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***"Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of his 65th anniversary"***

REMOVAL OF LEAD FROM INDUSTRIAL WASTEWATER BY ELECTROCOAGULATION USING SACRIFICIAL ALUMINIUM ELECTRODES

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Abstract. The aim of this study was to develop an ecological method for the removal of Pb^{2+} ions from industrial wastewater. The electrocoagulation (EC) process of Pb^{2+} has been studied, using an electrolytic flow cell (flow rate of 20, 40, 60 mL/min) equipped with sacrificial Al electrodes, operated under galvanostatic mode (current density of 5, 10 and 15 mA/cm^2). In all experimental conditions the concentration of Pb^{2+} was lowered below the maximum allowable concentration (0.5 ppm). The experimental results showed that the performances of the process are more strongly dependent on the applied current density than on the applied flow rate. The electrolytic flow cell has proved to be quite effective, allowing the complete removal of lead with a specific energy consumption of 3.08 kWh/kg Pb removed.

***Keywords**: lead contamination, sacrificial Al electrodes, lead removal, electrocoagulation.*

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INTRODUCTION

In the recent decades, the development of different types of industries, especially in Asian countries increased the amount of directly or indirectly discharged wastewaters into the environment [1, 2]. In many situations these wastewaters have high heavy metal concentrations, even exceeding the maximum allowable concentration, causing important environmental issues. The most of metals such as copper, nickel, lead, zinc and chromium tend to accumulate in living organisms leading to several health problems [3, 4]. Among the heavy metals, lead is one of the most dangerous since it is a neurotoxin that can accumulate in the soft tissues and bones through ingestion, causing serious brain disorders [5, 6]. There are different sources of lead pollution such as plating industries, depleted lead mines, dyes and refineries [7, 8]. Another major source of pollution is attributed to the uncontrolled degradation of electronic waste materials such as lead batteries or waste printed circuit boards [9, 10]. As a result, various techniques have been employed for the removal of heavy metals from industrial wastewaters among which the most important are: precipitation, adsorption, biosorption, ion-exchange, electrochemical and ion-exchange assisted membrane separation [11-14]. It is well known that an advanced removal of heavy metals can be achieved by means of electrochemical treatment, ion-exchange and reverse osmosis [15, 16]. The last two techniques are more expensive than electrochemical methods such as electrowinning, electrodialysis, and electrocoagulation (EC), which have been more frequently applied for heavy metal removal [17-19]. EC is a simple and efficient method where the flocculating agent is generated *in situ* by electro-oxidation of a sacrificial anode such as iron or aluminum [10, 20]. Moreover, EC offers an attractive and promising alternative considering its low environmental impact, high energy efficiency and the fact that it can be performed with minimal involvement of auxiliary materials. Thus, the treatment is done without adding any chemical coagulant or/and flocculants, preventing the generation of other wastewaters [21].

For the above reasons this study assesses the influence of current density and flow rate on the efficiency of lead removal *via* electrocoagulation. The most adequate operating conditions for the process were determined based on key technical performance indicators such as removal and cathodic current efficiency and specific energy consumption.

RESULTS AND DISCUSSION

Theoretical background

The removal of Pb^{2+} ions through electrocoagulation involves the following main electrochemical reactions:

Anode: $Al \rightarrow Al^{3+}_{(aq)} + 3e^{-}$ (1)

Cathode: $3H_2O_{(l)} + 3e^{-} \rightarrow 3HO^{-}_{(aq)} + 3/2H_{2(g)}$ (2)

At the cathode in parallel with hydrogen evolution the electrodeposition of lead can also take place as a secondary reaction:

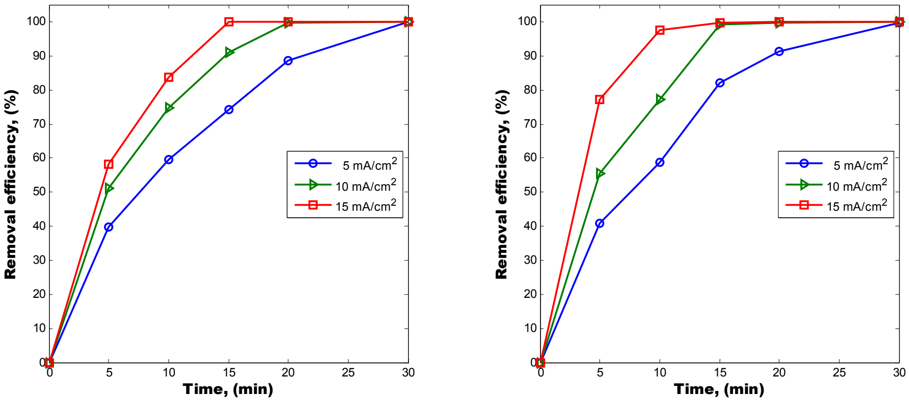
Cathode: $Pb^{2+} + 2e^{-} \rightarrow Pb_{(s)}$ (3)

