

RIGA TECHNICAL UNIVERSITY
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**ELECTROCHEMICAL DISINFECTION OF WATER USING
TITANIUM OXIDE CERAMIC ELECTRODES**

Summary of doctoral thesis

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Dr. sc. ing., Professor
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CONFIRMATION

I hereby confirm that I have developed this thesis, which was submitted for review in Riga Technical University, for obtaining a doctor's degree in engineering sciences. This thesis has not been submitted to any other university for obtaining any scientific degree.

Madars Reimanis.....(Signature)

Date:

The original thesis is written in Latvian language, it contains an introduction, review of literature sources (6 chapters), experimental part (6 chapters), results and discussion (9 chapters), conclusions, list of literature sources, 75 figures, 13 tables, 6 appendixes on 124 pages in total. The list of literature sources contains 135 titles.

NOTE OF GRATITUDE

Let me express my gratitude for the scientific supervisor of this thesis, professor, *dr. sc. ing.* Jurijs Ozoliņš, for choice of the contemporary subject, supervising the work, valuable advice, understanding and loyalty.

Many thanks to the director of RTU Institute of Material Sciences and Applied Chemistry, General Chemical Technology, professor, *dr. sc. ing.* Līga Bērziņa-Cimdiņa for loyalty, understanding, support, providing infrastructure and the possibility to work and perform the required research.

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URGENCY AND NATURE OF THE PROBLEM

The urgency of the subject is determined by the necessity to disinfect drinking water, in order to minimize multiplication of microorganisms in engineering water supply systems and eliminate the possibility of human infection, which could lead to significant economic losses along with deterioration of the public health and working abilities.

In the developed countries, this problem is mostly urgent for users of individual water wells and local water supply systems. Epidemiologic research shows that the number of infections while consuming low-quality drinking water from individual water wells is several times higher than while consuming water from the centralized water supply systems.

The necessity of water disinfection can also appear due to occurrence of environmental catastrophes, including floods, terroristic attack threats, military conflicts, as well as due to specific domestic conditions.

A significant number of Latvian citizens consume water from the individual wells and they have no access to the centralized water supply systems.

By improving drinking water microbiologic quality in de-centralized water supply systems, number of infections caused by poor water quality will be significantly decreased.

Goal of thesis: using titanium oxide (TiO_{2-x}) ceramic electrodes, develop an effective non-reagent electrochemical water disinfection method which can be used on local water collection venues, in emergency situations and for water preparation for specific applications.

For achieving the goal of thesis and for thesis development, the following tasks were set:

- 1) Analyze scientific literature sources about the subject related to thesis;
- 2) Determine main physical, chemical and electrochemical properties for the electro conductive TiO_{2-x} ceramics. Evaluate if the electrodes made from this materials are capable to disinfect water with electrolysis method;
- 3) Determine impact of various substance ions, dissolved in the water, on the water electrolysis process.
- 4) Determine water electrolysis impact on various microorganisms found in water;
- 5) Determine technologic parameters impact on the water electrolysis efficiency.
- 6) Based on the data of conducted experiments, create a mathematical model describing the water electrolysis process.
- 7) Develop a principle scheme of a continuous operation water disinfection device.

Scientific and practical importance of the thesis:

- 1) It was found that while using the TiO_{2-x} electrodes, even minor chlorine ions concentrations (7 – 9 mg/L) in the water during electrolysis can ensure a sufficiently high water disinfection efficiency with a lasting exposure.
- 2) Impact of various technological factors on electrolysis process and lasting disinfection exposure using TiO_{2-x} ceramic electrodes were studied. Based on the experiment results, a mathematical model, allowing disinfection efficiency prediction, was developed.
- 3) Based on the experiment data, a principle scheme of a continuous operation water disinfection device is developed.
- 4) Work results can be used as a basis for design and manufacturing of a commercial water disinfection device.

Scientific novelty of the thesis – for the first time, TiO_{2-x} ceramic electrodes, activated in a deep vacuum at the high temperatures, were obtained. Research results allow to state that titanium oxide ceramic electrodes do not impact water quality already at the minor chlorine ions

concentrations, and can ensure complete main microbiologic pollution indicator organisms inactivation. A mathematical model, which allows water disinfection process monitoring, has been developed.

Defendable statements:

- 1) Vacuum activated TiO_{2-x} ceramic can be used in water electrolysis devices as an electrode material;
- 2) Using TiO_{2-x} ceramic electrodes in minor chlorine ions concentrations containing water (7 – 9 mg/L) for electrolysis, a complete inactivation of the main microbiologic pollution indicator organisms can be achieved.

Thesis approbation:

The main scientific achievements and results of the thesis are presented on 20 international scientific conferences. 11 full text printed articles and 12 scientific conference theses were published about the subject of this thesis.

The main research results were demonstrated in 11 publications and full text conference theses brochures.

1. Rubenis K., Ozolins J., Pura A., Locs J., **Reimanis M.**, Narkevica I., Berzina-Cimdina L. The influence of the thermal treatment on the properties of TiO_2 ceramics obtained by extrusion. RTU zinātniskie raksti, Materiālzinātne un lietišķā ķīmija, 25. sējums, 2012, p.p. 71-75.
2. **Reimanis M.**, Ozoliņš J., Mālers J., Ēce L. Cietības ietekme uz ūdens elektrolīzi izmantojot titāna oksīda keramikas elektrodus. RTU zinātniskie raksti, Materiālzinātne un lietišķā ķīmija, 25. sējums, 2012, p.p. 66-70.
3. **Reimanis M.**, Ozolins J., Malers J., Locs J. and Juhna T. Water disinfection using $\text{Ti}_n\text{O}_{2n-1}$ electrodes. 2011 2nd International Conference on Environmental Engineering and Applications. International Proceedings of Chemical, Biological and Environmental Engineering, 2011, 17, p.p. 265-270, IACSIT Press, Singapore.
4. **Reimanis M.**, Malers J., Ozolins J. $\text{Ti}_n\text{O}_{2n-1}$ saturoša keramikas elektroda izmantošana ūdens elektroķīmiskajā apstrādē. Latvijas ķīmijas žurnāls, 2010, 3, p.p. 254.-260.
5. **Reimanis M.**, Mezule L., Malers J., Ozolins J., Juhna T. Model water disinfection with electrolysis using $\text{Ti}_n\text{O}_{2n-1}$ containing ceramic electrodes. Environmental Biotechnology, 2011, 7 (1), p.p. 34-40.
6. **Reimanis M.**, Malers J., Ozolins J. Preparation of water using electrochemical proceses. International Journal of Chemical and Environmental Engineering, World Academy of research and publication Press, 2010, 1 (1) p.p. 35-39.
7. **Reimanis M.**, Ozolins J., Malers J., Nikolajeva V. Influence of various physical - chemical treatment methods on microbial growth in water. In: 7th International Conference "Environment. Technology. Resources", Conference. Rezekne, Latvija, June 25-27, 2009. Proceeding. Rezekne, Rezekne Higher Education Institution Press, 2, 2009, 71-77.

8. Mezule L., **Reimanis M.**, Malers J., Ozolins J., Juhna T. Application of electrolysis with $\text{Ti}_n\text{O}_{2n-1}$ ceramic electrodes for disinfection of drinking water. The Scientific Proceedings of Riga Technical University, Material science and applied chemistry, 2009, 20, p.p. 123-131.
9. **Reimanis M.**, Ozoliņš J., Mālers J. Ūdens bioloģiskā piesārņojuma samazināšana pielietojot elektrolīzes procesā TiO_x saturošu keramikas elektrodus. RTU zinātniskie raksti, Materiālzinātne un lietišķā ķīmija, 18. sējums, 2008, p.p. 90.-96.
10. **Reimanis M.**, Mezule L, Malers J, Berzina-Cimdina L, Juhna T, Ozolins J. Preparation of water with electrolysis method using ceramic electrodes. In: IWA Specialist Conference "Water and Wastewater Treatment Plants in Towns and Communities of the XXI Century: Technologies, Design and Operation". Conference. Moscow, Russia, June 2-4, 2010. Proceeding [electronic resource]. Moscow, SIBICO International Ltd., 2010, p.p. 1-8.
11. **Reimanis M.**, Malers J., Ozolins J. Water preparation using electrochemical process. Conference on Emerging Technologies in Environmental Science and Engineering, [electronic resource], 2009, October, India, Aligarh: Department of Civil Engineering, A.M.U., 2009, p.p. 207.-214.

The main research results are demonstrated in 12 international conference theses.

1. **Reimanis M.**, Mezule L., Ozolins J., Malers J., Juhna T. Drinking water disinfection with electrolysis methods. International conference "ECOBALT 2012": Book of Abstracts, University of Latvia, Riga, Latvia, October 18-19, 2012, p.p. 67.
2. **Reimanis M.**, Ozolins J., Vindedze-Jonisenoka E., Sirsnina S., Malers J. The impact of individual technological parameters on the water electrolysis process. Riga Technical University 53rd International Scientific Conference dedicated to the 150th anniversary and The 1st Congress of World Engineers and Riga Polytechnical Institute / RTU Alumni : Book of Abstracts, Riga, Latvija, October 11-12, RTU Publishing House, 2012, p.p. 82.
3. **Reimanis M.**, Ozoliņš J., Mālers J., Ēce L. The effect of water hardness on the water electrolysis process using $\text{Ti}_n\text{O}_{2n-1}$ ceramic electrodes. The 52th International Scientific Conference of Riga Technical University: Book of Abstracts, Latvija, Rīga, 13-15 October, 2011, p.p. 101.
4. **Reimanis M.**, Malers J., Ozolins J. Water preparation using $\text{Ti}_n\text{O}_{2n-1}$ electrodes. EMEC 11 - The 11th European Meeting on Environmental Chemistry PORTOROŽ, Slovenia, 8-11 december 2010, p.p. 98.
5. **Reimanis M.**, Pavlova A., Locs J., Freimanis I., Berzina-Cimdina L., Ozolins J. Dense titanium oxide ceramics for water preparation with electrolysis. In: XIX-th International Baltic Conference "Materials Engineering&Balttrib *2010". Conference. Riga, Latvia, October 28-29, 2010. Proceeding, Riga, Latvia, Institute of Inorganic Chemistry, 2010, p.p. 36.
6. **Reimanis M.**, Malers J., Ozolins J. Water preparation using $\text{Ti}_n\text{O}_{2n-1}$ electrodes. In: XIX-th International Baltic Conference "Materials Engineering&Balttrib *2010". Conference. Riga, Latvia, October 28-29, 2010. Proceeding, Riga, Latvia, Institute of Inorganic Chemistry, 2010, p.p. 18.
7. **Reimanis M.**, Pavlova A., Malers J., Berzina-Cimdina L., Ozolins J. Electrical conductive $\text{Ti}_n\text{O}_{2n-1}$ ceramic extraction and use for water treatment with electrolysis. ELECTROCERAMICS

XII, abstract book [electronic resource], Norwegian University of Science and Technology, Trondheim, Norway 13th June - 16th June 2010, p.p. 151.

8. **Reimanis M.**, Mezule L., Malers J., Berzina-Cimdina L., Juhna T., Ozolins J. Preparation of water with electrolysis method using ceramic electrodes. IWA Specialist Conference “Water and Wastewater Treatment Plants in Towns and Communities of the XXI Century: Technologies, Design and Operation”, abstract book [electronic resource], Moscow, Russia on 2-4 June 2010, p.p. 1-2. (ISBN 978-5-9900677-9-0).

