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PRELIMINARY INVESTIGATIONS ON THE USE OF ELECTROCOAGULATION FOR HEAVY METALS REMOVAL FROM METAL PLATING WASTERWATER

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Abstract

The aims of the present paper was to investigate the possibility of using the electrocoagulation method (EC) for the removal of Ni2+ and Cr3+ ions from the wastewaters generated at an electroplating plant from Transylvania area. In the investigated wastewater samples, the concentration of Ni2+ and Cr3+ significantly exceeds the maximum consent limits established by Romanian Standard NTPA001/2002. The influence of the varying operating parameters, such as the applied current intensity (4,5 and 6 A), electrode material (Fe and Al) and the contact time (10 to 60 minutes) on the heavy metals removal was investigated. The results showed that the removal of the metals from electroplating wastewaters solution increases with increasing current density and operating time. Using iron electrodes, over 99.64% of nickel and 99.39% of chromium ions were removed efficiently by conducting the EC treatment at current intensity of 5A, pH of 8.09 and EC time of 60 min. By using aluminium electrodes, the removal efficiency of Ni2+ was 98.21%, at pH 6.02, a current intensity of 5A and an operation time of 60 min.

Key words: *electrocoagulation, chemical precipitation, iron electrodes, aluminium electrodes, removal efficiency.*

INTRODUCTION

Metal plating industry is one of the major chemical processes that discard large amounts of wastewaters that contain various types of harmful heavy metals such as chromium, nickel, copper, zinc (Al-Shannag et al., 2014). The most used methods for the treatment of metals polluted wastewater are precipitation and coagulation followed by the time-consuming sedimentation (Heidmann and Calmano, 2007). Various other methods based on physical, chemical and biological processes including adsorption, ion-exchange, reverse osmosis, filtration are also employed in the wastewaters treatment (Al-Shannag et al., 2014).

Precipitation of heavy metals in an insoluble form of hydroxides is the most economical method to treat the wastewaters containing heavy metals. It consists in the adjustment of the pH of wastewater and the addition of chemical coagulants, like aluminium or iron salts to remove pollutants as colloidal matter (Ferreira et al., 2013). Although the chemical coagulation technique is considered to be effective in treating industrial wastewater effluents, it has quite high cost. On the other hand, the addition of chemical coagulants to the wastewater may produce side-products that are considered as secondary pollutants (Al-Shannag et al., 2014). A variation of this method developed in the last years is electrocoagulation (EC) using iron or aluminium electrodes (Ferreira et al., 2013). During the electrocoagulation process, wastewater is subjected to a direct electrical field through sacrificial electrodes that are generally made of iron or aluminium. According to B. Al Aji et al (Al Aji et al., 2012) a range of coagulant species and hydroxides are formed which destabilize and coagulate the suspended particles or precipitate and adsorb dissolved contaminants. It is generally accepted that the EC process involves three successive stages (Al Aji et al., 2012) :

(1) Formation of coagulants by electrolytic oxidation of the electrode. The main reaction occurring at the metal anode is dissolution:

$M(s) \rightarrow M(aq)^{n+} + ne^-$

Additionally, water electrolysis occurs at the cathode and anode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ (cathodic reaction)

2H2O(l) → 4H+ (aq) + O2(g) + 4e- (anodic reaction)

(2) Destabilization of the contaminants, particulate suspension, and breaking of emulsions.
A direct electrochemical reduction of metal cations (Mn+) may occur at the cathode surface:
Mn+ + ne- → nM0

Furthermore, the hydroxide ions formed at the cathode increase the pH of the wastewater thereby inducing precipitation of metal ions as corresponding hydroxides and co-precipitation with hydroxides:
Mn+ + nOH- → M(OH)n(s)

