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Interpretation of results obtained from test purification of wastewater with zinc electrodes

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Abstract: Basic materials used for electrochemical purification of wastewater are iron and aluminium electrodes. In this paper, results obtained from analysis of wastewater samples before and after electrolysis with zinc electrodes are presented and compared with the results of aluminium electrodes and mixed metal oxide electrodes. In all experiments with zinc, the same materials were used as anode and cathode. After 7 min of electrolysis at only 0,018 A/dm^2, concentration of chloride in was reduced using zinc electrodes, and the efficiency of microorganisms removal is double, directly and indirectly. The effects of the main parameters in electrochemical cell with zinc electrodes – changes in the conductivity of the solution, variation of pH, turbidity of samples, removal of chloride and production of hypochlorous acid were investigated.

INTRODUCTION

Wastewater treatment is closely related to the standards and/or expectations set for the effluent quality. Wastewater treatment processes are designed to achieve improvements in the quality of the wastewater. One of the most effective ways for wastewater disinfection is by using chlorine. The disinfecting effect of free chlorine is based on the release of atomic oxygen according to (Chen, 2004):

$$HClO \rightarrow O + Cl^- + H^+ \quad (1)$$
$$ClO^- \rightarrow O + Cl^- \quad (2)$$

The wastewater used in this research contained high concentrations of chlorides. Our goal is an electrochemical production of chlorine.
First, chlorine is electrochemically produced from chloride ions dissolved in the water (Mendia, 1982):

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

The next step is the dissolution of chlorine in the water. The maximum amount of Cl_2 (g) which can be dissolved in water at 20 ºC is about 7.1 g or 0.1 mol/kg$_{water}$ (Halilović, 2015).
Solubility of Cl_2 in water was shown in Figure 1.

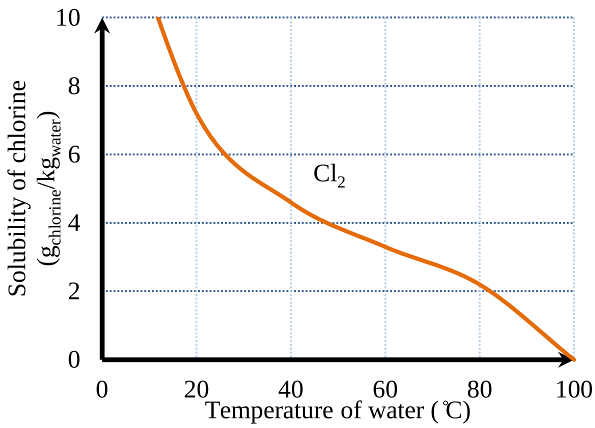

Figure 1: Solubility of Cl_2 in water, g$_{chlorine}$/kg$_{water}$

Our interest is found the best electrode material in this purpose.

Aluminum and iron metal salts are used in raw water and wastewater treatment. Both metals can form multivalent ions, Al^{3+}, Fe^{2+} and Fe^{3+}, and various hydrolysis products (Kostamo et al., 2003). Metal cations go through a series of hydrolytic reactions depending on the pH of the solution and mononuclear (Eq. 4) and polynuclear hydroxides form in the solution (Halilović, 2015).

$$Me^{3+}(aq) + nH_2O \leftrightarrow Me(OH)_n^{3-n} + nH^+(aq) \qquad (4)$$

It can be concluded that iron dissolved in Fe(II) form and dissolution followed Faraday's law. This was consistent with the results of other researchers (Sasson et al., 2009; Linares-Hernández et al., 2009; Bagga et al., 2008). This result was significant because it is known that Fe(II) is a poor coagulant and should be oxidized to Fe(III) form before it can be used to remove organic matter (Bratby, 2006).

