Latvian Journal of Chemistry, No 4, 2012, 296–304
DOI: 10.2478/v10161-012-0016-9

DRINKING WATER DISINFECTION WITH ELECTROLYSIS

M. Reimanis[1], L. Mezule, J. Ozolins[1],
J. Malers[1], T. Juhna[2]

[1] Riga Technical University, Faculty of Materials Science and Applied Chemistry, Institute of General Chemical Technology, Riga Technical University, Azenes iela 14/24, Riga, LV-1048, Latvia,
E-mail: madars.r@inbox.lv

[2] Riga Technical University, Department of Water Engineering and Technology, Azenes iela 16/20, Riga, LV-1048, Latvia

Nowadays electrochemical disinfection has gained an increasing attention as an alternative to conventional drinking water disinfection, since it is regarded as environmentally friendly, amendable to automation, inexpensive, easily operated and is known to inactivate a wide variety of microorganisms from bacteria to viruses and algae. We found that along with increasing the number of electrodes in our equipment from 2 to 24, the resistance of chlorine-generating electrolytic cell and specific work of electric current decreased. During the electrolysis the amount of generated Cl_2 increased along with the increase of chloride ion concentration in the solution and the intensity of electric current. The technological process parameters (flow rate, current intensity) have been established to obtain a predetermined amount of generated chlorine during the electrolysis process. A comparison of flow and circulating (3 times) regimes for electrolysis of tap water with chloride ion concentration below 10 mg/L showed that circulation is necessary to generate active chlorine (above 1 mg/L).

At the same time, when no circulation was performed, even a 0.9 A treatment was not enough to generate detectable levels of free chlorine. Electrochemical disinfection of tap water with non-stoichiometric titanium oxide electrodes was effective enough to inactivate both metabolically active and cultivable bacteria *E. coli* to undetectable levels within 15 minutes at 0.5 A current intensity.

Key words: *electrolysis, disinfection, oxidants, chlorine, technological parameters.*

INTRODUCTION

Nowadays electrochemical disinfection has gained an increasing attention as an alternative to conventional drinking water disinfection since it is regarded as environmentally friendly, amendable to automation, inexpensive, easily operated and is known to inactivate a wide variety of microorganisms from bacteria to viruses and algae [1–6]. If compared with chlorination (the use of gaseous chlorine or concentrated hypochlorite solution), no addition of chemicals is necessary, because the main disinfecting agents are produced from the naturally occurring ions found in the water itself [7].

The electrolysis of water is significantly influenced by electrode materials [8–14]. The possibility of using non-stoichiometric titanium oxide (with overall

formula Ti_nO_{2n-1}) ceramic electrodes for drinking water disinfection has been analyzed previously [15–19] and it has been shown that during electrolysis of water the amount of organic substances is reduced and oxidation properties ($KMnO_4$ index) change significantly [18]. The presence of chloride ions in water subjected to electrolysis significantly decreased the amount of cultivable bacteria *E. coli* [16]. The oxidizing substances formed during the treatment were shown to possess a long-lasting disinfecting effect. At the same time bacteriostatic effect of up to 10 days has been observed when water contained iodide ions prior treatment [15, 17].

When using a Ti_nO_{2n-1} electrode in the electrolysis process in the presence of chloride ions at such concentration range, that is common in raw waters [14], enough active chlorine can be created to kill more than 99% of *E. coli* within 15 minutes. The mathematical model for prediction of disinfection efficacy of *Escherichia coli* with electrolysis process have been developed [17]. However, the application of Ti_nO_{2n-1} electrodes so far has been limited to the use in continuously stirred batch systems that cannot be representative enough for disinfection of water in dynamics. Thus the aim of this study was to describe the use of TiO_{2-x} containing ceramic electrodes to treat natural (tap) water under dynamic conditions. and to show the influence of selected technological parameters (current intensity, number of electrodes, chloride ion concentration in water, water flow capacity and the specific electrical work required for electrolysis) on the effectiveness of the treatment process.

The experiments were carried out in laboratory scale using *Escherichia coli* as a model organism for disinfection experiments. The anode was synthesized in the Riga biomaterials innovation and development centre [20].

EXPERIMENTAL

Model solutions of chloride ions with concentrations from 0 to 250 mg/l were prepared by adding KCl to deionized water. Maximum concentration of chloride ions did not exceed the maximum concentration permissible for drinking water [21].

