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New UV irradiation and direct electrolysis—promising methods for water disinfection

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Abstract

UV irradiation as a method of disinfecting drinking, waste and feed waters is becoming more and more widespread. Besides the normally used low and medium pressure lamps, a new type has been recently developed, the microwave stimulated electrodeless lamp. This paper presents first results on drinking water disinfection using this new type of lamp. Its suitability for application could be shown in experiments with microorganisms of risk group one. Additionally, research results on the direct electrolysis of water for disinfection purposes are given. The combination of the two methods provides a promising approach to disinfection treatment of drinking water.

Keywords: Disinfection; UV irradiation; Electrolysis; Water treatment

1. Introduction

The disinfection of water is of vital importance for man's existence. At present, in many countries of the world, the need for disinfected drinking water already constitutes a huge problem. In the industrialised nations this problem has been solved in principle, although even here deviations from the norm occur from time-to-time.

Different methods of drinking water disinfection compete with one another. Besides the widely used chlorination or treatment by chlorine components, disinfection is carried out by ozonation or UV irradiation. Of these, UV irradiation is more frequently applied in Europe than in the United States [1]. In order to rule out, the regrowth of microorganisms, this water disinfection process requires a final chlorination step.

An evaluation of recent developments shows that the trend is to use less chlorine, the reasons being problems caused by overchlorination, odour, by-product formation, transport and storage risks. Alternative methods are the use of UV irradiation techniques and, to a certain extent, the application of stand-by electrolysers for the required amount of chlorine production. The direct disinfection of water by electrolysis has been discussed since the fifties [2], but has not yet found application in the drinking water treatment industry. New studies have been reported [3] and some authors consider diamond electrodes to be a promising alternative to traditional electrode materials, such as activated titanium [4].

UV reactors usually work with low pressure mercury lamps with a main spectral line of 254 nm. This is in good agreement with the absorption maximum of aminic acids [5]. The large number of publications in the literature demonstrate the relevance of this research topic. The following aspects have been treated: study of wavelength influence on microorganisms [5,6], the combination of UV irradiation with ultrasound [7], hydrogen peroxide [8] or micro-filters [9]. Further topics of interest are the behaviour of *Salmonellae* under special conditions [10], the use of pulsing radiation [11], design and modelling aspects [12] and the formation of by-products [13]. Besides the treatment of drinking water, many studies deal with the application of UV irradiation for the disinfection of feed water, municipal or industrial waste water, air systems and solid surfaces.

In contrast to normal lamps fired by electrodes, the new lamps can work without contacted electrodes [14]. Fig. 1 shows the working principle schematically. UV radiation is stimulated by microwaves. The spectrum of the resulting UV waves can be influenced by varying the content of the special filling (mercury and additives). Stimulation with a high frequency field is also possible. Fig. 2 shows the scheme of a working unit used for experiments with treated water

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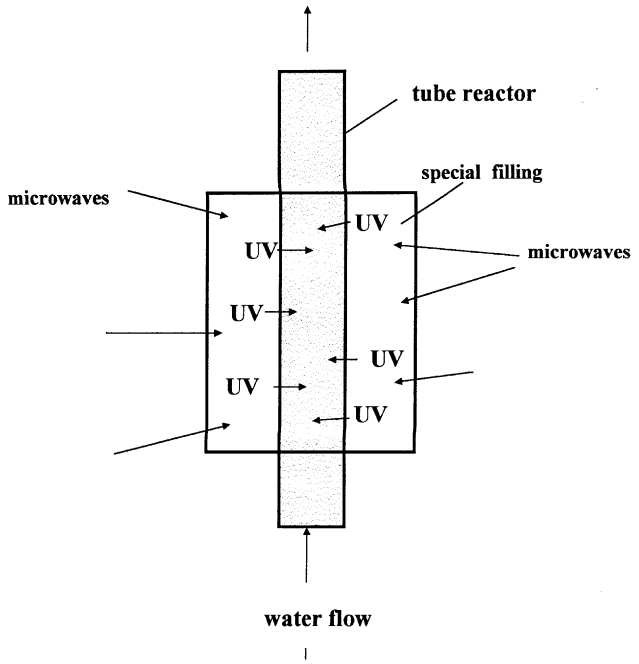

Fig. 1. Schematic sketch of electrodeless UV lamp.

recirculation. The advantages of the new lamps are longer lifetime, less inner deposits and good radiation energy dispersion as a result of their 'positive irradiation geometry' [14]. The disadvantages are higher energy consumption and problems connected with scale-up.