Water temperature had a significant effect on the dissolving speed of the aluminum electrodes. According to the results, the chemical dissolution of aluminium cathodes was affected by temperature. At low temperatures, chemical dissolution initiated more slowly than at higher temperatures (Vepsäläinen, 2012).
Vepsäläinen (2012) studies showed that increased removal of pollutants at high temperatures has been obtained by Yilmaz et al. (2008), and Vasudevan, et al. (2009), whereas Katal and Pahlavanzedah (2011) and El-Naas et al. (2009) reported the opposite effect in their studies.
Main reaction of electrocoagulation by aluminum anode in experiment with wastewater is (Halilović, 2015a):

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \qquad (5)$$

Our goal is to test zinc anode-cathode material for electrochemical disinfection and removal of chloride from wastewater.
Zinc standard redox potential is $E^o(Zn^{2+}/Zn) = -0.762$ V, which means that this material is relatively easily oxidized in aqueous solutions, that is, zinc is the reducing agent.

EXPERIMENTAL

Chemicals and instruments

Sodium thiosulfate, p.a. (Merck); potassium iodide, p.a. (Merck); starch, p.a. (Merck); hydrochloric acid, p.a. (Merck); sodium chloride, p.a. (Merck); conductivity meter (Iskra); pH meter (PHYWE); constanter (PHYWE); amperemeter (PHYWE); digital multimeter (DT9205A); magnetic stirrer (TEHTNICA ŽELEZNIKI); analytical balance (Mettler); thermometer; zinc anode and cathode and laboratory glassware were used for the experiment process.

Procedure

The effect of the main parameters in electrochemical cell with zinc electrodes - changes in the conductivity of the solution, variation of pH, turbidity of samples, removal of chloride and production of hypochlorous acid was investigated. Electrolysis duration for all experiments was 7 min. Dimension of used electrodes was 7 cm × 3 cm and the distance between the electrodes was 5 mm. The volume of the tested samples was the same, 0.4 dm^3. Experiments were carried out at 500 rpm on a magnetic stirrer. Scheme for electrolysis using zinc electrodes is given in Figure 2.

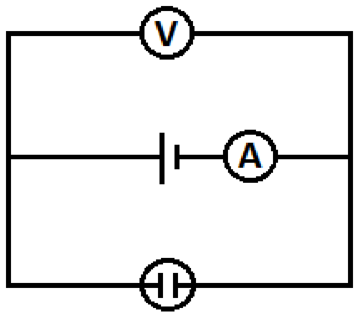

Figure 2: Scheme for electrolysis using zinc electrodes

The determination of chloride in wastewater

Determination of the chloride in the wastewater before and after electrolysis is carried out by titration method. The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. The reactions are:

$$Ag^+ + Cl^- \leftrightarrow AgCl_{(s)} \qquad (6)$$
$$2Ag^+ + CrO_4^{2-} \leftrightarrow Ag_2CrO_{4(s)} \qquad (7)$$

By knowing the stoichiometry and moles consumed at the end point, the amount of chloride in an unknown sample can be determined.

The decrease in total chloride is presented:

$$\omega(\%) = \frac{c_{Cl^-(before\ electrolysis)} c_{Cl^-(after\ electrolysis)}}{c_{Cl^-(before\ electrolysis)}} \cdot 100 \qquad (8)$$

The determination of hypochlorite

Hypochlorous acid reacts with iodide when the solution is acidic:

$$HOCl_{(aq)} + HCl_{(aq)} + 3I^-(aq) \rightarrow I_3^-{}_{(aq)} + 2Cl^-{}_{(aq)} + H_2O_{(l)} \qquad (9)$$

A dark blue complex is formed when triiodide is combined with starch.

