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TREATMENT OF WASTEWATER FROM CYANIDE-FREE ZINC PLATING

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Abstract: Wastewater from the electroplating process often contains high concentrations of heavy metals, and must be treated before being discharged into public sewage systems or natural recipients. In this research, rinsing wastewater after acid and alkaline zinc electroplating process was treated by the electrocoagulation process. The experiments were performed in a batch electrochemical reactor made of polypropylene with a volume of 250 cm³. During all treatments constant mixing was performed at a speed of 200 rpm. Different electrode pairs (anode-cathode) were used: Fe-Fe, Al-Al, Fe-stainless steel (SS), Fe-Cu, Al-SS, Al-Cu. The success of the electrocoagulation process, in terms of zinc removal from cyanide-free electroplating rinsing wastewater, achieved with electrode pairs was: Fe-SS > Fe-Cu > Fe-Fe, respectively. The initial concentration of zinc in the wastewater was 173.5 mg/L, and after 60 minutes of treatment with the Fe-SS electrode pair it was achieved removal efficiency of 99.8%, while the specific energy consumption was 6.10 kWh per m³ of treated wastewater, or 8.74 kWh per kg of removed zinc.

Keywords: electroplating, rinsing wastewater, electrocoagulation.

1. INTRODUCTION

Zinc and its alloys have been used for over a hundred years as protective and decorative coatings over a variety of metal substrates, primarily steel. Over the years there have been a number of processes developed for applying zinc coatings depending on the substrate, coating requirements and cost. Of these, electroplating is the most prevalent for functional and decorative applications [1].

In practice, acid and alkaline baths are used for zinc electroplating process. Acid baths are based on salts of: sulfuric, tetrafluoroboric and hydrochloric acid. Alkaline baths are: cyanid, zincate and pyrophosphate. Cyanide baths have a higher deposition power and higher cathodic current densities can be applied. Coatings from cyanide baths are more shiny, but the current efficiency is quite low, in contrast to the efficiency in acid baths [2].

It is important to note that in earlier years zinc coatings were applied mainly using cyanide baths, which posed a great danger to human health and the environment. In recent years, efforts have been made to develop technology that does not involve the use of cyanide, so the technology of cyanide-free electroplating has been developed. The cyanide-free electroplating process has proven to be very efficient for both technical and decorative purposes. Despite the fact that there are no extremely toxic cyanides in these baths, the problem is certainly the large amount of zinc that appears in the rinsing wastewater after the electroplating process.

The regulations on the discharge of wastewater into surface water and public sewage systems define permissible values for certain substances. According to the regulations for the Republika Srpska (RS), the concentration of zinc in wastewater that can be discharged into surface water is 1000 mg/m³

[3], while for public sewage systems the limit value of zinc is 2000 mg/m³ [4]. The regulations on the discharge of wastewater in the Federation of Bosnia and Herzegovina (FBiH) also define the limit value of zinc, which for both surface water and public sewage systems amounts 2000 mg/m³ [5].

Wastewater from the electroplating process usually contains metal in concentrations higher than the maximum permitted value, and must be treated before discharge into surface water or sewage systems. There are a number of treatment methods such as: electrocoagulation (EC), precipitation, coagulation, adsorption, biosorption, ion-exchange, electrodialysis, electrodeionization, and membrane separation that are used for treatment of waste electroplating effluents. Among all these techniques, EC has proved to be an excellent and prominent technique because of its simplicity in operation, low volume of generated sludge, and being cost-effective [6].

In the EC process, the coagulating ions are produced *in situ* involving three successive stages: (1) formation of coagulants by electrolytic oxidation of sacrificial electrode such as iron or aluminium, (2) destabilization of the contaminants, particulate suspension and breaking of emulsions, (3) aggregation of the destabilized phases to form flocs. Fe/Al gets dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze to polymeric iron or aluminium oxyhydroxides. In the EC, the anodic reaction involves the dissolution of metal, and the cathodic reaction involves the formation of hydrogen gas and hydroxide ions [7].

The EC process proved to be effective for the treatment of both wastewater after cyanide and cyanide-free electroplating process. The efficiency of EC process depends on numerous factors such as: electrode material, pH, supporting electrolyte, current density, temperature, treatment time, etc.

In the treatment of wastewater after cyanide electroplating, the pH, temperature, treatment time, and current density proved to be important process parameters. In one research on the treatment of zinc-cyanide electroplating rinse water, the optimal conditions for the EC process were a current density of 30 A/m², a pH 9.5, and a treatment time of 40 minutes. The temperature at which the process was carried out was 25°C. Also, it is important to mention that a higher efficiency of both zinc and cyanide removal was observed using the Fe sacrificial anode, compared to the Al sacrificial anode. The highest removal efficiency achieved is 85% and 99% for Fe electrodes, and 64% and 33% for Al electrodes, for cyanide and zinc, respectively [8].

One study focused on treatment of final rinse water of zinc phosphating from an automotive assembly plant in an electrochemical cell equipped with aluminium or iron plate electrodes in a batch mode by EC. For 15 minutes of treatment with iron electrodes at a current density of 60 A/m² and pH 3, phosphate removal efficiency was 97.7% and zinc removal efficiency was 97.1%. By using aluminium electrodes, at a same current density and pH 5, 99.8% of phosphate and 96.7% of zinc were removed in 25 minutes. The electrode consumptions increased from 0.01 to 0.35 kg electrode/m³ for Al electrode and from 0.20 to 0.62 kg electrode/m³ for Fe electrode with increasing current density from 10.0 to 100.0A/m². The energy consumptions were 0.18–11.29 kWh/m³ for Al electrode and 0.24–8.47 kWh/m³ for Fe electrode in the same current density range. It was concluded that increasing the current density would not significantly increase the efficiency of pollutant removal, and the costs would be significantly higher [9].

