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Influence of operating conditions and wastewater-specific parameters on the electrochemical bulk disinfection of biologically treated sewage at boron-doped diamond (BDD) electrodes

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ABSTRACT

The aim of this study was to investigate an electrochemical process for bulk disinfection of biologically treated sewage. The influence of operating conditions (current density and flow rate) on the electrochemical formation of free chlorine in the sewage was determined. Furthermore, the effect of wastewater-specific parameters on the inactivation of *Escherichia coli* was studied. The disinfection capacity is primarily influenced by the concentration of electrochemically produced free chlorine. The production rate of free chlorine is independent of the flow rate within the range of 25–125 $\mathrm{L\,h^{-1}}$. The investigations have also shown that the electrochemical disinfection of *E. coli* in secondary effluents with BDD electrodes proceeds effectively at an electric charge input of 0.1–0.15 $\mathrm{Ah\,L^{-1}}$ corresponding to an energy expenditure of 2.0–2.6 $\mathrm{kWh\ m^{-3}}$. The electrochemically generated concentration of free chlorine ($c = 0.4$–$0.6\,\mathrm{mg\,L^{-1}}$) is sufficient for an *E. coli* reduction of four log levels under the following conditions: after-reaction time of 15–20 min, $T > 6$°C, $\mathrm{pH} < 8.5$ and $\mathrm{DOC} < 22\,\mathrm{mg\,L^{-1}}$. The formation of organic by-products (AOX, THMs) was marginal to moderate. The inorganic by-products chlorate ($1.2\,\mathrm{mg\,L^{-1}}$) and perchlorate ($18\,\mathrm{mg\,L^{-1}}$) were produced in considerable concentrations.

Keywords: Electrochemical disinfection; Wastewater reclamation; *E. coli*; Boron-doped diamond electrode; Electrochemical oxidants; Disinfection by-products

1. Introduction

The importance of direct recycling of sewage for sustainable water resources management is commonly acknowledged [1]. In the decentralized field, this reuse would lead to the establishment of a secondary loop for different possible applications (e.g. for sanitary facilities). Secondary effluents after biological treatment still contain a multitude of pathogenic germs (e.g. faecal bacteria, protozoa, viruses, worm eggs, etc.) [2]. Hence, a disinfection prior to direct reuse is indispensable and stipulated in country-specific codes and legal regulations [3].

The disinfection processes employed in the centralized large-scale water treatment such as chlorination and ozonization exhibit decisive drawbacks in the decentralized field (e.g. system safety, necessity for chemical storage and formation of unwanted disinfection by-products). As regards the introduction of a particular disinfection method for smaller systems, various factors such as acquisition cost, operating safety, compactness and simple, low-maintenance operation are of outstanding significance. Membrane filtration methods [4,5] and UV irradiation [6–8] represent useful options in small-scale wastewater (WW)

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disinfection; however, their current application requires a lot of investment in maintenance and costs. Therefore, electrochemical disinfection could be a promising alternative for the local internal recycling of biologically treated (domestic) effluents. The main advantage of an electrochemical method in contrast to membrane filtration and UV irradiation is the maintenance of disinfection residuals (depot effect) due to the generated oxidizing species, which facilitates the storage of reclaimed water. Further potential key benefits could be the high disinfection performance for a wide variety of micro-organisms [9,10], no necessity for storage of chemicals, on-site generation of electrochemical oxidants only if necessary, higher tolerance in terms of fluctuating water quality parameters and the fact that it is easy to perform by a simple, space-saving and low-maintenance integration in existing small sewage systems. Most of the published studies in the field of electrochemical disinfection have focused on drinking water treatment and were often performed with model solutions [11]. The electrodes applied therefore are mostly dimension-stable anodes (DSA) that are coated with mixed oxides (MOX) [12]. In model waters containing chloride, MOX electrodes demonstrate a high-production rate of the strong germicide “free chlorine”. Their application in real waters, however, is possible only in a limited scope, since deposits of calcium carbonate and magnesium hydroxide occur on the cathode as a consequence of local pH value increases. The easiest and the most efficient method to prevent this disturbing effect consists in polarity reversal. However, this polarity reversal drastically reduces the durability of the conventional DSA materials [13].

