

Limits of UV disinfection: UV/electrolysis hybrid technology as a promising alternative for direct reuse of biologically treated wastewater

Daniela Haaken, Viktor Schmalz, Thomas Dittmar and Eckhard Worch

ABSTRACT

Although UV irradiation represents an energy efficient disinfection method, bacterial regrowth in UV irradiated secondary effluents is a serious problem for their direct reuse (e.g., for domestic or irrigation purposes). The decrease of the lethal UV fluence caused by coverings (scaling and biofouling) on quartz sleeves of UV lamps and/or fluctuating specific water parameters (suspended solids, transmittance or turbidity) results in a reversible inactivation of faecal coliforms (*Escherichia coli*). The reactivation of *E. coli* is increased with rising light intensity (≥ 470 Lux) and rising temperature (≥ 20 °C). The supplementation of UV disinfection with an electrolysis compartment ensures a reliable, sustained bacterial reduction and prevents reactivation of *E. coli* in UV irradiated ($H = 138\text{--}140 \text{ J m}^{-2}$) wastewater at a concentration of total oxidants of 0.5 mg L^{-1} . The electric charge input of 0.012 Ah L^{-1} was lowest on MOX (mixed oxide) electrodes compared to particle BDD (boron-doped diamond) and thin film BDD electrodes. The formation of organic by-products (adsorbable organically bound halogens, trihalomethanes) ranged from marginal to moderate. In contrast to BDD electrodes, no chlorite, chlorate and perchlorate were observed on MOX electrodes. The energy consumption of the UV/electrolysis hybrid reactor was 0.17 kWh m^{-3} .

Key words | bacterial regrowth, disinfection, disinfection by-products, UV/electrolysis hybrid technology, wastewater reuse

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INTRODUCTION

According to estimates of the United Nations Environment Programme (UNEP), in 2025 more than 1.8 billion people will be directly affected by the consequences of acute water shortage (water stress) (UNEP 2007).

Wastewater represents a valuable resource as regards its occurrence and composition. Thus, wastewater treatment and reuse are essential particularly in the newly industrializing and developing countries of the semiarid and arid climate zones. Over 90% of the annual water consumption is used for the irrigation of agricultural land to ensure the nutrition of the population (Cornel & Weber 2006).

Activities in the field of wastewater management are particularly beginning to focus on decentralized wastewater treatment. Innovative local wastewater management can be defined as the collection, treatment and direct reuse of water

from individual homes, clusters of homes or isolated communities and industries (Tchobanoglous & Angelakis 1996). Direct recycling provides the possibility to enhance the efficiency of water usage.

The direct usage of biologically treated wastewater is excluded due to the infectious risk caused by a multitude of pathogens (bacteria, viruses, worms, protozoa) (Popp 1998; Costán-Longares *et al.* 2008). A satisfactory reduction of pathogens can be attained by the application of specific disinfection methods.

Practical experience, partly with semi-industrial facilities, as well as economic and environmental reasons, lead to the conclusion that only a small number of conventional chemical disinfection methods applied in drinking water treatment are also suitable for advanced wastewater

treatment. In particular, the well-established disinfection procedures in central water treatment, such as chlorination and ozonation, suffer from decisive disadvantages, e.g., a necessity for the storage of toxic, polluting, partly explosive and oxidizing chemicals, the need of a substantial compliance of safety standards which requires complex control, measuring and monitoring equipment, as well as the formation of undesirable, partly carcinogenic disinfection by-products, e.g., trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chlorite, chlorate, etc., caused by chlorination processes (Koukouraki & Diamadopoulos 2002; Singer *et al.* 2002), and aldehydes, keto acids, hydroxy acids, esters, bromoorganics, bromate, etc., caused by ozonation processes (von Gunten 2003).

UV irradiation is an established and increasingly popular alternative to chemical disinfection of drinking water, domestic wastewater and industrial wastewater (Whitby *et al.* 1984; USEPA 1986, 1996, 1999; White *et al.* 1986; Kruithof *et al.* 1992; Hijnen *et al.* 2006; Antonelli *et al.* 2008).

However, unfavourable effects are the high potential for bacterial regrowth caused by the lack of a residual disinfectant as well as a diminished UV fluence. This diminished UV fluence results from, among other things, fluctuating specific water parameters, such as turbidity, total suspended solids (TSS), etc., and from coverings (biofouling, scaling) on the quartz sleeves of UV lamps which shorten the UV reactors' long-term operation significantly (Jesien 1998; Lin *et al.* 1999a, b; Sheriff & Gehr 2001). Furthermore, a reduced UV fluence leads to a reversible inactivation of faecal coliforms (*Escherichia coli*). They are reactivated by photo and dark repair mechanisms (Lindenauer & Darby 1994; Oguma *et al.* 2001; Zimmer & Slawson 2002; Queck & Hu 2008). As a result, this disinfection technology is of limited applicability for wastewater reclamation. However, UV irradiation represents a disinfection method that can be combined well with other disinfection procedures such as electrolysis. Bergmann *et al.* (2002) also proclaim this fact as promising and they motivate scientists for further specific research.