There are also studies on the treatment of real industrial wastewater from the electroplating process by the EC. In one such research, the goal was to remove metals, primarily nickel, zinc, and copper. The chemically treated electroplating wastewater was additionaly treated by EC. The laboratory EC reactor was composed of plate electrodes, a direct current source, a voltmeter, an electric pump, cables and electrolyte. All anodes and cathodes were connected in monopolar series. A comparison between iron and stainless steel electrodes for the removal of metals was investigated. Furthermore, the effect of different electric voltages, and contact time on metals removal efficiency were also examined. It was found that the optimum removal efficiency was achieved when a stainless steel electrode was used in the presence of ferric chloride as coagulant, at 10 volts, 30 minutes contact time, and pH 9 for synthetic solution. In a batch treatment system, the real industrial wastewater was treated at the predetermined optimum operating conditions; the removal of metals was 92.1%, 87.8% and 82.9% for Ni. Zn, and Cu respectively. By using a continuous flow reactor for the treatment of the same real wastewater and under the same operating conditions, metals removal rate increased to 98.9%, 97.4% and 96.6% for Ni. Zn, and Cu respectively [10].

A process focused on the removal of chromium, copper and zinc by EC and adsorption was investigated by Ayub et al. The electrochemical reactor consisted of 8 aluminium plates of appropriate size. Effect of pH, applied current, and contact time in the EC process were studied. For adsorption, the effect of parameters including adsorbent dose (TiO_2: activated carbon (AC)), pH and contact time were studied. It has been shown that pH is a very important parameter for process efficiency. The optimum conditions evaluated were pH around 4, applied current 2 A, and 60 min of electrolysis time. This experimental study showed that under the optimal conditions, 87.6% Cr, 100% Cu and 99.2% Zn were successfully removed. The adsorption percentages of these ions by TiO_2:AC increased sharply by increasing adsorbent dose. The results show that an optimum dose of 5 and 4 g/L of TiO_2:AC can remove about 97% Cr (VI), 97.45% Cu, and 96% Zn from the wastewater sample containing initially 50 mg/L concentration of each heavy metal. Electrocoagulation and TiO_2:AC adsorption achieved a high degree of Cr, Cu, and Zn removal and therefore can be utilized for the treatment of industrial effluents [11].

The mechanism of zinc removal by the EC process and the reaction kinetics were also the subject of research. Researches show that the Fe electrode generated more coagulant such as iron hydroxides in comparison with Al electrode at the same current density. The main removal mechanism of metals during electrocoagulation is the precipitation with metal hydroxide. Iron sludge is composed mainly of Fe_3O_4 and FeO(OH), and Al sludge is mostly AlO(OH) [12]. SEM and EDX analysis of the sludge produced after the EC process determined that besides the precipitation effect of aluminum hydroxide flocculation, electrochemical reduction of Zn^{2+} at the cathode also contributed to Zn^{2+} removal, especially at a high initial concentration. At low initial zinc concentrations, it was difficult to detect zinc on the cathode precipitate by EDX analysis, implying that the main removal mechanism is precipitation with metal hydroxide [13].

2. EXPERIMENTAL

The experimental part of this research is the application of the EC process in order to remove zinc from wastewater after the cyanide-free electroplating process. The wastewater sample was taken from a company whose activity is the surface protection of metals, from Bosnia and Herzegovina. The sample was composed of wastewaters after acid and alkaline (cyanide-free) electroplating.

The batch electrochemical reactors used for the treatments were made of polypropylene. The reactor volume was 300 cm³ each. During all wastewater treatments, constant stirring was performed at a speed of 200 rpm. Different electrode pairs (anode-cathode) were used: steel-steel (Fe-Fe), Al-Al, Fe-stainless steel (SS), Fe-Cu, Al-SS, Al-Cu. The useful surface area of the steel anode was 46.4 cm², and the aluminium anode 46.2 cm². The distance between the electrodes was 2 cm and the volume of the sample used in each treatment was 250 cm³. Digital BLANCO PS3010 (for treatments with Fe anodes) and programmable DC power supply GW Instek PSP 2010 (for treatments with Al anodes) were used as a source of direct current. Before each treatment electrodes were cleaned and degreased. Figure 1 shows the process of electrocoagulation.

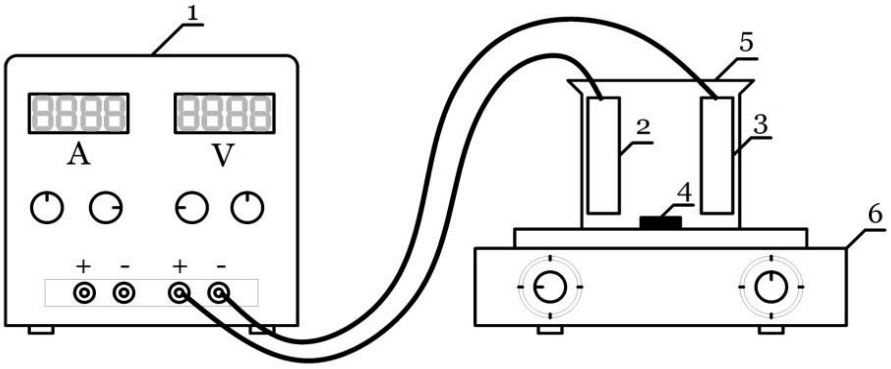

Figure 1. *Scheme of electrocoagulation process setup: 1 – source of electric power; 2 – anode; 3 – cathode; 4- magnetic stir bar; 5 – electrochemical cell; 6 – magnetic stirrer)*

Before all treatments, the wastewater samples were thermostated to a room temperature (20-25°C). A series of experiments were conducted lasting 5, 15, 30 and 60 minutes. All water samples were treated at a current density of 5 mA/cm², for each electrode pair.

