Glasnik hemičara i tehnologa Bosne i Hercegovine

Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

2017

48

Print ISSN: 0367-4444

Online ISSN: 2232-7266

UDC: ___

Original Scientific Paper

15-20

Electrochemical treatment of leather industry wastewater

Halilović, N.[a*], Krdžalić, E.[b,c], Bašić, A.[d,e], Dacić, M.[d,e], Avdić, N.[a]

[a]*University of Sarajevo, Faculty of Science, Department of Chemistry, Zmaja od Bosne 33-35, 71000 Sarajevo, B&H*

[b]*University of Zenica, Faculty of Metallurgy and Materials Science, Department of Chemistry, Travnička Cesta 1, 72000 Zenica, B&H*

[c]*Factory of glues, facades, inks KOMOCHEM, Donja Zimča 68, 71300 Visoko, B&H*

[d]*Faculty of Pharm and Health, University in Travniku, Dolac na Lašvi, Polje Slavka Gavrančića 17C, 72270 Travnik, B&H*

[e]*Institute for Biomedical Research and Diagnostics GENOM, Dolac na Lašvi, Polje Slavka Gavrančića 17C, 72270 Travnik, B&H*

Article info
Received: 20/04/2017
Accepted: 14/06/2017

Keywords:
Aluminum
Escherichia Coli
Copper
Chlorides
Electrocoagulation
Leather industry wastewater

***Corresponding author:**
E-mail: namir.halilovic@live.com
Phone: 00-387-61-495311

Abstract: Leather industry wastewater is contaminated with bacteria including *Escherichia Coli*. In this paper, results obtained from analysis of leather industry wastewater samples with use of copper electrodes are presented and compared with the results of use of aluminum electrodes and mixed metal oxide electrodes. In all experiments the same materials were used as anode and cathode except the two last where anode of the mixed metal oxides and steel cathode was used. Electrodes with platinum group metals or their oxides as active coatings are generally the best suited for electrochemical water disinfection. After 7 min of electrolysis at only 0.018 A/dm^2, Cl^- was reduced using both tested electrodes, the efficiency of microorganisms removal followed the order: Cu > Al. The electrochemical treatment of wastewater resulted in the production of chlorine gas and hypochlorite, which is microorganisms deactivator. Also, electrocoagulation by aluminum anode was used for water purification to reduce all pollutants, including chlorides and microorganisms.

INTRODUCTION

At the phase boundary between the electrodes and the water, the electric current leads to the electrochemical production of disinfecting species from the water itself (for example, ozone), or from species dissolved in the water (for example, chloride is oxidised to free chlorine). If electrochemical disinfection is applied to drinking water, industrial water, seawater or other solute-containing water, its effect is mainly based on the electrochemical production of hypochlorite and/or hypochlorous acid from the chloride content of the water (Kraft, 2008).

First, chlorine is electrochemically produced from chloride ions dissolved in the water (Mendia, 1982):

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The gas in low concentrations is an irritant to the mucous membranes, the respiratory system, and the eyes (Harms and O'Brien, 2010).

Chlorine hydrolyses in water and hypochlorous acid (HClO) is formed:

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

In the nomenclature of water disinfection, the sum of hypochlorous acid and hypochlorite concentrations is usually termed *free chlorine* or *active chlorine*. The disinfecting effect of free chlorine is based on the release of atomic oxygen according to (Chen, 2004):

$$HClO \rightarrow O + Cl^- + H^+$$

$$ClO^- \rightarrow O + Cl^-$$

Our goal was find the best anode-cathode material for electrochemical disinfection and removal of chloride from leather industry wastewater.

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; copper anode and cathode, aluminum anode and cathode (see Fig. 1 (a), (b), (c)), anode of the mixed metal oxides - MMO (RuO_2, IrO_2) and cathode of steel and laboratory glassware were used for the experiment process.

