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# Water disinfection using $Ti_nO_{2n-1}$ electrodes

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**Abstract.** Water disinfection with electrolysis is an alternative for water treatment, which is receiving increasing attention from drinking and industrial water producers. With this approach oxidants are produced from electrolysis of water molecule and some of dissolved chemical compounds. To carry out the process of electrolysis the using of $Ti_nO_{2n-1}$ containing ceramic electrodes is possible.
The obtained electrodes were used to form electrolytic cell. The total electrolysis cell resistance decreases if the current density applied to the electrolysis cell is increased. During electrolysis at constant current strength, the amount of chlorine, which is delivered in the process of electrolysis, was not dependent on the electrode surface. The technological parameters of process (flow rate, current intensity) have been established to obtain predetermined amount of released chlorine during electrolysis process. The specific work of electric current to release chlorine is decreased, if electrode surface area was increased and current intensity remains constant; but increased, if current density remained constant.

**Keywords:** electrolysis, disinfection, oxidants, chlorine, technological parameters.

## 1. Introduction

Biofilms, which are formed in presence of fast growing microorganisms, can cause problems in water supply systems [1]. To solve these problems, various methods for water disinfection are used, including electrochemical treatment of the water [2, 3, 4, 5, 6].

Nowadays electrochemical disinfection has gained increasing attention as an alternative for conventional drinking water treatment, because 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 (Jeong et al 2007, Jeong et al 2009). 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 water itself (Kraft et al 1999, Kwang et al 2006).

Electrolysis process is significantly influenced by several factors including electrode material [7, 8, 9, 10, 11, 12].

In works [13, 14, 15, 16] the possibility of using non-stoichiometric titanium oxide (with overall formula $Ti_nO_{2n-1}$) ceramic electrodes for electrochemical treatment of water with target to decrease the microbiological contamination were investigated. If conditions for producing ceramics are varied, the Ti/O rate changes and obtained ceramics have semiconductor properties [17].

The use of $Ti_nO_{2n-1}$ ceramic electrodes in electrolysis of water reduce the amount of organic substances as evidenced by significant changes of oxidation properties (KMnO4 index) [14]. If halogen ions (Cl-, Br-) are present in water during electrolysis, drastic decrease in Pseudomonas fluorescens colony forming units can be observed [18, 14, 15, 16]; the oxidizing substances formed during electrolysis have a long-lasting disinfecting effect. Using titanium oxide ceramic electrodes in electrolysis of water which contains iodine ions there is a bacteriostatic effect, which can last up to 10 days [14, 16].

When using a $Ti_nO_{2n-1}$ electrode in the electrolysis process with the presence of chloride ions, in concentration range [13, 16] which is common in raw waters, 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 has been developed. It was also found that obtained results can be described using a mathematical model.

The aim of this study was to describe the use of $Ti_nO_{2n-1}$ containing ceramic electrodes to treat water under dynamic conditions and to show the influence of selected technological parameters on the effectiveness of the treatment process.

## 2. Experimental

**Model solutions**

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 in drinking water [19].

As almost all natural waters contain $SO_4^{2-}$ ions that are stable during electrolysis process, to assess the influence of electric conductivity of solution potassium sulphate model solutions were prepared; the chosen maximum $SO_4^{2-}$ ion concentration did not exceed maximum concentration permissible in drinking water (<250 mg/l) [19].

**Determination of resistance of electrolytic cell**

Using 1 mmol/L $K_2SO_4$ solution current intensity is determined at constant current voltage. From the obtained measurements the resistance of electrolytic cell is calculated.

**Determination of specific resistance of electrolytic cell**

As anode has cylindrical shape the specific resistance of electrolysis cell is substituted with value obtained when the specific resistance of electrode and the distance between electrodes is multiplied – arbitrary specific resistance (j), that is proportional to specific resistance of electrolysis cell. Arbitrary specific resistance is determined using formula:

$$j = \rho \cdot l = R \cdot S \text{ , } \Omega \cdot m^2, \qquad (1)$$

Where, $\rho$ – electrode material specific resistance, R – resistance of electrolytic cell, Ω, l – distance between electrodes, m, S – surface area of electrodes, $m^2$.