2.1 Materials and chemicals

The wastewater from the electroplating process had a conductivity of 3.10 mS/cm and the use of supporting electrolyte (to increase electrical conductivity) was not necessary. All used electrode materials are made out of metals known compositions, and comply with prescribed standards, respectfully:

- aluminium (Al 99.5/EN AW-1050 A): 99,5% Al, 0,25%Si, 0,40% Fe, 0,05% Cu, 0,05% Mn, 0,05% Mg, 0,05% Ti, 0,07% Zn;
- steel (EN10130-91): 0,08% C, 0,12% Cr, 0,45% Mn, 0,60% Si;
- stainless steel (EN 1.4301 / AISI 304): max. 0,07% C, 18,1% Cr, 8,2% Ni);
- copper (EN 13601 / CW004A): min. 99,90% Cu, max. 0,001 P).

After each EC process, treated wastewater was filtered through filter paper, Filtres Fioroni, France (Ref.:0015A00007; size: 125 mm, qty.: 1000) and it was collected formed sludge.

The following parameters were determined for all samples before and after treatment: pH, conductivity, total dissolved solids (TDS), chemical oxygen demand (COD), and the concentration of certain metals: zinc, aluminium, manganese, nickel, chromium, silicon and phosphorus.

Electrical conductivity (σ), pH and TDS were measured using a multimeter (Consort C861) and COD measuring was performed by closed colorimetric reflux method on thermal block (COD Reactor, Hach, USA) and colorimeter (COD CheckItDirect, Lovibond, Germany) using standard cuvette (Test Tube LR, Lovibond, Germany). Metal concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (PerkinElmer Optima 8000 ICP-OES). The morphological characteristics of the sludge were evaluated by scanning electron microscope (SEM) analysis (Tescan Mira 3).

3. RESULTS AND DISCUSSION

The efficiency of the EC treatment was monitored by comparing the water quality parameters before and after treatment. The parameters that characterize the initial wastewater sample, as well as the maximum allowed values according to the regula-

Table 1. *The quality of the initial wastewater sample and limit values*

Parameter (unit)	Value in wastewater sample	Limit values in RS		Limit values in FBiH	
		surface water [3]	public sewage [4]	surface water [5]	public sewage [5]
σ (mS/cm)	3.1	-	-	-	-
pH	**2.12**	6.50 - 9.00	6.50 - 9.50	6.5 – 9.0	6.5 – 9.5
TDS (g/L)	1.78	-	-	-	-
COD (mg/L)	55	125	*	125	700
Zn (mg/L)	**173.5**	1.0	2.0	2.0	2.0
Al (mg/L)	0.529	1.0	**	3.0	3.0
Cr (mg/L)	**0.615**	0.1	1	0.5	0.5
Ni (mg/L)	**0.112**	0.01	0.05	0.5	0.5
Mn (mg/L)	0.431	0.5	0.5	1.0	1.0
Si (mg/L)	6.47	-	-	-	-
P (mg/L)	1.06	3.0	5.0	2.0 (a)	5.0

**COD is not standardized, it is regulated by a permit, taking into account all technical and economic factors that influence the choice of treatment plant, as well as the penetration of groundwater into the sewage system, as a result of which the concentration of organic substances in the inflow to the plant can be low*

***without limits*

(a) this value is reduced by 1 mg/L for sensitive areas

tions on the discharge of wastewater into surface water and public sewage systems in the RS [3, 4] and the FBiH [5] are shown in table 1.

The efficiency of EC treatments is expressed through the removal efficiency of certain parameters and is calculated according to the following equation:

$$E_r = \frac{\gamma_i - \gamma_f}{\gamma_i} \cdot 100\% \quad (1)$$

where are γ_i and γ_f are the initial and the final concentration/value of certain parameter, expresed in units shown in table 1.

The main goal of the treatment was to remove the highest possible concentration of zinc by the EC process, with the shortest possible treatment time and the lowest possible energy consumption. The energy consumed to remove pollutants unit is one of the most important technological performance indicators of electrochemical reactor, because it affects the overall cost of treatment. Specific energy consumption (W_{sp}) is calculated by the following equations:

$$W_{sp} = \frac{U \cdot I \cdot t}{m}\left[\frac{kWh}{kg_{polu\,tan\,t}}\right] \quad (2)$$

$$W_{sp} = \frac{U \cdot I \cdot t}{V}\left[\frac{kWh}{m^3}\right] \quad (3)$$

where: *U*- voltage (V), *I*- applied current (A), *t*- electrolysis (treatment) time (h), *V*- volume of wastewater (m^3), *m*- mass of removed pollutant (kg).

The current density used during all treatments was 5 mA/cm², and was chosen from the range based on literature recommendations [9,15]. Before wastewater treatment pH was not adjusted. The influence of the electrolysis time and the type of electrode material on the values and treatment efficiency in terms of the removal/reducing of certain parameters (σ, pH, TDS, COD, Zn, Mn, Al, Cr, Si, P, Ni) was examined.

3.1. The effect of the EC treatment on σ, pH, TDS, COD values

Electrical conductivity depends on the concentration of dissolved substances in water, dissociation, electrical charge and mobility of ions and temperature. It was experimentally determined that the treatment with all tested electrode pairs led to a decrease in the conductivity of the wastewater. The lowest conductivity was obtained with the Al-SS electrode pair. After 60 minutes of this treatment, the electrical conductivity was 1.272 mS/cm, or it was reduced by 59%.

It is well known that the EC process leads to a slight increase in the pH value of the treated water, because aluminium or iron hydroxides are formed by the electrolytic dissolution of sacrificial iron or aluminium anodes and water reduction to hydrogen gas and OH^- on the cathode [15]. During the EC process with all examined electrode pairs, there was an expected increase in the pH value of the treated water, with the highest value of 5.32 achieved using the Fe-Fe pair for 15 minutes of treatment. After 60 minutes of treatment with all tested electrode pairs, the pH ranged from 4.13 to 4.42, which is about 2 units lower than the value allowed by the regulations [3], [4] and [5].