9. **Reimanis M.**, Malers J., Ozolins J. Water preparation using electrochemical process. International Conference on Emerging Technologies in Environmental Science and Engineering, 2009, October, India, Aligarh: Department of Civil Engineering, A.M.U., 2009, p.p. 63.-64 (ISBN: 978-93-80043-42-5).

10. Reimanis M., Mezule L., Malers J., Ozolins J., Juhna T. Water disinfection with electrolysis using Ti_nO_{2n-1} containing ceramic electrodes. Second International Environmental Best Practices Conference and AGFES Educational Workshop, 2009, September, Poland, Krakow: abstract book, September 2009, p.p. 26.

11. Pavlova A., **Reimanis M.**, Berzina-Cimdina L., Ozolins J., Barloti T., Teters V. Fabrication of a conductive ceramic and its use in water treatment technology. International Baltic Sea Region conference „Functional materials and nanotechnologies”, 2009, march – April, abstract book, Latvia, Riga: Institute of Solid State Physics University of Latvia, 2009, p.p. 196.

12. **Reimanis M.**, Berzina-Cimdina L., Ozolins J., Malers J. Influence of electrolysis process on propagation of microorganisms in water. 49th Annual Conference International symposium on Microbial biotechnology: diversity, genomics and metagenomics, 2008, November, India, Delhi: Association of Microbiologists of India, 2008, p.p. 138-139.

BRIEF SUMMARY OF THE LITERATURE SOURCES REVIEW

The first chapter “Water quality and main factors that impact it” contains a general description of water quality definition along with the review of the main factors that can impact it. It also reviews general information about bacteriologic water pollution [1, 2].

In the second chapter “Water pollution and its development”, a water pollution description is given, and the pollution development mechanisms are described. This chapter reviews and thoroughly analyzes different pollution kinds.

The third chapter “Microbiological pollution” reviews details of water microbiological pollution caused by pathogenic bacteria. In water supply systems, these bacteria are located in a bio-film that protects them from disinfection effect. The problem is urgent for individual water wells and local water supply systems [3]. Analysis of indicator microorganisms is applied in order to determine water microbiological pollution [4].

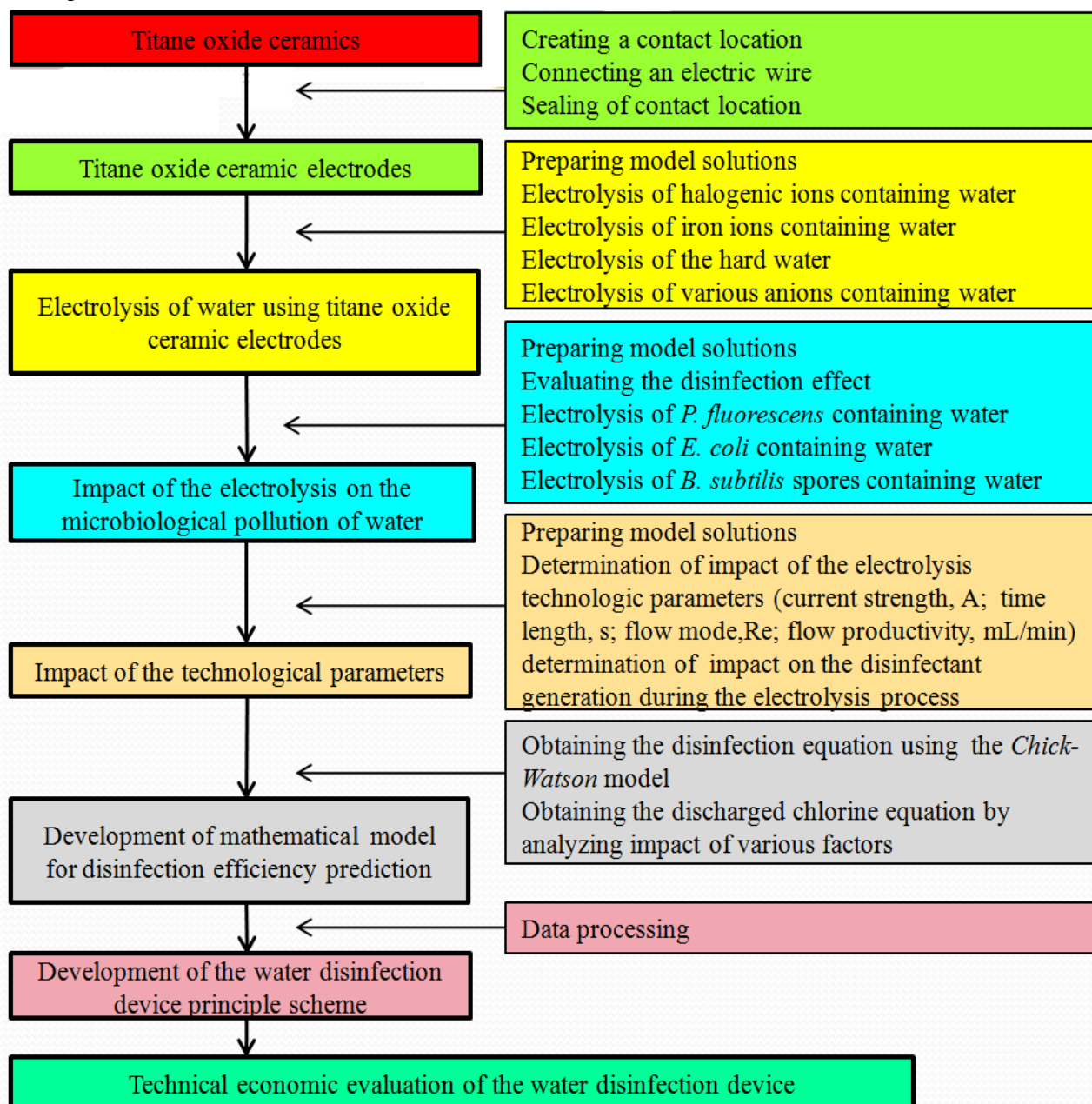
The most popular water purification and disinfection methods – chemical (chlorination and ozonizing of water) and physical (ultrasound processing, ultrafiltration, ultraviolet ray processing and electrolysis) are reviewed and compared in the fourth chapter “Water purification and disinfection methods”.

The fifth chapter “Titanium oxide ceramic for electrode materials manufacturing” reviews the general properties of titanium dioxide, titanium oxide ceramic and their electrical properties.

Based on the analysis of literature sources, it was found that titanium oxide is a sufficiently effective material for manufacturing electrodes, and the electrodes made from this material can be used for the electrochemical disinfection of the water by means of electrolysis.

EXPERIMENTS

Work process scheme



Performed analysis and research methods

1. Micro photographing with a MZ16 A stereo microscopy.
2. Micro photographing with a MIRA/TESCAN scanning electron microscopy (SEM).
3. Determination of electrode potential and voltamperogramming using „VoltaLab” PGZ 301 radiometer.
4. Processing the voltamperogram curves with Radiometer Analytical SAS, VolaMaster, software, version 5.6.0.
5. Analyzing crystal phase of the sample with X-ray diffractometer (XRD) Pananalitical X’pert PRO with a Cu cathode lamp radiance in a 2 θ range from 10 to 70°.
6. Element composition analysis with an electron microscopy (SEM) MIRA/TESCAN.
7. Determination of calcium and magnesium presence using the LVS ISO 6059:1984 standard.

8. Determination of iron presence using the LVS ISO 6332:2000 standard.
9. Determination of permanganate index using the LVS EN ISO 8467:2000 L/A standard.
10. Determination of chlorine presence using the LVS EN ISO 7393-3:2000 and LVS EN ISO 7393-1:2001 standards.
11. Determination of alkalinity using the LVS EN ISO 9963-1995 standard.
12. Processing the experimental data and obtaining mathematical coherences using the *Systat Software Inc. TableCurve 3D* software, version 4.0.
13. Determination of the amount of bacteria capable to build colonies.
14. Determination of amount of metabolically active – breathing bacteria, using the inking-up method and *FISH*.
15. The cell division ability determined using a modified *DVC* method and *FISH*.
16. The cell analysis was performed using the epifluorescent microscopy *Leica DM, LB*.
17. Pictures of the microorganisms in an epifluorescent microscopy were taken, using the *CoolSNAP Pro, Media Cybernetics* camera.
18. Microorganism pictures were edited using the *Image Pro Plus v. 4.5.1.* software.

Water electrolysis devices built

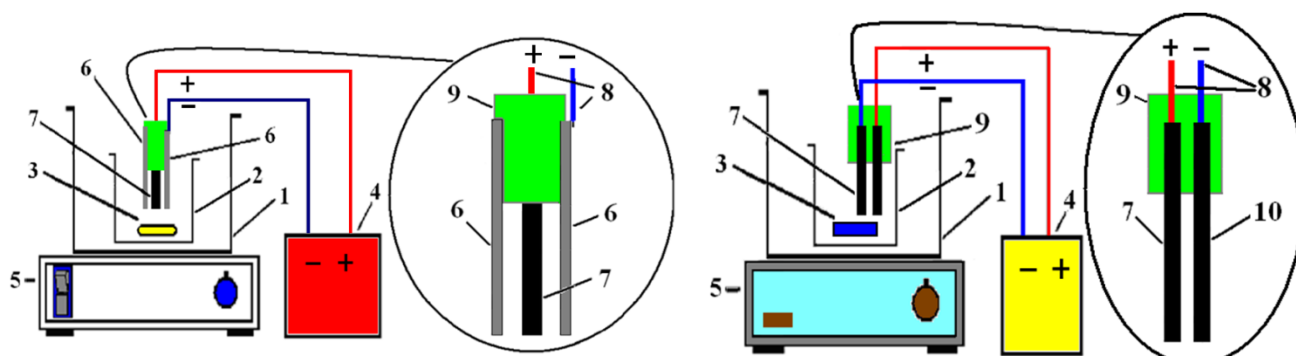


Figure 1. Scheme of the experimental electrolysis device in static mode: 1 – thermostat, 2 – electrolytic cell, 3 – magnet, 4 – DC source with a controllable voltage and the electric current strength, 5 – magnetic mixer, 6 – highly alloyed stainless steel cathode (AISI 304), 7 – TiO_{2-x} containing ceramic anode, 8 – electric wires, 9 – epoxy resin, 10 – TiO_{2-x} containing ceramic cathode

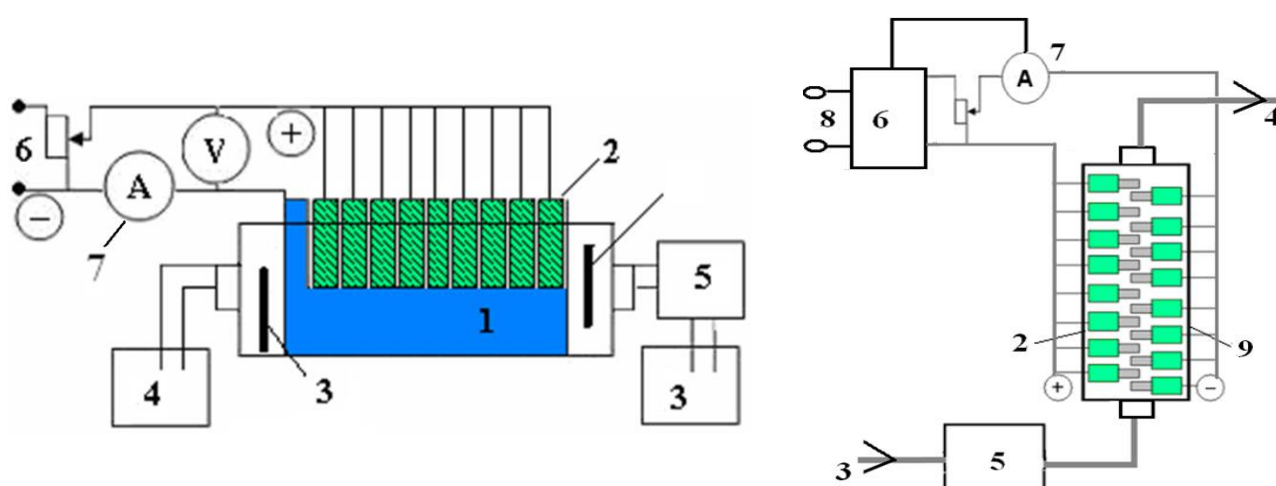


Figure 2. Experimental electrolysis device scheme in dynamic mode: 1 – stainless steel cathode, 2 – TiO_{2-x} containing ceramic electrodes, 3 – analyzed solution, 4 – processed solution, 5 – pump, 6 – the electric current source, 7 – amperemeter, 8 – the mains voltage, 9 – organic glass case