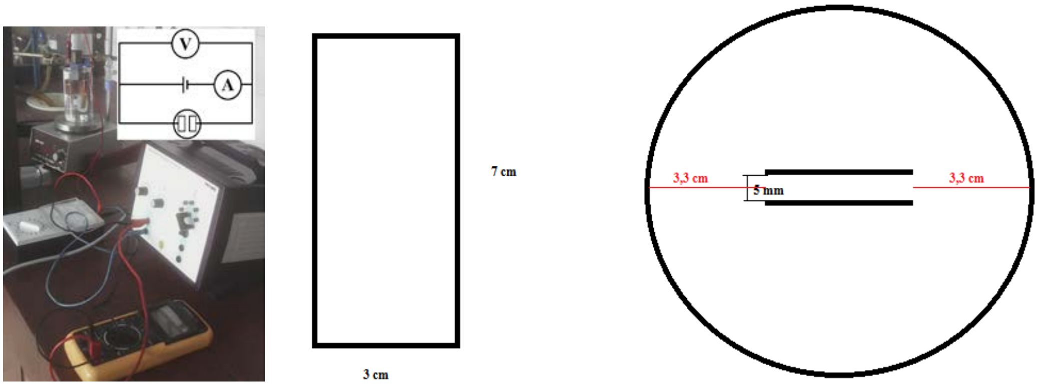


Figure 1: **(a)** Scheme and apparatus for electrolysis using Al and Cu electrodes. **(b, c)** Dimensions of used electrodes and position in laboratory glass.

Procedure

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 as shown by Fig. 1 (b, c). Scheme for electrolysis using aluminum, copper and MMO electrodes is given in Fig. 1 (a). The volume of the tested samples was the same, 0,4 dm^3. Experiments were carried out at 500 rpm on a magnetic stirrer.

The determination of hypochlorite in standard solution of chloride after electrolysis

Hypochlorous acid reacts with iodide when the solution is acidic:

$$HOCl\,(aq) + HCl\,(aq) + 3I^-\,(aq) \rightarrow I_3^-\,(aq) + 2Cl^-\,(aq) + H_2O(l)$$

Tridiodide, I_3^-, is a dark red complex. A dark blue complex is formed when triiodide is combined with starch.

$$I_3^- + \text{starch} \rightarrow [I_3^-][\text{starch}]$$

As result of these three reactions a dark blue complex formation is observed. Its concentration is proportional to the amount of sodium hypochlorite in the solution. In the next step, the starch-triiodide product is titrated by sodium thiosulfate to form a colorless solution of iodide, dithionate, and uncomplexed starch (Chang, 2010):

$$[I_3^-][\text{starch}] + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} + \text{starch}$$

Copper anode and cathode, aluminum anode and cathode, anode of the mixed metal oxides - MMO (RuO_2, IrO_2) and cathode of steel are used in determining hipohloritne acid as a product of electrolysis of Cl- standard solution, which concentration was 0,05 mol/dm^3(this concentration was detected in leather industry wastewater). Apparatus for electrolysis is shown in Fig. 1 (a).

The determination of chloride in sample of leather industry wastewater by Mohr method

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 (Skoog et all., 1996). The reactions are:

$$Ag^+ + Cl^- \leftrightarrow AgCl(s)$$
$$2Ag^+ + CrO_4^{2-} \leftrightarrow Ag_2CrO_4(s)$$

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:

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

The determination of *Escherichia Coli* and total bacterias in sample of leather industry wastewater

The nutrient pads are made of biologically inert cellulose cardboard that does not bind the nutrient medium chemically or physically. Growth of microorganisms can therefore develop freely. All equipment must be sterile.
We used two standards:
Endo-NPS: Medium selective for *Escherichia Coli* and coliform bacteria in water (DIN EN ISO 9001, 2008).
and is used white membrane filter with pores of 0,45 mm. Application of bacteria are carried out by filtering 100 mL of sample on a Buchner funnel using white membrane filter. The filter is transferred by pincette to an inert bacterial surface. Before transporting the filter, it is necessary to add water on the dehydrated base, 3 to 5 ml of distilled water. Incubation of the seeded filtrate sample takes 24 hours at 37°C or 42-44°C. E. coli develops dark red colonies on green metallic shiny surface.