Also, during the treatment, a decrease in TDS was observed with an increase in the duration of the EC process. The results showed that all treatments resulted in a decrease in the TDS, which indicates that the EC process is effective in reducing the amount of dissolved and suspended substances from wastewater. The highest reduction in TDS value was observed with the Al-SS electrode pair, where the TSD value was 0.865 g/L, or it was reduced by 51.4%.

Wastewater from the electroplating process mainly shows a high COD due to the presence of compounds such as various additives, metal precipitates and metal-cyanide complexes. Therefore, the removal of these compounds, containing heavy metals, is necessary in order to reduce COD of the electroplating effluent in a permissible discharge limit and thus control pollution and its impact on the environment [16]. The initial COD value of the untreated sample was 55 g/L, which is in line with the maximum allowed concentrations according to the regulations in RS and FBiH, but it was interesting to examine how the COD of the treated water would change by using different electrode pairs during EC treatment. The results showed that Al-SS electrode pair achieved the best results. After 60 minutes of treatment, 65.4% of the initial COD value was reduced.

3.2. The effect of the EC treatment on Zn, Al, Mn, Si, Cr and Ni concentration

The change in the concentration of certain metals from the wastewater after the EC process was monitored, and it was tested whether the water after treatment was of satisfactory quality (according to the regulations in RS and FBiH), and the specific energy consumption of certain treatments was also presented.

The results presented in Fig. 2 show that all electrode pairs with Fe anode and Al-Al electrode pair were efficient in terms of reducing the concentration of Zn in the treated water compared to the initial value. Fe anode shows higher efficiency compared to Al anode, which is in accordance with previous research [7, 8].

The results (Fig. 2) also show that the use of electrode pairs with SS or Cu cathode at shorter treatment times results in an increase in Zn concentration compared to the initial value. Without additives, alkaline zincate baths produce powdery non-adherent deposits which have no use in commercial plating. Additives must be added in optimum concentrations to obtain adherent, bright and uniform zinc coatings. It was necessary to replace the complexing effect of toxic cyanide ions with other complexing agents such as EDTA, gluconate, tartrate and triethanolamine. However, the use of these additives caused problems in the removal of heavy metals in wastewater treatment. Modern additives for alkaline zinc baths are often organic compounds that, when added in small amounts, can modify crystal growth, thereby changing the properties of the coating [17].

In the company from which the wastewater sample was taken, EDTA is used as a complexing agent in the bath for alkaline Zn electroplating. The increase in Zn concentration is most probably caused by the electrochemical destruction of the Zn-EDTA complex. In the EC process, pollutant removal is majorly due to adsorption, coagulation, and floatation, and there is no proof advanced oxidation process involved in the EC process. However, the ability of the EC process to make the pH of the treated effluent neutral or almost neutral from an acidic or alkaline state can lead to the degradation of some components by the peroxycoagulation process [18]. The Electro-Fenton (EF) process is an electrochemical advanced oxidation process in which hydrogen peroxide and ·OH are generated in an electrolytic cell *in situ*, and the optimal pH for this process is 3, which was the pH at shorter EC times in this research (5, 15 min). In the EF process, the reaction between Fe^{2+} (generated by electrolytic dissolution of the sacrificial Fe anode) and hydrogen peroxide (generated at the cathode) produces a hydroxyl radical, which is responsible for the degradation of the metal complex. Although mainly carbon materials are used as

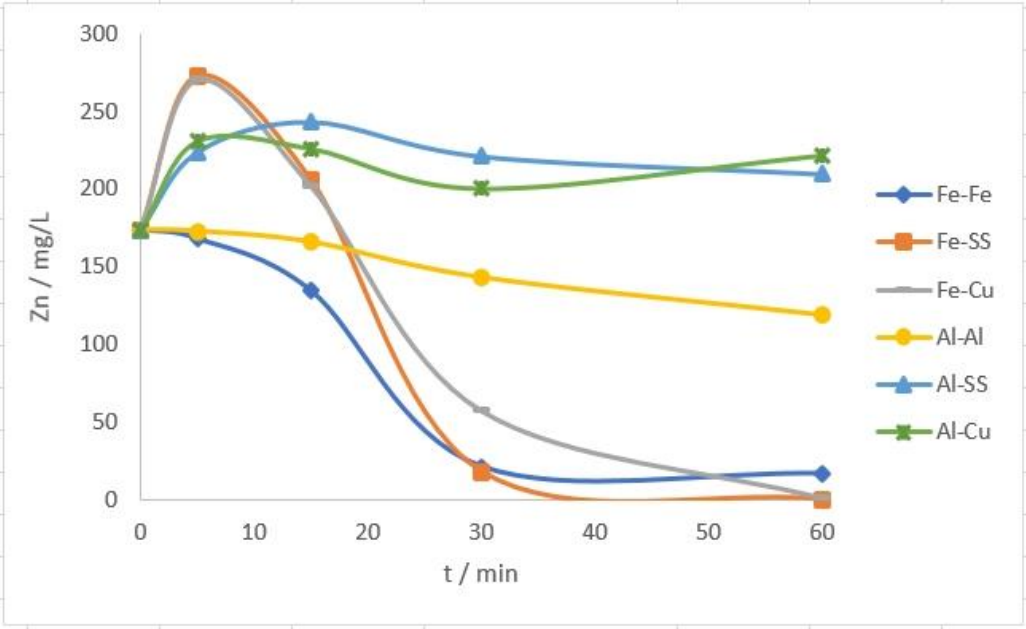

Figure 2. *Change in zinc concentration depending on the treatment time and the electrode pair*