The combination of the conventional or new UV irradiation technique and direct disinfection electrolysis could be a promising innovation for drinking water disinfection. The aim of this paper is to document some of its fundamental aspects.

2. Experimental details

2.1. Experiments with microwave stimulated UV lamps in batch mode

Two glass reactors in the shape of a double wall container with an inner volume of 11 cm^3 (radius 12.7 mm) by UMEX GmbH were used in this study. The first reactor emitted the UV light of 254 nm wavelength, the second of 220 nm. The reactor was placed inside a microwave oven with an electric power input of 750 W. Prepared microorganism suspension of 10 cm^3 were transferred to the inner reaction compartment and the microwave was switched on. A reaction time of 1 s was used. In selected experiments, the suspension was stepwise irradiated in both reactors giving different main wavelengths. The irradiation time was set at 1 s for each reactor. The delay between the individual irradiations was reduced to the duration of the sample transfer between the reactors.

2.2. Experiments with microwave-stimulated UV lamps in a flow-through mode

The reactor used in this series of experiments was basically identical to that used during previous series of experiments. The main difference consisted in its construction as a flow-through channel (Fig. 2) with an inner diameter of 75 mm and a flow length of 195 mm. In this case, the electric input power of the microwave oven was 800 W. The reactor type emitting 254 nm irradiation was used. Prior to each experiment the apparatus was disinfected with 0.1% peracetic acid. The volume of the solution treated was 10 dm^3. Tap water was used as the solvent. The water temperature was kept constant at 25 °C by means of a Lauda RM6 cryostat. In order to provide sufficient homogenisation of the solution, the experiments were started after a 3 min pre-mixing period. Samples were taken at 1, 3, 5, 10 and 30 min after the start of the experiment and were analysed with respect to the remaining microorganisms.

2.3. Water disinfection by direct electrolysis

An activated titanium anode (ATA) with an active layer based on mixed iridium oxides was compared to boron-doped diamond and Pt anodes relative to the amount of chlorine and hydrogen peroxide generated. The ATA was shaped like a rotating disk electrode and was used at 300 rotations per minute (rpm). The counter-electrode consisted of the same material. The electrolyte volume was 0.4 dm^3.

Platinum electrodes in the shape of two smooth foils 2 cm × 2 cm were both the anode and the cathode. The electrolyte volume was again 0.4 dm^3. Its motion was provided by a magnetic stirrer (500 rpm).

In the case of the boron-doped diamond electrode, the experimental arrangement was identical to that for Pt electrodes. The diamond electrode consisted of an extended mesh (0.2 cm × 2.5 cm × 4.8 cm). Activated titanium was used as the counter-electrode.

After 5 min of electrolysis, a sample was taken and immediately analysed with respect to its chlorine and hydrogen peroxide content.

The undivided flow-through electrochemical cell consisted of a glass cylinder (diameter 47 mm, length 250 mm). The electrode stack was located in the centre of the cylinder parallel to the electrolyte flow direction. The distance between individual electrodes was set at 3 mm. Iridium based mixed oxide activated titanium electrodes were used as both anodes and cathodes. Their dimensions were 1 mm × 30 mm × 100 mm. The temperature was kept constant at 25 °C by means of a Hake S/F3 thermostat. Statron 3231 was used as a stabilised power source.

2.4. Microorganisms studied

The viability of the following cell types was studied during the UV irradiation experiments in a batch mode