Standard *TTC-NPS*: For colony count determinations of water and waste water for pure cultures (DIN EN ISO 9001, 2008).

Standard is designed for the determination of the bacteria: *Escherichia Coli, Pseudomonas aeruginosa, Staphylococcus aureus*. Application of bacterias is carried out by filtering 100 mL of sample on a Buchner funnel using a membrane filter with pores of 0,45 microns, and then the filter is transferred by pincette to an inert bacterial surface. Incubation of the seeded filtrate sample takes 48 hours at 30°C or 48-72 hours at 20°C. Bacterias develope pink colonies on the surface. These points are visible to the eye.

The determination of conductivity and pH of NaCl standard solution and sample of leather industry wastewater

These parameters were determined before and after electrolysis with copper, aluminum and MMO electrodes for samples of wastewater and for standard samples of NaCl (c = 0,05 mol/dm^3) because of comparison.

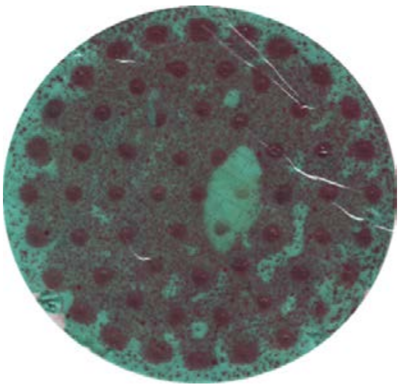
RESULTS AND DISCUSSION

Results of experiments are showed in Table 1 and Figure 2, 3, and 4.

Table 1: Results of determination of hypochlorite, pH and conductivity of NaCl standard solution and sample of leather industry wastewater. Minus(-) refers to the reduction of the initial value of the parameter after experiment.

Electrode pair (A, K)	Cl^- standard samples of NaCl = 0,05 mol/dm^3			Leather industry wastewater				
	HOCl [mol/dm^3]	ΔpH (pH_0=7,14)	Δκ (mS/cm)	ΔpH (pH_0=8,43)	Δκ (mS/cm)	Reduction of chloride [%]	Destruction of *E. coli* [%]	Destruction of all bacterias [%]
Cu$_{500\ o/min}$	86,7 · 10^{-5}	3,84	0,152(-)	x	3,168	17,8	100	100
Al$_{500\ o/min}$	2,3 · 10^{-5}	1,11	0,159	0,67(-)	0,022	75,8	>90	>80
MMO	90 · 10^{-5}	1,91	0,25	x	x	x	x	x

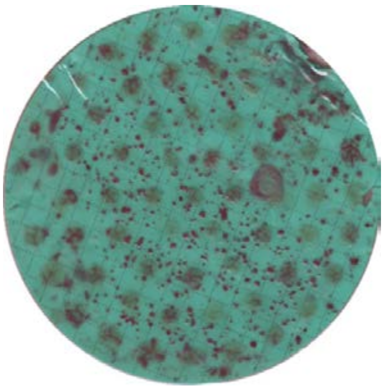
(a)



(b)

Figure 2: **(a)** A test for total bacteria in wastewater before experiment. **(b)** A test for *E.coli* in wastewater before experiment. Each red dot on nutrient pad is a colony of bacteria.

(a)



(b)

Figure 3: **(a)** A test for total bacteria after experiment with Al anode-cathode pair. **(b)** A test for *E. Coli* after treatment with Al anode-cathode pair. Each red dot on nutrient pad is a colony of bacteria.