RESULTS AND DISCUSSION

Titanium oxide ceramic structure and physical properties

Samples thermal treatment in deep vacuum conditions results in a dramatic reduction of the specific electrical resistance value (Figure 3). Reduction of resistance can be explained by formation of oxygen vacancies and release of electrons in the TiO_2 crystal lattice [5]. Formation of oxygen vacancies in deep vacuum conditions, similar to thermal treatment of TiO_2 in a reducing environment, significantly increases its electro conductivity [6]. A known relation between the descriptive material properties and its electro conductivity is observed. Along with the increasing of the ceramic sample density with the increase of thermal treatment temperature and average grain diameter, sample's specific electric resistance also reduces: averagely from $0,76 \Omega \cdot \text{m}$ in the sample that was thermally treated in the air environment at the 1100°C temperature, before the thermal treatment in the high vacuum conditions; until $0,1 \Omega \cdot \text{m}$ in the sample that was thermally treated in the air environment at the 1350°C , before the thermal treatment in the high vacuum conditions.

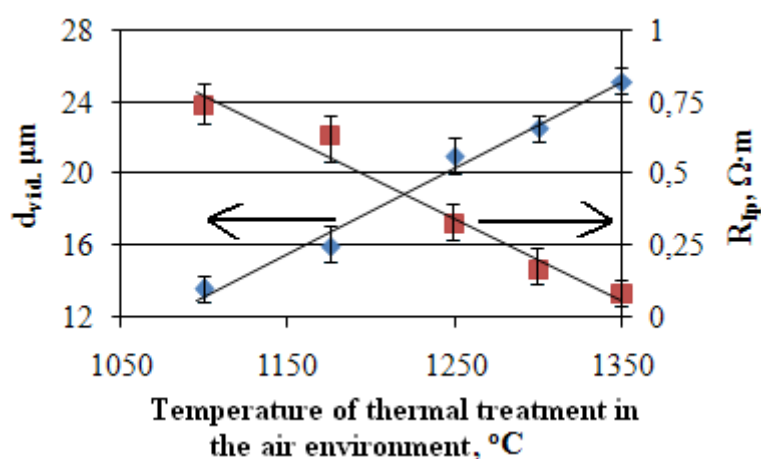


Figure 3. Average grain diameter (◆ – d_{vld}) and the specific electric resistance (■ – R_{ip}) depending on the thermal treatment temperature in the air environment and the following thermal treatment in the deep vacuum conditions at the 1075°C

It was found that thermal treatment of the ceramic samples in the deep vacuum conditions causes electric resistance reduction of ceramic, which allows using obtained titanium oxide ceramic as an electrode material in electrolysis devices.

For the experiment, voltamperograms were taken from TiO_{2-x} electrodes in the 1 mol/L H_2SO_4 and 1 mmol/L KCl solutions, increasing the voltage for 100 mV/s (Figure 4).

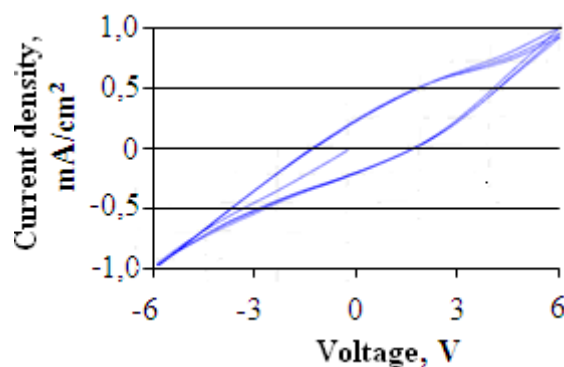


Figure 4. Voltamperogram of the TiO_{2-x} electrode in the 1 mol/L H_2SO_4 solution, with voltage increased for 100 mV/s

Voltamperograms taken from the TiO_{2-x} electrodes demonstrate formation of the hysteresis loop; also, further hysteresis cycles match the previous ones, which can be explained by a slight oxidizing of the TiO_{2-x} electrode surface which is reflexive, and by the fact that no remaining oxide layer is forming on the electrode surface. The similar voltamperograms were taken from the samples in both 1 mol/L H_2SO_4 , and 1 mmol/L KCl solutions.

In order to compare electrode materials, it is necessary to evaluate their efficiency of chlorine release during the electrolysis process, eliminating the device construction impact. For a comparison, a parameter which shows, how many mg Cl_2 forms from a 1 ampere-hour large charge (mg $\text{Cl}_2/\text{A}\cdot\text{h}$), running through an anode electrode is used. The efficiency of electrode material may vary depending on the chlorine ions concentration in the analyzed solution, achieving larger values at the larger chlorine ions concentrations. Chlorine release efficiency of the TiO_{2-x} ceramic electrodes upon the flowing charge was determined at the various chloride concentrations which are allowed to present in drinking water.

Comparing experimentally obtained chlorine outcomes with the mentioned in the literature [7], it was found that electrochemically generated chlorine may form on the TiO_{2-x} ceramic anode, its outcome can be compared with those mentioned in the literature and considered a very good outcome on IrO_2 and $\text{IrO}_2/\text{RuO}_2$ electrode materials [7] (see Table 1).

Table 1

Active chlorine release outcome on a single A·h					
Cl^- , mg/L	mg Cl_2/Ah				
	Pt*	BDD*	IrO_2^*	$\text{IrO}_2/\text{RuO}_2^*$	TiO_{2-x}
0	0	0	0	0	0
20	0,5	1	20	24	20
60	1	3	50	64	50
120	5	12	102	87	82
180	12	15	126	100	94

In his studies, Kraft [7] found that the IrO_2 and $\text{IrO}_2/\text{RuO}_2$ release chlorine more than 10 times better than Pt and BDD electrodes, and are prospective as electrode materials for electrochemical generation of chlorine from water. We have experimentally found that at the small chloride ions concentrations (less than 60 mg/L), the TiO_{2-x} ceramic electrodes, during electrolysis, release electrochemically generated chlorine in the same amount as the $\text{IrO}_2/\text{RuO}_2$ electrode, and are only slightly behind the IrO_2 electrode. As far as the cost of the TiO_{2-x} anatase powder, used for manufacturing the TiO_2 ceramic electrode, is much lower than the cost of material used in manufacturing of IrO_2 electrodes, it can be stated that the TiO_{2-x} ceramic is prospective for electrode manufacturing and realization of water disinfection with the electrolysis method.

Titanium oxide ceramic electrodes manufacturing technology development

In order to use titanium oxide ceramics as electrodes, one should add an electro conductive material to them. It usually requires additional research, since it cannot be achieved by direct brazing, and mechanical pressing cannot always guarantee a good contact. The electrode was manufactured from extruded and thermally processed in vacuum titanium oxide bars with connected and sealed electric wires at one end, according to the scheme (see Figure 5).

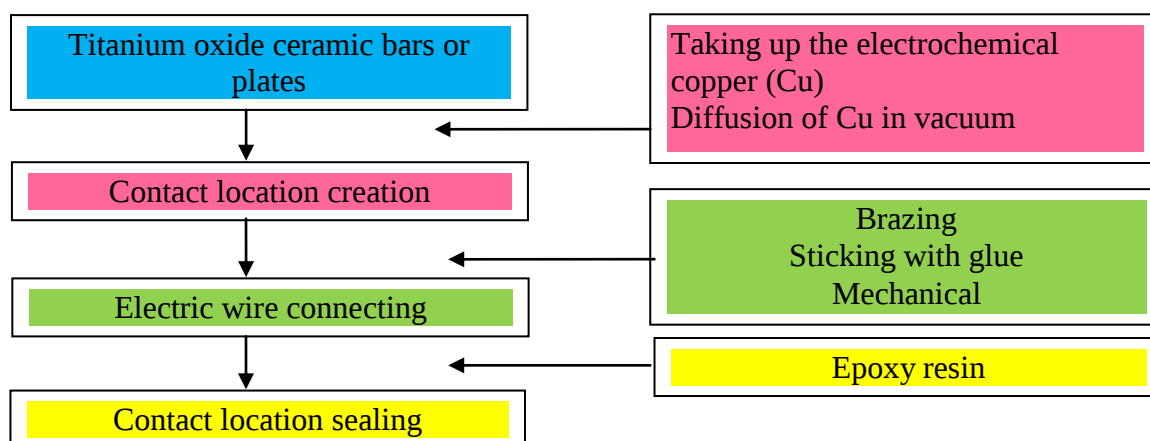


Figure 5. Electrode manufacturing scheme: a – copper is taken up the titanium oxide bars by diffusing it in vacuum or by electrolysis; b –electric wire is connected with the copper-covered bars by sticking with glue, brazing or screwed mechanically; c – contact location sealing

Electrolysis of water, using the titanium oxide ceramic electrodes

In order to determine impact of the different halogen ions on the electrolysis process, different halogen ion containing model solutions were electrolyzed (Cl^- , Br^- , I^-) (Figure 6). The initial ion concentration was 1 mmol/L at equal process parameters ($j = 8.1 \text{ mA/cm}^2$, $t^\circ = 25^\circ \text{ C}$), with intensive mixing.

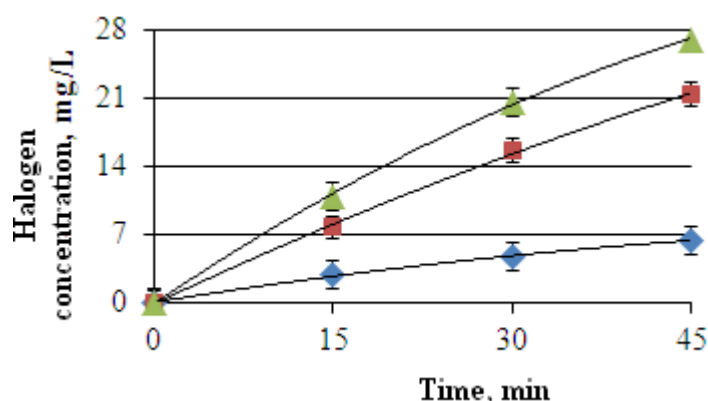


Figure 6. Variations of total released halogen amount depending on the electrolysis lengths for various halogen ions containing solutions: $\blacklozenge$ – Cl^- ; $\blacksquare$ – Br^- ; $\blacktriangle$ – I^- . The initial halogen ions concentration 1 mmol/L

As it is seen from Figure 6, amount of released halogen increases along with the increasing time of the electrolysis.