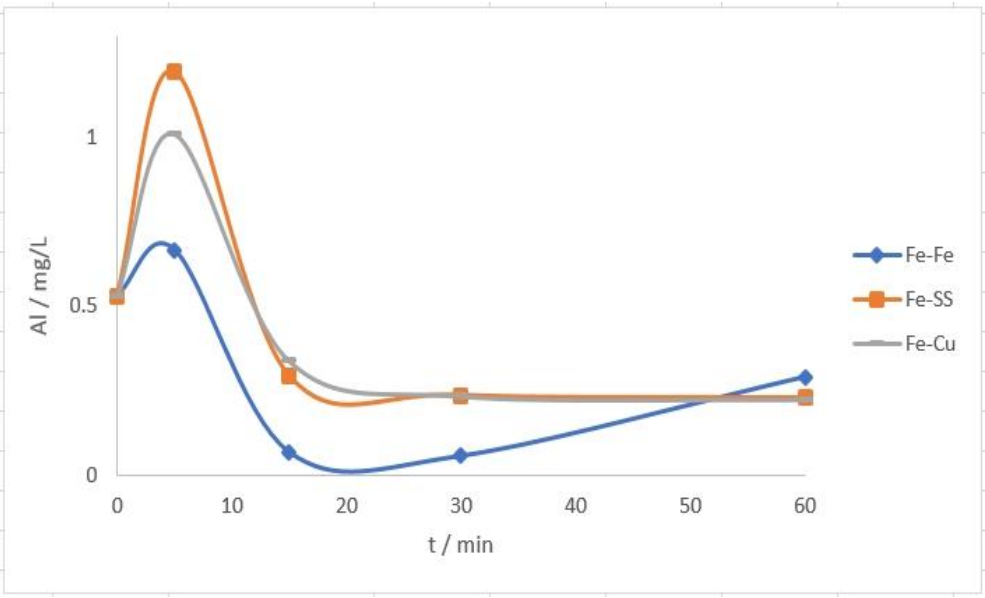

Figure 3. *Change in aluminium concentration depending on the treatment time and the electrode pair*

cathodes for the EF process, there is a certain number of studies where stainless steel was successfully used as the cathode [19].

The highest zinc removal efficiency was achieved with the Fe-SS electrode pair and amounts 99.8% after 60 minutes of treatment. For this treatment energy consumption was 6.10 kWh/m^3, or 8.74 kWh/kg$_{Zn}$. The concentration of Zn after this treatment (0.213 mg/L), as well as 60 min of treatment with the Fe-Cu electrode pair (0.962 mg/L) was within the limits defined in [3], [4] and [5]. Energy consumption of 8.74 kWh/kg$_{Zn}$ (Fe-Fe) at a current density of 5 mA/cm^2 (50 A/m^2) corresponds to the range of energy consumption (0.24–8.47 kWh/m^3) obtained in the research by Kobya et al. for the treatment of waste rinse water after zinc phosphate coating with Fe anode and in the range of current density from 10.0 to 100.0 A/m^2 [9].

To evaluate the efficiency of aluminium removal, only electrode pairs with Fe anode are taken into account, since the use of Al anode leads to electrolytic dissolution in accordance with Faraday's law and, consequently, an increase in the concentration of aluminium in the treated water. The concentration of aluminium in the untreated water was satisfactory according to the current regulations, and after treatment it was additionally reduced (Figure 3). The highest aluminium removal efficiency is observed with the Fe-Cu electrode pair, 58.03%, while with the Fe-SS electrode pair it is slightly lower and amounts to 57.1%. The treatment lasted 60 minutes and the energy consumption for the most efficient treatment (Fe-Cu) was 8.07 kWh/m^3.

Both anodes contain a certain amount of manganese, 0.05% in the Al anode and 0.45% in the Fe anode. The electrolytic dissolution of the sacrificial anodes leads to the expected increase in manganese concentration in the treated water, as shown in Figure 4. After all treatments, the concentration of Mn was higher than concentration allowed by regulations, except in the case of the Al-Al electrode pair, where during all treatments the concentration was <0.5 mg/L and in line within the maximum allowed limit values.

The highest manganese removal efficiency was achieved by EC with Al-Al electrode pair. For 30 minutes of treatment final concentration of manganese was 0.142 mg/L and energy consumption was 3.71 kWh/m^3.

In the composition of both used anode materials there is certain percent of silicon, 0.25% in the Al anode and 0.60% in the Fe anode. However, although Si was probably released by the electrolytic dissolution of the anodes, the treatments were still effective and there was a simultaneous removal of Si, which can be seen by the decrease in concentration compared to the initial value in untreated water (Fig. 5). The lowest silicon concentration was achieved by EC with Fe-Fe (0.151 mg/L) and Fe-SS (0.098 mg/L). The treatment lasted 60 minutes, and