Tap water was taken from Riga Water Supply System (Latvia) which contains chloride ions in concentrations from 8 to 9 mg/L. Quality parameters of drinking water are given in Table 1.

Table 1. **Quality parameters of drinking water used in this study with the permissible range according to legislation [21]**

Parameter	Value	Permissible range
1	2	3
Total hardness, mmol/L	3.7	not specified
calcium ions, mg/L	52.0	not specified
magnesium ions, mg/L	13.0	not specified
total alkalinity, mmol/L	2.35	not specified
total mineralization, mmol/L (g/L)	3.95	not specified
sulphate ions, mg/L	60.0	< 250
hydrogen carbonate ions, mg/L	143.0	not specified
iron ions (total), mg/L	0.49	< 0.2
manganese ions, mg/L	0.02	< 0.05

End of Table 1

1	2	3
oxidizability ($KMnO_4$), mg O/L	2.60	< 5
nitrate nitrogen, mg/L	1.20	< 11
nitrite nitrogen, mg/L	< 0.005	< 0.15
ammonium nitrogen, mg/L	0.13	< 0.4
Hydrogen sulphide, mg/L	< 0.05	
Colour, turbidity	colourless, clear	without major changes
pH	7.4	6.5–9.5
Conductivity at 25 °C, mS/cm	0.39	< 2.5

The total and free chlorine concentrations was determined with volumetric methods [22, 23].

Water electrolysis was done in specially constructed electrolytic cell for water treatment under dynamic conditions with the flow rate of 0.01 m/s (Fig. 1.).

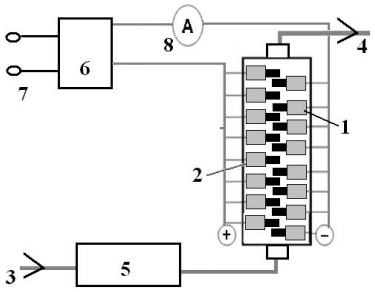

Fig. 1. Experimental electrolysis unit with TiO_{2-x} electrodes for dynamic conditions:
1 – Plexiglas casing; *2* – TiO_{2-x} ceramic electrodes; *3* – bowl with a stock solution;
4 – electrolyzed solution; *5* – pump; *6* – power supply; *7* – supply voltage; *8* – ammeter.

Ceramic TiO_{2-x} electrodes in the shape of cylindrical bar are used as anodes and cathodes in the electrolysis unit. The number of ceramic anodes and cathodes is equal (12 and 12), and each has a surface area of 11.8 cm^2 (for the total area of 282.7 cm^2). The total internal volume of the electrolysis unit is 320 cm^3. A rectifier (HQ Power, PS5005; 0–50 V; DC; 0–5 A) was used as the current source. The electrolysis process was carried out at current intensity within the range of 0.1–0.9 A, temperature 21 ± 2 °C, and pH 7.0 ± 0.5.

Before each microbiological experiment the electrolysis unit was washed with plenty of sterile distilled water (at least 4 litres) and after each experiment – with ~13 mmol/L KCl solution (I = 0,4 A, Q = 0.218 L/min) to generate active chlorine and remove any potential microbiological pollution.

To a 0.5 L of pre-filtered (0.2 μm pore size, *E. coli* free) tap water prewashed overnight culture of *E. coli* cells was added (final concentration of ~$1.1 \cdot 10^6$ cells/mL). Prior of the electrochemical treatment the sample was circulated in the system for 10 minutes (flow rate 55 mL/min), then the current was turned on, the first 0.4 mL were discarded and 100 mL collected for cell inactivation analyses. During the study, 0.1, 0.5 and 0.9 A current intensity treatment regimes were tested. Additionally, a modification of the

system was prepared to allow sample circulation (15 min) in the electrolysis unit (0.3 or 0.5 A).

In all samples free chlorine and total chlorine concentration was analyzed using DPD colorimetric method [23]. For microbiological analyses all samples were neutralized with excess sodium thiosulphate.

Cultivable *E. coli* concentration was estimated by the plate count technique, where 10-fold dilutions were inoculated onto TBX medium (Oxoid Ltd, UK) and incubated for 24 hours at 37 °C. Typical blue/green colonies were counted and results expressed as CFU per milliliter. All sample analyses were repeated three times.

