ANALYSIS OF ELECTROCOAGULATION PROCESS EFFICIENCY OF COMPOST LEACHATE WITH THE FIRST ORDER KINETIC MODEL

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ABSTRACT

Large quantities of leachate are generated from the water release during the decomposition of the biodegradable waste. The composition of compost leachate is very complex and its treatment is necessary before releasing into the environment. The possibilities of treating compost leachate by electrocoagulation have been extensively studied. The scope of this work was to investigate applicability of the first order kinetic model for degradation of metal and organic compounds from compost leachate by electrocoagulation process. Experimental results showed 75 % removal efficiency of Cu^{2+} and 65 % of Zn^{2+}, while chemical oxygen demand was reduced by 36 %. According to obtained kinetic parameters, simulation of metal removal efficiency was performed in batch reactor. This way optimal electrocoagulation time which is needed for 95 % efficiency of metal removal was determined at 120th min for Zn^{2+} and 102nd min for Cu^{2+}.

Keywords: *compost leachate, metal removal efficiency, electrocoagulation*

INTRODUCTION

Compost leachate is generated during the decomposition of the biodegradable waste. The aqueous leachate cannot be released into the environment due to its hazardous nature. The composition of compost leachate is very complex and its treatment is necessary before releasing into the environment. Using the electrocoagulation (EC) process for compost leachate treatment has a lot of advantages [1]. The process is easy to operate, it is involved in simple equipment, it is offering a short retention time and it requires only a small space which contributes to low operating costs as compared to conventional ponding system or chemical coagulation. Despite being easy to operate, EC is complex technology processes which consist of three fundamental technologies: coagulation, flotation and electrochemistry. Due to the synergistic effect of different technologies, EC mechanisms that are used to remove pollution from wastewater have not yet been defined and differ for each

wastewater. Electrocoagulation was chosen due to promising results in treating industrial waste water [1]. Using this technique there has been a little consideration of the factors that influence the effective removal of ionic species, particularly metal ions and organic matter (Chemical oxygen demand, COD) from wastewater [2]. EC reactor with aluminium or iron electrodes could also be used and the process could be optimized by varying the current, the distance between the electrodes, and electrode area and pH value of the treated wastewater. Successful removal, up to 95 %, of metal ions such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+} and Ni^{2+} was achieved after 45 min of electrocoagulation in EC reactor with iron electrode [3]. At the distance of 1.5 cm, Cu^{2+} was removed at 95 % and Zn^{2+} at 80 % in 60 min [4]. 99 % of Zn^{2+} removal was achieved, while Cu^{2+} and Ni^{2+} were removed by 70 % when the combination of iron and aluminium electrode was applied [5]. With a relatively low energy consumption of 0.35 kWh/m^3, 50 mg/L of Zn^{2+} was removed in 20 min of EC treatment [6]. COD could be removed by electrocoagulation in combination with hybrid expanded granular sludge bed and fixed-bed bioreactor [7]. It was reported that after 75 min at the 3 cm distance between aluminium electrodes at 20 V, the COD removal reached 92 %.

The scope of this work was to investigate applicability of the first order kinetic model for degradation of metal and organic compounds from compost leachate by electrocoagulation process. Batch reactor with two aluminium electrodes was applied. Difference in potential enables the release of Al^{3+} ions from anode. Heavier suspended particles formed sludge at the bottom of reactor, while hydrogen bubbles removed volatile substances by floating to the solution surface. Nonlinear regression analysis of experimental data (at different current, electrode size, electrode distance and leachate pH) was performed in order to determine the reaction rate constant. Dynamic simulation of EC process removal efficiency of Zn^{2+} and Cu^{2+} from leachate according to the first order kinetic model was performed.