In the 1970s and 1980s, Reis and Kirmaier described technical applications of the electrochemical disinfection having, however, been shifted into the background due to lengthy problems with the electrodes' operability (Reis 1976; Reis & Henninger 1951; Kirmaier *et al.* 1984). Only in recent years have scientists succeeded in eliminating the technical

problems by conducting extensive development work on this method. Most of the published studies in the field of electrochemical disinfection have focused on drinking water treatment and were often done with model solutions (Martinez-Huitle & Brillas 2008). The electrodes applied therefore are mostly dimensionally stable anodes being coated with mixed oxides (MOX) (Kraft 1999; Kraft *et al.* 1999a, b, 2003; Kraft 2008) or boron doped diamond (BDD) electrodes (Kraft *et al.* 2000, 2003; Kraft 2008; Haenni *et al.* 2001; Furuta *et al.* 2004, 2005; Panizza & Cerisola 2005). Electrochemical disinfection is largely based on the dominant effect of electrochemically generated free chlorine (Schmalz *et al.* 2009). Continuous bulk disinfection with a subsequent reaction time of the germicides promises the highest degree of effectiveness (Haaken *et al.* 2012). However, current studies on electrochemical disinfection of biologically treated wastewater at BDD electrodes show that a number of disadvantages are inherent to this method. Thus, it was observed that temperature, pH value and dissolved organic carbon (DOC) concentration strongly affect the disinfection capacity. Low temperatures (6 °C), raised pH values (>8.5) and increased DOC concentrations (>22 mg L⁻¹) hamper the electrochemical disinfection and require higher concentrations of free chlorine or longer disinfection periods. However, this measure is limited by the formation of undesirable disinfection by-products, such as adsorbable organically bound halogens (AOX), chlorate and perchlorate (Haaken *et al.* 2012). Hence, the application of the electrochemical disinfection of biologically treated wastewater is possible only to a limited extent.

The UV/electrolysis hybrid technology as an innovative combined method might compensate the disadvantages of the single procedures due to the synergistic effect of UV irradiation and electrolysis.

Against this background, the potential eligibility of the UV/electrolysis hybrid technology for wastewater reclamation was investigated. The UV disinfection represents the primary disinfection method within the hybrid reactor. The additional electrochemical treatment of the UV irradiated wastewater should ensure a disinfection residual due to the formation of long-lived oxidizing germicides and thus suppress the reactivation mechanisms of faecal coliforms in reclaimed wastewater. Therefore, the extent of photo and dark repair of the indicator bacteria *E. coli* after UV irradiation under varying conditions (light intensity, pH,

temperature) and its prevention using UV/electrolysis hybrid technology were examined in the present study.

MATERIAL AND METHODS

Reagents and chemical analyses

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

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 × 250 mm, eluent 20 mM KOH, flow rate 0.25 mL min⁻¹). 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).

The photometric determination of free chlorine and total oxidants was carried out by means of *N,N*-diethyl-*p*-phenylene diamine (DPD) method (EN ISO 7393-2) utilizing a UV/VIS Photometer (Unicam Co., UK).

The trihalomethanes (THMs) were quantified by gas chromatography–mass spectrometry (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.

Preparation of the coliform (*E. coli*) stock suspension and spiking of biologically treated wastewater

In order to realize a stable initial bacterial concentration in each assay, it was essential to cultivate coliforms from the sewage and then spike the water with them. The proportion of *E. coli* within the total of coliforms amounted to around 50%. To this end, 0.1 mL of a fresh sewage sample (wastewater treatment plant, Dresden, Germany) was spread on selective agar for coliform germs (MacConkey Agar, Merck, Germany) and incubated for 20 hours 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 glycerine, filled in Greiner tubes and stored at –70 °C. The working culture was produced by adding 1 mL of the test culture to 50 mL of the nutrient broth and incubating it for 5 hours 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). This layer was 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 9 × 10⁹ CFU mL⁻¹. This bacteria concentrate was spiked to wastewater to get an initial concentration of approximately 1–3 × 10⁵ *E. coli* in 100 mL.

The quantitative determination of the *E. coli* was conducted by means of the Colilert-18/Quanti-Tray procedure (IDEXX, USA).

Triplicate measurements of the disinfection and reactivation experiments exhibited a good reproducibility of the microbiological method within a 95% confidence interval.