The HO^{-} formed at the cathode can react with Al^{3+} and Pb^{2+} ions, inducing their precipitation and co-precipitation as corresponding hydroxides. Freshly formed amorphous $Al(OH)_{3(s)}$ (sweep flocs) have large surface areas, which are beneficial for the adsorption and trapping of Pb^{2+} ions. According to the literature [10], the adsorption of Pb^{2+} ions on $Al(OH)_3$ flakes can be described by the following reaction:

$$Al(OH)_3 + Pb^{2+} \rightarrow Al(OH)O_2Pb + 2H^{+} \quad (4)$$

The influence of current density and flow rate on process performances

The removal efficiency of Pb^{2+} ions was evaluated under batch electrocoagulation using different current densities and flow rates. It was found that the increase of current density lead to more rapid removal of Pb^{2+} ions regardless the applied flow rate. Figure 1 shows that the removal efficiency values obtained at 5 and 15 mA/cm^2 differ most in the initial stage of the process, being with 40 % higher after the first 5 minutes for the current density of 15 mA/cm^2.



a

b

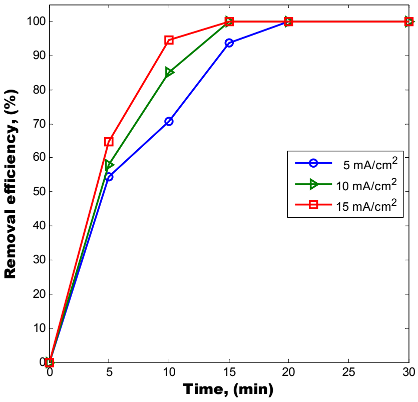


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Figure 1. Removal efficiency for various current densities at different flow rates: a - 20 mL/min; b - 40 mL/min; c - 60 mL/min.

It can be also observed that the difference in removal efficiency values between the highest and the lowest current densities decreases in time and with flow rate increase, reaching a minimum of 10 % after 20 minutes. This tendency can be accounted to the fact that current density determines the generation rate of metal hydroxides and the growth of flocs. Therefore the amount of produced coagulating agent increases as current density increases. However, the removal efficiency does not follow linearly the increase of current density considering that an increase of current density by three times did not increase the removal efficiency three times. This can be explained considering that the adsorption of Pb^{2+} ions is a much slower step than the generation of $Al(OH)_3$ flocs. As a result, the removal efficiency values increase only moderately with the increase of current density, even if the amount of coagulant agent and available surface area for Pb^{2+} ion adsorption increases. It can be also observed that the removal efficiency reached 100 % in just 30 minutes for all the combinations of current density and flow rate values. On the other hand, the period of time in which a complete removal of Pb^{2+} ions was achieved decreased as the applied current density and flow rate increased.

Still, operating at high current densities has negative impact on the process considering the dependency of electrode potentials and cell voltage on the applied current density. As the data from Table 1 indicates, electrode potentials increase with the increase of current densities. This can be attributed to the increase of cathode over potential for hydrogen evolution and more advanced passivation of the aluminum anode. Similar tendency can be noticed in the case of the cell voltage which also increases with the increase of current density due to the higher ohmic drop. In contrast, the increase of flow rate has a positive effect on the electrochemical parameters of the process which can be accounted to the more intensive mass transport of electroactive species.

Table 1. Electrode potentials and cell voltage vs. electrolyte flow rate and current density

Flow rate, (mL/min)	U_b, (V)			U_{el}, (V)			U_{ce}, (V)		
	i, (mA/cm^2)			*i*, (mA/cm^2)			*i*, (mA/cm^2)		
	5	10	15	5	10	15	5	10	15
20	5.10	7.07	9.29	2.11	2.75	3.09	-1.88	-2.13	-3.81
40	4.97	7.09	9.16	2.03	2.67	2.76	-1.72	-2.14	-2.89
60	4.88	7.07	9.00	2.04	2.08	2.45	-1.63	-1.84	-2.23