**Determination of total chlorine concentration**

Total chlorine concentration was determined using the volumetric method [20].

**Experimental setup**

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

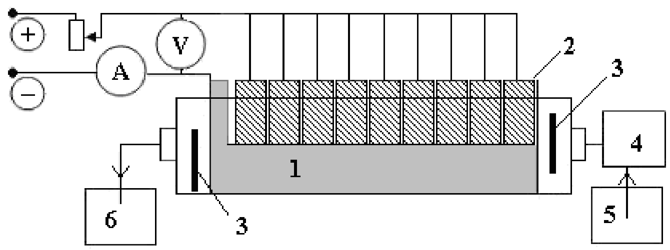


Fig.1. Experimental EL equipment setup for dynamic conditions: 1 – stainless steel cathode; 2 – $Ti_nO_{2n-1}$ containing ceramic anodes; 3 – parting section walls; 4 – pump; 5 – container for untreated solution; 6 – container for electrolyzed solution.

In the EL equipment $Ti_nO_{2n-1}$ containing ceramic electrodes in the shape of cylindrical bar are used as anodes (surface area 12.4 $cm^2$). The number of ceramic anodes can be varied from 1 to 9. Cathode is made of stainless steel (AISI 304) with total surface area 190 cm$^2$. Rectifier HQ Power, PS5005 (0 – 50 V DC, 0 – 5 A) was used as a current source. The $Ti_nO_{2n-1}$ containing ceramic electrodes used in the research described in this article was specially made for these purposes [17].

## 3. Results and discussion

Technological parameters that characterize electrolysis device under dynamic conditions are: electric resistance, intensity of release of disinfecting substances and the specific electrical work required for electrolysis process. The intensity of release of disinfecting substances was characterized using the release rate of chlorine.

The electrical resistance of electrolysis device depends on the surface area of electrodes. When 1 mmol/L $K_2SO_4$ solution is electrolyzed using constant current density (8.1 mA/cm$^2$), the resistance of electrolysis cell decreases in inverse rate to the surface of electrodes. Changes in resistance (R) can be described by Equation 1, because the arbitrary specific resistance of electrolysis cell (j) does not change.

If electrolysis is carried out under constant current intensity (0.1 A) and the number of electrodes is increased, the current density decreases as well as the resistance of electrolysis device (although this decrease cannot be described using Equation 1). When current density is changed, the arbitrary specific resistance of electrolysis cell (j) also is changed (see Fig. 2). At low current densities the changes in (j) are more marked.

If surface area of electrodes is changed, the amount of total released chlorine from electrolyzed solution is affected.

If solution containing chloride ions is electrolyzed (see Fig.3) at constant current intensity (0.1 A), the changes in surface area of electrodes do not affect the amount of released chlorine. If electrolysis is carried out under constant current density (8.1 mA/cm$^2$), the amount of released chlorine increased 3.5 times (from 1.4 mg/L to 4.5 mg/L) as electrode surface area is increased 9 times.

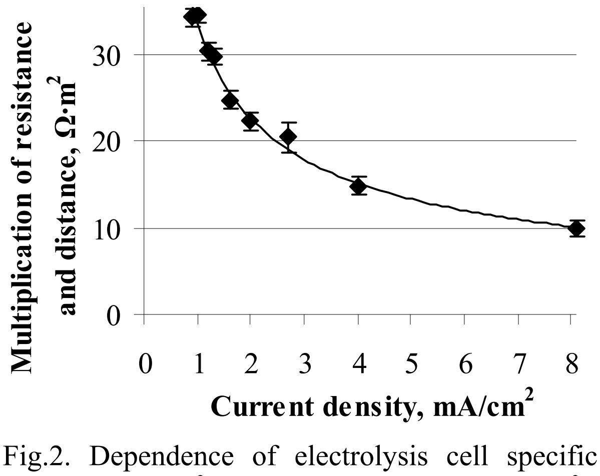


Fig.2. Dependence of electrolysis cell specific resistance (Ω·m$^2$) on current density (mA/cm$^2$). Potassium sulphate concentration is 1 mmol/L.