The metabolically active *E. coli* concentration was estimated by staining with CTC in accordance with the procedure described by Reimanis *et al.* [16]. In brief, samples were stained for 2 hours in the dark with CTC (5-cyano-2,3-ditolyl tetrazolium chloride, Fluka, BioChemika) with a final concentration of 4 *mM*. Then the sample was filtered through 25-mm-diameter 0.2-µm-pore-size filter, fixed and stained with 10 µg/mL DAPI. Actively respiring and non-respiring cell numbers were determined with epifluorescence microscope (DAPI Ex: 340/380 nm; Em: >425 nm, fluorescent formazan crystals Ex: 545 ± 30 nm; Em. 610 ± 37 nm).

RESULTS AND DISCUSSION

Technological parameters that characterize the electrolysis device under dynamic conditions are: electrical resistance, intensity of disinfecting substance release, the specific electrical work required for electrolysis process and disinfection efficiency against bacteria. The intensity of disinfecting substance release was characterized by the release rate of chlorine. The efficiency of the electrolysis cell was characterized by the amount of chlorine generated and expressed as the fraction of theoretically possible chlorine amount and the required specific work performed by current in the process.

Previously electrochemical disinfection with fecal pathogen *Escherichia coli* in a model system with a single electrode has been evaluated [16]. Despite the fact that *Escherichia coli* is not particularly resistant to disinfection, when compared to other waterborne pathogens such as *Cryptosporidium* spp., this bacterium is used as an indicator of hygienic quality of drinking water, and therefore it is of interest for water industry. The results showed that treatment for 30 minutes at low current intensity was enough to reduce cultivable *E. coli* amount by more than 5 orders of magnitude [16]. Analyses on applying the same treatment conditions with the exception that 2 pairs of electrodes were used showed that within 30 minutes no cultivable *E. coli* can be found in the system. At the same time a mere 10-fold decrease of metabolically active cells was observed, which corresponded to previous results [16]. The results showed that if the number of electrodes was increased and constant current intensity was applied (0.1 A), the amount of released chlorine remained practically constant, but the specific work of electric current needed to generate free chlorine decreased 2.7 times (Fig. 2.). The specific work of electric current decreased, because the total resistance of electrolysis cell decreased. Thus, further experiments were conducted using 24 electrodes.

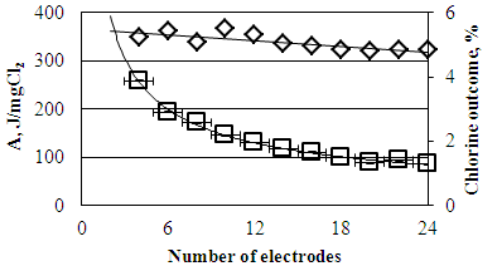

Fig.2. The specific work of electrolysis (□) and the released amount of chlorine (◊) (expressed in % of theoretical) as a function of the number of electrodes. Current intensity 0.1 A. Concentration of chloride ion 1 mmol/L.

The intensity of generation of disinfecting substances and, herewith, the efficiency of electrolysis process in the water supply systems can vary, if the concentration of chloride ions and parameters of electric current in the solution are changed. To test the formation of active chlorine from chloride ions, KCl salt in concentrations similar to those in drinking water was added to the water. The solution was electrolyzed using permanent process parameters (pH 7.5 ± 0.5, T = 25 °C, Q = 0.055 L/min).

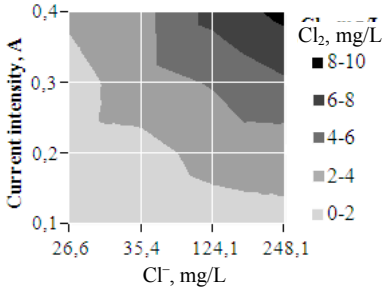

Fig. 3. The amount of Cl_2 released during electrolysis as a function of chloride ion concentration (mg/L) and electric current intensity (A). Flow capacity 55 mL/min.

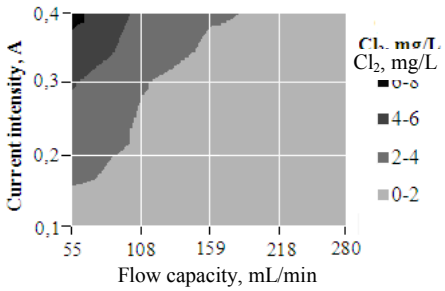

Fig. 4. The amount of Cl_2 released during electrolysis as a function of current intensity (A) and flow capacity (Q). KCl concentration 26.6 mg/L.