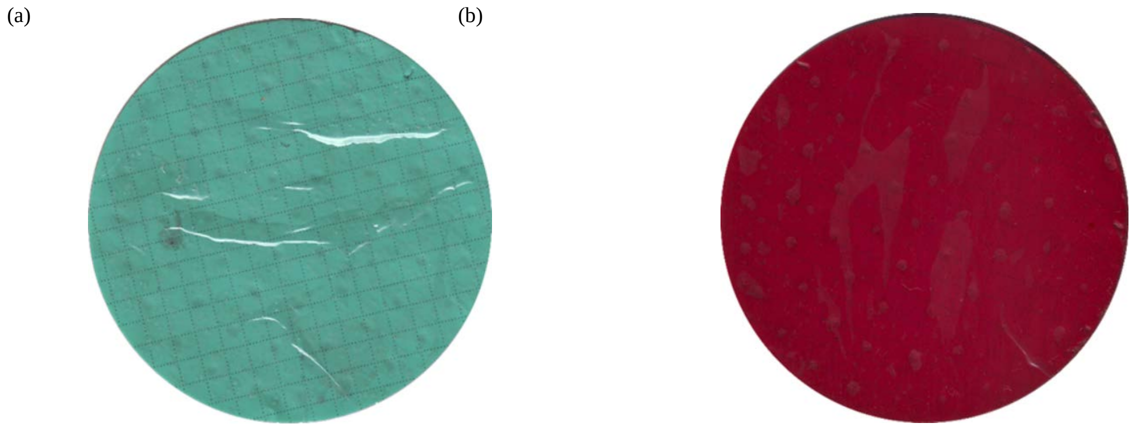


Figure 4: **(a)** A test for total bacteria after treatment with Cu anode-cathode pair. **(b)** A test for *E. Coli* after treatment with Cu anode-cathode pair.

Electrodes with platinum group metals or their oxides as active coatings are generally the best suited for electrochemical water desinfection as shown by the results in Tab. 1. ($c_{HOCl} = 90 \cdot 10^{-5}$ mol/dm^3). MMO comes before aluminum and copper electrodes because in this experiment formed hydroxide does not react with the metal ion of MMO electrodes.

MMO electrodes are very expensive, so we will not discuss them for use in wastewater treatment but can be used for the production of HOCl.

After 7 min of electrolysis at 0,018 A/dm^2, Cl^- was reduced and, using both tested electrodes, the efficiency of microorganisms removal followed the order: Cu>Al (comparison of the number of red dots on Fig. 2, Fig. 3 and Fig 4 showed in Tab 1).

While microbial inactivation mechanisms have not been clearly explained, it is evident that there exist synergistic effects on water disinfection when Cu^{2+} and Ag^+ are provided simultaneously (Younggy, 2014).

After the electrolysis with Cu, pH of NaCl standard solution is measured, and its value was 10,98 (see ΔpH=3,84 for NaCl solution in Tab. 1), so it is important to mention the following reaction is not favored and OH^- ions do not accumulate to a significant extent:

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2\ (s)$$

The anode is surrounded by an acidic medium and the primary reaction is the formation of the dichloride. NaOH, which accumulate, increases the pH.

During the electrolysis in NaCl solution, a copper anode is oxidized froming the protective layer (Naumczyk et all., 1996; Antonijević, et all., 2009):

$$2Cu^+ + H_2O \rightarrow Cu_2O + 2H^+$$
$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2\,e^-$$

followed by the reaction:

$$Cu^+ + Cl^- \rightarrow CuCl$$
$$2CuCl \rightarrow Cu + CuCl_2$$
$$CuCl + Cl^- \rightarrow CuCl_2^-$$

Cu^{2+} inactivate microorganisms, including pathogens, as an active disinfectant which are shown in Fig 5 (see Fig. 4).