Novel boron-doped diamond electrodes (BDD electrodes) exhibit a high durability against periodic polarity reversals. Furthermore, such BDD electrodes possess an extraordinarily high electrochemical, mechanical and thermal stability [14,15]. Thus, short-lived germicides such as the free radicals $^\bullet OH$, $^\bullet O_2^-$ or $^\bullet OOH$ [16] and more stable germicides, e.g. Cl_2, ClO^-, HClO, O_3, H_2O_2, or $S_2O_8^{2-}$, can be produced electrochemically [17]. In chloride-containing waters, the formation mechanism of free chlorine at the BDD electrode is characterized by an indirect oxidation of the chloride ions [18]. Our previous studies have demonstrated that the implementation of disinfection with the BDD electrodes in biologically treated sewage is largely based on the dominant effect of electrochemically generated chlorine [19]. Moreover, the obtained results substantiate the fact that continuous bulk disinfection with subsequent after-reaction of the germicides with bacteria promises the highest degree of effectiveness.

Since it is known that free chlorine can react with organic material to form chlorinated organic compounds on the one hand and can be oxidized to chlorite, chlorate and perchlorate on the other, the formation of such unwanted disinfection by-products (DBPs) has to be investigated prior to each application of this technology [20,21]. The formation of adsorbable organically bound halogens (AOX) was proven in our previous studies [19].

The objective of the present study was to determine the influence of operating conditions such as current density, flow rate and parameters specific to WW like dissolved organic carbon (DOC), pH value and temperature on electrochemical disinfection of biologically treated sewage by using the technical set-up delineated. Furthermore, the formation of DBPs was examined.

2. Materials and methods

2.1. Reagents and chemical analyses

All chemicals used were of reagent grade and could be applied without further purification.

Photometric determination of free chlorine was carried out by means of the *N,N*-diethyl-*p*-phenylenediamine (DPD) method (EN ISO 7393-2) utilizing a UV/VIS Photometer (Unicam Co., England).

The DOC concentration was measured with the device TOC-5000 (Shimadzu, Japan). The determination of the sum parameter AOX was carried out using the device TOX-10Σ (Abimed, Germany). Anion concentrations were measured by an ion chromatograph DX 500 (DIONEX Co., USA) equipped with a conductivity detector and an IonPac AS 19 column ($2 \times 250\,mm$, eluent 20 mM KOH, flow rate $0.25\,mL\,min^{-1}$).

The trihalomethanes (THMs) were quantified by GC/MS (Thermo Scientific, USA).

The standard deviations of the analytical methods applied were found to be 4.5% for the DPD method (free chlorine), 5% for the determination of DOC, 10% for the anion analyses (e.g. chloride, etc.) by ion chromatography, 8% for the determination of THMs by GC/MS and 15% for the determination of AOX.

The temperature was measured with a digital thermometer GTH 175/Pt (Greisinger Co., Germany). The pH value was measured with the pH meter 761 Calimatic (Knick Co., Germany).

2.2. Preparation, assay and inactivation kinetics of coliforms (*Escherichia coli*)

In order to realize a stable initial concentration of the germs in each assay, it was essential to breed coliform germs from the sewage and wastewaters used in the experiments were spiked with them. The proportion of *E. coli* within the total of coliforms amounted to ca. 50%.