EXPERIMENTAL

Compost leachate characterization and analytical methods

Compost leachate samples were taken from the local compost company of Kogal, Slovenia. Compost contained wetted organic matter from kitchen waste (leaves, food waste). From the compost pile, the water passed into the stabilization ponds. Compost leachate samples were taken three times during the 3 weeks from each pond. Leachate contained a lot of organic substances which were dissolved or undissolved in the solution. The main characteristics are collected and displayed in Table 1.

Table 1. Parameters of compost leachate

Parameter	Unit	Value
pH	/	5.4 ± 0.3
κ	mS/cm	19 - 24.3
TSS	g/L	20 - 90
γ (Cu^{2+})	mg/L	0.4 - 11
γ (Zn^{2+})	mg/L	6.1 - 20
COD	mg/L	50000 - 80000
BOD_5*	mg/L	40000 - 60000

* Biochemical oxygen demand

The high organic content is in range from 50 to 80 g/L, O_2 expressed as chemical oxygen demand (COD), pH value was around 5.4 ± 0.3, and total suspended solids (TSS) up to 90 g/L, Zn^{2+} concentration up to 20 mg/L, Cu^{2+} concentration up to 11 mg/L, other metals such as Cd^{2+}, Ni^{2+}, Cr^{6+} and Pb^{2+} were all below 1 mg/L [8].

Physicochemical parameters of untreated and treated compost leachate were determined. All measured parameters and standard methods are shown in Table 2.

Table 2. Measured parameters, equipment and standard for determination physicochemical parameters

Parameter	Unit	Equipment	Standard
conductivity, κ	mS/cm	WTW LF537	SIST EN 27888
pH	/	pH meter WTW Multi 3410	DIN 38 404-C5
TSS	mg/L	Glass fibre filter, oven Nabertherm	ISO 11923
COD	mg/L O_2	thermoreactor MERCK, spectroquant TR 620	SIST ISO 6060
BOD_5	mg/L O_2	dilution and seeding	SIST ISO 5815
γ (Zn^{2+})	mg/L	spectrometer SPECTRO CIROS VISION ICP-AES	SIST ISO 11885
γ (Cu^{2+})	mg/L	spectrometer SPECTRO CIROS VISION ICP-AES	SIST ISO 11885

EC reactor configuration

The batch EC reactor that was applied for the treatment of the compost leachate had a total volume of 1 L with two aluminium electrodes immersed into the compost solution and it was connected to DC power supply. Area/volume ratio used in experiment was 15 m^2/m^3, the width of electrode was 5 cm and the height 12 cm. The electrical current was measured at constant voltage. A magnetic stirrer was used to provide mixing of the solution. The scheme of the EC reactor is shown in Figure 1.
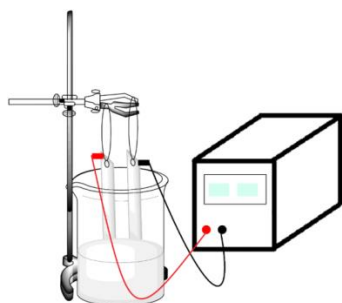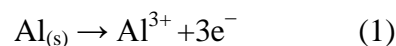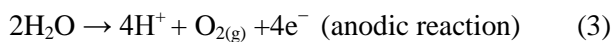

Figure 1. Scheme of electrocoagulation batch reactor (DC power and reactor with electrodes)

The main reaction occurring at the aluminium anode is dissolution [9]:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \qquad (1)$$

Additionally, water electrolysis occurs at the cathode and anode:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \text{ (cathodic reaction)} \quad (2)$$

$$2H_2O \rightarrow 4H^+ + O_{2(g)} + 4e^- \text{ (anodic reaction)} \qquad (3)$$

A direct electrochemical reduction of metal cations (Me^{n+}) may occur at the cathode surface:

$$Me^{n+} + ne^- \rightarrow nMe^0 \qquad (4)$$

In addition, anodic metal ions and hydroxide ions generated at the electrode surfaces react in the bulk wastewater to form various hydroxides and built up polymers:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)} \qquad (5a)$$

$$n\,Al(OH)_{3(s)} \rightarrow Al_n(OH)_{3n(s)} \qquad (5b)$$
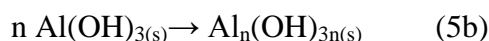
Al species are capable of removing organic compounds, while equation 5 is mostly adequate for metal removal [9].