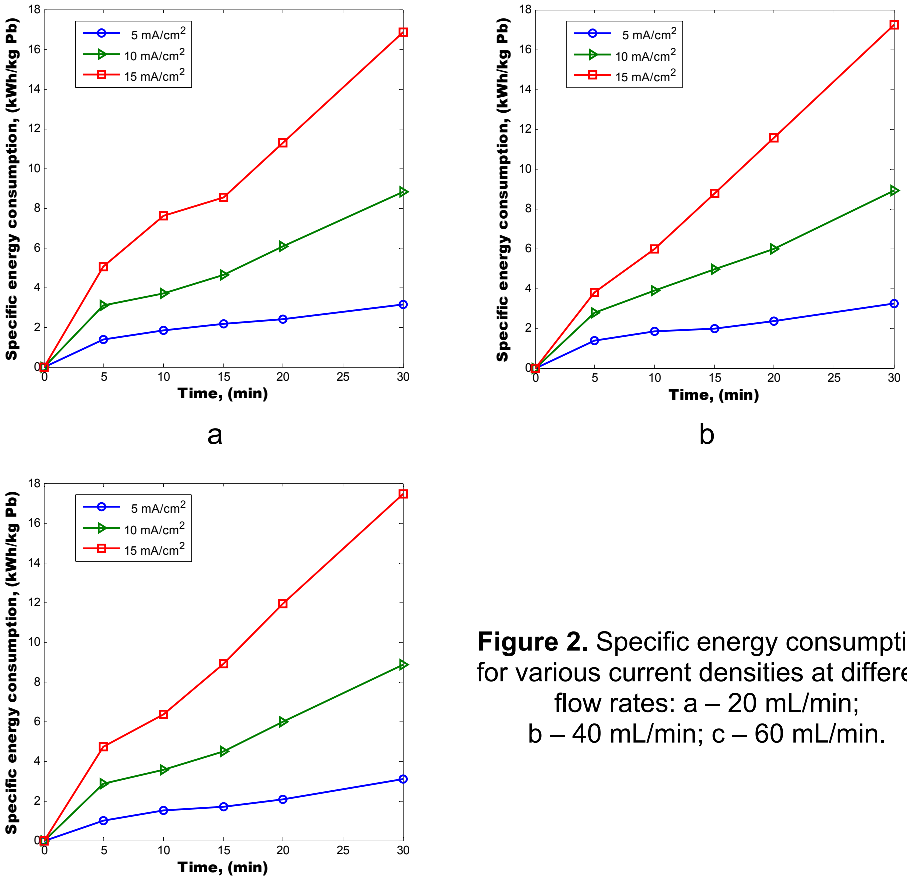
According to eq. (3) the removal of Pb^{2+} ions from the solution also involved the electrodeposition of metallic lead. In order to quantify the importance of lead electrowinning compared to the removal of Pb^{2+} ions by electrocoagulation a new performance criteria was introduced. The extraction efficiency was defined as the ratio between the amount of electrodeposited Pb and the total amount of Pb removed from the solution. The results from Table 2 show that at the lowest flow rate and current density almost 5 % of Pb^{2+} ions were removed by electrowinning. Also as it was expected the extraction efficiency drops as flow rate and current density increases. The extraction efficiency values are decreasing with 63 % by increasing the current density from 5 to 15 mA/cm^2 and with 17 % by increasing the flow rate from 20 to 60 mL/min. The more significant influence of current density can be accounted to enhancement of hydrogen evolution with the increase of current density while flow rate increase involves only the intensification of Pb^{2+} ions adsorption. This is also sustained by the cathodic current efficiency which follows the same tendency as the extraction efficiency. The low values of these two parameters it is also related to the fact that Pb^{2+} ions concentration is very low and decreasing during the process.

Table 2. Extraction and current efficiency vs. electrolyte flow rate and current density

Flow rate, (mL/min)	Extraction efficiency, (%)			Current efficiency, (%)		
	i, (mA/cm^2)			*i*, (mA/cm^2)		
	5	10	15	5	10	15
20	4.62	2.80	1.67	1.89	0.58	0.23
40	4.39	2.38	1.49	1.80	0.49	0.21
60	3.82	1.93	1.42	1.56	0.40	0.20

In order to determine the combined effect of the previously discussed parameters the specific energy consumption for the removal of Pb^{2+} ions was also evaluated for all the experimental conditions. The specific energy consumption was defined as the amount of energy consumed for the removal of one kg of Pb^{2+} ions from the treated effluent. Figure 2 shows that the specific energy consumption increases in time regardless the applied flow rate or current density. This can be attributed to the fact that the amount of Pb^{2+} ions removed decrease in time, especially during the second part of the experiment. Moreover, as flow rate increases the difference between the specific energy consumption after 5 and 30 min of processing become even larger due to the faster removal of Pb^{2+} ions at higher flow rates.