To this end, 0.1 mL of a fresh sewage sample (WW treatment plant, Dresden, Germany) was spread on selective agar for coliform germs (MacConkey Agar, Merck, Germany) and incubated for 20 h at 37°C. Some colonies were collected through an inoculating loop and inserted in a nutrient solution consisting of pancreatic peptone and meat (SIFIN, Germany). This solution was kept for 5 h in an incubator at 37°C. The test culture thus created was mixed with glycerin, filled in Greiner tubes and stored at −70°C. The working culture was cultivated by adding 1 mL of the test culture to 50 mL of the nutrient broth and incubating it for 3 h at 37°C. Thereafter, 0.1 mL of this solution was spread on an agar plate and grown to a bacterial layer at 36°C for 24 h (DEV nutrient agar). The grown layer was then washed with a 5 mL solution prepared with 8.5 g NaCl and 20 mL phosphate buffer (pH = 7.3). This final suspension had a durability of 7 days and contained from 1 to 10×10^9 CFU mL^{-1}. This bacteria concentrate was spiked to WW to get an initial concentration of approximately 10^5 *E. coli* 100 mL^{-1}.

The quantitative determination of *E. coli* was conducted by means of the Colilert-18/Quanti-Tray procedure (IDEXX Laboratories, Inc., USA). The level of inactivation was expressed as a log reduction of the ratio N/N_0, where N is the number of germs after disinfection and N_0 is the initial number of germs. Triplicate measurements of the disinfection experiments exhibited good reproducibility of the microbiological method within a 95% confidence interval.

2.3. Experimental procedures

All of the electrochemical experiments were performed under galvanostatic conditions using an undivided flow-through cell, into which four latticed BDD electrodes (BDD layer on niobium substrate, Condias GmbH, Germany) were integrated (Fig. 1). These electrodes were used as cathodes and anodes with an effective overall surface area ($A_{\text{Anode}} = A_{\text{cathode}}$) of 54 cm^2. The volume of the flow-through electrolysis cell (2) was 120 mL, whereas the volume of the reservoir (1) and the collection receptacle (5) was of 10 L. The WW was set to the desired temperature by means of a thermostat.

For disinfection experiments, the WW was taken from a municipal sewage treatment plant in Dresden. Selected chemical parameters of these WWs are summa-

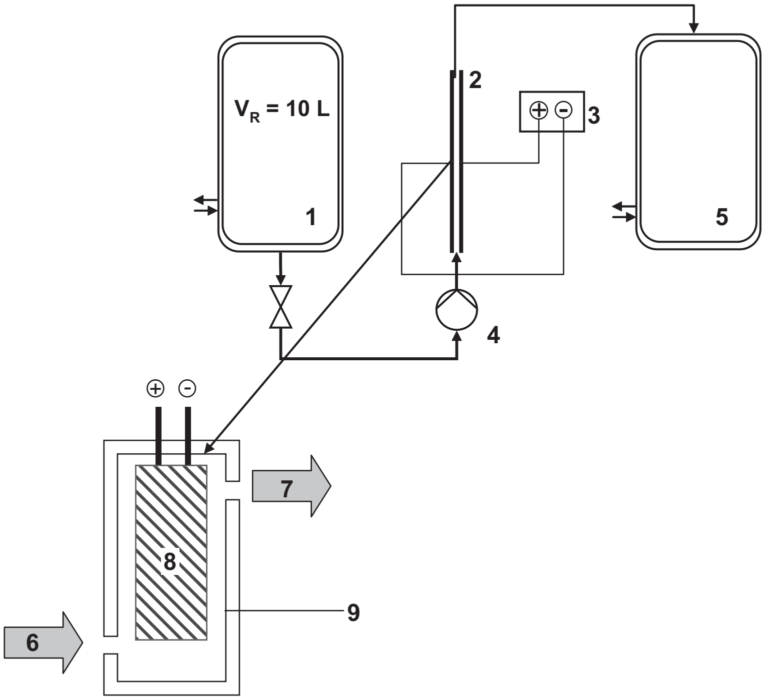

Fig. 1. Experimental set-up: 1, reservoir ($V_R = 10$ L); 2, flow-through electrolysis cell; 3, power supply; 4, pump; 5, collection receptacle; 6, inlet; 7, outlet; 8, BDD electrodes ($A_{\text{Anode}} = 54\ \text{cm}^2$); 9, volume of the electrolysis cell ($V_{\text{Cell}} = 0.12$ L).

