenol harmful to the environment. The higher the chloride concentration, the faster the measured removal rates.

Further electrolysis of organic (sulfamethxazole) was done by Radjenovic et al., who measured a four times faster removal kinetic by chloride attendance in Na2SO4 and 13 times in NaNO3 anolyte. This is probably due to the effective electrochlorination. A study of the formed intermediates at the BDD compared to a Pt-anode exemplified by 2,6-dichlorobenzamide in chloride medium is done by Madsen et al. In the presence of chloride ions, a mixture of degradation intermediates was detected, since the initial oxidation of organic always took place through active chlorine, independent of the electrode.

Wu et al., who investigated chloride-containing and chloride-free dye wastewater at the BDD and dimensionally stable anodes (DSA), had come to a similar conclusion. In the presence of chloride, secondary pollution occurs at both electrodes. In chloride-free wastewater, BDD is more efficient due to complete mineralization. Further literature noted that for all considered process parameters in the literature above a chlorine formation occurred at the BDD anode. This resulted in an increased rate of organic degradation through the formation of oxidative chlorine species in Refs. 13, 15–18, but some studies attest a better mineralization without chloride species and the effect must be examined individually. In case of the present study, the valuable NaCl of the MDA wastewater would be consumed and chlorinated organic products would be formed.

Recent publications have recognized the knowledge gap regarding the more detailed understanding of chloride ions at defined process parameters regarding the diverse chlorine species at the BDD.

Such an investigation was done by Farhat et al., who evaluated the implication of chloride ions to the electrooxidation of surrogate and resorcinol at pH 2 to pH 7 in a sulfate solution. The pure sulfate solution and its organic components served as a benchmark, next to a pure nitrate solution. It could be observed, that an increasing pH from 2 to 7 reduced the amount of chlorinated organics.

Mostafa et al. investigated the electrochlorination in water treatment and analyzed various volatile chlorine species during the electrolysis of 0.6 M NaCl and 0.6 M NaClO4 and evidenced the competition between O2, Cl2 and •OH. At a pH value greater 12, no volatile chlorine was detected, only oxygen formation. However, only the gaseous chlorine compounds Cl2, ClO and ClO2 were considered. Mostafa indicates that hydroxyl radicals are formed only up to pH 7 or 8, in the higher pH value the oxygen development would begin.

This is in contradiction to numerous publications, which have the fastest degradation in the alkaline environment or a competitive degradation kinetic. In addition, the dissolved chlorine species (compared to the considered gaseous species by Mostafa) are more relevant in electrochemical wastewater treatment and this publication therefore focuses on them.

However, aiming NaCl as recyclable material besides the demineralized water, chlorine formation should be avoided as far as possible. A chlorine formation during organic degradation would result in forming of chlorinated hydrocarbons and would make the subsequent handling more difficult, for example at the desired use in CAE.

A publication, which describes the degradation of organic compounds with in-situ generated oxidizing agents at a BDD in NaCl and organic pollutants containing wastewater without the formation of chlorine species and chlorinated products, does not exist. The present publication is precisely aimed at this application.

### Experimental

In this contribution, the influence of varying temperatures and pH value on the electrochemical behavior of a NaCl solution at BDD anodes was investigated. For this aim, different electrochemical measurements were done at varied electrolysis conditions. These include cyclovoltammetric (CV) curves in a half-cell setup, further laboratory electrolysis in technical relevant terms and the analysis of the electrolyte.

Half-cell measurements.—The half-cell tests were carried out in a commercially available flexcell, which houses a three-electrode arrangement (Gaskatel, Germany). The working electrode is exchangeable and has an active electrode area of 3.14 cm². The investigated working electrode was a commercially available BDD electrode by Condias (Germany) type Diachem (boron-doped diamond layer on a niobium carrier, the thickness of the diamond layer is 12 μm), as counter electrode a coated platinum wire (by Gaskatel, Germany) was used.

For comparison, a titanium electrode with a ruthenium oxide (Ti/RuO2) coating was investigated, which is a state of the art anode for the (intended) chlorine development. DeNora (Italy) produced the coating of this DSA.