This is useful because the result of these reactions is the formation of a dark blue complex. In the next step, the starch-triiodide product is titrated by sodium thiosulfate to form a colorless solution of iodide, dithionate, and uncomplexed starch:

$$[I_3^-][starch] + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} + starch \qquad (10)$$

Zinc anode and cathode was used in experiment for determining hypochlorous acid as a product of electrolysis of NaCl, which concentration was 0.05 mol/dm^3 (this concentration is defined as the most common in the wastewater). The obtained results were compared with results for same wastewater reported by other (Halilović et al., 2015b) for electrochemical cell of aluminum anode and cathode and, otherwise, for anode of the mixed metal oxides (RuO_2, IrO_2) and cathode of steel.

Conductivity of the solution, pH, turbidity of samples
These parameters were determined before and after electrolysis with zinc electrodes for samples of wastewater and for samples of NaCl (c = 0.05 mol/dm^3) because of comparison.

RESULTS AND DISCUSSION

Results of chemical analysis of solution of NaCl and wastewater obtained with volumetric method are given in Tables 1. and 2.

Table 1: Results of determination of hypochlorite, pH and conductivity of NaCl with zinc electrodes.

Electrode pair (A, K)	HOCl [mol/dm^3]	ΔpH (pH_0=7,14)	Δκ (mS/cm)
Zn	$3.7 \cdot 10^{-5}$	2.04	0.08
Al*	$2.3 \cdot 10^{-5}$	1.11	0.159
MMO*	$90 \cdot 10^{-5}$	1.91	0.25

*Values reported by other (Halilović et al., 2015b). MMO – mixed metal oxide

Conductivity of NaCl (c = 0.05 mol/dm^3), which is subjected to electrolysis, before electrolysis amounted to 2.930 mScm^{-1}. Some of the reactions that take place during electrolysis of chloride are:

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (11)
Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (12)

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH \quad (13)$$

Formation of NaOH increases the pH of the solution (ΔpH in Table 1). Compared to the other electrodes mentioned in the tables 1, zinc showed the biggest change in pH. The conductivity of the solution is also increased due to an increase in the concentration of OH^- ions (Δκ in Table 1) in the order: aluminum > MMO > zinc. This sequence can be explained by Figure 3.

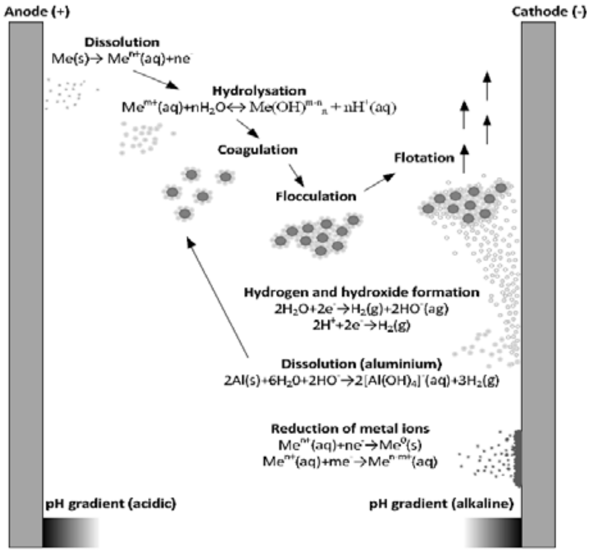

Figure 3: Schematic representation of typical reactions during the electrochemical treatment (Kraft, 2008)

MMO comes before zinc because in this experiment formed hydroxide does not react with the metal ion of MMO electrodes. Aluminum is the first in the series because of the reactions shown in Figure 3.
Electrolysis of NaCl solution with Zn electrodes is created gray-white solution in which the white precipitate was formed gradually. Aluminum gives more sludge because of properties that will be mentioned below.
The essence of the disinfectant action of chlorine, consists in oxidizing-reduction processes, which occur during the interaction of chlorine and its compounds with organic matter of microbial cells (Kraft, 2008). Because of this, we determined the amount of formation of hypochlorite (Table 1) and decrease of chloride in wastewater (Table 2).

Table 2: Results of determination of chloride before and after electrolysis of wastewater with zinc electrodes.