In order to compare obtained results in case of halogen ions with the results obtained when the ions contained in solution were inert during the electrolysis, the sulfate ion was chosen (by dissolving K_2SO_4).

During the electrolysis of analyzed solutions, pH rapidly increases, achieving during the first 15 minutes values from 8 to 9.5, which can be explained by intensive releasing of H_2 (Figure 7). The oxidizing-reduction potential also tends to increase. During the electrolysis, while corresponding halogen releases (Cl_2 , Br_2 , I_2), increasing of the solution oxidizing-reduction potential is observed (Figure 8), which can exceed 700 mV. The increasing of the oxidizing-reduction potential can be explained by the oxidizing of the halogen ion up to a free halogen. We should note that an average oxidizing-reduction potential value of 200-300 mV is characteristic to non-processed drinking water.

A more rapid increasing of the oxidizing-reduction potential is observed in case of solution containing Br^- ions. An opposite effect is observed at the solutions that contain SO_4^{2-} ions, their oxidizing-reduction potential values reduce until they achieve almost -200 mV. Performing electrolysis to the solution containing ions of Cl^- a sufficiently regular growth of the oxidizing-reduction potential value, depending on the electrolysis length is observed. Determining the relationship between variations of the oxidizing reduction values and the amount of halogen released during the electrolysis, including Cl_2 , the oxidizing-reduction potential can be used for process control and management.

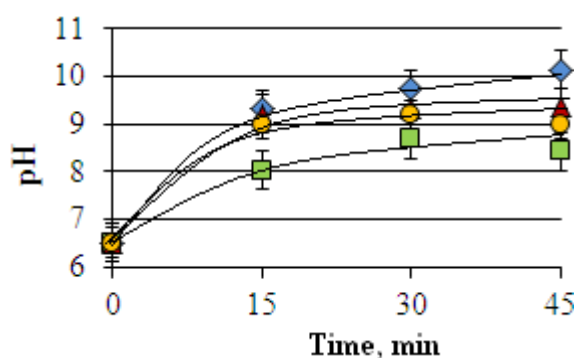


Figure 7. pH variations of the solution during the electrolysis process. The solution contains the following ions: $\blacklozenge$ – SO_4^{2-} ; $\blacksquare$ – Cl^- ; $\blacktriangle$ – Br^- ; $\bullet$ – I^- . Initial concentration 1 mmol/L, current strength 0.1 A

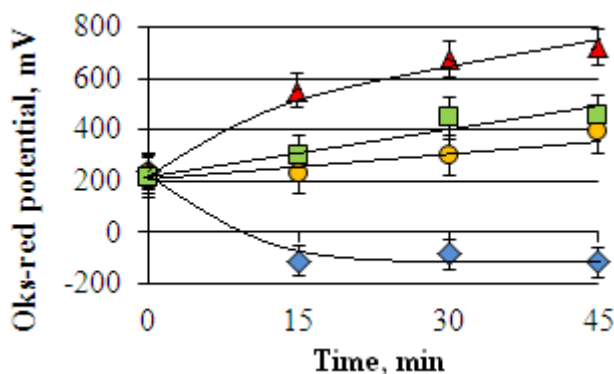
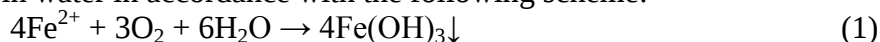


Figure 8. Oxidizing-reduction (Oks-red) potential changes of the solution during electrolysis. The solution contains the following anions: $\blacklozenge$ – SO_4^{2-} ; $\blacksquare$ – Cl^- ; $\blacktriangle$ – Br^- ; $\bullet$ – I^- . Initial concentration 1 mmol/L, current strength 0.1 A

Iron ions impact on water electrolysis process

In water, iron ions can consume the electrochemically generated chlorine and oxygen during oxidizing [8], which is mainly explained by oxidizing of Fe^{2+} in presence of oxidizer and creation of the insoluble Fe^{3+} compounds in water in accordance with the following scheme:



Fe^{2+} ion oxidizing can be intensified by water electrolysis. The bivalent ions that present in water could react on chlorine that was generated during the electrolysis process and reduce the amount of released chlorine. Oxygen that is released at the anode during the water electrolysis process, can act in the similar way, as it was mentioned before (see Equation 1). Performing the electrolysis of solution containing 35 mg/L chloride ions and 0.5 mg/L Fe^{2+} ions, no significant iron ions impact on the amount of released chlorine was observed. However, it was found that the electrolysis of solution with the further filtration through the quartz sand significantly reduces the total iron ions amount in the analyzed solution samples (Figure 9) and can be used for water deferrization.

As it can be seen on Figure 9, filtering through the quartz sand reduces amount of iron ions up to 20 times, but electrolysis of solution with the further filtering through a layer of quartz sand reduces overall iron ions concentration for 40-50 times. It can be explained by water saturation with oxygen during the electrolysis process, and only part of it is used for oxidizing of iron ions right on. Afterwards, when the solution is filtered through the layer of sand, an increased oxygen concentration advances Fe^{2+} ions oxidization. With the total iron ion concentration increasing in the processed solution, its concentration variation reduces during the electrolysis.

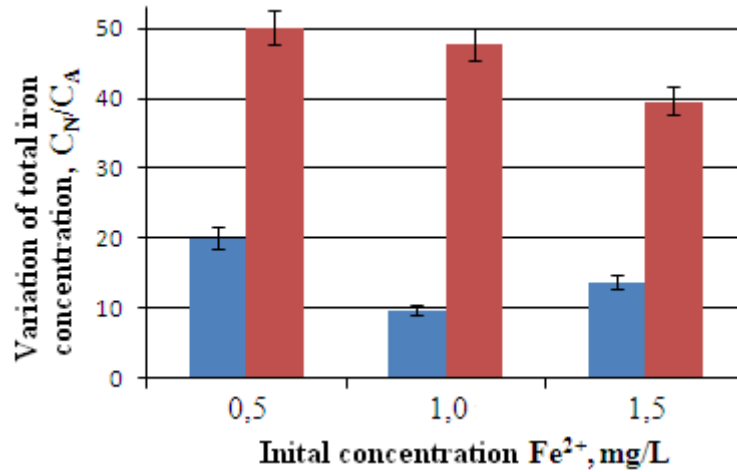


Figure 9. Total variation of iron ion concentration in the analyzed solutions: ■ – filtering through quartz sand; ■ – electrolyzing with the further filtering through quartz sand. C_N , C_A – total iron concentration in the initial and respectively processed solution, mg/L, $C_N = 0.5$; 1.0; 1.5. Electrolysis is performed at the current strength 0.09 A and flow speed 0.01 m/s 10 min

Water hardness impact on electrolysis process

When electrolyzing hard water, sediments are forming on the cathode electrode [9]. This work studies how the ions that ensure water hardness (Ca^{2+} and Mg^{2+}) and flow characteristics impact the intensity of disinfecting substance generation.

Sediments formation on electrode was modeled by electrolyzing $\text{Ca}(\text{HCO}_3)_2$ and MgSO_4 solutions.

With the CaCO_3 sediments forming on electrode, concentration of Ca^{2+} and HCO_3^- ions in the electrolyzed solution reduces, which causes solution's electro conductivity reduction. With the length of electrolysis increasing, the electro conductivity of the solution reduces; a more dramatic reduction is observed when electrolyzing the solution longer than for 15 minutes (Figure 10).

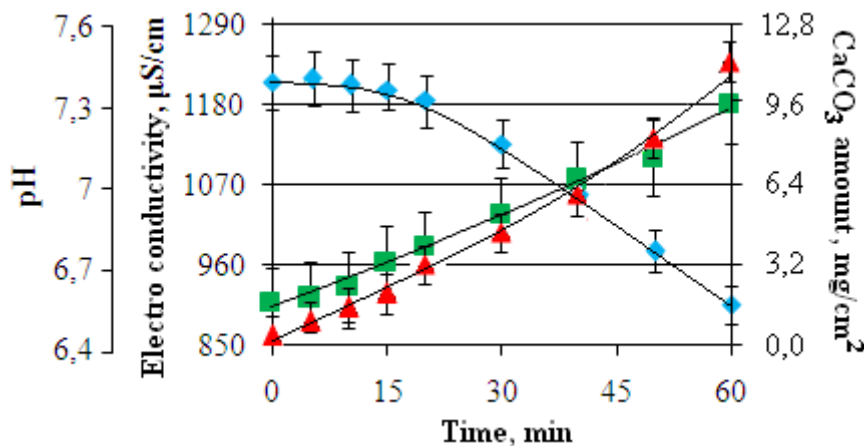


Figure 10. Electro conductivity of the electrolyzed solution (◆), amount of CaCO_3 sediments (▲) on electrode surface and solution pH (■) variations depending on the electrolysis length. Initial $\text{Ca}(\text{HCO}_3)_2$ solution concentration – 4.5 mmol/L, current strength 0.1 A, $\text{Re}_c = 18\,000$

Naturally, with the electrolysis length increasing, flowing current charge increases and reactions that it causes on the electrode surface become more intensive. During the electrolysis, the gases that were released at the electrodes (H_2 , O_2) can reduce CO_2 solubility in water, which causes transformation of $\text{Ca}(\text{HCO}_3)_2$ into an insoluble form of CaCO_3 . Hydrogen, released at the cathode,

reduces the H^+ ion concentration, and the alkalinity of solution increases (see Figure 10), which also advances insoluble $CaCO_3$ generation on the electrode in the form of the sufficiently thick sediments (Figures 10 and 11).

With the $Mg(OH)_2$ sediments forming in case of $MgSO_4$ solution electrolysis, there is a solution electro conductivity growth observed in the beginning of the process, which is opposite, comparing with the electrolysis of the $Ca(HCO_3)_2$ solution. The pH value of the electrolyzed solution quickly reduces, which can be explained by sedimentation of $Mg(OH)_2$ (see Figure 12).

The amount of the $Mg(OH)_2$ sediments released on the cathode increases with the electrolysis length increasing, similar to the case of electrolysis of the $Ca(HCO_3)_2$ solution, and is explained by the increase of intensity of the charge flowing through and the reaction it generates.

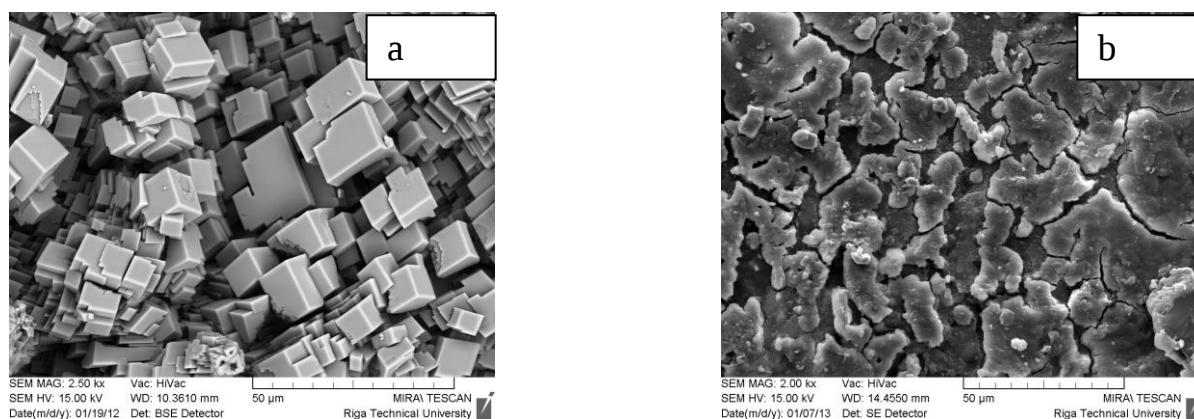


Figure 11. SEM microphotographs of the sediments formed on the electrode surface during electrolysis:

a – $CaCO_3$, b – $Mg(OH)_2$. Processing for 1 h with current strength of 0.1 A, $Re_c = 18\ 000$

Structure and morphology of sediments formed on the electrode surface were analyzed, using X-ray structure analysis and scanning electron microscopy. $CaCO_3$ and $Mg(OH)_2$ sediments formed during electrolysis of calcium hydrogen carbonate and magnesium sulfate prove the maximums, characteristic to the $CaCO_3$ calcite crystal modification, and diffraction maximums, characteristic to the $Mg(OH)_2$ brucite crystal modification, observed on the sample XRD diffractograms.