At constant current density, specific energy consumption increases by 200 % for the flow rate of 60 mL/min while for the other two flow rates it only doubles between the initial and final stages of the experiment. The results also revealed that specific energy consumption depends more on the applied current density than on the flow rate considering that it increased by 5 times between the lowest and highest current densities.



a

b

c

Figure 2. Specific energy consumption for various current densities at different flow rates: a – 20 mL/min; b – 40 mL/min; c – 60 mL/min.

CONCLUSIONS

The study proved that the complete removal of Pb^{2+} ions from aqueous solutions can be performed efficiently by EC using an electrolytic flow cell in batch operation. The results revealed that in parallel with the precipitation of Pb^{2+} ions the process also involved the electrodeposition of metallic lead which accounted to 1.5-4 % of the removed Pb^{2+} ions. It was found that process performance is more strongly dependent on current density than electrolyte flow rate or duration of the experiment.

As it was expected, the increase of current density increases the amount of flocs which makes the removal of lead ions to be done in a shorter time but with higher specific energy consumption. Nevertheless, the increase of flow rate even if reduces the requested time for the removal of Pb^{2+} ions with less extent than current density it decreases the specific energy consumption as well.

Considering the importance of the specific energy consumption it can be concluded that the complete removal of Pb^{2+} ions, in the applied experimental conditions, can be done the most efficiently at 60 mL/min and a current density of 5 mA/cm^2.

EXPERIMENTAL SECTION

EC experiments were performed using a plexiglas undivided electrochemical reactor equipped with parallel Al plate electrodes with a nominal surface area of 12.5 cm^2 (Figure 3). The inter-electrode gap between the electrodes was 20 mm. Cathode and anode potentials were measured using two Ag/AgCl/KCl_{sat} reference electrodes.

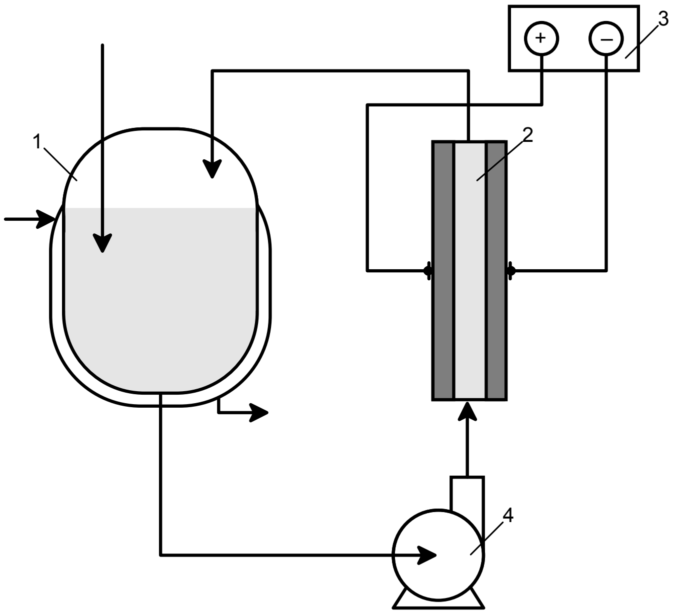


Figure 3. The experimental set-up for the EC process using sacrificial Al electrodes: 1 - thermoregulated reservoir; 2 - electrochemical cell; 3 - power supply; 4 - pump

Tests were performed under galvanostatic conditions, at different values of applied current densities (i = 5, 10, 15 mA/cm^2), using a computer controlled DXC 236 potentiostat (Datronix Computer) equipped with a PCI 6024E (National Instruments, U.S.A.) data acquisition board. All experiments were performed at room temperature over a period of 30 minutes using 100 mL synthetic wastewater solutions containing 500 mg/L Pb^{2+} and 1 g/L $NaNO_3$. The solutions were made by using analytical grade chemicals and double distilled water. The electrolyte containing 500 mg/L Pb^{2+} ions was recirculated through the electrochemical reactor at a flow rate of 20, 40 and 60 mL/min by using a Reglo-Digital-Ismatec peristaltic pump. During the EC process, the electrolyte was sampled at different time intervals in order to determine the evolution of Pb^{2+} ion concentration in time. At the end of each experiment the cathodic deposit was dissolved in concentrated HNO_3 solution. The Pb content of the samples and of the solution with the cathodic deposits was quantified by an atomic absorption spectrophotometer (Avanta PM - GBC).

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