Table 1
Chemical parameters of the applied secondary effluents

Chemical parameter	WW 1	WW 2	WW 3	WW 4
κ in $\mu S\,cm^{-1}$	1,293	1,151	964	916
pH	7.3	7.0	7.3	7.1
DOC in $mg\,L^{-1}$	8.3	13.5	21.8	9.2
β (Cl^-) in $mg\,L^{-1}$	173	173	132	129
β (Br^-) in $mg\,L^{-1}$	nd	nd	nd	nd
β (SO_4^{2-}) in $mg\,L^{-1}$	167	144	136	142
β (NO_2^-)in $mg\,L^{-1}$	nd	0.7	4.2	2.4
β (NO_3^-) in $mg\,L^{-1}$	42	29.5	13.9	38.1
β (PO_4^{3-}) in $mg\,L^{-1}$	nd	nd	nd	nd
β (free chlorine) in $mg\,L^{-1}$	nd	nd	nd	nd
β (ClO_2^-) in $mg\,L^{-1}$	nm	nm	nd	nd
β (ClO_3^-) in $mg\,L^{-1}$	nm	nm	nd	nd
β (BrO_3^-) in $mg\,L^{-1}$	nm	nm	nd	nd
β (ClO_4^-) in $mg\,L^{-1}$	nm	nm	nd	nd
β (BrO_4^-) in $mg\,L^{-1}$	nm	nm	nd	nd
β (NH_4^+) in $mg\,L^{-1}$	nd	nd	nd	nd
AOX in $\mu g\,L^{-1}$	22	27	20	30
β (TCM) in $\mu g\,L^{-1}$	nm	nm	0.1	0.1
β (BrDCM) in $\mu g\,L^{-1}$	nm	nm	nd	nd
β (DBrCM) in $\mu g\,L^{-1}$	nm	nm	nd	nd
β (TBrM) in $\mu g\,L^{-1}$	nm	nm	nd	nd
β_{total} (THMs) in $\mu g\,L^{-1}$	nm	nm	0.1	0.1

Note: nm, not measured; nd, not detectable; TCM, Trichloromethane; BrDCM, Bromodichloromethane; DBrCM, Dibromochloromethane; TBrM, Tribromomethane; THMs, Trihalomethanes.

rized in Table 1 that shows a typical composition of biologically treated WWs.

Within a series of experiments, the same charge was used for the respective inspection of a certain survey parameter.

The applied operation mode of the disinfection process combines the continuous addition of electrochemically generated disinfectants with subsequent after-reaction in batch mode (Fig. 1). Six litres of the WW was channelled via the flow-through electrolysis cell (2) into a collection receptacle (5). After 5 L had passed through the electrochemical cell, the sampling was directly conducted in the effluent of the electrolysis cell. Different residence times of the electrochemically created germicides of 0, 5, 10, 15 and 20 min were realized. These residence times were set in all experiments, except while investigating the influence of the pH value. With a view to studying the influence of pH on disinfection, residence times of 0, 4, 6 and 12 min were selected. The concentration of free chlorine was immediately determined at the given time point. A $Na_2S_2O_3$ solution ($1.5\,g\,L^{-1}$) was added to quench the oxidants in each microbiological subsample.

To determine the influence of current density and flow rate on the production rate of free chlorine, current densities (j) of 15, 30, 45, 60, 75, 90 and $105\,mA\,cm^{-2}$ and flow rates ($\dot{V}$) of 25, 50, 75, 100 and $125\,L\,h^{-1}$ were applied to WW 1.