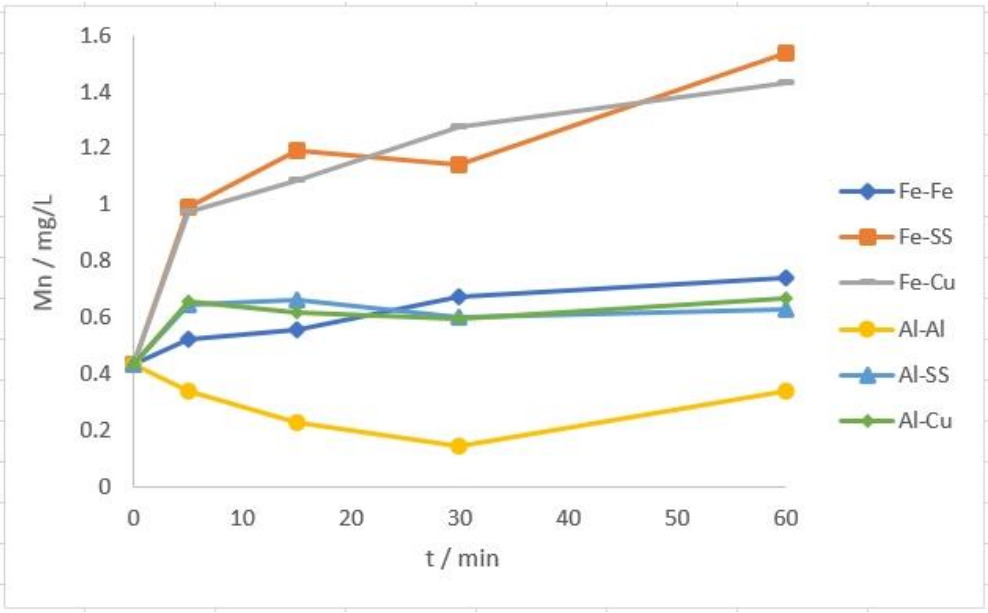

Figure 4. *Change in manganese concentration depending on the treatment time and the electrode pair*

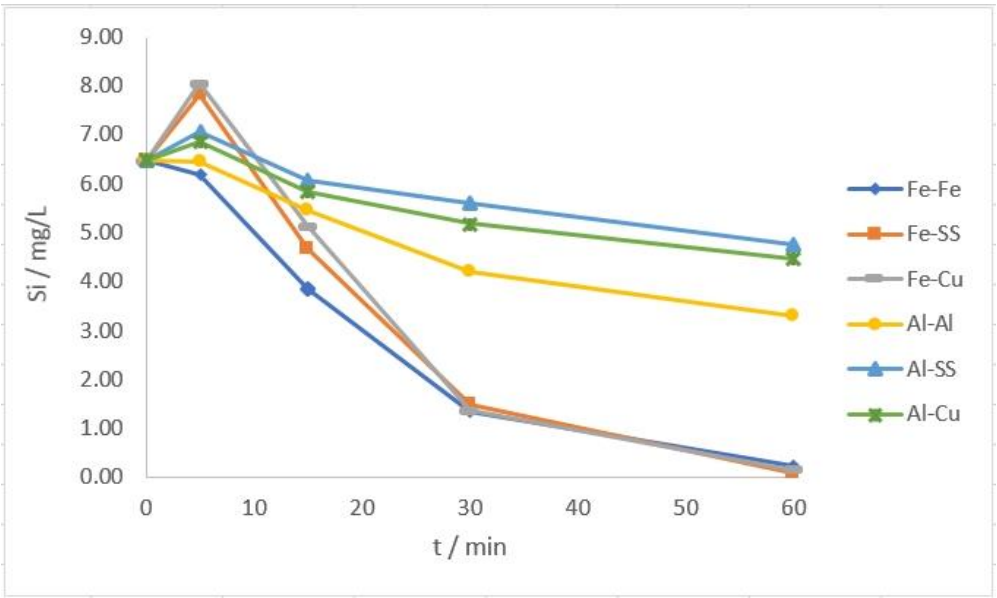

Figure 5. *Change in silicon concentration depending on the treatment time and the electrode pair*

achieved silicon removal efficiencies were 97.66% and 98.48%.

Phosphorus is a natural nutrient, but released in large amounts into surface waters causes eutrophication. EC is successfully used to remove phosphorus from various types of wastewater and is economic and effective both with iron and aluminium anodes [20]. The concentration of phosphorus in this wastewater was satisfactory, but the treatment certainly proved to be extremely effective in reducing the concentration of phosphorus (Figure 6). The Fe-Fe was the most efficient electrode pair for removing phosphorus from wastewater. The 15 minutes EC treatment resulted in the complete removal of phosphorus from the wastewater (100%).

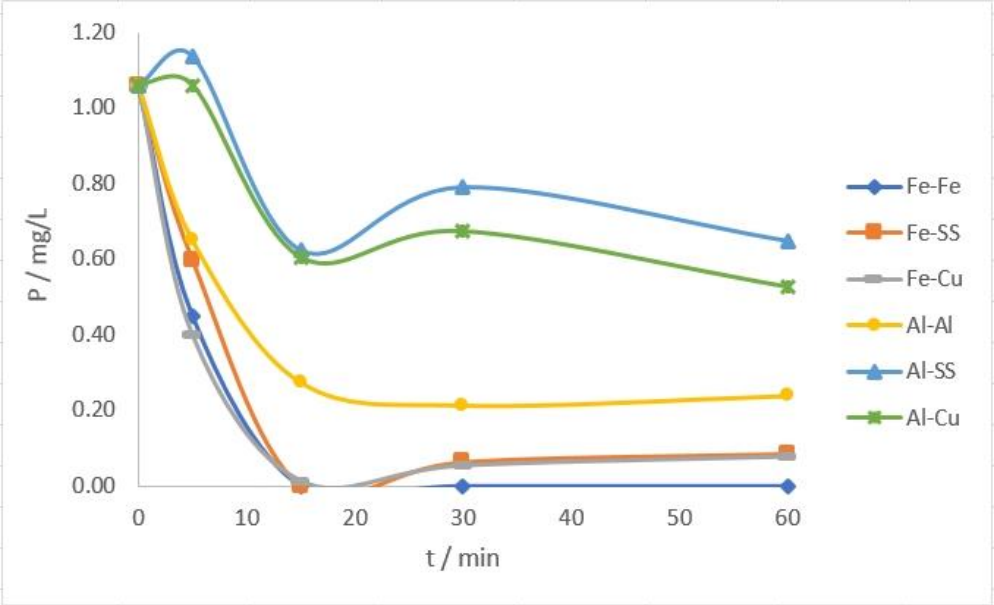

Figure 6. *Change in phosphorus concentration depending on the treatment time and the electrode pair*