(3) Aggregation of the destabilized phases to form flocs.
Electrocoagulation has been successfully applied for the removal of various heavy metal ions, like Ni(II), Cr(VI), Cu (II) from industrial or synthetic wastewaters.
Electrocoagulation process have advantages and disadvantages. In an electrocoagulation process, no addition of chemicals is necessarily needed. The volume of sludge produced by EC is smaller compared to that produced in classical chemical process and it can be easily removed by decantation. A major disadvantage of EC process is that the 'sacrificial electrodes' are dissolved into wastewater streams as a result of oxidation and need to be replaced periodically. Other disadvantages: the use of electricity may be expensive in many places, an impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit, and high conductivity of the wastewater suspension is required.
In present paper, it was aimed to remove Ni and Cr ions from metal plating wastewater through electrocoagulation. The impact of EC time, direct current intensity, pH and electrical conductivity on Ni and Cr ions removal by electrocoagulation was investigated.

MATERIAL AND METHODS

Wastewater composition

The studied wastewater was provided by a metal plating station from Transylvania. The pH and electrical conductivity of the wastewater were measured using a pH-meter (Hanna instruments) and a Cond 315i conductivity-meter (Hanna instruments), respectively. Chemical composition of the wastewater samples was determined in laboratory by X-ray fluorescence spectrometry (XRF) using a Quant'X ARL spectrometer (Thermo Scientific, USA).
Electrocoagulation experiments
For EC experiments, a system formed by 4 electrodes connected at a power source was used. For this process, were used iron electrodes and aluminium electrodes,
respectively. The iron (97mm x 30mm x 4mm) and aluminium (98mm x30 mm x 1,5 mm) electrodes were weigh before and after each experiment. They were vertically positioned in a Berzelius flask filled with 400 ml wastewater, in a parallel arrangement. A saturated calomel electrode was used as reference electrode. A magnetic stirrer with speed rotation 200-300 rpm was also used. The total effective surface area of electrodes immersed in wastewater was around 76.8 cm2 for iron electrodes and 99.2 cm2 for aluminium electrodes. This system was connected at a power supply providing voltage and electrical current in range of 10 pA to 600 mA , Gill AC Serial Instruments. Current densities used for EC treatment using aluminium electrodes were: 3.7 A/dm2 (at 4A), 5 A/dm2 (at 5A) and 5.6 A/dm2 (at 6A), while the current density used the iron electrodes was 6.5 A/dm2 (at 5A).

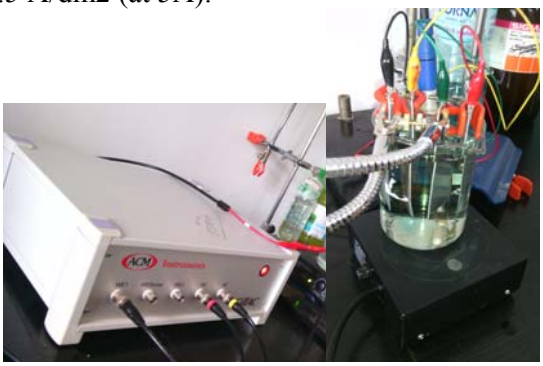

Figure 1. Electrocoagulation experimental set-up

The heavy metal ions removal was measured in terms of percent removal efficiency defined as:

$$RE(\%) = 100 * \frac{C_0 - C}{C_0} \%$$

where C0 and C are the concentrations of metals in the original wastewater sample and in the treated one at the given EC time (t), respectively.

Table 1. Average chemical composition and physicochemical parameters of plating wastewater sample

Parameter	Wastewater	Maximum consent limits*
pH	3.08	6.5 - 8.5
Ni (ppm)	280	1
Cr^{3+} (ppm)	165	1
Fe (ppm)	12	5
Ca (ppm)	82	300
Conductivity (mS cm^{-1})	2.73	

*According to Romanian Standard NTPA 001/2002.[5]

Samples of wastewater (10 ml) were taken during EC process at specified times, filtered through filter paper and then analysed by X-Ray Fluorescence (XRF).

RESULTS AND DISCUSSIONS

Characterisation of plating wastewater samples

The physical and chemical characteristics of the metal plating wastewater used in this study are listed in Table 1.