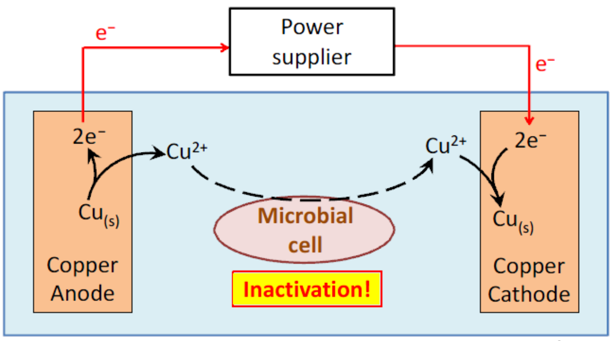


Figure 5: Illustration of electrochemical disinfection. Cu^{2+} released at the anode inactivates microorganisms. Simultaneously, Cu^{2+} is recovered as metallic copper at the cathode (Vepsäläinen, 2012)

At the anode, metallic copper is oxidized to aqueous Cu^{2+} ions (Fig. 5). The aqueous Cu^{2+} ions released from the anode inactivate microorganisms (including pathogens) as an active disinfectant. Simultaneously, Cu^{2+} ions migrate toward the cathode where Cu^{2+} is reduced to metallic copper (reaction below). With this recovery of Cu^{2+} ions at the cathode, the disinfected water from the reactor will have sufficiently low Cu^{2+} concentration that are safe for human consumption (Halilović and Avdić, 2015) (this is reason for destruction of bacterias showed in Fig. 4).

$$Cu(s) \rightarrow Cu^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

In experiment with NaCl standard solution, κ (mS/cm^3) decreased primary because of reaction between Cu^{2+} and chlorides from solution (Δκ for NaCl standard solution in Tab. 1).

In experiment with aluminum electrodes, pH decreased and come close to zero (0,67(-) in Tab.1) because of reaction OH^- with metal ions in sample of leather industry wastewater. Also, the additional reasons for this kind of behavior are processes as electrocoagulation, electroflotation and electroflocculation that affects metal ions that are released from the anode.

Electrocoagulation process involves the separation of solid particles from the solution. The process takes place with the formation of coagulants by electrolytic dissolution of electrodes made of aluminum. Aluminium seems to be a more suitable electrode material for electrocoagulation applications because it produces Al(III) species (Kraft, 2008; Vepsäläinen, 2012) (this is reason for reduction of bacteria showed in Fig. 3, the other reason is the formation of HOCl).

Electrocoagulation: $Al^{3+} + 3OH^{-} \rightarrow Al(OH)_3$

The reduction of pH in alkaline effluents is the result of hydroxide being precipitated and the formation of $Al(OH)_4^-$ by the equation (Gardić, 2007):

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$

In the case of electrolysis of NaCl standard solution, the acidic environment is formed around anode, but during the mixing of the solution pH rises. In the end of the experiment pH was 8,25; and at the end the pH rises as in the previous examples. It is evident that in electrolysis with Al lower pH is observed when compared with other electrode materials, Cu and MMO (see Tab. 1).

The explanation is in the reaction of OH^- ions with Al^{3+} ions to form a particle coagulant. It acts as a seed for the removal of solid particles from the solution. Aluminum ions in a water solution will give a large number of compounds of the mesh patterns of Al-O-Al-OH structure, which are capable of adsorbing the chemical pollutants such as F-, or similar ions. Aluminum is commonly used in the treatment of drinking water, and the iron in the treatment of waste water (Chen et al., 2000).

CONCLUSIONS

The electrochemical treatment of wastewater produced in a leather industry resulted in the production of chlorine gas and hypochlorite, which is a microorganisms deactivator. Also, electrocoagulation by Al and Cu anode has been in use for water production or wastewater treatment to reduce all pollutants, including chlorides and microorganisms. With this technology, metal cations are produced on the electrodes through electrolysis and these cations form various hydroxides in the water depending on the water pH.