Experimental procedures

The UV/electrolysis hybrid module was equipped with a UV flow reactor (UMEX GmbH, Germany) as well as an electrolysis flow cell (galvanostatic conditions) having been operated in continuous mode (Figure 1). A 20 W low pressure mercury UV lamp with a UVC efficiency of 32.9% and a sensor for measuring the UV irradiance were integrated into the UV flow reactor (length = 36 cm, inner radius = 1.9 cm, $V_{\text{irradiated}} = 0.27$ L). The following electrode materials were components of the electrochemical disinfection unit:

- Thin film BDD on Nb substrate (Condias GmbH, Germany, $A_{\text{eff, anode}} = A_{\text{eff, cathode}} = 54$ cm²).
- Plastic based particle BDD (pro aqua Diamantelektroden Produktion GmbH, Germany, $A_{\text{eff, anode}} = A_{\text{eff, cathode}} = 100$ cm²).
- Ir/Ru mixed oxide on Ti substrate (De Nora GmbH, Germany, $A_{\text{eff, anode}} = A_{\text{eff, cathode}} = 301$ cm²).

Anode and cathode were made up of the same material. The reservoir and the collection receptacle had a volume of 10 L.

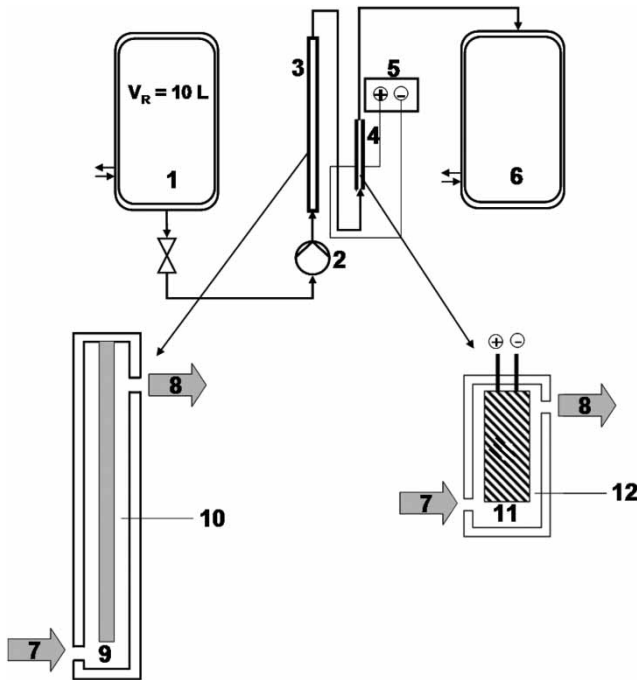


Figure 1 | Experimental set-up: 1 – reservoir ($V_R = 10$ L), 2 – pump, 3 – UV flow reactor, 4 – electrolysis flow cell, 5 – power supply, 6 – collection receptacle, 7 – inlet, 8 – outlet, 9 – low pressure mercury UV lamp (20 W), 10 – UV irradiated volume ($V = 0.27$ L), 11 – BDD or MOX electrodes ($A_{\text{eff, anode}} = A_{\text{eff, cathode}} = 54$ – 301 cm 2), 12 – volume of the electrolysis cell ($V_{\text{cell}} = 0.12$ – 0.35 L).

For the disinfection experiments, wastewater (WW) was taken from a municipal sewage treatment plant in Dresden. Selected chemical parameters of the wastewater and the model water used for the characterization of the electrodes are summarized in Table 1.

Experimental examinations involving photo and dark repair of *E. coli* in UV irradiated wastewater were conducted as follows.

The influence of lighting conditions on the repair of *E. coli* was examined by exposing the bacteria to a sublethal UV fluence of 150 J m^{-2} since, in practice, the reduction of the lethal UV fluence ($\geq 400 \text{ J m}^{-2}$) to a sublethal level is often a result of fluctuating, high TSS concentrations of the biologically treated wastewater. Afterwards, samples were stored for 1–48 hours at light intensities of 470 and 4,200 Lux (daylight fluorescent lamp: Philips TL-D90/965, 18 W) as well as under dark conditions at 20°C .