The influence of sewage-specific parameters such as temperature, pH value and DOC on the disinfection capacity was studied according to the respective chloride concentrations of sewage at current densities of 83, 148 and $167\,mA\,cm^{-2}$ and at a flow rate of $60\,L\,h^{-1}$.

The influence of temperature on electrochemical disinfection efficiency was studied at 6, 20 and 30°C (WW 2).

The investigation of the pH dependence of the electrochemical disinfection was carried out at pH = 5.7, 7.6 and 8.5 (WW 2). These values were adjusted with sulphuric acid ($1\,mol\,L^{-1}$) or sodium hydroxide ($1\,mol\,L^{-1}$), respectively, and remained constant during electrolysis.

The influence of dissolved organic compounds of the WW on the disinfection efficiency was determined at DOC concentrations of 9 and $22\,mg\,L^{-1}$ (WW 3, WW 4).

Samples for the determination of the DBPs were taken after the electrochemical treatment of WW 3 and WW 4 at $j = 167\,\mathrm{mA\,cm^{-2}}$ and $\dot{V} = 60\,\mathrm{L\,h^{-1}}$.

3. Results and discussion

3.1. *Influence of operating conditions (current density and flow rate) on the production rate of free chlorine*

Due to the high concentration of chloride in WW 1–WW 4, free chlorine is the main oxidant/germicide (other secondary oxidants such as ozone and hydrogen peroxide could not be detected) [19]. Thus, the production rate of free chlorine under various operating conditions (current density and flow rate) was examined.

It became apparent that the production rate of free chlorine (concentration of free chlorine normalized to the electric charge input) is independent of the flow rate (25–125 $\mathrm{L\,h^{-1}}$) within the range of applied current densities (15–105 $\mathrm{mA\,cm^{-2}}$) (Fig. 2). Consequently, the influence of mass transport on the production rate of free chlorine is marginal.

3.2. *Influence of wastewater-specific parameters on the E. coli inactivation efficiency*

3.2.1. *Influence of temperature*

It could be observed that the disinfection time is considerably reduced as the temperature rises (Fig. 3).

At a temperature of 30°C, the limiting value of 100 faecal coliforms (mainly *E. coli*) per 100 mL sewage was already undercut after a residence time of < 5 min. At 6°C, this limiting value was not reached even after a 20-min residence time. Merely a reduction of *E. coli* one log level down was achieved.

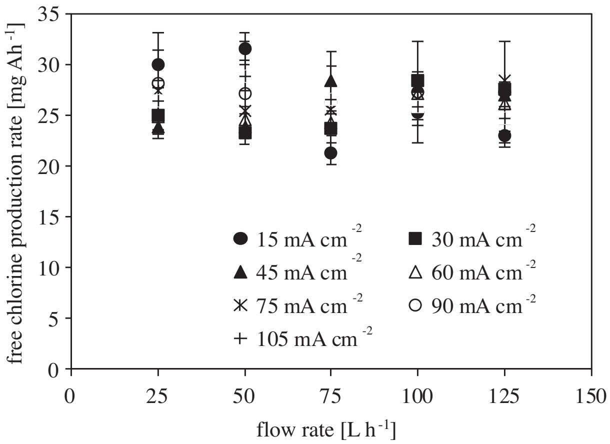

Fig. 2. Production rate of free chlorine in dependence on flow rate and current density (WW 1, $T = 20$°C).

The *E. coli* reduction depending on the temperature can moreover be characterized with the so-called CT value (concentration × residence time). It takes into account the germicide concentration (e.g. free chlorine) averaged over time as well as the effect of the disinfectant residence time on the germs. For this reason, the CT value is often applied to assess the effectiveness of certain disinfectants on different micro-organisms [22]. Furthermore, this parameter depends on several factors such as pH value, temperature and micro-organisms' species.