Half-cell measurements were performed under standard conditions (25 °C, 1 atm). In order to ensure a constant temperature of the electrolyte despite heat generation, the cell was cooled by a cryostat system via a double heat exchanger jacket. The reversible hydrogen electrode (RHE, Gaskatel GmbH) and a Hg/HgO electrode (1 M NaOH) were used as reference electrodes.

While the RHE was integrated directly into the flexcell, the connection to the Hg/HgO reference cell was realized via an additional Luggin capillary. To avoid a chlorine denoting gas mixture (Cl2 + H2)
during the decomposition of the NaCl solution, the reaction solution was covered with nitrogen.

The experiments were performed with an “IM6” potentiostat (Zahnner Elektronik GmbH, Germany).

Laboratory electrolysis and cell design.—A laboratory electrolysis cell was set up and operated for further investigations of the BDD electrode reactions. The cell with an active area of 100 cm² was operated with a planar Diachem BDD (by Condias, Germany). This is also a diamond electrode on the carrier material niobium, which has a trifle diamond coating of 12 μm in total. A Ti/RuO₂ anode was also used for comparison (coating by DeNora, Italy).

In combination with the mentioned anodes, a commercially available oxygen depolarized cathode (ODC) from Covestro AG (Germany) was used, which performs the oxygen reduction to hydroxide ions. For more information on the silver-based ODC refer to.⁷⁻⁹

For the reaction chamber separation, a Flemion 133 cation exchange membrane (by Asahi Glass Co., Japan) was utilized. The total electrode distance was 12 mm, resulting in an 8 mm distance between anode and membrane and 4 mm between membrane and cathode. The schematic structure of the laboratory electrolysis cell is shown in Figure 1.

A centrifugal pump, a gas separator, a heating tube, a voltage sensor and a temperature sensor completed the electrolyte circuit. The ODC was supplied with technically pure oxygen (over-stoichiometric) at a differential pressure of 59 mbar in the gas compartment. The power supply model was “Genesys” by TDK Lambda.

To enable operation within the membrane specification, the temperature of the tests was set at 60°C. To increase further homogeneous mixing a bypass behind the centrifugal pump was used. The inner volume flow was set to 80 l/h (anolyte) and 15 l/h (catholyte).

During the tests, anode and cathode potentials vs. RHE were measured and the cell voltage was recorded.

Analysis-methods.—For the laboratory evaluation, samples were taken at defined intervals from the anolyte and catholyte in order to determine the pH value by acid-base titration (0.1 M HCl or 0.1 M NaOH as measurement solution). Furthermore, the total organic carbon (TOC), the total chlorine concentration and the NaCl concentration were determined in the anolyte.

The TOC content was determined using a TOC device from Elementar (model vario TOC cube). Firstly, the samples were diluted (dilution factor of five) with deionized water and acidified with concentrated hydrochloric acid (32 wt%). The analysis was then carried out in accordance with the operating instructions. The TOC concentration was analyzed threefold for each sample and the mean value was determined.

For the analysis of the chloride concentration, the chloride determination according to Mohr using 0.1 M silver nitrate solution was used.¹⁰

The analysis of sodium hypochlorite/hypochlorous acid and chloride is carried out by the total chlorine determination in bleach.¹¹ For this purpose, each sample of 1 ml was filled to a volume of 300 ml with water and was stabilized with a tiny amount of NaHCO₃. Subsequently, the titration with arsenic acid (0.05 M) was done, until the spot test on potassium iodide starch paper no longer shows any coloring.

In addition to the above-mentioned analytical methods, ultrasensitive detection of organic compounds was performed using GERSTEL’s Twister analysis. First, the organics are extracted (in the alkaline and acidic milieu) onto a sorbent coated stirring rod. After the subsequent thermal desorption of the stirring rod coating follows a gas chromatography analysis. This was carried out by an external laboratory of CURRENTA GmbH (Germany).

The flow state within the electrolysis cell (Reynolds number) given in the following explanations was determined according to V. Schmidt.¹²

Used chemicals and wastewater.—During the tests sodium chloride, sodium hydroxide and sodium sulfate from Sigma-Aldrich (No. 433209, S0899 and S6264) were used. The pure organic substances were obtained from Sigma-Aldrich also, aniline (No. 242284), phenol (No. P4161), EPP (No. 596310), sodium formate (No. S2140) and MDA (No. 32950).