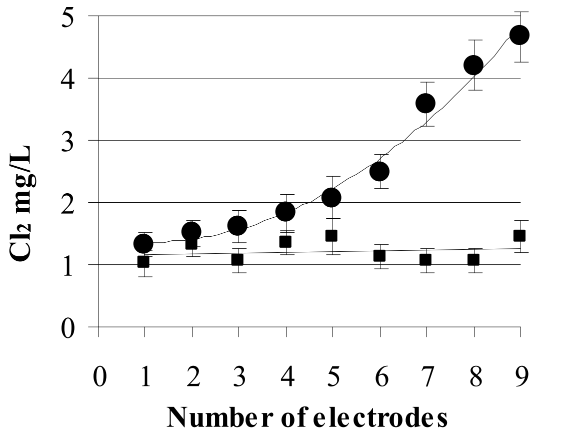


Fig.3. Dependence of concentration of released chlorine on the number of electrodes connected: ● – at constant current density (8.1 mA/cm$^2$), ■ – at constant current intensity (0.1 A). Concentration of chloride ion is 1 mmol/L.

Practically all natural waters have some salt dissolved in it and the presence of dissolved salts affects the electric conductivity of water. To ascertain how the electric conductivity changes the amount of released chlorine during electrolysis process, to 1 mmol/L KCl solution various amounts of $K_2SO_4$ were added to increase the electric conductivity of solution (see Fig. 4).

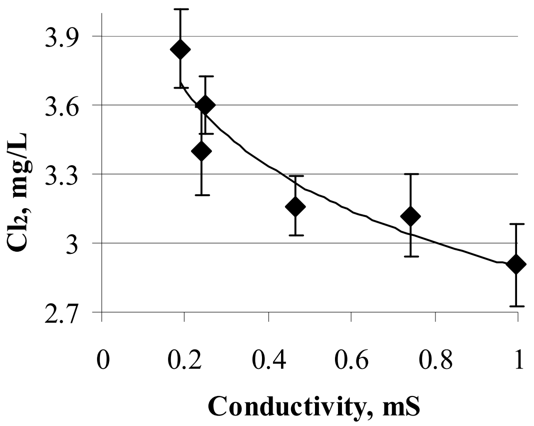


Fig.4. Dependence of amount of released chlorine on electric conductivity of solution at constant current density (8.1 mA/cm$^2$). Concentration of chloride ion is 1 mmol/L.

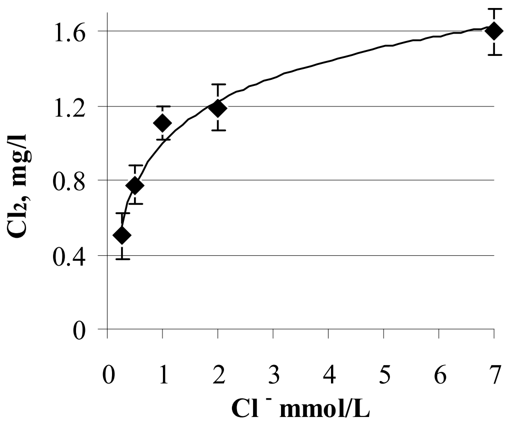


Fig.5. Dependence of the amount of released $Cl_2$ on chloride ions concentration in solution at constant current density (2.7 mA/cm$^2$).

As it can be seen in Fig. 4., if electric conductivity of solution increases, the amount of released chlorine decreases substantially. If the electric conductivity of water is increased 6 times, the amount of released chlorine decreases 1.3 times. This fact can be explained by promotion of other reactions on anode that decreases the amount of active chlorine. In natural water the concentration of chloride ions can substantially differ and this affects the amount of released chlorine in EL process. As it can be seen in Fig. 6., at constant electric density, if the amount of chloride ions is increased from 0.25 mmol/L to 7 mmol/L, the amount of released chlorine increases more than 3 times.