At an *E. coli* reduction of one log level, the average CT value at 20°C is ca. 3 $\mathrm{mg\,min\,L^{-1}}$, at 6°C, however, it is 7 $\mathrm{mg\,min\,L^{-1}}$. For a bacterial count reduction of five log levels, the average CT value at a temperature of 20°C with 6 $\mathrm{mg\,min\,L^{-1}}$ accounts for more than thrice the CT value at 30°C (2 $\mathrm{mg\,min\,L^{-1}}$). It becomes apparent that the CT value shrinks at rising temperature thus increasing the effectiveness of free chlorine and consequently augmenting the disinfection capacity.

To explain the strong temperature dependence of the electrochemical disinfection of sewage, chemical and biological aspects have to be considered. The fact that germs show a better metabolic activity at higher temperatures than at lower temperatures is well established. At low temperatures, the free chlorine can penetrate the bacteria only in a complicated fashion, or, to put it differently, it can only enfold its effect very restrictedly. Consequently, the disinfection time is considerably longer than at high temperatures.

Moreover, it was examined to what extent the fraction of the potent germicide HClO, as part of the free chlorine, changes at high and low temperatures. This fraction could furthermore represent a decisive indication of the temperature dependence of the disin-

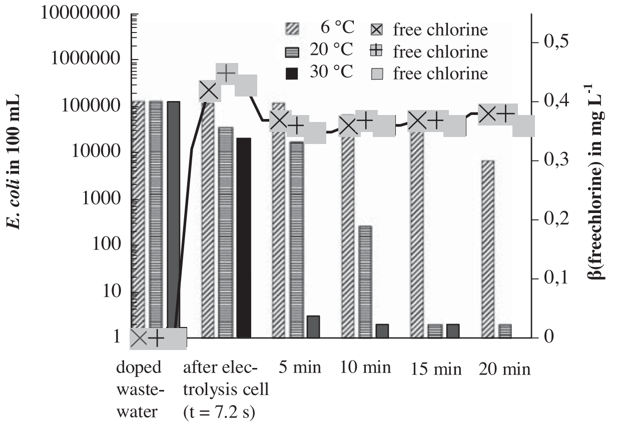

Fig. 3. *E. coli* inactivation and formation of free chlorine in dependence on temperature (WW 2, $\dot{V} = 60\,\mathrm{L\,h^{-1}}$, $j = 83\,\mathrm{mA\,cm^{-2}}$, $T = 6$, 20, 30°C, residence time = 5, 10, 15, 20 min).

fection. To verify this hypothesis, the pK_a values of HClO were compared for temperatures of 6, 20 and 30℃. A negligibly small alteration (pK_a(6℃) = 7.74, pK_a(20℃) = 7.58, pK_a(30℃) = 7.50) was discerned [23]. Consequently, the different disinfection periods cannot be explained by an altered composition of the free chlorine at varying temperatures.

3.2.2. *Influence of pH*

The pH were set to values that represent weakly acidic as well as weakly basic conditions (pH = 5.7, 7.6, 8.5). With an increasing pH value, the disinfection of WW is retarded (Fig. 4).

In an acidic medium, an *E. coli* reduction of four log levels is attained after a residence time of 4 min, whereas in a weakly basic environment (pH = 7.6) the same result is achieved only after 12 min. Thus, the residence time and the resulting CT value (7 mg min L^{-1}) are three times higher under basic than under acidic conditions (2.4 mg min L^{-1}). In another elevation of the pH value to 8.5, an *E. coli* reduction of solely 2.6 log levels is observed after 12 min. For all tested pH environments, the concentration of free chlorine was constant (0.6 mg L^{-1}). At a given total concentration of free chlorine, the ratio of HClO to ClO^- depends on the pH according to the acid/base equilibrium. It is well known that the germicidal effect of hypochlorous acid is 80 times greater than that of hypochlorite [24]. Therefore, the pH-dependent change in the free chlorine composition has to be considered in order to interpret the observed results. The pK_a value of the hypochlorous acid equals 7.5 ($T = 20^\circ$ C). Hence, the disinfection periods, and thus the CT values, are smaller in an acidic environment than in a basic environment.