Covestro AG provided real wastewater from a MDA production plant. The most important components of the wastewater are the valuable substance NaCl with up to 99.5 g/l and the demineralized water. The most significant organics to be degraded are phenol, aniline, diaminodiphenylmethane (MDA), sodium formate as well as various short- and long-chain aliphatics.

Results and Discussion

Half-cell measurements.—Comparison of BDD and Ti/RuO₂.—The electrochemical behavior of the BDD in a neutral Na₂SO₄ solution and neutral NaCl solution are shown in Figure 2 and are compared to the CV of the Ti/RuO₂ electrode. To protect the Ti/RuO₂ electrode, the CV was only run between −2 V and +2.5 V, for the tests at the BDD the full potential range of the potentiostat was used (−4 V to +4 V).

In all three cases the left curve forms the oxidative path (with increasing potential) and the return path is given by the right curve - as exemplified by the CV of BDD in NaCl (arrow 1 and 2).

While the Ti/RuO₂ electrode starts the chlorine development as expected from about 1.5 V vs. RHE, the overvoltage at the BDD is significantly higher. The comparison shows that the CV diagram of the BDD implies an additional peak (at about 1.9 V vs. RHE). However, this reaction seems to be strongly inhibited and the system response with regard to the current density is low. Due to the high concentration of chlorine anions it is assumed that the formation of

![Figure 1. Schematic drawing of the used laboratory electrolysis cell based on a planar BDD (red), an ODC (blue) and cation exchange membrane (gray). The desired reactions and exemplary subsequent products are sketched.](image-url)
Figure 2. CV curves of a Ti/RuO₂ anode and BDD electrode in 0.5 M NaCl (neutral pH), as well as the BDD in 0.5 M Na₂SO₄ (neutral pH) electrolyte, 25°C, sweep rate of 100 mV/s, E vs. RHE.

chlorine only occurs in the further course (E > 2.25 V vs. RHE), which was confirmed by the analysis of a sample taken in the higher potential range.

As expected, the CV curve of BDD in neutral Na₂SO₄ electrolytes does not show a current increase until E > 2.85 V vs. RHE. The hydroxyl radical formation begins.

Unfortunately, OH⁻ formation sets in at a significantly higher potential than the chlorine development in the NaCl electrolyte.

Compared to the standard potential of chlorine formation of E° = 1.36 V, the overvoltage of the BDD is about five times the value of the investigated titanium electrode.

It is noted that the flattening of the CVs is caused by mass transport limitations and the level can be affected by electrolyte temperature.

**Influence of temperature and pH value.**—To investigate the electrochemical potential window of the chlorine formation at the BDD, the electrolyte temperature and pH values were varied.

Since the temperature variations (in neutral 0.5 M NaCl with 30°C, 50°C and 62°C) only show that the mass transport limitation is delayed (higher current densities are possible) and the peak of the reaction is slightly more pronounced at E vs. 2.1 V, a figure is not shown.

Figure 3 shows the most important test results of pH variation with a comparison of the neutral and the alkaline milieu (pH 6.6 to pH 14.3). In the very strong alkaline media the CV starts with a drastic increase in current density by a potential of approx. 1.9 V vs. RHE. The potential of the reaction is very close to the reaction which seems to be strongly inhibited in Figure 2.

To ensure that the observed potential shift is not due to a malfunction of the RHE, the measurement was repeated against Hg/HgO. The results are also shown in Figure 3 in the corrected form (converted to RHE conditions) by Nernst equation. The measurement versus Hg/HgO confirm the observations.

Furthermore, the CV of the strongly alkaline NaCl is similar to a CV of a pure NaOH solution at the BDD.

**Laboratory-cell measurements.**—In order to further investigate the electrochemical behavior, laboratory cell experiments were carried out.

Both the TOC degradation of the individual ingredients of the MDA process water and the membrane hazardous EPP organic were investigated, as well as complex real MDA wastewater. A 10 wt% NaCl solution and the pure organic substance serve as electrolyte for the TOC decomposition experiments of the individual decomposition tests. The pH value of the solutions was adjusted with caustic soda. A 1 M NaOH was used as the catholyte.