The influence of temperature between 10 and 30°C and the effect of pH between 5.7 and 8.1 on the reactivation of *E. coli* were examined by storing the UV-treated samples

Table 1 | Selected chemical parameters of the applied secondary effluents and of the model water

Chemical parameter	WW 1	WW 2	MW
κ in $\mu\text{S in cm}^{-1}$	1,212	1,411	1,482
$\text{SA}_{\text{C}_{254}}$ in m^{-1}	18.8	19.0	nm
$T_{254, \text{unfiltered}}$ in %	64	65	nm
TSS in mg L^{-1}	8.1	8.2	nm
pH	7.2	7.0	nm
DOC in mg L^{-1}	9.1	9.2	nm
β (Cl^-) in mg L^{-1}	140	130	150
β (SO_4^{2-}) in mg L^{-1}	147	170	480
β (NO_2^-) in mg L^{-1}	nd	nd	nd
β (NO_3^-) in mg L^{-1}	73	38	nd
β (PO_4^{3-}) in mg L^{-1}	10	1.5	nd
β (free chlorine) in mg L^{-1}	nd	nd	nd
β (ClO_2^-) in mg L^{-1}	nd	nd	nd
β (ClO_3^-) in mg L^{-1}	nd	nd	nd
β (ClO_4^-) in mg L^{-1}	nd	nd	nd
β (NH_4^+) in mg L^{-1}	nd	nd	nm
AOX in $\mu\text{g L}^{-1}$	22	27	nm
β (TCM) in $\mu\text{g L}^{-1}$	0.1	0.1	nm
β (BrDCM) in $\mu\text{g L}^{-1}$	nd	nd	nm
β (DBrCM) in $\mu\text{g L}^{-1}$	nd	nd	nm
β (TBrM) in $\mu\text{g L}^{-1}$	nd	nd	nm
β_{total} (THMs) in $\mu\text{g L}^{-1}$	0.1	0.1	nm

nm, not measured; nd, not detectable.

$\text{SA}_{\text{C}_{254}}$, spectral attenuation coefficient at 254 nm (unfiltered WW); $T_{254, \text{unfiltered}}$, transmittance at 254 nm (unfiltered WW); TSS, total suspended solids; AOX, adsorbable organically bound halogens; DOC, dissolved organic carbon.

THMs, trihalomethanes; TCM, trichloromethane; BrDCM, bromodichloromethane; DBrCM, dibromochloromethane; TBrM, tribromomethane.

(WW 1, WW 2, $H = 150 \text{ J m}^{-2}$) at a light intensity of 4,200 Lux and under dark conditions for 48 hours.

The characterization of the electrochemical unit was realized with model water (MW, Table 1).

The electrochemical production rate of free chlorine as well as of total oxidants at various electrode materials (thin film BDD, particle BDD and MOX electrodes (Ir/Ru/Ti)) was determined at a flow rate of 100 L h^{-1} and current densities of 50, 70 and 100 mA cm^{-2} . In the process, the particle BDD electrodes were supplied indirectly with direct current compared to thin film BDD and MOX electrodes (Ir/Ru/Ti). BDD particles of the particle electrode were embedded in a nonconductive plastic matrix. Therefore, the electrolysis cell

was operated in a bipolar set-up via MOX electrodes (Ir-Ru/Ti) which acted as contact electrodes.

To examine the prevention of bacterial regrowth, the UV irradiated wastewater (WW 1, $H = 150 \text{ J m}^{-2}$) was treated electrochemically and the minimum concentration of total oxidants suppressing the reactivation of coliforms was determined. The examinations were conducted at temperatures between 10 and 30 °C and at pH values ranging from 5.7 to 8.1. Furthermore, the expenditure of energy and the formation of unwanted organic (AOX, THMs) and inorganic (chlorite, chlorate and perchlorate) by-products were investigated.

RESULTS AND DISCUSSION

Limits of UV disinfection of biologically treated wastewater – reactivation of *E. coli* after UV irradiation

Influence of light intensity

Since *E. coli* in controls, present in the same concentration as undamaged *E. coli* bacteria in UV disinfected samples (400–600 *E. coli* in 100 mL, $H = 150 \text{ J m}^{-2}$), did not show any reproduction within 1–48 h (data not shown), the reactivation, as illustrated in Figure 2, is, first and foremost, due to DNA repair of reversibly damaged *E. coli*. It becomes apparent that the reactivation significantly depends on the given lighting conditions. The lower the light intensity, the

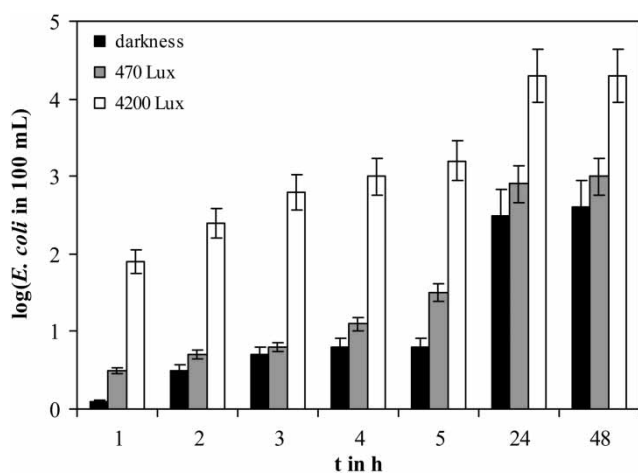


Figure 2 | Time course of *E. coli* reactivation after UV irradiation (WW 1, $H = 150 \text{ J m}^{-2}$, $T_{254} = 64\%$) at various light intensities ($E = 0, 470$ and $4,200 \text{ Lux}$, $\vartheta = 20 \text{ }^\circ\text{C}$).