As it can be seen in Table 1, the plating wastewater is acidic (pH =3.08), present a high conductivity and contains various heavy metal ions (Ni, Cr and Fe). The concentrations of nickel and chromium in the plating wastewater exceed more than 165 to 280 times the maximum consent limits established by Romanian Standard NTPA001/2002.

Electrocoagulation

It is well-known that EC process is affected by several operating parameters, such current intensity, the nature of the electrodes, pH and the operating time. In this study, these parameters were explored in order to evaluate a treatment technology for Ni2+ and Cr3+ removal from the real wastewater.

In the first stage, experimental studies were carried out using iron electrodes at 5 A the different operating times between 10 to 60 minutes, at the original pH (3.08) of the wastewater. The variation of the residual metals concentration and the removal efficiency values during EC time are presented in Figure 2.

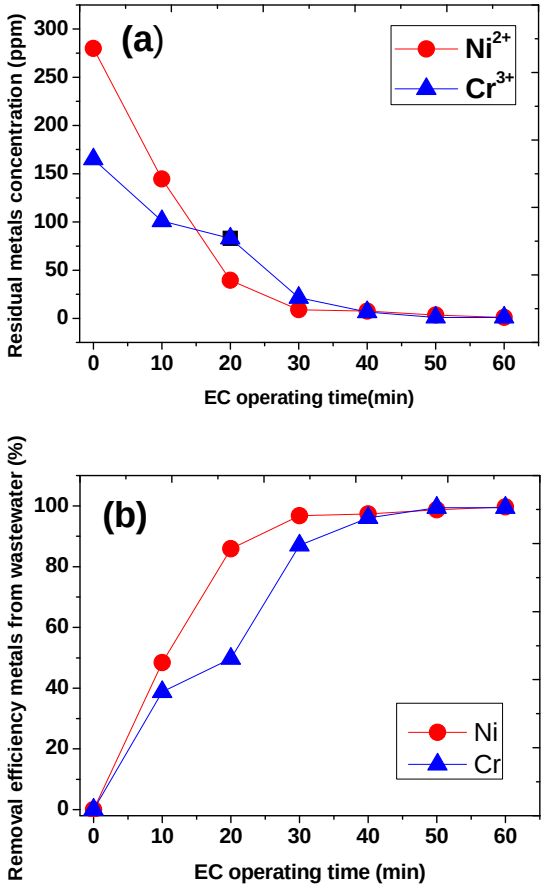

Figure. 2. The variation of residual metals concentration (a) and of the removal efficiency values (b) during EC time; iron electrodes, I=5A (i=6.5 A/dm^2).

It is depicted in Figure 2 that there is a dramatic reduction in the heavy metal ion concentrations within the first 30 min. For example, after 20

min of EC treatment, the Ni2+ ion concentration decreased from an initial concentration of 280 to 39,5 ppm and Cr3+ ion concentration decreased from initial concentration 165 to 83 ppm. Although, in investigated experimental conditions, the metals concentration exceeds 39.5 times for Ni2+ and 83 times for Cr3+ the maximum admissible limit according with NTPA001, the removal efficiency for both metals is significant. The concentration reduction was enhanced by increasing the EC time above 30 min. In the investigated experimental conditions, in the first 10 minutes of electrocoagulation, the removal efficiencies values for Ni2+ and Cr3+ are 48,39% and 38,78%, respectively. However, the RE values progressively increase during the increases of EC operating time and attain the maximum values of 99,64% for Ni2+ and 99,39% for Cr3+.