3.2.3. *Influence of DOC*

The applied sewage contains dissolved organic compounds reacting with free chlorine. This fact becomes apparent in comparison of the production of free chlorine at varying DOC values (Fig. 5).

As a result of an increasing DOC level from 9 to 22 mg L^{-1}, the concentration of free chlorine decreases by 72%. The effectiveness of the electrochemical disinfection is thereby reduced. At a DOC concentration of 22 mg L^{-1}, only a 1.7 log reduction was observed after a residence time of 15 min. At a DOC concentration of 9 mg L^{-1}, however, a four log germ reduction was attained due to a higher concentration of free chlorine. Consequently, the DOC level constitutes a decisive influencing factor for the disinfection of sewage.

3.3. *By-product formation during the disinfection process*

Because of the demonstrated dominant role of chlorine species in the electrochemical WW disinfection process, the control of organic and inorganic by-product formation is of great concern.

After the electrochemical treatment (WW 3 and WW 4, $j = 167\,\mathrm{mA\,cm^{-2}}$, $\dot{V} = 60\,\mathrm{L\,h^{-1}}$, residence time = 20 min) chlorite was not detectable. It is a short-lived component that could be indirectly oxidized by, for example, hydroxyl radicals or directly oxidized at the anode via chlorate to perchlorate [20]. The concentration of chlorate was 1.3 mg L^{-1} whereas that of perchlorate reached 18 mg L^{-1}.

Currently, there are no regulated thresholds for chlorite, chlorate and perchlorate in reclaimed WW. However, the WHO [25] recommends guideline values of 0.7 mg L^{-1} for chlorite as well as for chlorate in drinking water. For perchlorate, the US-EPA specifies

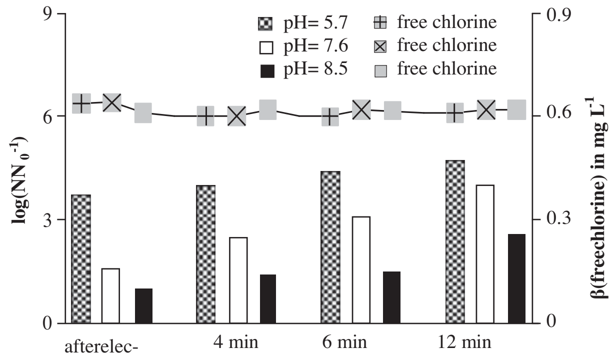

Fig. 4. Inactivation of *E. coli* and formation of free chlorine in dependence on pH (WW 2, $\dot{V}$=60 L h^{-1}, j = 148 mA cm^2, T = 20℃, residence time = 4, 6, 12 min).

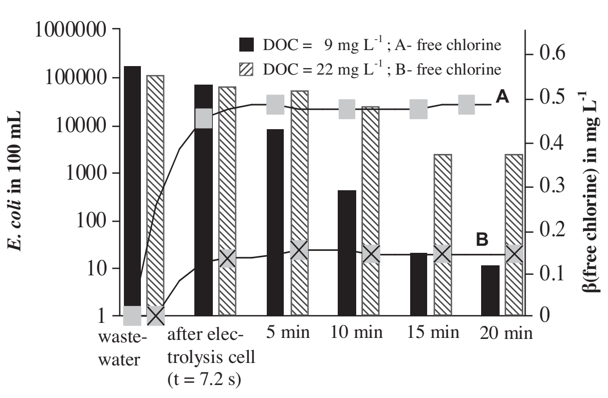

Fig. 5. Inactivation of *E. coli* and formation of free chlorine in dependence on DOC (WW 3, WW 4, $\dot{V}$=60 L h^{-1}, j = 167 mA cm^{-2}, T = 20℃, residence time = 5, 10, 15, 20 min).

a reference dose of 0.0007 mg kg^{-1} d^{-1}, which equates to a drinking water equivalent level of 24.5 μg L^{-1} [26]. The formation of chlorate and perchlorate is critical due to their toxic effects on human beings (haemolytic anaemia, thyroid dysfunction). Furthermore, bromate and perbromate could not be detected.