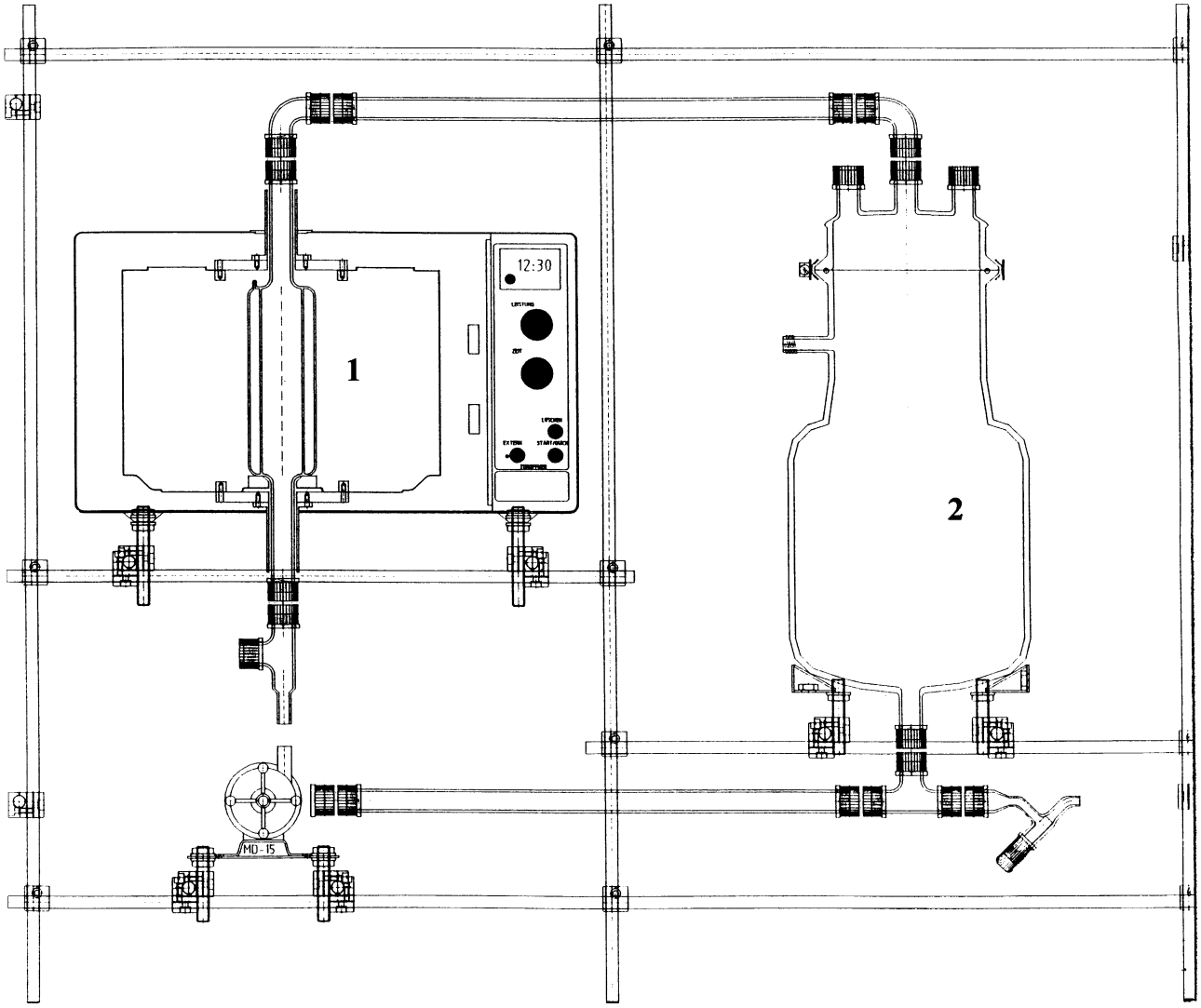

Fig. 2. Microwave stimulated flow-through UV reactor in the stand with solution recirculation: (1) UV reactor, (2) water reservoir.

arrangement: *Escherichia coli* DSM 498, *Bacillus subtilis* DSM 347, *Saccharomyces cerevisiae* Kolin and *Saccharomyces cerevisiae cyc*^{R}R103.

During the experiments in the flow-through reactor the following microorganisms were studied: *E. coli* DSM 498, *B. subtilis* DSM 2277, *Saccharomyces cerevisiae* Kolin and spores of *B. subtilis* DSM 2277.

Escherichia coli DSM 498 cells were used in the electrolysis experiments.

2.5. Microorganism cultivation and analytical methods

The organisms were pre-cultivated for 24 h in a special medium (SIFIN nutrient broth and wort broth for yeast cells) at 30 °C, grown at the same temperature for 20 h and twice washed and centrifuged. The effect of the disinfection methods used on the microorganisms both from the logarithmic and the stationary growth periods was tested.

After the experiments, samples were diluted, plated on wort and nutrient agar medium and incubated for 48 h at 30 °C (*E. coli* cells at 37 °C). Afterwards the colonies were counted.

An analysis of the samples of water treated by direct electrolysis with respect to the free chlorine and hydrogen peroxide content was carried out photometrically by special chemical sets from Macherey & Nagel.

3. Results and discussion

Table 1 summarises the concentration of the individual microorganisms in an original suspension and after treatment at different individual wavelengths in a batch irradiation reactor. The concentrations after treatment with two different wavelengths combined are given for comparison.