SEM microphotographs show explicit $CaCO_3$ formations, characteristic to the calcite crystal modification, as well as the crystal modification of $Mg(OH)_2$ brucite (see Figure 11).

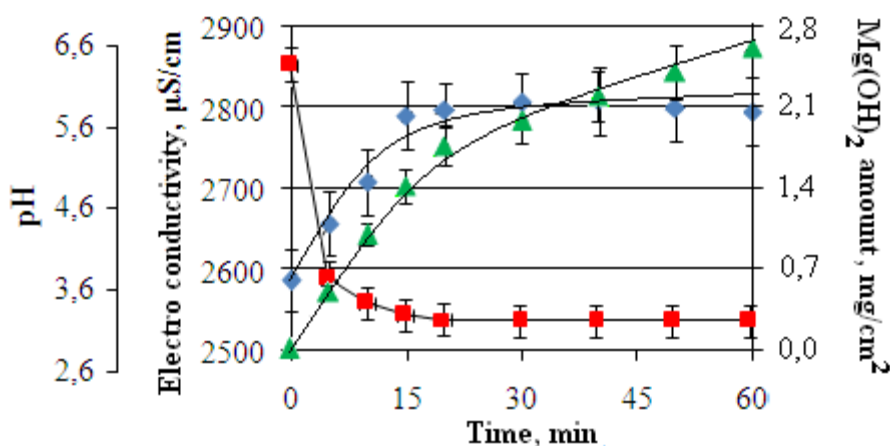


Figure 12. Variations of the electro conductivity of the electrolyzed solution (◆), amount of $Mg(OH)_2$ sediments (▲) on electrode surface and solution pH (■) depending on the electrolysis length. Initial concentration of $MgSO_4$ solution - 15 mmol/L, current strength 0.1 A, $Re_c = 18\ 000$

Forming of sediments on electrode during the electrolysis process can impact the amount of released chlorine and therefore the disinfection efficiency. Water hardness impact on the the released chlorine amount is evaluated by adding calcium hydrogen carbonate to the model solution 1 mmol/L KCl (Figure 13).

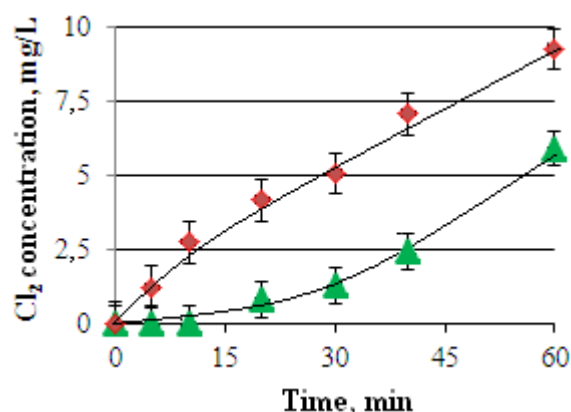


Figure 13. Chlorine release dependence from the electrolysis length and initial concentration of Ca^{2+} ions: $\blacklozenge$ – 0 mmol/L; $\blacktriangle$ – 4.5 mmol/L. Current strength 0.1 A, $\text{Re}_c = 18\,000$

As it can be seen, the chlorine release kinetics during the electrolysis process from a solution not containing ions of calcium and from a solution containing 4.5 mmol/L of Ca^{2+} (which corresponds with very hard water characteristics) are substantially different. In case of hard water, release of chlorine can be detected after the first 10 minutes of process running. It can be explained by various side reactions on the electrode surface, in which chlorine, produced during the electrolysis process, can be involved; for example:



One of the electrode cleaning approaches from sediments released during the electrolysis is variation of poles of attached electric wires. To achieve that, a solution that contained $\text{Ca}(\text{HCO}_3)_2$ was electrolyzed for 1 hour, during which, as it was mentioned above, CaCO_3 sediments were formed on the cathode of the electrolytic cell; that can be proven by increasing of the Ca^{2+} ions concentration in the solution obtained by dissolving sediments in the acid. After one hour of electrolysis, electrode current pole was changed (see Figure 14). After pole variation, a cathode which was located in the basic environment became an anode which is located in the acidic environment.

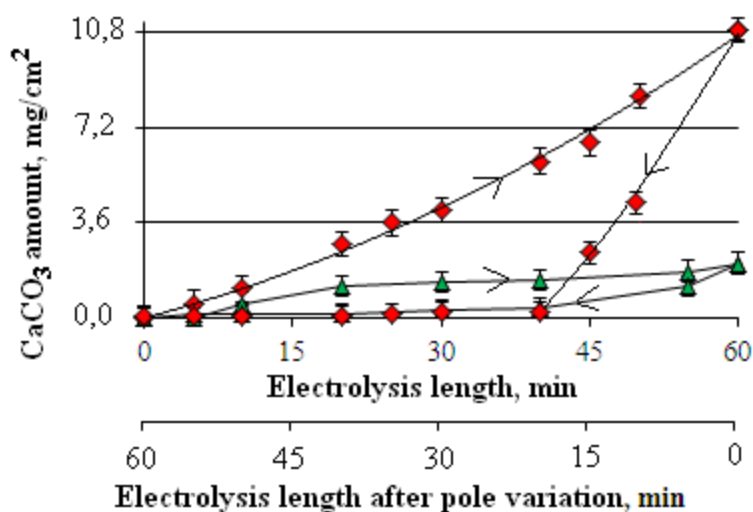


Figure 14. Variation of the CaCO_3 sediments amount on the electrode surface before and after variation of the current pole depending on the electrolysis length and flow mode: $\blacktriangle$ – $\text{Re}_c = 0$; $\blacklozenge$ – $\text{Re}_c = 18\,000$. Current strength 0.1 A

The sediments dissolve well in an acidic environment and easily detach from the electrode already during the first 10-15 minutes after current pole variation. Intensive electrolyzed solution turbulence advances both formation of sediments and electrode cleaning from those after current pole variation. With the electrode length increasing, amount of sediments on the cathode increases as well, reducing water hardness. Obviously, vigorous mixing of electrolyzed solution advances the performance of the above described reaction. As opposed to the impact of Ca^{2+} ions on chlorine release, presence of Cl^- ions in CaCO_3 and sedimentation of $\text{Mg}(\text{OH})_2$ does not impact the kinetics. Similar to the case of CaCO_3 sediments, also in the case of $\text{Mg}(\text{OH})_2$ sediments, the electrode is free from them in 10-15 minutes after current pole variation.

Water anions impact on electrolysis process

Presence of various ions in the water not only changes its electro conductivity, but can also impact the release of chlorine during the electrolysis process.

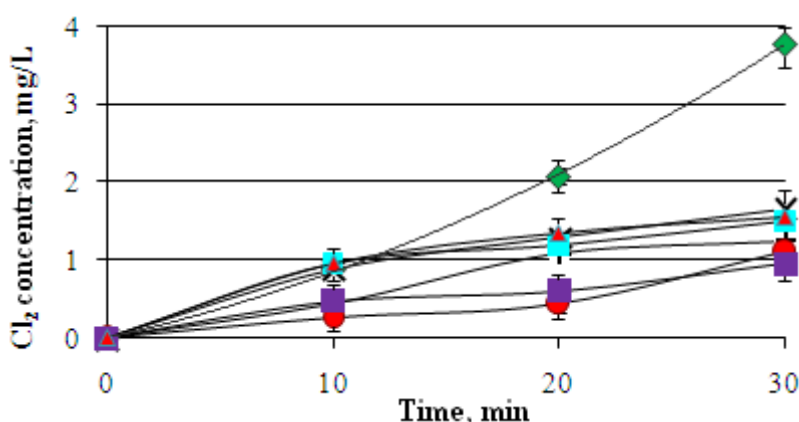


Figure 15. Amount of released chlorine depending on the electrolysis time and presence of the other ions in the solution. $I = 0.1\text{A}$, concentrations of used ions in the solution - 1 mmol/L

◆ - Cl^- ; + - HPO_4^{2-} ; X - NO_3^- ; ■ - H_2PO_4^- ; ▲ - SO_4^{2-} ; ● - PO_4^{3-} ; ■ – all ions.

Performing water solution electrolysis which, apart from ions of Cl^- contains several ions of other kinds (Figure 15), it was found that in all the cases the amount of the released chlorine reduces. Also, impact of separately used anions on the chlorine release is similar. Obviously, presence of different anions in the solution, similar like in case of the hard water, advances the side reaction performance on the anode which reduces formation of active chlorine.

Electrolysis impact on water microbiological pollution

In this work, impact of the electrolysis parameters on the cells of certain microorganisms, their metabolic activity, cultivation ability and ability to divide is studied.

At first we have chosen *Pseudomonas fluorescens* (*P. fluorescens*) bacteria which is fairly widely spread in water supply systems and easily submits to disinfection with classical water disinfection approaches.

In the solutions containing Cl^- or Br^- ions, a significant bacteria colony forming units (CFU) reduction is observed. In solutions containing SO_4^{2-} ions, disinfection effect of electrolysis is hardly observed, which allows concluding that disinfection effect depends on halogen compounds in water generated during the electrolysis, and not on the current flowing through the solution (see Figure 16).

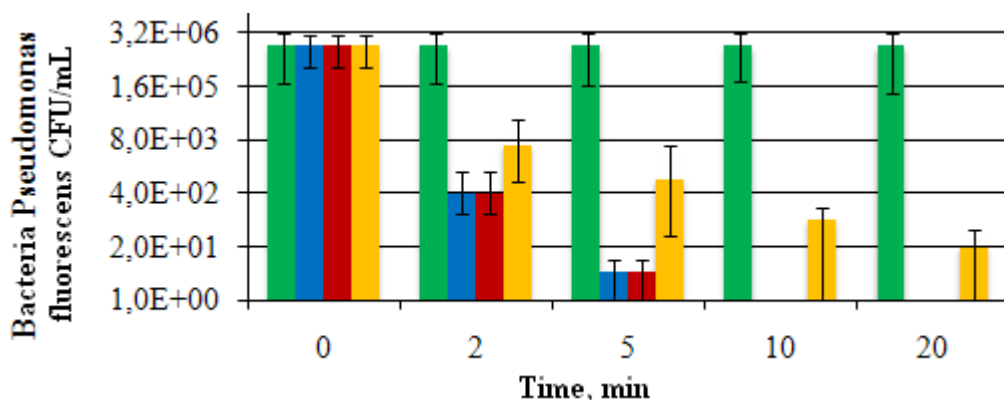


Figure 16. Variations of the cultivable CFU of *P. fluorescens* depending on the electrolysis length, in the solutions containing ■ – SO_4^{2-} , ■ – Cl^- , ■ – Br^- , ■ – I^- ions with initial concentration 1 mmol/L. Current strength 0.1 A

As the Figure 16 shows, during the Cl^- and Br^- ions containing water electrolysis, number of *P. fluorescens* CFU is reduced for more than 99.9% during the first minutes of disinfection; after 10 minutes of disinfection, no more *P. fluorescens* CFU are detected.