The increase in chloride ion concentration and electric current intensity during the electrolysis resulted in an increased amount of generated Cl_2. (Fig. 3). To maintain a constant concentration of disinfecting substances in the solution, the concentration of chloride ions or the provided electric current intensity must be altered. Disinfectant generation rate and, hence, the efficiency of water electrolysis process may change, due to changing water and power consumption characteristics. Specified disinfectant concentrations in solution can be ensured by varying the flow capacity and the current intensity. As can be seen from Figure 4, the generated Cl_2 in the electrolysis process increased when water consumption Q was reduced and the applied current increased. The obtained relationship allowed to predict the concentration of Cl_2 achievable by changing the electrolysis parameters.

Since tap water also contains various solvated salts (as ions), the electric conductivity of water increases and the amount of released chlorine during the electrolysis process decreases. To effectively generate chlorine during electro-chemical treatment and to obtain optimum efficiency, the current intensity and flow capacity must be changed (Table 2).

The increase in current intensity (Table 2) causes the increase of the amount of released total chlorine. Free chlorine formation was not detected in flow regime, what could be explained by the small amounts of released free chlorine and large quantities of organic matter (tap water oxidizability amounts to 2.6 g ($KMnO_4$ index)) reacting with all free chlorine formed. Free chlorine was generated only during the circulating flow regime (15 minutes, passing 3 times through the device) indicating the importance of the contact time in the electrolysis process.

Table 2. **The amount of total and free Cl_2 released during tap water electrolysis**. Flow capacity 55 mL/min

Treatment regime	Current intensity, mA	Chlorine, mg/L	
		total	free
Flow	100	0.0	0.0
Flow	300	4.4	0.0
Flow	900	6.5	0.0
Circulating	100	0.3	0.0
Circulating	300	1.8	0.0
Circulating	500	4.4	1.2

First to analyse the efficiency of electrochemical treatment with 24 electrodes, drinking water containing the *E. coli* culture was pumped through the electrolysis unit at a flow rate of 55 mL/min. The results indicated that when 0.1 A current was applied, no reduction in both cultivable and metabolically active *E. coli* cells was obtained (Fig. 5). This can be explained by insufficient chlorine levels generated. The increase in current intensity (0.3 A) allowed to detect 4.37 mg/L of total chlorine after the treatment and a 10-fold reduction in cultivable counts. At the same time, no detectable amounts of free active chlorine were determined in this assay. Further studies with increased current intensity showed that a current of 0.9 A was sufficient to obtain more than 5 orders of magnitude decrease in cultivable amounts, and complete removal of metabolically active cells. However, at the same time an increase in temperature and pH (from 7.1 to 8.8) was observed, which would not be acceptable for drinking water.

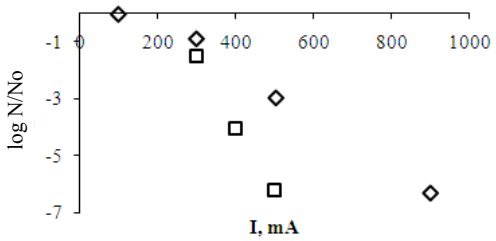

Fig. 5. Estimated cultivable *E. coli* log reduction in tap water after electrochemical treatment in a cell containing 24 electrodes: flow (□), circulating or 15 min treatment (◊). Concentration of chloride ion 1 mmol/L.

As shown in Fig. 2, the 24-electrode cell was not able to generate more chlorine than 1 electrode during an equal length of time, thus prolonged sample

circulation (15 minutes, 55 mL/min) was introduced. This was enough to obtain the same inactivation rate (>5 orders of magnitude cultivable, no metabolic activity) by using a 0.5 A current instead of 0.9 A. At the same time pH increased only from 6.9 to 7.4, and no significant increase in temperature was observed. Additionally, 1.3 mg/L of free chlorine was obtained on average after 15 minutes.

Thus, by changing configuration of the electrolysis unit and applying natural drinking water with constantly changing quality parameters, it is necessary to adjust the operation conditions to obtain optimal disinfection efficiency. Besides, the treatment regime must be effective enough to neutralize all potentially harmful microorganisms and simultaneously avoid generating elevated chlorine levels. Our studies using the 24 electrode cell showed that the treatment time can be decreased from 30 minutes [16] to 15 minutes to fully inactivated viable *E. coli* in tap water.