less regrowth of bacteria was observed. According to that, the extent of photo repair at 470 Lux is reduced by a factor of 1.5–3.5 compared to 4,200 Lux. The degree of reactivation is lowest in darkness. Under these conditions, bacteria are reactivated by 2.7 log levels. However, at a light intensity of 4,200 Lux, the degree of reactivation amounts to 4.3 log levels within 24 h. A further increase of storage time leads to a marginal enhancement of regrowth so that a maximum value results within 24–48 h. Both photo and dark repair are enzymatic processes. A large number of various enzymes are involved in dark repair. The photoreactivation is primarily catalysed by the photolyase enzyme (Lindenauer & Darby 1994).

The higher the light intensity, the more energy per time unit is available for the photolyase enzyme to monomerize the pyrimidine and thymine dimers of the bacterial DNA generated during UV irradiation. Thus, the extent of reactivated bacteria increases according to rising light intensity.

Influence of temperature

Due to seasonal fluctuations of temperature, its influence on photo and dark repair has been investigated within a range between 10 and 30 °C. It could be observed that the degree of reactivation increases with rising temperature (Figure 3).

At 10 °C, the extent of *E. coli* reactivation is lowest both under light and dark conditions. At light it is 1.3 log levels and in darkness 1.6 log levels lower than at 30 °C. At

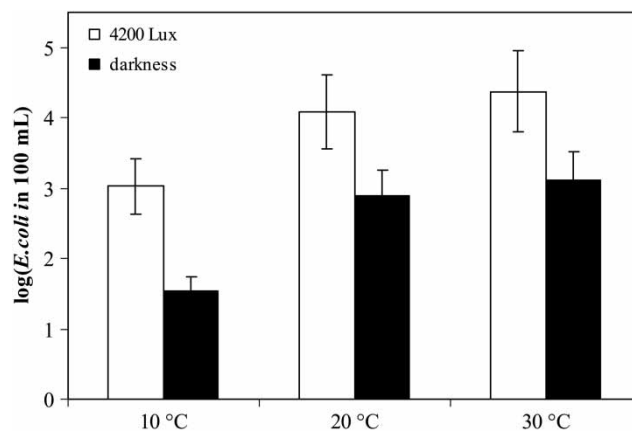


Figure 3 | Photo ($E = 4,200 \text{ Lux}$) and dark repair of *E. coli* after UV irradiation (WW 1, $H = 150 \text{ J m}^{-2}$, $T_{254} = 64\%$) and 48 hour storage in dependence on temperature.

20 °C and 30 °C, bacterial regrowth shows a comparable extent. In general, the extent of *E. coli* reactivation is reduced by a factor of 1.2–1.5 in darkness compared to light conditions.

The increase of bacterial regrowth at rising temperature is the result of rising reaction rates of enzymatic processes with increasing temperature on the one hand. On the other, the formation of enzyme dimer complexes, being a precondition for DNA repair, depends on temperature (Lindenauer & Darby 1994). The higher the temperature, the more preferentially and faster the dimer complexes are formed.

Influence of pH

The determination of the pH effect on photo and dark repair was realized at pH values within a range between 5.7 and 8.1 (typical pH range for biologically treated wastewater).

It follows from Figure 4 that the extent of photo and dark repair is largely independent of the pH value. The degree of photoreactivated *E. coli* amounts to 4.0–4.2 log levels. The reactivation under dark conditions reaches 3.0–3.3 log levels.

The comparable bacterial regrowth at the given pH range can be explained by the unchanging activity of the enzymes required for the repair processes. Thus, a significant binding of the photolyase enzyme to pyrimidine dimers of the UV damaged DNA is possible within a broad pH range between 5.5 and 8.5 (Sancar *et al.* 1985).