Since the electrolysis of iodide ions containing solution demonstrates poorer disinfection characteristics than the chloride and bromide containing ones, and bromide ions are less common in the natural waters, only water solutions containing Cl^- ions were used in the further experiments. As the test model microorganism for evaluation of water pollution, *Escherichia coli* were used; it is also used as the drinking water hygienic quality indicator. In this work, impact of the electrochemical disinfection on metabolic activity, ability to cultivate and ability to divide of the *E. coli* bacteria was studied.

In order to determine how the electric current impacts *E. coli* vitality, and are there other chemical compounds with disinfection properties created as a result of this impact, variations of *E. coli* were measured by adding *E. coli* cells and sulfate ions (SO_4^{2-}) to distilled water in various concentrations. All the samples were electrolyzed for 15 minutes at minor current strengths ($j = 8.1 \text{ mA/cm}^2$, $\text{pH } 7 \pm 0.2$, $t^\circ = 23 \pm 2^\circ \text{C}$).

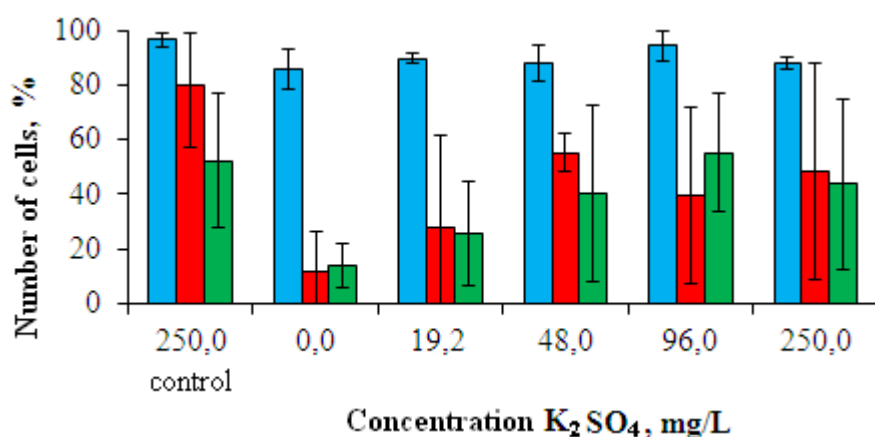


Figure 17. Number of *E. coli* cells, %: metabolically active - breathing (■), cultivable (■) and DVC positive – with the ability to divide (■). Processed for 15 minutes at current strength 0.1 A

The obtained results show that presence of SO_4^{2-} ions in electrolyzed solution does not ensure a significant reduction of *E. coli* bacteria amount (see Figure 17).

KCl was added to the analyzed water that contained *E. coli* bacteria, creating model solutions of various concentrations (from 6.8 to 100 mg/L Cl^-). The chosen KCl concentrations corresponded

to the ones in real water, where the maximum allowed chloride ions concentration cannot exceed 250 mg/L.

The obtained results prove that disinfection efficiency is the result of creation of oxidizable chlorine compounds and not the impact on radicals' creation in water because of energy applied. The obtained results show that disinfection efficiency is resulted by oxidizable compounds formed by chlorine and not the impact of the electric energy on radicals' formation in the water.

Chloride ion concentration impact on disinfection efficiency during the electrolysis process, analyzing the *E. coli* cells, is shown on the Figure 18. It is clearly seen that already at the concentration around 7 mg/L Cl^- electrolysis passivates *E. coli*, they are no longer cultivable, do not demonstrate an ability to divide and do not breathe, meaning that they are not viable. Chloride ions concentration in the solution corresponds with the concentration which is characteristic to ground and underground waters.

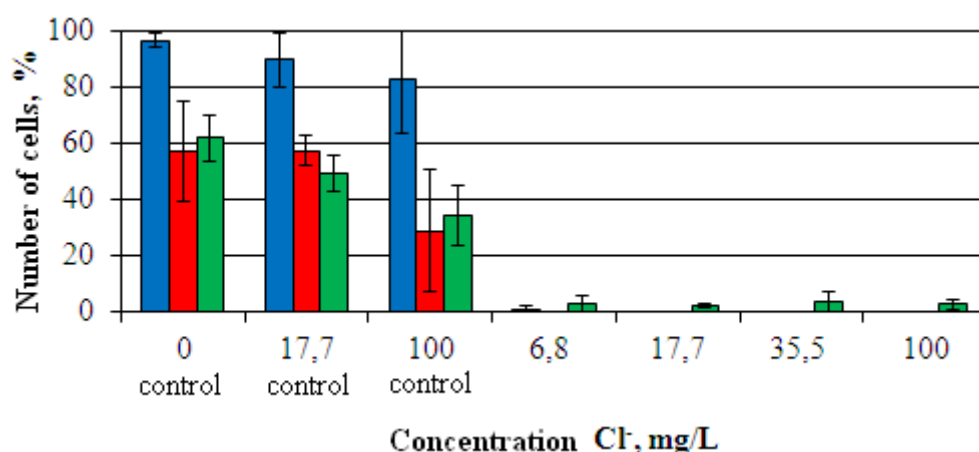


Figure 18. Chloride ion concentration impact on disinfection efficiency, analyzing *E. coli* cells, %: metabolically active – breathing (■), cultivable (■) and DVC positive – with an ability to divide (■). Processed for 15 minutes with the current strength of 0.1 A.

Current strength impact on *E. coli* cells was analyzed by processing it for 15 minutes at the chloride ion concentration of 6.8 mg/L (Figure 19.). Evaluating obtained results, it can be seen that increasing current strength over 0.02 A is sufficient for all the *E. coli* cells deactivation. It's to be noted that the cultivation ability of the bacteria is eliminated at first, then the cells lose their ability to divide and afterwards lose the breathing ability (are no longer viable).

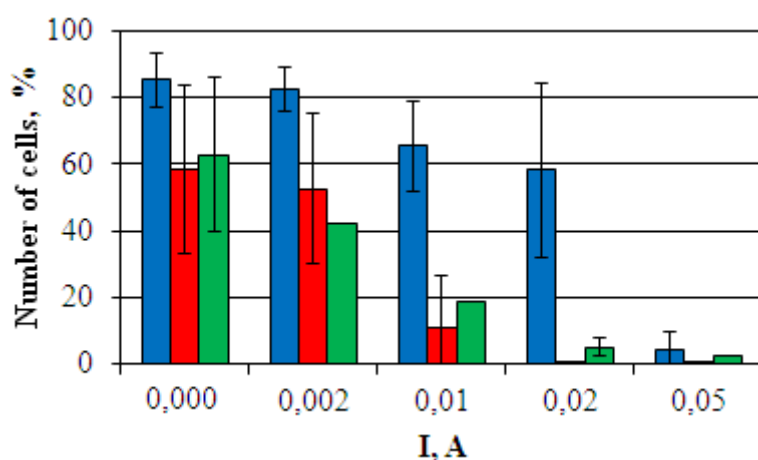


Figure 19. Impact of the current strength on the disinfection efficiency, analyzing the *E. coli* cells %: metabolically active - breathing (■), cultivable (■) and DVC positive – with an ability to divide (■). Initial concentration of chloride ions 6.8 mg/L

Kinetics of water disinfection was analyzed on the samples with chloride ion concentration of 6.8 mg/L, which were processed with 0.02 A electric current. The previous experiments shown that the concentration of the released chlorine is approximately 0.5 mg Cl_2/L . Afterwards, when this concentration is achieved in the sample, *E. coli* concentration reduces exponentially. The ratio, at which the concentration reduction of *E. coli* occurred, was similar at both cultivable and able to divide cells. After 15 minutes, neither of the mentioned kinds of *E. coli* cells was detected in the samples. However, breathing cells concentration went down with a different tendency: more rapid in the beginning and almost stopped after 3 minutes after the experiment beginning (Figure 20).

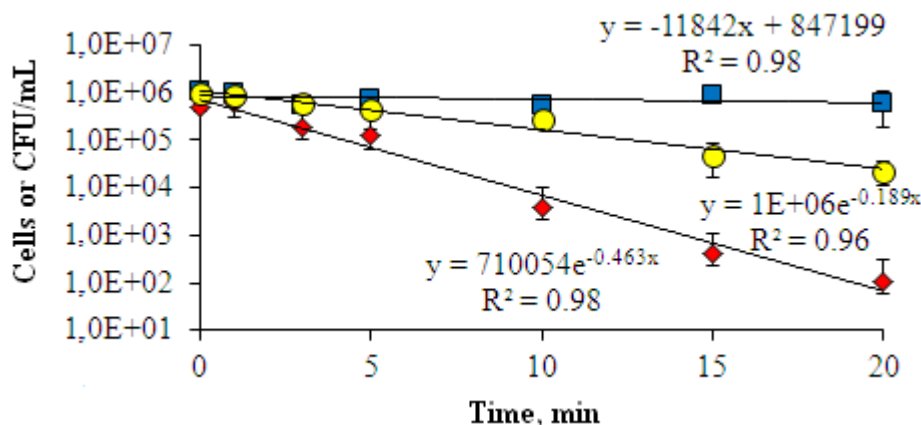


Figure 20. Disinfection efficiency depending on the time (initial chloride ions concentration 6,8 mg/L, current strength 0.02 A, pH 7 ± 0.2 , $t^0 = 23 \pm 2^\circ \text{C}$). *Escherichia coli*: breathing ability (■), ability to divide (●), cultivability (◆)

In this work, we have also analyzed *Bacillus subtilis* spore viability after electrolyzing in low chloride ions concentration water. *B. subtilis* spores were chosen, since they are considered one of the most disinfection resistant species. Also, *B. subtilis* has similar properties like *Bacillus anthracis*, which is pathogenic to humans and may cause anthrax and filter into drinking water like a bioterrorism agent.

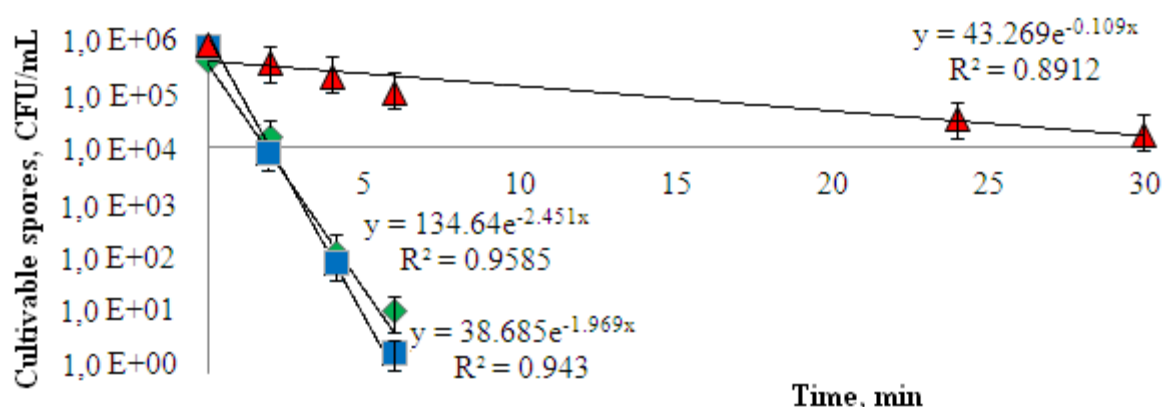


Figure 21. Impact of the solution pH on the electrolysis disinfection efficiency, analyzing the amount of colony forming *Bacillus subtilis* bacteria units: pH 6 (■), pH 7 (◆) and pH 8 (▲). Current strength 0.1 A

Electrolysis was performed at various solution pH values. At pH 8, the poorest efficiency has been observed (reduction is significantly less than 99%), cultivable spores (figure 21) were detected after 30 hours, which could be related to the dissociation of hypochlorite acid at the higher pH values [10]. Electrolyzing solution at pH 7 and pH 6 *B. subtilis* spore cultivability reduction for 99% was achieved already after 1 h.