Electrode pair (A+K)	$c(Cl^-)$** [mol/dm^3]	$\omega_{total\ removal\ of\ chloride}$[%]
Zn	0.0141	33.18
Al*	0.0051	75.8

*Values reported by other (Halilović et al., 2015b)
** $c(Cl^-)_{before\ electrolysis}$ = 0,0211mol/dm^3

After 7 min of electrolysis at 0.018 A/dm^2, Cl^- was reduced in all experiments. The reasons are electrocoagulation, electroflotation and electroflocculation effects of metal ions that are released from the anode. Compared to aluminum, zinc did not show substantial removal of chloride (Table 2). Aluminum shows very good electrocoagulation effect. MMO is not tested on wastewater because of high price of material.
The presence of ZnO in the protective film on the electrode can be explained by the following equations (Antonijević et al., 2009):

$$Zn^{2+} + H_2O \rightarrow ZnO + 2H^+ \quad (14)$$
$$Zn + H_2O \rightarrow ZnO + 2H^+ + 2e^- \quad (15)$$

In the NaCl solution, Cl^- react with the zinc anode according to the following reaction:

$$Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)} \quad (16)$$

From an aqueous solution of zinc, it crystallizes as the dihydrate, $ZnCl_2\ 2H_2O$ and it is very difficult to remove traces of water from the dihydrate. $ZnCl_2$ is used for wood preservatives.

Secondary reaction on anode, when used in the experiment a magnetic stirrer, is:

$$Zn_{(s)} + 2H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} + H_{2(g)} \quad (17)$$

However, due to the existence of the Na^+ ions in the solution, the reaction is insignificant compared to the reaction:

$$Na^+ + OH^- \rightarrow NaOH \quad (18)$$

After the electrolysis, pH of NaCl is measured, and its value was 9.18, so it is important to mention the following reaction:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_{2(s)} \quad (19)$$

CONCLUSIONS

The electrochemical treatment of wastewater resulted in the production of chlorine gas and hypochlorite, which is a microorganisms inactivator.

The concentration of hypochlorous acid produced by electrolysis, after dissolving chlorine, following order: MMO > Zn > Al and it increased compared to the theoretically expected. The reason is the mixing of solution, the impact of the hydroxide, the temperature and the participation of secondary reactions.
Compared to aluminum, zinc did not show substantial removal of chloride. The reason is because Al(III) shows very good electrocoagulation effect and Zn(II) is a poor coagulant.
The largest increase in conductivity mixed metal oxide electrode occurs due to the inertia of the material, and there is no dissolution of the anode. It resulting the generation of NaOH, and OH^- ions are responsible for the increased conductivity compared to Al and Zn.
Due to the large loss of zinc ions by electrolysis from the anode and the same is not reduced at the cathode due to the mixing of the solution, a zinc electrode is not applicable to the waste water purification at high current densities.

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Summary/Sažetak

Osnovni materijali koji se koriste za elektrohemijsko prečišćavanje otpadne vode su željezne i aliminijske elektrode. Ovaj rad sadrži interpretaciju rezultata dobijenih analizom uzoraka otpadne vode prije i poslije elektrolize sa elektrodama od cinka i usporedbu istih sa rezultatima elektrolize otapadne vode koristeći elektrode od aluminija u prvom i elektrodu miješanih metalnih oksida u drugom slučaju. U svim eksperimentima je cink korišten kao anoda i katoda. Poslije 7 minuta elektrolize na samo 0,018 A/dm^2, koncentracija hlorida je smanjena koristeći elektrode od cinka, a efekat na uklanjane mikroorganizama je dvostruk (direktan i indirektan). Istraženi su efekti glavnih parametara u elektrohemijskoj ćeliji u kojoj su korištene elektrode od cinka – promjene u provodljivosti uzoraka, pH, promjena mutnoće uzoraka, uklanjanje hlorida i nastanak hipohloritne kiseline.