Table 1
Results of irradiation in the batch type UV reactor

Wavelength (nm)	*Bacillus subtilis*	*Bacillus subtilis*	*Saccharomyces cerevisiae* Kolin	*Saccharomyces cerevisiae* cyc^RR103	Growth phase
Before irradiation (col./ml)					
	4×10^7	5×10^7	5×10^5	3×10^5	
After irradiation (col./ml)					
254	2×10^4	6×10^3	3×10^3	1×10^3	Logarithmic
220	1×10^5	4×10^7	5×10^5	2×10^5	Logarithmic
254/220	4×10^4	2×10^4	2×10^5	1×10^3	Logarithmic
220/254	4×10^3	2×10^2	2×10^2	6×10^2	Logarithmic
Before irradiation (col./ml)					
	1×10^6	3×10^7	2×10^5	7×10^3	
After irradiation (col./ml)					
254	7×10^3	1×10^3	4×10^2	0	Stationary
220	1×10^6	2×10^7	2×10^5	2×10^3	Stationary
254/220	1×10^2	8×10^3	7×10^2	10	Stationary
220/254	0	4×10^2	10	0	Stationary

As expected, the disinfection at 254 nm is much more efficient than at 220 nm. It is interesting to note that, only in the cases of 254 nm wavelength and the combination variants with 254 nm irradiation in the second step, were the microorganisms completely removed; the exception was *E. coli* bacteria from the log phase. The combination 220 nm/254 nm, as compared with the 254 nm/220 nm variant, generally proved to be more effective by 2–3 decadic degrees (maximum of 1 for the yeast). This can be explained by the repairing mechanisms of formed DNS dimeres to monomeres at wavelengths differing from the adsorption maximum [15].

The main disadvantage of the batch experimental arrangement is the limitation of the reaction time because of the rapid overheating of the treated water and the disaggregation of the microorganism suspension. This is one of the reasons for initiating the thermostated experiments in an irradiation flow-through reactor with liquid recirculation (Fig. 2).

A flow-through arrangement is generally more suitable for practical application. Using this arrangement a concentration of *B. subtilis* and *E. coli* cells was reduced reproducibly even over seven orders of magnitude (Fig. 3). Only the spores did not reach the disinfection criterion of four orders of magnitude. This result was expected because most of the spores exist in a stable encapsulated form, which makes them relatively resistant to UV irradiation. Nevertheless, they are used for testing and calibrating purposes [16].

The efficiency of electrochemical water disinfection can be enhanced by using a divided electrolytic cell. This is because separator avoids reduction of the oxidising species ($OH^{\bullet}$, Cl_2) on the cathode. It seems more practical, however, to use an undivided electrolyser. The results presented relate to the latter case.

The experimental results of direct electrolysis indicate that disinfection does not occur by way of direct electron transfer between the electrode and the microorganisms adsorbed on its surface. Microorganism destruction is caused by electrochemically generated oxidising species, such as radicals, hydrogen peroxide, ozone and chlorine-containing products.

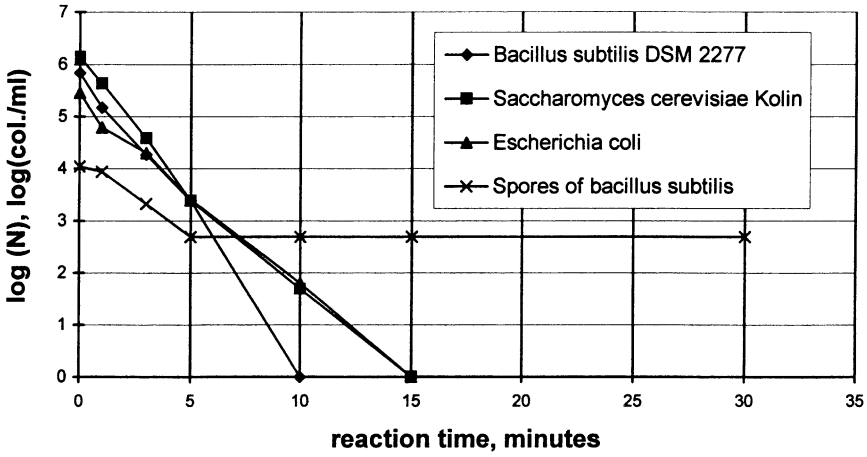

Fig. 3. Number of surviving microorganisms in dependence on irradiation time, flow-through arrangement.