**Comparison of BDD and Ti/RuO₂.**—The degradation effect and the prevailing chloride concentration when using the BDD is compared with the dimensionally stable titanium anode (Ti/RuO₂) in Figure 4. In both cases, the pH value of the electrolyte was not adjusted and real MDA wastewater served as anolyte. The pH value dropped during the experiment from pHₐ = 13.1 to pHₑ = 1 as expected.

It should be mentioned that a different geometry (compared to above) was used for these tests. It was necessary to increase the gap distance to ensure a quick evacuation of the formed chlorine gas, preventing a chlorine gas cushion in the anode half shell. An increased distance of 14 mm between anode and membrane was used in order to integrate larger outlet diameters and a better gas removal.

Under the influence of anodic chlorine generation, both electrodes show an almost congruent degradation behavior, the consumption of existing chloride ions is also almost identical. Therefore, the hydroxyl radical yield seems negligible for organic treatment in the present operating case (pH ≤ 13.1) at the BDD. In both cases, the onset
of perceptible chlorine odor was perceived after some time in the experiment.

Influence of pH value on organic degradation.—In order to investigate the observed potential shift further, the pH value of the anolyte was adjusted in subsequent experiments in such a way that it is kept strongly alkaline over the test time despite the proton consumption/generation.

Figure 5 shows the organic degradation at the BDD electrode in the highly alkaline media.

Three tests are summarized and the mean value and the standard deviation are shown and the quantity of total chlorine measured is also shown.

During the degradation test at 6 kA/m² a cell voltage of about 4 V was obtained with an anode potential of relatively constant 3 V. A slight increase in cell voltage and potential occurred due to the continuous change in electrolyte composition and in particular in pH. The value decreased from 14.8 to 14.25 during the experiment (refer to “MDA-ww 1” in Figure 6) of 5 h. The TOC concentration fell by 94.79% within the 3 h shown in Figure 5, before it remained nearly constant.

The results confirm the observations of the half-cell experiments that a different electrochemical behavior of the NaCl-solution at the BDD can be forced by a very high pH value. It is possible to reduce the TOC of the real wastewater by almost 95% without generating chlorine in any form.

Figure 6 summarizes further experiments of the same form, with regard to the total chlorine concentration as a function of the pH value. It illustrates that two operating ranges are possible with a NaCl electrolyte at the BDD anode.

If the pH value fell below 14.2 during the test, chlorine development started immediately. A chlorine-free (ClO⁻ free) working range exists at a pH > 14.2 and a chlorine-comprising (ClO⁻) working range is set at a pH < 14.2 at a BDD anode.

The details of the further experiments are shown in Table I. It is obvious that a large proportion of the pure substances aniline, phenol, MDA and sodium formate could also be decomposed in an artificial wastewater without chlorine generation. Table I summarizes also the Reynolds numbers (Re) of the experiments. The viscosity was determined according to the average NaOH concentration during the experiment for the Re calculation. The flow conditions in the anode half shell were Re > 2000 in all experiments and therefore in the transition area or in the full turbulent area.

Analysis of electrolysis products based on EPP-degradation.—In another series of experiments, EPP salt was dissolved in 10 wt% NaCl solution and the degradation effect was also investigated. This artificial wastewater was decomposed at the BDD at operating regions 1 and 2 (referring Figure 6). In both tests the degradation was carried out at 4 kA/m².

Without chlorine development the TOC was reduced by 45.86% after 30 Ah/l (27.85 mg/l to 14.36 mg/l). Despite more specific charges the TOC remained almost constant in the further test procedure. In the operating range 2 the TOC could be reduced more under the same specific charge of 30 Ah/l, by 60.6% (36.37 mg/l to 14.32 mg/l), but to a similar final concentration despite the differences in the initial sample weight.