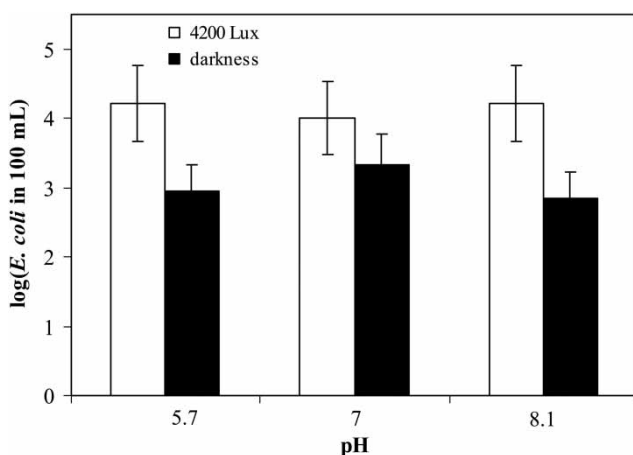


Figure 4 | Photo ($E = 4200$ Lux) and dark repair of *E. coli* after UV irradiation (WW 2, $H = 150$ J m⁻², $T_{254} = 65\%$) and 48 hour storage ($\vartheta = 20$ °C) in dependence on pH value.

Prevention of bacterial regrowth by UV/electrolysis hybrid technology

Screening of electrodes

The dominating role of electrochemically generated free chlorine in the disinfection process of biologically treated wastewater could be verified by Schmalz *et al.* (2009). Bound chlorine (e.g., chloramines) as well as further oxidants produced by anodic oxidation, such as chlorine dioxide, peroxydisulfate, etc., could act as disinfectants in addition to free chlorine. These further oxidants exhibit a cross-sensitivity to the photometric determination of total chlorine (Bergmann 2006; Schmalz *et al.* 2009). Therefore, the production rate of total oxidants ($C_{\text{total oxidants}}/Q_v$) was investigated in addition to the production rate of free chlorine ($C_{\text{free chlorine}}/Q_v$). It becomes apparent from Figure 5 that the production rate of free chlorine and total oxidants is highest at particle BDD electrodes (BDD/par) with 80–92 mg (Ah)⁻¹. The formation of free chlorine and total oxidants per Ah at particle BDD electrodes (BDD/Nb) is 7–8 times higher than at thin film BDD electrodes. In general, the production rate of free chlorine and total oxidants is largely unaffected by the current density in a range between 50 and 70 mA cm⁻².

Electric charge input and expenditure of energy

Examinations involving the electrolysis of the UV irradiated, biologically treated wastewater ($H = 150$ J m⁻², $T_{254} = 58\%$) at an electric charge input within a range of 0.0033 and 0.012 Ah L⁻¹ showed that the reactivation of the *E. coli* (4,200 Lux) is reduced when the electric charge input is increased (Figure 6).

The photoreactivation of the *E. coli* after 72 h ($\vartheta = 20$ °C, pH = 7.2) amounts to 4 log levels at the lowest electric charge input of 0.0033 Ah L⁻¹ that is comparable with the extent of photoreactivation after UV irradiation. Increasing the charge input by the factor 2.5 results in a reduction of bacterial regrowth by 0.5 log levels. In contrast, a charge input of 0.012 Ah L⁻¹ prevents the photoreactivation of *E. coli*. The same findings were observed for dark repair (data not shown). The prevention of photo and dark repair results from the irreversible damage of the bacterial DNA

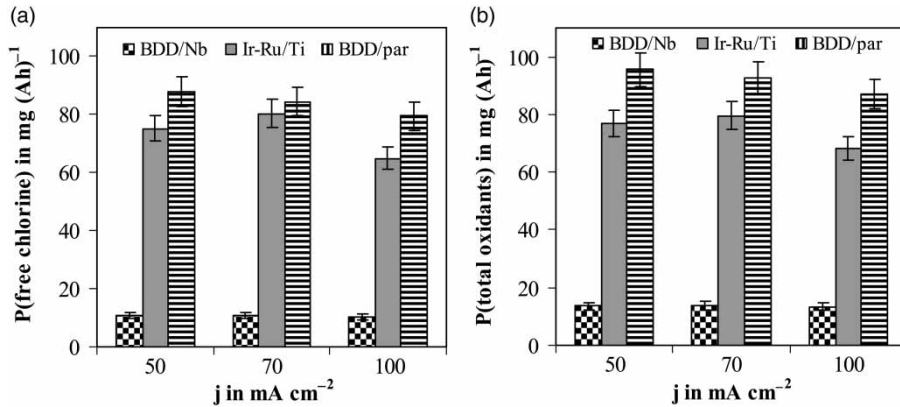


Figure 5 | Production rate of free chlorine (a) and total oxidants (b) on various electrode materials in dependence on current density (MW, $\beta(\text{Cl}^-) = 150 \text{ mg L}^{-1}$, $\beta(\text{SO}_4^{2-}) = 480 \text{ mg L}^{-1}$, $V = 100 \text{ L h}^{-1}$).