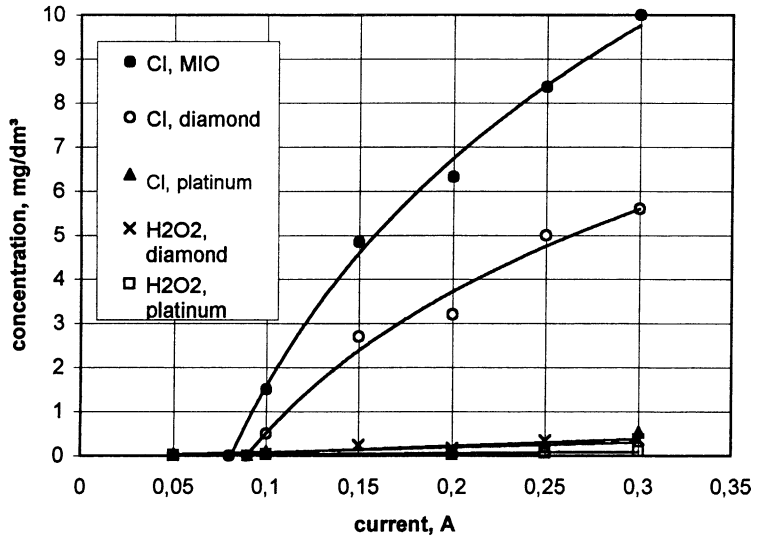

Fig. 4. Production of total chlorine and hydrogen peroxide in dependence on cell current for different electrodes (diamond, platinum, modified iridium based mixed oxide), treated volume: 0.4 dm^3; starting concentration (mg/dm^3)—chloride: 100; sulphate: 100; sodium salts in demineralised water, pH = 7; T: 298 K.

Therefore, in the first period the efficiency of the production of these compounds was studied. The total concentration of hypochlorite ions, hypochlorous acid and dissolved chlorine form an amount of active chlorine. Total chlorine is the sum of active chlorine and bonded chlorine due to reactions with other impurities. Chlorine dioxide is detected separately.

The results presented demonstrate the influence of a large variety of parameters, such as electrode material, cell type, electrical conditions, concentration ranges, etc. Fig. 4 summarises the concentrations of total chlorine and hydrogen peroxide versus electrolytic current for several different electrode materials and working conditions. The findings show that the formation of hydrogen peroxide is marginal, especially on the platinum electrode. The use of the remaining electrodes only slightly increases its concentration.

In the particular case of synthetic water with a chloride content of 100 mg/dm^3, used during the study, the formation of total chlorine is very low on the platinum electrode. A sufficiently high amount of chlorine was produced on the diamond electrode. However, the greatest efficiency of chlorine production was obtained using a modified iridium-based, mixed oxide ATA. A non-modified ATA was also tested. In

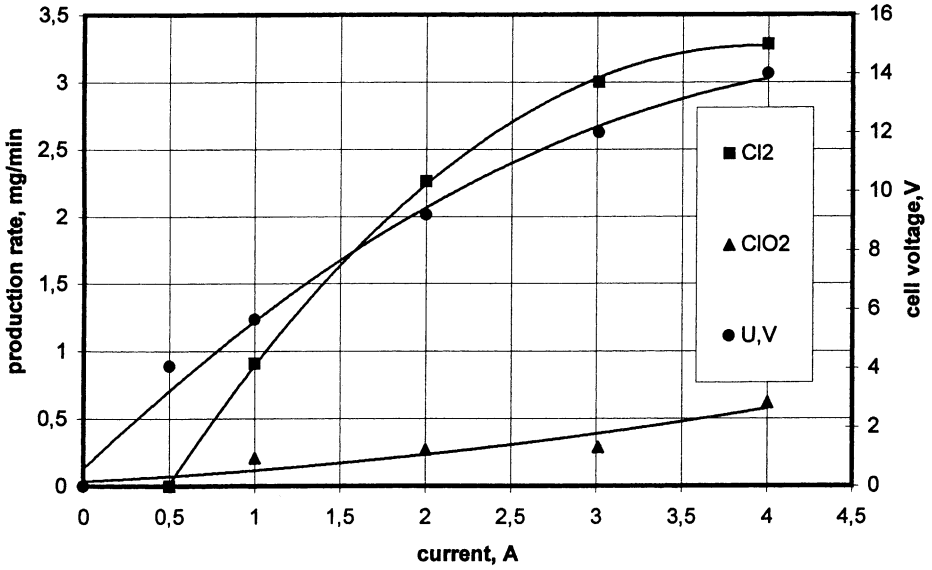

Fig. 5. Chlorine dioxide and free chlorine production in the flow-through reactor with electrodes stack and cell voltage in dependence on cell current, flow rate: 1 dm^3/min; concentrations (mg/dm^3)—chloride: 48; sulphate: 240; potable water, pH = 7; T = 298 K.