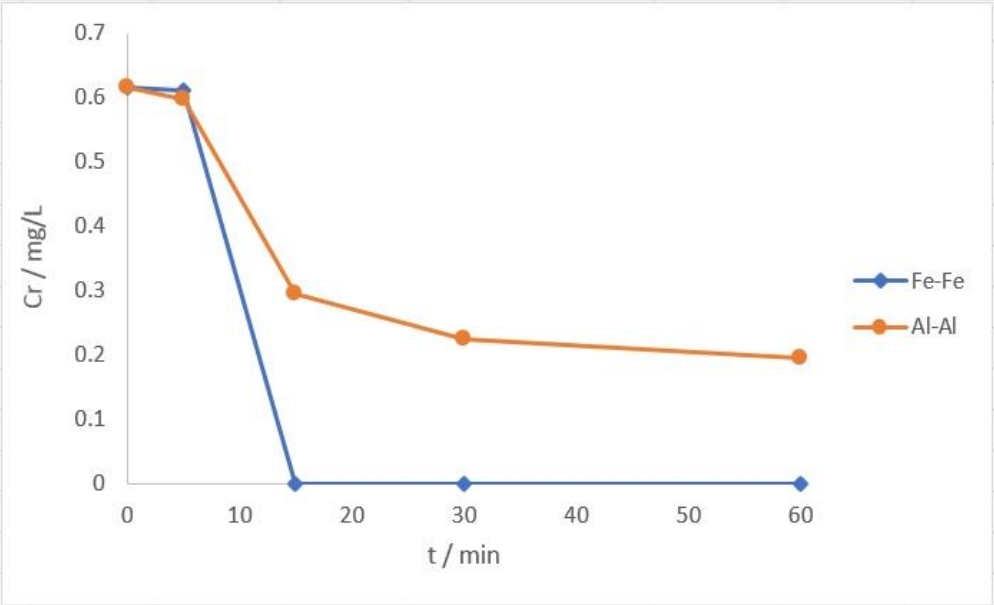

Figure 7. *Change in chromium concentration depending on the treatment time and the electrode pair*

The concentration of total chromium in the wastewater was higher than the limit concentrations (table 1). Based on previous research, EC has proven to be a very effective treatment for removing chromium from wastewater. For 30 minutes of wastewater treatment with an initial chromium concentration of 50 mg/L with an Al-Al electrode pair, a removal efficiency of 43.9% was achieved, while with the Fe-Fe pair, 97.9% of chromium removal was achieved in just 5 minutes of treatment, at the current density of 20 mA/cm^2 [21]. Since the aforementioned anode materials were effective in removing chromium at a concentration that was ten times higher than the concentration present in this wastewater, only two electrode pairs were tested, as shown in Figure 7. Complete removal of chromium was achieved in

15 minutes by EC with Fe-Fe electrode pair. As expected, the efficiency of chromium removal with the Al-Al electrode pair was lower, but the chromium concentrations after the treatment were within the regulations limits.

In this set of experiments, the concentration of nickel after treatment was also examined. The nickel removal efficiency of 43.75% was achieved with the Al-Al electrode pair in 60 minutes of treatment, but the Ni concentration after the treatment was not within the regulations permitted limits. The Fe-Fe electrode pair proved to be less efficient for the removal of nickel from the wastewater sample by the EC process, with the highest efficiency of 15.1%.

3.3. Review of the success of the treatments

How successful the tested electrode pairs were in reducing the concentration/value of certain parameters is shown in Table 2. It can be seen that the Fe-SS electrode pair has the most achieved efficiency after 60 minutes of treatment.

Table 3 shows whether, after 60 minutes of treatment with the Fe-SS electrode pair, the water has satisfactory quality defined by regulations in the Republic of Srpska and the Federation of Bosnia and Herzegovina. Based on the results presented in the table 3, it can be seen that the water after the electrocoagulation treatment meets the prescribed quality,

Table 2. *The most efficient electrode pair after 60 minutes of treatment*

Electrode pair	σ (ms/cm)	TDS (g/L)	mg/L							
			COD	Zn	Al	Cr	Ni	Mn	Si	P
Fe-Fe						x				x
Fe-SS				x	x	-	-		x	
Fe-Cu						-	-			
Al-Al							x	x		
Al-SS		x	x			-	-			
Al-Cu	x		x			-	-			

- not monitored

Table 3. *Quality of treated water*

Parameter	Value after 60 min of treatment	Limit values in RS		Limit values in FBiH	
		surface water	public sewage	surface water	public sewage
σ (ms/cm)	1,63	✓	✓	✓	✓
pH	**4,13**	x	x	x	x
TDS (g/L)	0,962	✓	✓	✓	✓
COD (mg/L)	60	✓	✓	✓	✓
Zn (mg/L)	0,213	✓	✓	✓	✓
Al (mg/L)	0,227	✓	✓	✓	✓
Cr (mg/L)	-	-	-	-	-
Ni (mg/L)	-	-	-	-	-
Mn (mg/L)	**1,535**	x	x	x	x
Si (mg/L)	0,098	✓	✓	✓	✓
P (mg/L)	0,086	✓	✓	✓	✓

- not monitored

except for the pH value which is lower than the limit and Mn whose concentration has increased due to the electrolytic dissolution of the iron anode. Total Cr and Ni parameters were not determined for this set of experiments, but it is almost certain that Cr is in the allowed concentration, since the Fe-Fe electrode pair removed 100% of the present chromium in only 15 min of treatment. The concentration of Ni in the untreated sample was 0.112 mg/L, which is higher than the maximum allowed concentration according to the regulations in the RS, but is lower than the allowed concentration prescribed in FBiH (0.5 mg/L). The company from wich sample was taken is located in the Federation of Bosnia and Herzegovina, so it can be considered that the water is of satisfactory quality in terms of this parameter as well.