CONCLUCIONS

1. The increase in number or surface area of ceramic non-stoichiometric titanium oxide electrodes caused a decrease of electrolysis cell resistance and of the specific work done by electric current to generate chlorine.

2. The amount of chlorine released during electrolysis increased along with the increase of chloride ion concentration in the solution and the intensity of electric current.

3. The technological parameters of the process (flow rate, current intensity) have been established to generate a predetermined amount of chlorine during the electrolysis process.

4. Circulation of water through electrolysis cell for 15 minutes (3 times) during the treatment allowed to generate active chlorine in amounts above 1 mg/L with 0.5 A current intensity. At the same time, when no circulation was performed, even a treatment with current of 9 A was not enough to generate detectable levels of free chlorine.

5. Electrochemical disinfection of tap water with non-stoichiometric titanium oxide electrodes was effective enough to inactivate both metabolically active and cultivable *E. coli* to undetectable levels.

Acknowledgements

This work has been partly supported by the European regional development fund within the project "Development of innovative water processing technology using nanostructured ceramics", No. 2010/0257/2DP/2.1.1.1.0/10/APIA/VIAA/012.

REFERENCES

1. Jeong, J., Kim, C., Joon, J. (2009). The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes. *Water Res.*, *43*, 895–901.
2. Marselli, B., Gomez, J.G., Michand, D., Rodrigo, M., Comninellis, C. (2003). Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. *J. Electrochem.*

Soc., *150*, D79-D83.

3. Kraft, A., Stadelmann, M., Blaschke, M., Kreysig, D., Sandt, B., Schroder, F., Rennau, J. (1999). Electrochemical water disinfection Part I: Hypochlorite production from very dilute chloride solutions. *J. Appl Electrochem*., *29*, 861–868.
4. Kraft, A., Blaschke, M., Kreysig, D., Sandt, B., Schröder, F., Rennau, J. (1999). Electrochemical water disinfection. Part II: Hypochlorite production from potable water, chlorine consumption and the problem of calcareous deposits. *J. Appl. Electrochem*., *29*, 895–902.
5. Tröster, I., Fryda, M., Herrmann, D., Schäfer, L., Hänni, W., Perret, A., Blaschke, M., Kraft, A., Stadelmann, M. (2002). Electrochemical advanced oxidation process for water treatment using DiaChem® electrodes. *Diamond and Related Materials*, *11*, 640–645.
6. Shi, H. X., Qu, J.H., Wang, A.M., Ge, J.T. (2005). Degradation of microcystins in aqueous solution with in situ electrogenerated active chlorine. *Chemosphere*, *60*, 326–333.
7. Martínez-Huitle, C.A., Brillas, E. (2008). Electrochemical Alternatives for Drinking Water Disinfection. *Angew. Chem. Int. Ed., 47*, 1998–2005.
8. Bergmann, M.E.H., Koparal, A.S. (2005) Studies on electrochemical disinfectant production using anodes containing RuO_2. *J. Appl. Electrochem.*, *35*, 1321–1329.
9. Chen, X., Gao, F., Chen, G.J. (2005). Comparison of Ti/BDD and Ti/SnO_2–Sb_2O_5 electrodes for pollutant oxidation. *J. Appl. Electrochem.*, *35*, 185–191.
10. Jeong, J., Kim, J.Y., Cho, M., Choi, W., Yoon, J. (2007). Inactivation of *Escherichia coli* in the electrochemical disinfection process using a Pt anode. *Chemosphere*, *67*, 652–659.
11. Jeong, J., Kim, C., Yoon, J. (2009). The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes. *Water Res.*, *43,* 895–901.
12. Palmas, S., Polcaro, A. M., Vacca, A., Mascia, M., Ferrara, F. (2007). Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes. *J. Appl. Electrochem.*, *37*, 1357–1365.
13. Zaggout, F.R., Ghalwa, N.A. (2008). Removal of *o*-nitrophenol from water by electro-chemical degradation using a lead oxide/titanium modified electrode. *J. Environm. Manag., 86,* 291–296.
14. Kraft, A. (2008). Electrochemical water disinfection: a short review. *Platinum Metals Rev*., *52* (3), 177–185.
15. Reimanis, M., Malers, J., Ozolins, J. (2010). Preparation of water using Electrochemical Processes. *Intern. J. Chem. Environmental Eng., World Acad. res. publ. Press.*, *1* (1), 35–39.
16. Reimanis, M., Mezule, L., Malers, J., Ozolins, J., Juhna, T. (2011). Model water disinfection with electrolysis using Ti_nO_{2n-1} containing ceramic electrodes. *Environ. Biotechnol.*, *7* (1) 34–40.
17. Reimanis, M., Ozolins, J., Malers, J., Locs, J., Juhna, T. (2011). Water disinfection using Ti_nO_{2n-1} electrodes. 2011 2nd Intern. Conf. Environ. Eng. Appl., 12–14 August 2011. Intern. Proc. Chem., Biolog. Environm. Eng., vol. *17*, 265–270, Singapore: IACSIT Press.
18. Reimanis, M., Ozolins, J., Malers, J., Nikolajeva, V. (2009). Influence of various physical-chemical treatment methods on microbial growth in water. In Proceedings of 7th International Conference "Environment. Technology. Resources". Rezekne: Rezekne Higher Education Institution Press, 71–77.
19. Smith, J.R., Walsh, F.C. (1998). Electrodes based on Magneli phase titanium oxides: the properties and applications of Ebonex® materials. *J. Appl. Electrochem*., *28*, 1021–1033.
20. Pavlova, A., Berzina-Cimdina, L., Locs, J., Barloti, J., Teters, V. (2009). Investigation of the electrical properties of vacuum annealed titanium oxide-containing ceramics. *Proc. Appl. Cer.*, *3* (4), 187–190.
21. Council Directive 98/83/EC of 3 November, 1998. *Offic. J. Eur. Comm.,* 1998, *5* (12).
22. Water quality. Determination of free chlorine and total chlorine. (1990). Part 3: Iodometric titration method for the determination of total chlorine. ISO 7393-3:1990, Intern. Stand. Org., Geneva, Switzerland.
23. Water quality. Determination of free chlorine and total chlorine. Part 1: Titrimetric method using *N,N*-diethyl-1,4-phenylenediamine. LVS EN ISO 7393-1:2001. Intern. Stand. Org., Geneva, Switzerland. 2000.