In the case of the real water, other various ions can be found in the solution along with the chloride ions as it was proven earlier, that can take part in side reaction on the electrodes, reducing the amount of released chlorine and the disinfection efficiency during the electrolysis process.

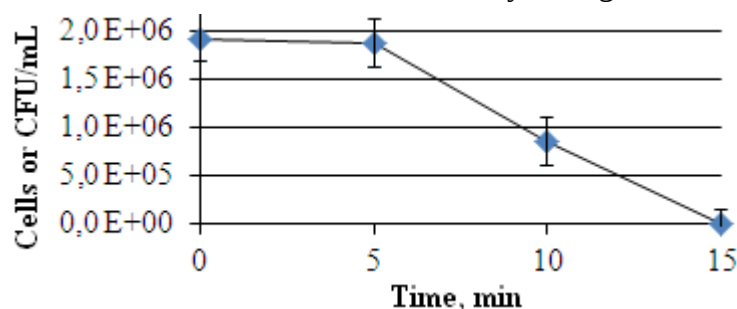


Figure 22. Well water disinfection efficiency depending on length (chloride ions concentration 9 mg/L, current strength 0.1 A, pH 7 ± 0.2 , $t^0 = 20 \pm 2^\circ \text{C}$).

Electrolyzing private well water containing 9 mg/L Cl^- ions and other ions that are characteristic to drinking water, the chlorine amount required for disinfection is formed in the water. As the Figure 22 shows that in 15 minutes, cultivability of *E. coli* bacteria reduces for more than 6 log, completely disinfecting the water. The obtained results allow affirming that natural water containing chloride ions in even smaller concentrations can be disinfected with electrolysis.

In general, electrochemical disinfection of drinking water using TiO_{2-x} electrodes at the low concentrations is the most effective at pH 6, which can also be observed at the traditional chlorination. This research confirms that the electrochemical disinfection is more effective for neutralization of bacteria spores – the most resistant forms of microorganisms, however, for this method to be used in wider circumstances, possible forming of by-products should be investigated and disinfection efficiency of deactivation of biofilm-forming bacteria assessed, for these bacteria are hazardous for the drinking water quality.

Technological parameters impact on water processing with electrolysis in dynamic regime

One of the factors that can impact the amount of released chlorine during the electrolysis is the electrode surface area. Electrolyzing a solution with chloride ion concentration of 1 mmol/L, it is observed that, at a constant current strength, number of electrodes (area) hardly impacts the amount of released chlorine (Figure 23).

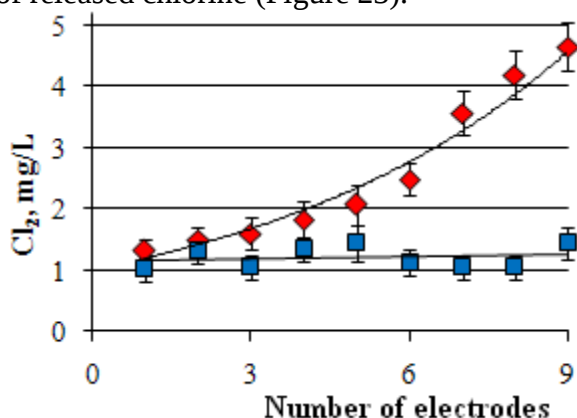


Figure 23. Released chlorine concentration depending on the number of attached electrodes: $\blacklozenge$ – at constant current density 8.1 mA/cm^2 ; $\blacksquare$ – at constant current strength 0.1 A. Chloride ions concentration 1 mmol/L, flow speed 0.01 m/s

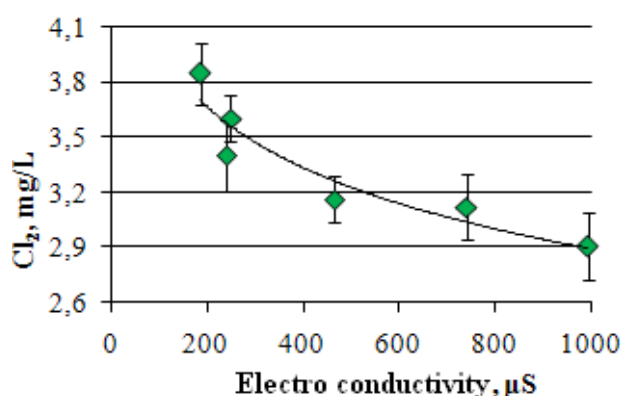


Figure 24. Released chlorine amount depending on the solution electro conductivity with a constant current density 8.1 mA/cm^2 . Chloride ions concentration 1 mmol/L, flow speed 0.01 m/s

Whereas, performing electrolysis in the same conditions at constant current density, amount of released chlorine increases when the electrode surface area increases. With the electrode surface area increased 9 times, amount of the released chlorine increases 3.5 times from 1.4 mg/L up to almost 4.5 mg/L.

With solution electro conductivity directly related to the other ions presence in solution increasing, released chlorine amount significantly reduces (Figure 24). Increasing the water electro conductivity for 6 times reduces the chlorine release for 1.25 times. Other ions presence advances the side reactions on the anode, reducing the active chlorine forming.

Intensity of the disinfection substance generation and electrolysis efficiency in the water engineering systems may change with the water consumption and current parameters changing. The water flow speed determines length of the electric current work. By variation of the flow speed and electric current strength, it is possible to ensure a certain concentration of the disinfection substance in the solution.

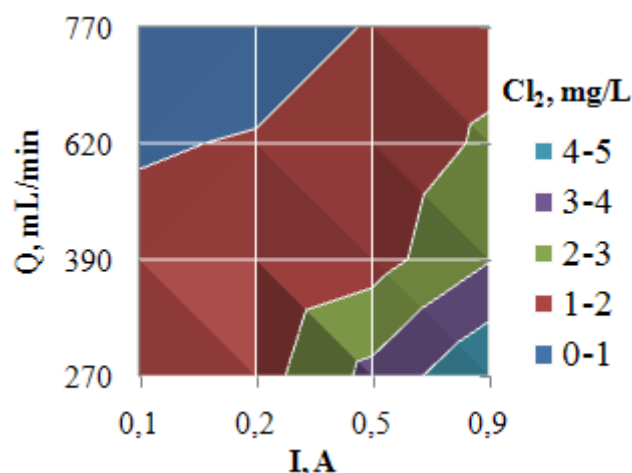


Figure 25. Isofields of Cl_2 amount released in electrolysis process depending on the flow regime Q (mL/min) and current strength (A). Chloride ions concentration 1 mmol/L

As figure 25 shows, the amount of Cl_2 released during the electrolysis increases when, in certain boundaries, water consumption Q is reduced and the electric current strength increased. The obtained coherences allow predicting Cl_2 concentrations required for effective disinfection ensuring by variation of electrolysis parameters.

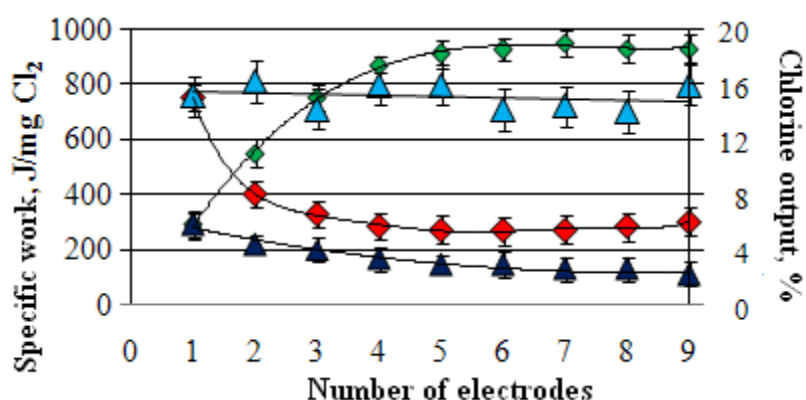


Figure 26. Specific electrolysis process work outcome and released chlorine (out of theoretically possible at the current) depending on number of electrodes: $\blacklozenge$ – specific electrode process work and $\blacklozenge$ – outcome of released chlorine at constant current density 8.1 mA/cm^2 ; $\blacktriangle$ – specific electrolysis process work and $\blacktriangle$ – outcome of released chlorine at constant current strength 0.1 A . Initial chloride ions concentration 1 mmol/L

Electrolytic cell efficiency is characterized by chlorine amount released in electrolysis process, out of theoretically possible, and consumed specific current work for realization of the process.

During electrolysis, at constant current strength (0.1 A), increasing number of electrodes (area), amount of released chlorine hardly changes, but the specific work of electric current for release of chlorine reduced for 2.7 times (Figure 26). The reduction of current specific work is explained by reduction of total electrolytic cell resistance. Realizing electrolysis at the constant current density and increasing number of electrodes, the amount of released chlorine reduces, but specific work of electric current to release chlorine increases. Performing electrolysis at a certain current density, with electrode surface area increasing, a current strength also grows which increases the energy consumption for electrolyzing.

Mathematical model development for electrochemical disinfection efficiency prediction

Using the data obtained in the experiment and *Chick – Watson* disinfection model [11], an equation describing efficiency of water electrochemical disinfection in the electrolytic cell using TiO_{2-x} ceramics was obtained. The correlation ratio of 0.66 was determined, which allows to describe disinfection processes with the following equation:

$$N = N_0 e^{(-0.66Ct)}, \text{ where} \quad (3)$$

N – *E. coli* concentration after disinfection, CFU/mL;

N_0 – initial *E. coli* concentration before disinfection, CFU/mL;

C – total chlorine concentration in the water sample, mg/L;

t – contact time, min;

0.66 – correlation factor

Processing the experimental data with *Systat Software Inc. TableCurve 3D*, version 4.0, we obtained an equation which describes a total amount of obtained chlorine.

Accepting the initial condition that water flow productivity is 0.055 L/min, the fundamental equation is obtained (4) in which, amount of released chlorine depends on the applied current strength and concentration of chloride ions in the solution.

$$C_{\text{Cl}_2} = (0.173 - 3.463 \cdot I + 0.0126 \cdot C_{\text{Cl}^-} + 18.75 \cdot I^2 - 0.000067 \cdot (C_{\text{Cl}^-})^2 + 0.785 \cdot I \cdot C_{\text{Cl}^-}), \text{ where} \quad (4)$$

C_{Cl_2} – amount of released chlorine, mg/L;

I – applied current strength, A;

C_{Cl^-} – concentration of chloride ions in the solution, mg/L.