3.4. Morphological characteristics

After collecting and drying the sludge after EC treatment, the surface morphology of the electrocoagulated precipitates was investigated by SEM (Figure 8).

Morphologies of the precipitated sludges after EC process using Fe and Al anodes are evidently different. Precipitate obtained using Fe anode has uneven rough surface morphology (Figure 8a), while the precipitate obtained from Al anode has flat layered surface morphology (Figure 8b). The differences in precipitates come from the differences in nature of precipitated Fe and Al hydroxides from Fe and Al anodes, respectively. Fe hydroxides tend to form particle or grain-like structures [22], while Al hydroxides form platelet-like structure [23]. Fe hydroxides should contain trapped Zn ions in the form of hydroxides precipitated together with Fe hydroxides, consisting of Fe, Zn and O as the main components of the precipitate. On the other hand, Al hydroxides should contain Al and O as a dominant elemental components coexisting with the Zn ions trapped in the Al hydroxides. Zn arise from the electrocoagulated sludge whose concentrations decreased from initial 173,5 mg/L to 0.213 mg/L and 119.2 mg/L using Fe and Al anodes, respectively. Hence, these differences in surface morphologies mainly come from the morphological differences in the structures of Fe and Al hydroxides.

4. CONCLUSION

Based on the experimentally obtained results the following can be concluded:

− The success of the EC process, in terms of zinc removal from cyanide-free electroplating rinsing wastewater for 60 minutes of treatment, was achieved with electrode pairs Fe-SS > Fe-Cu > Fe-Fe > Al-Al > Al-SS > Al-Cu.

− Steel electrode proved to be more efficient as an anode material, in contrast to aluminium, and the electrode pair of Fe-SS achieved the highest effi-

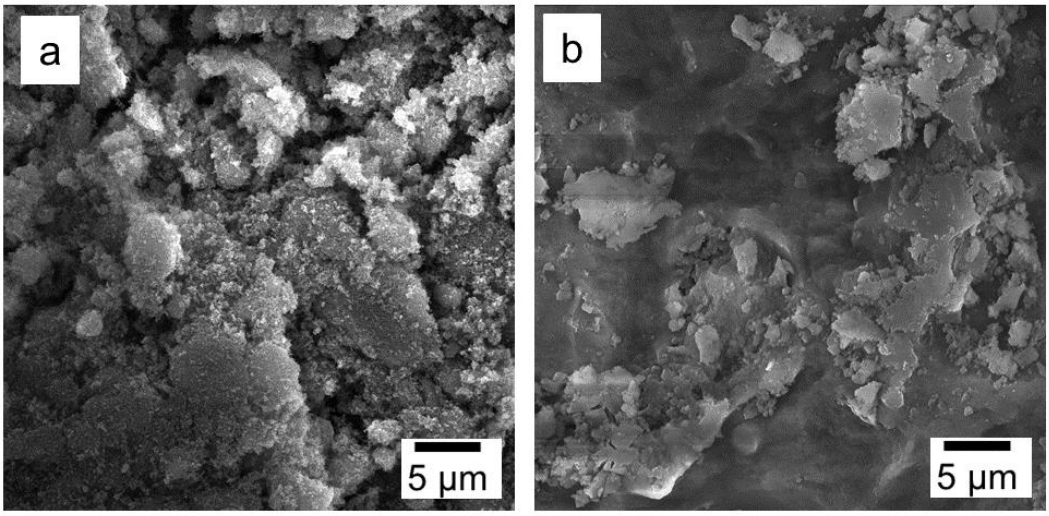

Figure 8. *SEM micrographs of electrocagulated precipitates.*
(a) Precipitate after EC using Fe-SS electrode pair
(b) Precipitate after EC using Al-Al electrode pair.

ciency for the removal of certain process parameters.

− The specific energy consumption for 60 min of treatment with the Fe-SS electrode pair amount 6.10 kWh/m³ of treated wastewater, or 8.74 kWh/kg of removed Zn, which can be considered a low energy consumption.

− After 60 minutes of treatment with Fe-SS pair, the treated water was of satisfactory quality according to all tested parameters, with the exception of the pH, which is slightly acidic, and the concentration of Mn which increased.

− By adjusting the pH value of the treated water to the alkaline range (legally allowed up to 9.5), the resulting Mn could be precipitated, and such water can be discharged into natural recipients or public sewage systems.

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ТРЕТМАН ОТПАДНЕ ВОДЕ БЕЗЦИЈАНИДНОГ ЦИНЧАЊА

Сажетак: Отпадне воде из процеса галванизације често садрже високе концентрације тешких метала, те се као такве морају третирати прије испуштања у јавне канализационе системе или природне реципијенте. У овом истраживању испирне отпадне воде послије киселог и алкалног цинчања третиране су процесом електрокоагулације. Експерименти су извођени у шаржном електрохемијском реактору израђеном од полипропилена и запремине 250 cm^3. Приликом свих третмана вршено је константно мијешање брзином од 200 о/мин. Кориштени су различити електродни парови (анода-катода): Fe-Fe, Al-Al, Fe-нерђајући челик (SS), Fe-Cu, Al-SS, Al-Cu. Успјешност процеса електрокоагулације, у смислу уклањања цинка из отпадне воде безцијанидног цинчања, остварена са различитим електродним паровима је Fe-SS > Fe-Cu > Fe-Fe. Почетна концентрација цинка у отпадној води износила је 173,5 mg/L, а након 60 минута третмана са електродним паром Fe-SS остварена је ефикасност уклањања од 99,8%, при чему је специфични утрошак електричне енергије за је износио 6,10 kWh по m^3 третиране отпадне воде, односно 8,74 kWh по 1kg уклоњеног Zn.

Кључне ријечи: галванизација, испирне отпадне воде, електрокоагулација.

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