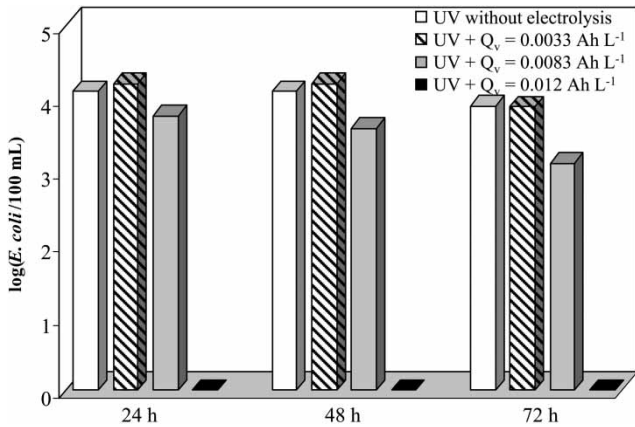


Figure 6 | Photoreactivation ($E = 4,200 \text{ Lux}$) of *E. coli* after UV/electrolysis (WW 1, $H = 150 \text{ J m}^{-2}$, $T_{254} = 64\%$, $Q_v = 0.0033\text{--}0.012 \text{ Ah L}^{-1}$, $j = 0.7\text{--}2.3 \text{ mA cm}^{-2}$, MOX-electrodes) and 24–72 hour storage ($\vartheta = 20^\circ \text{C}$).

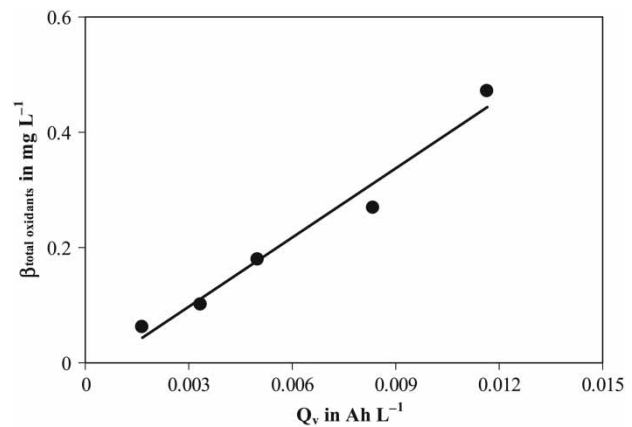


Figure 7 | Concentration of electrochemically generated total oxidants in dependence on the electric charge input (WW 1, $T_{254} = 64\%$, $c_{\text{Chlorid}} = 140 \text{ mg L}^{-1}$, $\text{DOC} = 9.0 \text{ mg L}^{-1}$, $\vartheta = 20^\circ \text{C}$, MOX-electrodes).

caused by the electrochemically generated total oxidants. Free chlorine was observed in marginal concentrations ($\leq 0.1 \text{ mg L}^{-1}$) directly after the electrolysis cell. This germicide would have to interact with the bacteria for 60 min to cause an irreversible *E. coli* reduction of 5 log levels (Haaken et al. 2012). Since free chlorine was already not observed after a few minutes, the prevention of bacterial regrowth is the result of the germicidal effect of bound chlorine (e.g., chloramines) as well as of other electrochemically generated oxidants (e.g., hydrogen peroxide, chlorine dioxide).

Furthermore, a linear enhancement of the concentration of total oxidants with increasing charge inputs has been observed (Figure 7). Thus, a concentration of total oxidants of 0.1 mg L^{-1} was determined at an electric charge input of

0.0033 Ah L^{-1} , whereas an electric charge input of 0.012 Ah L^{-1} results in a concentration of 0.5 mg L^{-1} .

As a further result of this examination, photo and dark repair of *E. coli* (24–72 hours) are prevented at pH levels of 5.7–8.1 and temperatures ranging from 10 to 30°C at a minimum concentration of total oxidants of 0.5 mg L^{-1} . Germicide concentrations lower than 0.5 mg L^{-1} caused no irreversible damage of coliforms within 72 hours (bacteria can be protected by microbial aggregation or particles).

Since the production rate of total oxidants is affected by the electrode material, the electric charge input and expenditure of energy needed for a germicide concentration of 0.5 mg L^{-1} varies. The detailed data are summarized in Table 2.