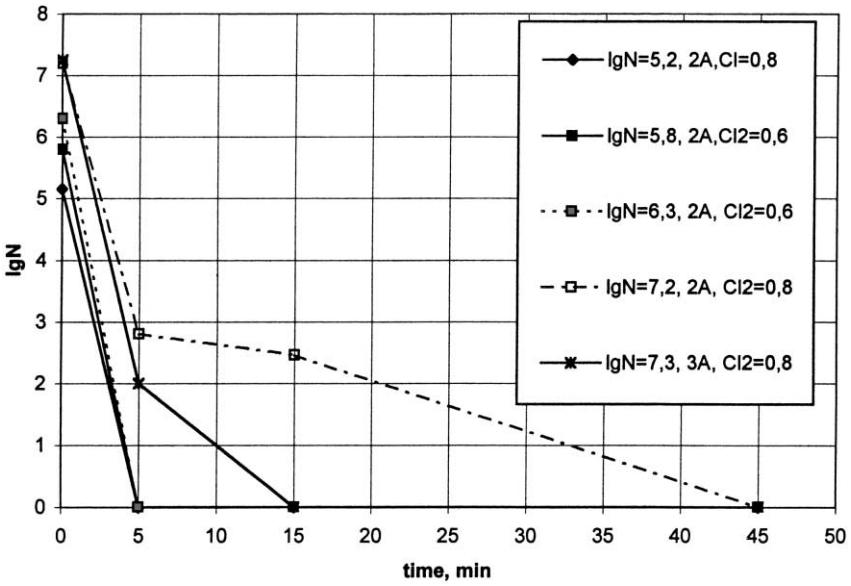

Fig. 6. Cell lethality vs. time for different starting concentration values of *E. coli*, free chlorine measured after single pass, flow rate: 3 dm^3/min, same water quality as for the experiments in Fig. 5.

this case, chlorine production efficiency was very low and the results are not presented here.

Fig. 5 demonstrates the dependence of the free chlorine and chlorine dioxide formation in a flow-through cell, after a single pass through it, with modified iridium-based, mixed oxide ATA in dependence on the applied current. The results shown were obtained for a flow rate of 1 dm^3/min. Local tap water was used as an electrolyte. A remarkable production of chlorine dioxide and a significant formation of free chlorine, enhanced by increased current, can be observed. With measured cell voltage between 0 and 14 V, specific energy consumption can be calculated in the range of 0.3 kWh per cubic meter and energy costs (only for electrolysis, without pumping energy) of 0.02 Euro/kWh. These values are acceptable with respect to the possible practical application of small and medium-sized disinfection equipment. The calculation is based on results from experiments with a chloride concentration of 50 mg/dm^3. It was found that in a chloride concentration range of 0–200 mg/dm^3 a linear correlation between total chlorine formation and chloride concentration exists. This makes an analysis of running costs possible for different conditions in this chloride concentration range.

Exemplarily, Fig. 6 shows the cell lethality of *E. coli* after the treatment in the flow-through reactor described. The starting cell concentration in a stirred reservoir tank before the electrolyser inlet was a variable parameter. The values of the free chlorine concentration (mg/dm^3) were obtained from immediate analysis of reactor outlet samples. They indirectly show a starting reaction inside the reactor during the short residence time. The reaction continues for 5–45 min, depending on the considered experiment. Normal tap water was chosen for disinfection. For each case, a cell number reduction down to zero can be reached with a flow rate of 3 dm^3/min. The detailed optimisation and analysis of kinetics orders will be the subject of further research.

4. Conclusions

The results presented show that both the new UV irradiation technique and optimised direct electrolysis offer an attractive alternative to conventional methods for drinking water disinfection. At present the former method cannot compete economically with the UV irradiation units currently used. On the other hand, direct disinfection electrolysis works efficiently even with low chloride concentrations in the treated water. The disinfecting effect results from the reactions of microorganisms with electrochemically formed oxidants, mainly containing chlorine as an active compound. Process parameters, such as current densities, flow rate, current reverse regime, electrode material and geometric parameters, are significant factors with regard to reactor and process design. Further research is needed in order to obtain essential information on long-term behaviour, scale-up, determination of irradiation density distribution, and kinetics of product formation and cell destruction. Finally, improved quantification of efficiency and a larger number of microorganism groups also have to be tested.

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