Removal efficiency (η) of metal ions (Zn^{2+}, Cu^{2+}) and COD was calculated according to equation 6:

$$\eta = \frac{\gamma_0 - \gamma_1}{\gamma_0} \cdot 100 \% \qquad (6)$$

where is: η - removal efficiency (%), γ_0 - initial concentration (ions) (mg/L), γ_1 - final concentration (ions) (mg/L).

Kinetic model

Nonlinear regression analysis was used to describe the Zn^{2+} and Cu^{2+} removal in the EC process. The first order kinetic model has been used to simulate experimental data [10]:

$$\frac{d\gamma}{dt} = k \cdot \gamma \qquad (7)$$

Kinetic parameters k for both ions were determined from EC experiments with different current and different initial concentration of Zn and Cu ions. Based on the obtained kinetic parameters, simulation of removal efficiency was performed according to the first order kinetic model in the batch reactor. This model in nondimensional form is shown in equation 8:

$$\frac{d\eta}{d\tau} = 1 - \eta \qquad (8)$$

where is: τ − non-dimensional time for batch reactor ($k \cdot t$).

In order to compare the first and second order kinetic models, the same procedure was performed for second order kinetic model in batch reactor according to equation 9:

$$\frac{d\eta}{d\tau} = \left(1 - \eta\right)^2 \qquad (9)$$

Taking into consideration the initial condition $\eta(t = 0) = 0$, removal efficiency function was obtained by using W.R. Mathematica software. The time for 95 % removal efficiency was determined for both ions.

RESULTS AND DISCUSSION

The batch EC reactor was filled with brown coloured leachate that changed its colour during the electrocoagulation process. Conductivity, pH and current were measured during 60 min of electrocoagulation with aluminium electrodes. The results of measurements are presented in Table 3. The voltage 15 V was applied which was higher than reported [6] when model solutions were treated, but lower as 20 V in case of organic pollutants removal from high strength wastewater [7]. Even though the model solutions suggested the removal of only metals, the aim of our study was to decrease the content of organic compounds expressed as COD, which was huge, determined at 85.4 g/L O_2. The main share of electric energy consumption was due to organic colloids removal. The initial pH value was 5.4 which means that monomeric Al-species such as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ are present in the solution. Organic compounds adsorbed on Al-species to form flocs and settle to the bottom as precipitate. Current increased at first from 1.3 A to approximately 2.0 A after 30 min and then stabilized at 2.17 A. It is assumed that organic substances hindered electricity transfer between electrodes and due to this resistance temperature also increased for 5 °C. As metals were removed, more OH^- ions remained in bulk solution and therefore pH increased in accordance with another study [6].

Table 3. Measurements of conductivity, pH and current in time dependence

t /min	κ / mS/cm	pH	I /A
0	22.0	5.4	1.32
5	22.2	5.5	1.54
10	22.4	5.6	1.68
15	22.6	5.6	1.85
20	22.7	5.7	1.93
25	22.7	5.7	1.98
30	22.8	5.7	2.04
35	22.9	5.8	2.10
40	22.9	5.8	2.13
45	23.0	5.8	2.17
60	23.0	5.8	2.17

During electrocoagulation, a lot of foam was formed, as shown in Figure 2. It was removed physically with a spoon.