Apparaently the Cu and Al act directly or indirectly to the bacteria and Cu is dominant with direct action of Cu^{2+} ions with respect to Al^{3+} ions. On the other hand, aluminum is better and more suitable coagulant as anodic-cathode material. The efficiency of microorganisms removal followed the order Cu>Al, but because of price and electrocoagulation effect, Al anode-cathode pair is good candidate for use in purification of leather industry wastewater.

The highest concentration of certain hypochlorous acids formed by electrolysis following order:

$$\text{MMO } (IrO_2, RuO_2) > Cu > Al$$

and increased compared to the theoretically expected, because of the mixing, the influence of the base, the temperature and the participation of secondary reactions.

Due to the large loss of Cu^{2+} ions to be separated by electrolysis from the anode and the same is not reduced at the cathode due to the mixing of the solution, a copper electrode is not applicable to the waste water purification at high current densities.

REFERENCES

Antonijević, M. M., Gardić, V., Milić, S. M., Alagić, S. Č., Stamenković, A. T., Jojić, M. (2009). *Protection of materials*, Technical Faculty Bor, Beograd, Serbian, p. 28.

Chen, G. (2004). *Separation and Purification Technology*, 38, 11–41.

Chang, N. (2010). *Chemistry*, TCU of New York Winter, New York, USA, p. 8.

Chen, X., Chen, G.H., Yue, P.L. (2000). *Separation and Puriication Technology*, 19, 65–76.

DIN EN ISO 9001: Endo-NPS (2008).

DIN EN ISO 9001: Standard TTC-NPS (2008).

Gardić, V. (2007). *The application of electrochemical methods for wastewater treatment,* Protection of materials, 48, 49-58.

Halilović, N., Avdić, N. (2015). *The electrochemical removal of chloride and disinfection of leather industry wastewater*, Master thesis, Sarajevo: Natural-Matematics Faculty, Department of Chemistry, p. 29.

Harms, L. L., O' Brien, W. J. (2010). *White's handbook of chlorination and alternative disinfectants*, Wiley, Hoboken, New Jersey, p. 28.

Kraft, A. (2008). *Platinum Metals Review*, 52 177–185.

Mendia, L. (1982). *Wat. Sci. Tech*., 14, 331-344.

Naumczyk, J., Szpyrkowicz, L., Zilio-Grandi, F. (1996). *Wat. Sci. Tech.* 34, 17-24.

Skoog, D. A., West, D. M., Holler, F. J. (1996). *Fundamentals of Analytical Chemistry*, Thomson Learning, Inc, USA.

Vepsäläinen, M. (2012). *Electrocoagulation in the treatment of industrial waters and wastewaters*, VTT SCIENCE 19, Espoo, Finland, p. 77.

Younggy, K. (2014). *Safe drinking water*, McMaster University, Hamilton, Ontario, p. 1-3.

Summary/Sažetak

Otpadna voda kožarske industrije je zagađena bakterijama uključujući Ešerihiju Koli. Ovaj rad sadrži rezultate prikupljene tretiranjem uzoraka otpadne vode elektrodama od bakra, aluminija i metalnih oksidnih elektoda. U svim eksperimentima su korišteni parovi elektroda istog sastava, osim u poslednjem u kome je korištena anoda od metalnih oksida i čelična katoda. Elektrode platinske grupe metala i njihovi oksidi kao aktivne prevlake su se pokazali naučinkovitijim za dezinfekciju vode. Poslije 7 min elektrolize pri 0.018 A/dm^2, koncentracija Cl^- jona je smanjena koristeći obe vrste elektroda, a uklanjanje mikroorganizama prati red Cu > Al. Elektrohemijskom obradom otpadne vode nastaje gas hlorin i hipohlorit, koji je inaktivator mikroorganizama. Također, elektrokoagulacija izazvana aluminijumskom anodom je iskorištena za pročišćavanje vode za smanjenje svih zagađivača, uključujući hloride i mikroorganizme.