The intensity of formation of disinfecting substances and subsequently the efficiency of electrolysis process in engineering water supply systems can change if consumption of water and current parameters is changed.

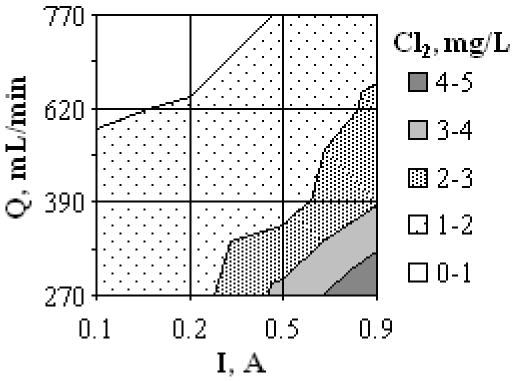


Fig.6. Isofields of amount of $Cl_2$ released in EL process depending on water flow Q (mL/min) and current intensity (A). Concentration of chloride ion is 1 mmol/L.

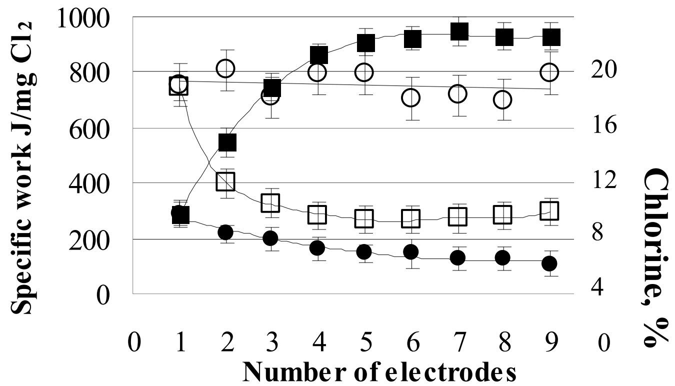


Fig.7. The specific work of electrolysis and amount released chlorine (expressed in % of theoretically possible amount released) as a function of number of electrodes used: ■ – specific work and □ – amount of released chlorine at constant current density (8.1 mA/cm$^2$); ● – specific work and ○ – amount of released chlorine at constant current intensity (0.1 A). Concentration of chloride ion is 1 mmol/L.

The speed of water in flow determines the duration at which the water is treated, and by changing intensity of electric current the amount of disinfecting substances in water can be controlled.

As it can be seen in Fig. 6., the amount of released $Cl_2$ increases when the amount of water consumed is decreased and applied current intensity is increased. The obtained dependences allow to forecast the amount of released $Cl_2$ concentration when parameters for EL are changed.

Efficiency of electrolysis cell is characterized by the amount of chlorine released expressed as a part of theoretically possible amount of released chlorine and the required specific current work in the process.

During electrolysis at constant current intensity (0.1 A), if the number of electrodes is increased, the amount of released chlorine remains practically constant, but the specific work of electric current needed for the release of chlorine decreases 2.7 times (see Fig. 7.). The specific work of electric current decreases because the total resistance of electrolysis cell decreases.

During EL process if current density remains constant, when the number of electrodes is increased, the amount of released chlorine decreases, but the specific work of electric current for the release of chlorine increases (see Fig. 7.). During EL process if current density remains constant, if the surface area of electrodes is increased, the current intensity increases and this causes the increase of electric energy required for EL process.

## 4. Conclucions

When ceramic electrodes containing non-stoichiometric titanium oxide are used for electrolysis cell, the total resistance of electrolysis cell decreases, if the current density applied to electrolysis cell is increased.

If electrolysis is conducted using constant current intensity, the amount of released chlorine does not depend on the surface area of electrodes, because it depends from current density. The presence of other ions in solution hinders the release of chlorine.

The technological parameters of the process (flow rate, current intensity) have been established to obtain predetermined amount of released chlorine during electrolysis process

The specific work of electric current to release chlorine is decreased, if electrode surface area is increased and current intensity remains constant; but increases, if current density remains constant.

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