The amount of released chlorine is also influenced by flow productivity. An equation which describes impact of the flow regime on released chlorine amount is obtained by bringing in the equation ratio k_1 , which changes depending on flow productivity. The ratio is calculated separately at all the chloride ions concentrations in water and applied current strengths and, it was found that k_1 changes only depending on the flow productivity (Figure 27). For a more convenient determination of the ratio, k_1 value variations were plotted depending on productivity (Figure 27), thus making it possible to determine an appropriate ratio depending on the desired flow dynamics in a simple way. By bringing in an additional ratio in the equation 4, the following equation is obtained:

$$C_{\text{Cl}_2} = (0.173 - 3.463 \cdot I + 0.0126 \cdot C_{\text{Cl}^-} + 18.75 \cdot I^2 - 0.000067 \cdot (C_{\text{Cl}^-})^2 + 0.785 \cdot I \cdot C_{\text{Cl}^-}) \cdot k_1, \text{ where} \quad (5)$$

k_1 – empirically obtained ratio.

An equation which could also describe other ions impact (analyzed using sulfate ions) on the released chlorine amount was obtained by bringing in the k_2 ratio that changes depending on sulfate ions concentration in the water, into the equation. The ratio was calculated depending on sulfate ions concentration in the water (Figure 28). Implementing the newly obtained ratio k_2 to the equation 5, the equation 6 was obtained:

$$C_{Cl_2} = (0.173 - 3.463 \cdot I + 0.0126 \cdot C_{Cl^-} + 18.75 \cdot I^2 - 0.000067 \cdot (C_{Cl^-})^2 + 0.785 \cdot I \cdot C_{Cl^-}) \cdot k_1 / k_2, \text{ where } (6)$$

k_2 – empirically obtained ratio

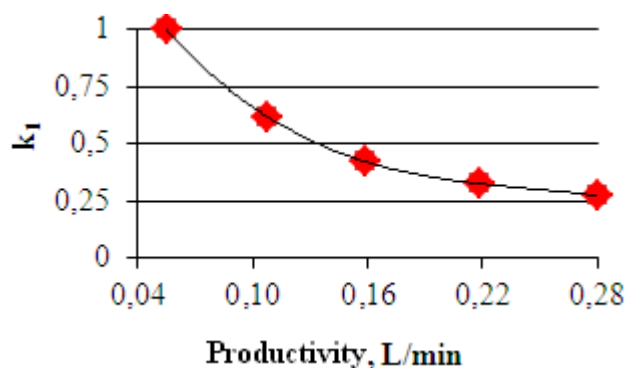


Figure 27. Ratio value depending on water flow productivity

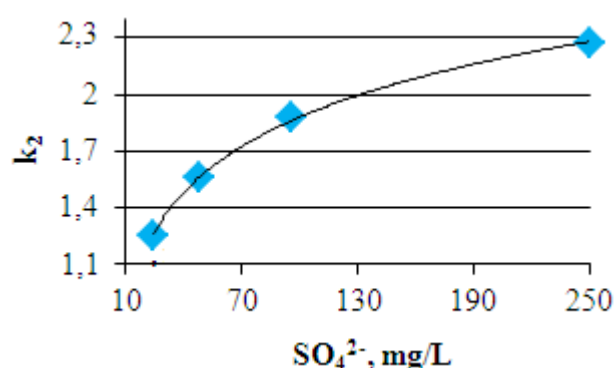


Figure 28. Ratio value depending on sulfate ions concentration

Using equations 5 and 6 allows water disinfection process prediction and management. Obtained equation 6 is valid within a certain set of chosen parameters (applied current strength 0.1 – 0.4 A, chloride ions concentration 0~250 mg/L, productivity may vary from 0.055 L/min until 0.280 L/min, and sulfate ions concentration is 24 – 250 mg/L).

Principle water disinfection device scheme and its technical economic assessment

Based on the experimental data obtained as a result of this work, a principle water disinfection device scheme was developed (Figure 29) and its technical economic assessment was performed.

Processed water is fed into the device through the intake point (1) which is followed by a pump (2) in case if the electrolysis device is not connected to water supply. Processed water is filtered before entering the electrolytic cell using a cartridge type mechanical filter (3). Electrolytic cell (7) consists of ceramic cathode and anode electrodes connected into line (5) located opposite each other; number of those may vary from 20 to 30. Electrodes are made from TiO_{2-x} ceramics (6). Strength of electric current applied to the cell is controlled by amperemeter. (9). In order to ensure a long-term function of device, current strength of one pair of electrodes cannot exceed 0.1 A; when working at a maximum power, cell voltage cannot exceed 24 V. Electrolysis is automatically controlled by using connection between released chlorine amount and electrolyzed fluid ORP determined by a specific ORP sensor (10). Applied current strength of electrolytic cell (A), sensor ORP (mV) and flow detector signals are analyzed and controlled by a control console (11) switched to a current source (AC converter, accumulator) (13). Analyzing chlorine leak amount in waters, current strength applied to electrolytic cell may be increased or reduced. Flow detector (14) controls the fluid flow through the electrolytic cell so that the current could be turned down automatically by the control console – it would not allow uncontrollable formation of gas during the electrolysis on the electrode surface in a closed system.

Developed water disinfection device can be used on the local water collection venues, in emergency situations and for water preparation for specific needs.

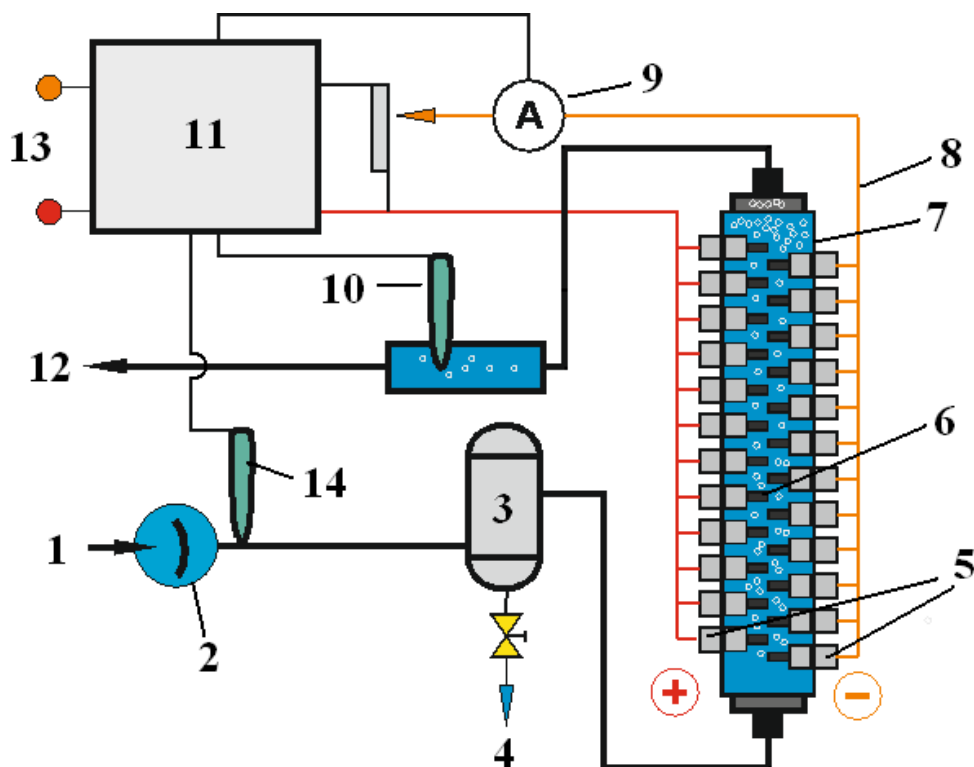


Figure 29. Technological scheme of water disinfection device: 1 – disinfected water; 2 – pump; 3 – mechanical filter; 4 – sewerage output; 5 – electrodes; 6 – TiO_{2-x} ceramics; 7 – electrolytic cell; 8 – electric wires; 9 – amperemeter; 10 – Oxidizing-reduction potential (ORP) sensor; 11 – control console; 12 – disinfected water; 13 – direct current source; 14 – flow detector.

In this work, social economic analysis of electrochemical disinfection method was performed as against situation when no water purification activities were conducted – zero alternative. Zero alternative is a typical situation for Latvian citizen's individual water supply systems.

Device cost is assessed as 150.0 LVL for a unit (no VAT included), its service time is 15 years and it is considered that all the devices will be sold during the first 5 years. Base year is 2012. Data is taken from main macroeconomic indicators and economic forecasts found at Financial Ministry home page [12]. State social discount rate for the next 15 years is 5.5%. GDP growth [12] in comparative prices was used for numeric data prediction. Development costs of device were accounted. As Table 2 shows, installation of electrolytic device brings 492868,- LVL benefit to state due to productivity growth and 40317191,- LVL from device sale. Device production costs are 32253753,- LVL. Dividing sales profit onto production costs brings a positive 1.26 large benefit and expense ratio. Installation of devices in decentralized households in 15 years would bring both productivity growth benefits to the state and profit for the device manufacturer.

Table 2

Main economical benefits and expenses

Economical benefit*	Total value (Lats, discounted)	% no total profit amount
1. Benefit from export proportion increase in the economic sector	0	0
3. Benefit from productivity growth	492 868	1
4. Benefit from material and energy consumption reduction on one produced unit	0	0
4. Benefit from environmental pollution reduction	0	0
5. Benefit from product sale	40 317 191	99
Expenses	Total value (Lats, discounted)	% no total profit amount
1. Product development costs	300 000	1
2. Product manufacturing costs	32 253 753	99

* Against the zero alternatives – product, technology is not implemented, project is not executed.

CONCLUSIONS

1. For water disinfection with electrolysis, thermally processed in deep vacuum conditions TiO_{2-x} ceramics can be used. It is electro conductive and can be used as an electrode material. Experimental voltamperograms of TiO_{2-x} ceramic electrodes and measured potentials show that the electrodes are stable in electrolytic conditions that ensure water disinfection.
2. Efficiency of TiO_{2-x} ceramic electrodes releasing chlorine at small chloride ions concentrations in the water can be compared to precious metal electrode materials considered prospective in the scientific literature sources. Amount of released Cl_2 increases with chloride ions concentration increasing in the solution and electric current intensity and electrolysis time increasing.
3. Charge that flows through solution impacts solution pH and oxidizing-reduction potential. Oxidizing-reduction potential significantly increases during electrolysis due to halogen ions contained in the used solution. Knowing the water chemical composition, ORP meter can be used for total chlorine concentration determination after electrolysis.
4. Dominating ions in the water reduce the amount of chlorine generated during electrolysis process. Amount increase of water hardness forming ions (Ca^{2+} , Mg^{2+}) and HCO_3^- in the water advances formation of sediments (CaCO_3 and $\text{Mg}(\text{OH})_2$) on cathode electrode and reduces total electrochemically generated chlorine amount during the electrolysis process.
5. Using TiO_{2-x} electrodes for electrolysis, if solution contains chloride ions with concentration equal to natural waters concentration (7 – 250 mg/L), a sufficient active chlorine amount is generated to eliminate more than 99% of *Escherichia coli* and *Pseudomonas fluorescens* bacteria in the solution in 15 minutes. It was found that electrolysis method can also be applied for deactivation of *Bacillus subtilis* spores in the water. The research shows that chloride ions containing electrolyzed water has a remaining disinfection effect that lasts for several days.
6. It is more energy efficient to increase the electrode number in the electrolytic cell, since then total electric resistance of electric cell reduces, but amount of released Cl_2 remains almost the same, therefore specific current activity for discharging 1 mg of Cl_2 reduces.
7. Based on the experimental data and using *Chick – Watson* disinfection model, mathematical equation allowing prediction of electrochemical disinfection was developed.

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