DZERAMĀ ŪDENS DEZINFEKCIJA ELEKTROLĪZĒ

M. Reimanis, L. Mežule, J. Ozoliņš, J. Mālers, T. Juhna

K O P S A V I L K U M S

Mūsdienās ūdens elektroķīmiskajai dezinfekcijai, kā alternatīvai tradicionālajām dezinfekcijas metodēm, tiek pievērsta liela uzmanība, jo tā ir videi draudzīga, viegli automatizējama, salīdzinoši lēta, viegli vadāma un ir zināma tās dezinficējošā iedarbība uz plašu mikroorganismu klāstu – no baktērijām līdz vīrusiem un aļģēm. Eksperimentāli konstatēts, ka, palielinot elektrodu skaitu elektrolīzes iekārtā no 2 līdz 24, tās pretestība un strāvas īpatnējais darbs samazinājās. Izdalītā Cl_2 daudzums elektrolīzes laikā palielinājās, palielinoties hlorīda jonu koncentrācijai šķīdumā un elektriskās strāvas stiprumam. Variējot elektrolīzes procesa tehnoloģiskos parametrus (ūdens plūsmas ātrumu, strāvas stiprumu), iespējams sasniegt noteiktu izdalītā hlora daudzumu. Salīdzinot ūdens, kurš satur hlorīda jonus mazāk par 10 mg/L, apstrādi ar elektrolīzi caurplūdes režīmā ar cirkulācijas režīmu (3 reizes), konstatēts, ka ūdens apstrādi vēlams veikt cirkulācijas režīmā, lai būtu iespējams saražot vairāk aktīvā hlora (koncentrācijā, lielākā par 1 mg/L).

Noteikts, ka process, veicot ūdens apstrādi ar elektrolīzi caurplūdes režīmā pat, ja strāvas stiprums 0,9 A, nenodrošināja aktīvā hlora veidošanos detektējamos daudzumos. Elektroķīmiskā dezinfekcija, izmantojot nestehiometriskā titāna oksīda elektrodus, bija pietiekami efektīva, lai pilnībā inaktivētu metaboliski aktīvās un kultivējamās *E. coli* baktērijas 15 minūšu laikā, ja strāvas stiprums 0,5 A.