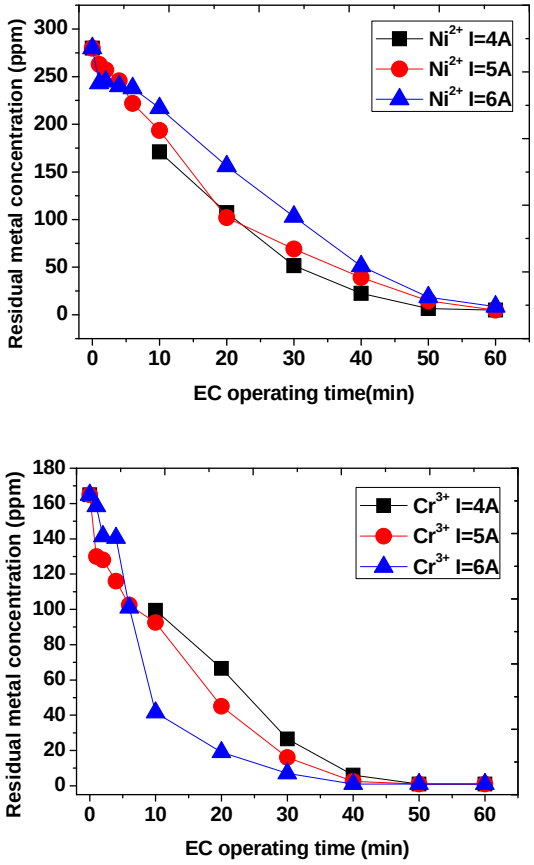

Figure. 3. The variation of residual metals concentration during EC time using aluminium electrodes at various current intensities (4-6 A).

In the second stage, electrodes made of aluminium were used in the EC experiments. Figure 3 presents the residual metals concentration and the removal efficiency values during EC time, at various current intensities(4-6A).

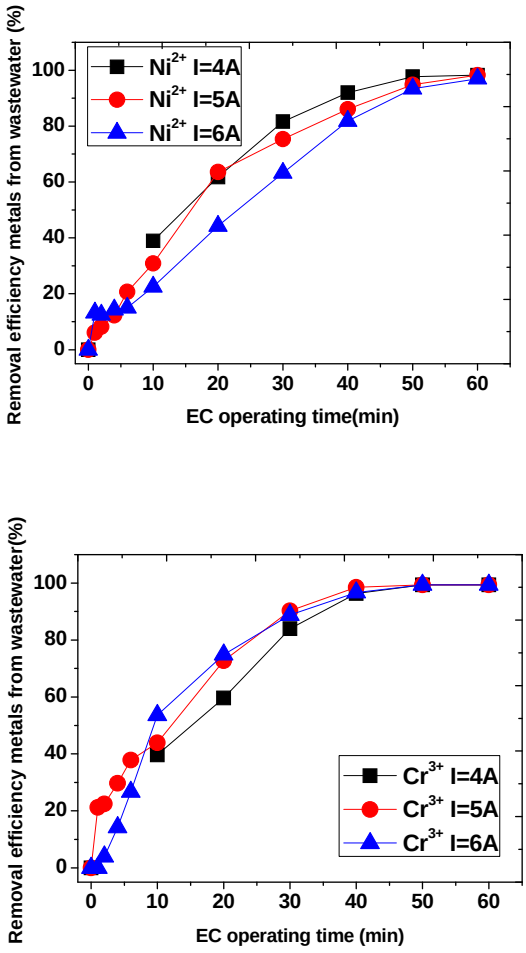

Figure. 4. The variation the removal efficiency values during EC time using aluminium electrodes at various current intensities.

Figure 3 clearly shows that aluminium electrodes are more effective in the reducing of the metal ions concentration from the plating wastewater. The decrease of metals concentrations is inversely with increasing EC operating time.

EC treatment at 4A illustrated in Figure 3 shows an obvious decreasing metal ions conc. during EC operating time. After 40 minutes of EC process, Ni2+ conc. decreased from initial conc. 280 ppm to 22.5 ppm and Cr3+ from 165

ppm to 1 ppm. After 40 minutes, the removal efficiency value for Ni2+ is 91.96% and for Cr3+ is 96.36%. The EC treatment had a progressive increasing of removal efficiency, it was reached the maximum values of 98.21% for Ni2+ and 99.39% for Cr3+, after 60 minutes.