The total concentration of the THMs (1.2 μg L^{-1}) was negligible and even significantly lower than the threshold of 80 μg L^{-1} being defined in international drinking water regulations [27].

The AOX value of the biologically treated sewage without disinfection was 20–30 μg L^{-1}. The application of the electrochemical disinfection yields a quadruplication or quintuplication of the AOX concentration (100–127 μg L^{-1}), which originates predominantly from the chemical reactions of the electrochemically produced free chlorine with the organic compounds of the sewage.

4. Conclusions

The results of this study have shown that the efficiency of electrochemical disinfection with BDD electrodes is mainly influenced by the concentration of the formed free chlorine. The production rate of free chlorine at flow rates within the range of 25–125 L h^{-1} varies between *ca*. 24 and 30 mg $(Ah)^{-1}$. These results indicate a marginal influence of the mass transport on the production rate of free chlorine.

The disinfection capacity is substantially influenced by the WW-specific parameters such as temperature, pH and DOC. The disinfection effect of free chlorine improves considerably within the studied temperature range of 6–30 °C. For a germ count reduction by one log level, the average CT value, which characterizes the efficiency of germicides, is ca. 7 mg min L^{-1} at 6 °C. This value declines by ca. 50% (3 mg min L^{-1}) at a temperature increase to 20 °C, and by another 93% (0.2 mg min L^{-1}) at 30 °C.

Compared to sewage with a moderately acidic pH value of 5.7 (CT value of 2.4 mg min L^{-1}), the CT value (7 mg min L^{-1}) for a germ reduction by four log levels is elevated by a factor of 3 under weakly basic conditions (pH = 7.6). With the increase of DOC from 9 to 22 mg L^{-1}, the concentration of free chlorine drops by 72% due to reactions with the competing dissolved organics of the sewage, which in turn results in a diminished disinfection capacity. Chlorine-consuming processes contribute to a rise in the AOX value to a maximum of 127 μg L^{-1}. The total concentration of THMs (1.2 μg L^{-1}) was negligible. In contrast to this, the inorganic by-products, chlorate (1.3 mg L^{-1}) and perchlorate (18 mg L^{-1}), were formed in considerable concentrations.

Summarizing, the investigations have demonstrated that the electrochemical disinfection of *E. coli* in secondary effluents ($T > 6$ °C, $pH < 8.5$, $DOC < 22$ mg L^{-1}) proceeds effectively at an electric charge input of 0.1–0.15 Ah L^{-1} corresponding to an energy expenditure of 2.0–2.6 kWh m^{-3}.

Nevertheless, a careful approach to the use of BDD electrodes in electrochemical disinfection is recommended due to the formation of chlorate and perchlorate. It is difficult to control or reduce the formation of chlorate and perchlorate regardless of the cell design. The specific electrochemical reactions at BDD electrodes—mainly based on radical mechanisms—lead to these undesired by-products. Only a reduced electric charge input can diminish the formation of chlorate and perchlorate on the one hand, but lowers the disinfection efficiency drastically on the other. As a result of this, the after-reaction time has to be increased. Furthermore, the potential for the generation of chlorate and perchlorate depends on the electrode material.

In experiments with MOX electrodes carried out by the authors (data not shown), a reduced formation of chlorate and no perchlorate could be observed at concentrations of free chlorine ranging from 0.4 to 0.6 mg L^{-1}. This is due to a different electrochemical mechanism compared to BDD electrodes (without ROS). Since processes of advanced oxidation are considered to be promising for environmental protection, more care has to be taken for studies on the analysis of by-products (e.g. chlorate, perchlorate).

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