Table 2 | Electric charge input and expenditure of energy of the UV/electrolysis hybrid reactor for the prevention of *E. coli* reactivation (20 W low pressure mercury lamp, $\beta_{\text{total oxidants}} = 0.5 \text{ mg L}^{-1}$, $\vartheta = 10\text{--}30 \text{ }^\circ\text{C}$, $\text{pH} = 5.7\text{--}8.1$)

	Thin film BDD electrode	Particle BDD electrode	MOX electrode
I in A	5	5	5
U in V	19.5	31	10
Q_v in Ah L ⁻¹	0.075	0.025	0.012
$E_{\text{UV+electrolysis}}$ in kWh m ⁻³	1.76	0.88	0.17

It follows from Table 2 that the UV/electrolysis hybrid reactor operating with MOX electrodes requires a 2–6 times lower electric charge input and shows a 5–10 times lower energy consumption compared to BDD electrodes.

This result demonstrates that the electrode material is a decisive criterion for a moderate energy consumption of the hybrid reactor. However, further long-term studies are necessary.

By-product formation

The formation of selected inorganic and organic by-products at BDD and MOX electrodes is summarized in Table 3.

The inorganic by-products chlorite and chlorate could neither be detected at MOX electrodes nor at particle BDD electrodes within the applied experimental conditions. Using thin film BDD electrodes, chlorate was measured in a concentration of 0.4 mg L^{-1} and perchlorate was found in a

Table 3 | Formation of selected inorganic and organic by-products (20 W low-pressure mercury lamp, $\beta_{\text{total oxidants}} = 0.5 \text{ mg L}^{-1}$)

	Thin film BDD electrode	Particle BDD electrode	MOX electrode
β (ClO ₂ ⁻) in mg L ⁻¹	nd	nd	nd
β (ClO ₃ ⁻) in mg L ⁻¹	0.4	nd	nd
β (ClO ₄ ⁻) in mg L ⁻¹	4.2	0.5	nd
AOX _{directly after UV/electrolysis} in $\mu\text{g L}^{-1}$	56.9	75.3	50.1
AOX _{24 h} in $\mu\text{g L}^{-1}$	135	115	124
β_{total} (THMs) in $\mu\text{g L}^{-1}$	nd	nd	nd

nd, not detectable.

THMs, trihalomethanes (trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane).

AOX, adsorbable organically bound halogens.

concentration of 4.2 mg L^{-1} . At particle BDD electrodes, a perchlorate concentration of 0.5 mg L^{-1} could be determined. On the contrary, perchlorate could not be observed at MOX electrodes.

Chlorite is a short-lived intermediate. Thus, it was not observed at MOX and BDD electrodes. In contrast to MOX electrodes, BDD electrodes work with a wide potential window (up to 2.8 V for oxygen generation and about -1.3 V for hydrogen generation) so that electrochemically produced reactive oxygen species (e.g., hydroxyl radicals) can indirectly oxidize chlorite via chlorate to perchlorate (Tröster *et al.* 2004; Bergmann & Rollin 2007). Moreover, thin film BDD electrodes need the highest electric charge input to produce the required minimum total oxidants concentration of 0.5 mg L^{-1} . This further contributes to a higher perchlorate concentration compared with particle BDD electrodes.

The AOX production directly after the electrolysis cells amounts to $50\text{--}75 \mu\text{g L}^{-1}$. An increase of the AOX concentration up to $115\text{--}135 \mu\text{g L}^{-1}$ was observed after 24 hours. However, no THMs could be observed.

CONCLUSIONS

The synergistic utilization of the combination of UV irradiation using a 20 W low pressure mercury lamp and electrochemical treatment using MOX electrodes represents an energy-efficient technology for decentralized wastewater reclamation. The supplementation of UV disinfection with an electrolysis unit ensures a reliable, sustained bacterial reduction being precondition for a sufficient storability and secure utilization of reclaimed wastewater as process and irrigation water. The unwanted reactivation of reversibly UV damaged faecal coliforms (*E. coli*), whose extent is considerably increased with rising light intensity and rising temperature, is completely prevented at a concentration of total oxidants of 0.5 mg L^{-1} ($T = 10\text{--}30 \text{ }^\circ\text{C}$, $\text{pH} = 5.7\text{--}8.1$). For this, an expenditure of energy of 0.17 kWh m^{-3} is needed.

The formation of inorganic and organic by-products using MOX electrodes is marginal to moderate. Nevertheless, a careful approach to the use of MOX electrodes in

the disinfection by UV/electrolysis is recommended due to the formation of AOX.

In the UV/electrolysis hybrid module, the UV unit can be located upstream or downstream of the electrolysis cell. Downstream positioning of the UV lamp could contribute to reduce the coverings on the quartz sleeves of the UV lamps due to the continuous wetting with a solution of total oxidants. As a result, this includes the possibility of increasing the cleaning intervals contributing to a low-maintenance long-term operation of the UV/electrolysis hybrid reactor. Studies on this subject and on possible limits of the UV/electrolysis hybrid technology (e.g., the influence of total suspended solids) are currently being conducted.

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