At the end of the experiment, the samples of the anolyte were given to a TWISTER analysis, the results are shown in Figures 7 to 10. The test in the operating range 2 (with formation of chlorine) shows a low residual concentration of EPP as well as numerous chlorinated hydrocarbons. Thus, in the acid (Figure 7): trichlorobutane (red marker 2), hexachloroethane (3) and dichlorobenzaldehyde (4) could be identified. The identified dichlorobutane (1) is due to the acidification of the sample with HCl and will not be rated. Furthermore, in the alkaline (Figure 8) analysis of the same sample hexachloroethane (5) could be found.
Table I. Experimental details of (further) TOC-degradation experiments.

| type of organic | $j$ [kA/m$^2$] | specific charge [Ah/l] | TOC$_0$ [mg/l] | TOC-degradation [%] | Re anolyte [-] | Re catholyte [-] |
|----------------|---------------|------------------------|----------------|---------------------|----------------|----------------|
| MDA-ww 1       | 6             | 180                    | 68.46          | 94.24               | 2169.7         | 1128.3         |
| Anilin 2       | 4             | 20                     | 19.92          | 73.10               | 2971.1         | 1101.9         |
| Phenol         | 5             | 50                     | 30.55          | 74.89               | 2842.7         | 1083.0         |
| Na formate     | 4             | 25                     | 24.48          | 97.52               | 2862.4         | 1088.6         |
| MDA            | 5.5           | 18.33                  | 0.48$^*$       | 99.99               | 2728.2         | -              |

*$^*$Due to the very low solubility, only a small amount of MDA could be dissolved in the highly alkaline electrolyte.

In contrast, in the analysis of the chloride-free operation range of the wastewater no chlorinated hydrocarbons (Figures 9 and 10) were detected.

This confirms the previous investigations regarding the impact of the pH value on the total chlorine concentration and generation. This underlines that an operating area has been identified in which organic substances can be degraded in a NaCl solution without chlorine emissions or chlorinated side products.

The investigations show a very specific degradation behavior regarding the organic substances. While nearly 95% of the MDA wastewater could be purified, the artificial wastewater with EPP (aiming PC wastewater) could only be reduced to a TOC concentration of approximately 14 mg/l.

In case of the MDA wastewater a reuse of the treated wastewater seems promising, possibly also in case of the EPP wastewater, because only aliphatic compounds remain at the newly found operating range 1. Future studies should evaluate, whether the aliphatic degradation products still contain ion-exchange active groups, otherwise membrane degradation would not happen.

For the intended reuse of the (MDA or PC) wastewater in a CAE must be verified that the remaining residual concentration (TOC) after electrochemical BDD-treatment has no negative impact on CAE performance and long-term experiments should be carried out.

Conclusions

To recycle NaCl from organically contaminated process water streams, the organics must be removed to a minimum, for example for reusing in a CAE.

It was investigated whether anodic chlorine formation can be prevented at the diamond anode, while a purification is simultaneously done by the formed oxidants at the BDD.

By avoiding anodic chlorine generation, the valuable material NaCl would be preserved, the oxidizing yield at the diamond electrode not reduced and the handling of purified process water would be facilitated through non-existing chlorinated hydrocarbons.

CV investigations reveal that the BDD has a considerable overvoltage with respect to the formation of chlorine. This overvoltage is not high enough to ensure that the hydroxyl radical formation takes place before chlorine formation.

However, an operating point was determined by varying the process parameters, which allows the purification of organic substances without the formation of chlorine emissions and therefore without chlorinated hydrocarbons and products in general.

The degradation tests showed that the organics sodium formate, aniline, phenol, MDA and EPP can be largely degraded in this operating range.

The mechanism behind the purification effect is not sufficiently understood. It is possible that the pH dependent hydroxyl radical formation takes place before the chlorine formation at the suggested operating point or ozone formation occurs at the operation conditions.
To reach this chlorine-free (Cl₂, HOCl, OCl⁻) purification at the BDD, the pH value of the anolyte must be above 14.2 at an operating temperature of 60°C.

Future investigations must consider which oxidizing agent is formed and why the chloride ions have not been oxidized in the identified operating range.

In addition, further experiments should be carried out in optimized cells. In particular, a diamond electrode should be used on expanded metal basis, as well as significantly higher volume flows or rather flow velocities (up to 170 cm/s according to Ref. 33) to achieve an even higher level of turbulence and thus improved mass transfer.

It must be examined for new process chains based on the described electrochemical purification, whether the residual concentration and species does not lead to any negative consequences in the subsequent process, which is fed with the recycled process water.

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