During EC experiment at 5A, Ni2+ and Cr3+ ions concentration had a gradual decrease.

After 20 min of EC treatment, at current intensity 5A, the Ni2+ ion concentration decreased from an initial concentration of 280 to 102 ppm, and Cr3+ decreased from 165 to 45 ppm. However, in these investigated conditions, the Ni2+ concentration exceeds 102 times the maximum admissible limit while the Cr3+ concentration is 45 times higher than the limits imposed by NTPA001/2002. After the first 20 minutes, the values of the removal efficiency for Ni2+ is 63,57% and for Cr3+ is 72,72%. As the electrocoagulation process progress, the RE values progressively increasing to maximum values of 98,21% for Ni2+ and 99,39% for Cr3+, respectively.

The EC process done at 6A, show significant variation for Cr3+ ions concentration. In first 10 minutes of EC treatment, Cr3+ have a dramatic decrease from initial conc. 165 ppm to 41.5 ppm, removal efficiency value being at this point 53.63%. This value of Cr3+ concentration is 41.5 times higher than the maximum consent admissible, according with NTPA001. Forward, the Cr3+ conc. is decreasing progressively, reaching the maximum limit, 1 ppm and removal efficiency is increasing to 99.39%. The Ni2+ conc. have a constant decreasing from initial conc. 280 ppm to 8.5 ppm, removal efficiency being 96.96%, after 60 minutes of EC treatment.

As it could be seen in Figures. 2(a) and 2(b), the concentration of Ni2+ decreased from 280 ppm to 1 ppm, while the concentration of Cr decreases from 165 ppm to 1 ppm, after 60 minutes of electrocoagulation disregarding the value of the applied current intensity.

Using aluminium electrodes, the removal efficiency for Ni^{2+} ions was 98.21 % at a solution pH of 6.02, conductivity of 2.358 mS, current intensity 5A ($i = 5$ A/dm^2) for 60 min, but the nickel concentration is 5 times higher than the maximum consent limit (1 ppm) (Figure 4). On the other hand, EC treatment with iron electrodes had better results, at the same current intensity (5A) for 60 minutes and the maximum consent limit were reached for both metal ions.

It is obvious from Figure 3 that EC treatment on metal plating wastewater achieved high removal efficiency for both heavy metals from the electroplating wastewater. By increasing the applied current and operating time, the residual concentrations of the heavy metals significantly decreases, in some cases below the maximum consent limits established by NTPA001/2002. In order to maximize the removal efficiency in the operating conditions of this study, the current intensity must higher than 4A ($i > 3.7$ A/dm^2) and EC treatment time should be in the range of 30-60 minutes.

Figure 5. Sludge resulted from EC with iron electrodes (right) and aluminium electrodes (left).

An end-use of resulted sludge from EC process (Figure 5) must by sustainable to reduce the negative impact over the environment. However, sludge management and reuse became an interesting area for many researchers in the last few years, especially when the sludge contains economic compounds like metallic hydroxides as in present study (Al-Shannag et al., 2014).

CONCLUSIONS

This study aimed at analysing the potential of electrocoagulation process for the removal of Ni2+ and Cr3+ ions from the wastewaters generated at a metal plating station from Transylvania. An electro-reactor was used with four iron or aluminium electrodes in a monopolar configuration. Two of the electrodes were designated as cathodes meanwhile the other two as anodes. The results showed that the removal efficiency of heavy metal ions

increases with increasing both electrocoagulation (EC) operating time and the applied current. In the investigated experimental conditions, disregarding the nature of the used electrodes, over 98% of nickel and chromium were removed by conducting the EC treatment during 60 minutes at 5A, especially in the case of aluminium electrodes.

In conclusion, the electrocoagulation process is an efficient treatment method for the removal of heavy metal ions from real metal plating wastewater. Since the existing literature concerning the removal of toxic metals from real industrial wastewaters by electrocoagulation is quite limited and thus this research field requires further investigations.

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