Figure 2. Foam formed during electrocoagulation

Initial sample contained 8.1 mg/L Zn^{2+} and 4.3 mg/L Cu^{2+}. Samples were taken after 20, 40 and 60 min of electrocoagulation and the concentrations of metals were determined at 4.5, 3.1 and 2.8 mg/L Zn^{2+} and 1.8, 1.0 and 0.8 mg/L Cu^{2+}, respectively. Compost leachate contained a lot of organic compounds, which could hinder the adsorption capability of Al^{3+} ions which were released from anode into the leachate by adhering on Al^{3+}. From 85.4 g/L O_2 the COD was reduced after one hour of electrocoagulation down to 54.6 g/L O_2. The efficiency was only 36 %. BOD reduction was practically the same (35 %). A share of organic compound was removed by the gas bubbles, while a lot of foam was formed. It had to be physically removed. Figure 3 shows leachate at the beginning, after one hour of electrocoagulation treatment and the third one after 1 hour of EC and one hour of settling. It is seen that the settling time was very important regarding suspended solids removal. It was assumed that Zn^{2+} and Cu^{2+} were removed according to reactions expressed in equation (5) and also as precipitate in form of $Zn(OH)_2$ and $Cu(OH)_2$. Since a lot of organic compounds did not settle and remained in the solution, it is assumed that also complexes were formed between organic compounds and metals which remain in the solution.

Figure 3**.** Changing of compost leachate during electrocoagulation in dependence of time (left at the beginning, in the middle after 1 hour of EC and right after 1 hour of EC and 1 hour of settling)

Nonlinear regression analysis of experimental data of EC process with different current and initial concentration of both ions was performed in order to determine the reaction rate constant. Kinetic parameter k_{Zn} was 0.0256 min^{-1} and k_{Cu} was 0.0292 min^{-1}. According to the obtained kinetic parameters,

simulation of removal efficiency was performed (equation (8) and (9)) and time for 95 % removal efficiency was determined for both ions. Results of the first order kinetic model showed that 95 % heavy metal removal efficiency could be achieved in the 120th min for Zn^{2+} and in the 102nd min for Cu^{2+}. Results of simulation removal efficiency according to the first and second order kinetic model for batch reactor and EC experimental results are shown in Figure 4 (Zn^{2+}) and Figure 5 (Cu^{2+}).
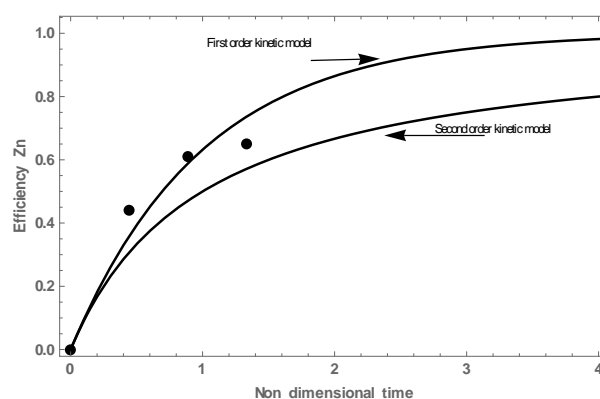

Figure 4. EC experimental results of removal efficiency (points) as well as the first and the second order kinetic model of removal efficiency (line) for Zn^{2+} ion
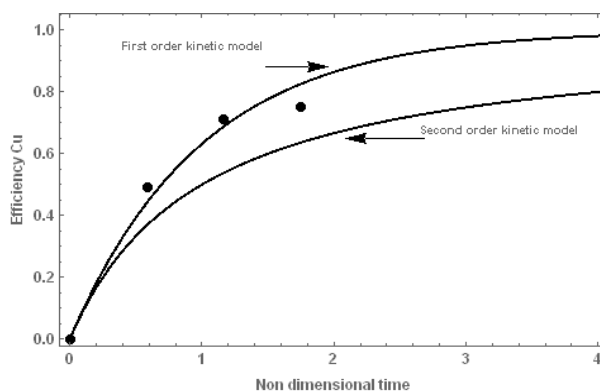

Figure 5. EC experimental results of removal efficiency (points) as well as the first and the second order kinetic model of removal efficiency for Cu^{2+} ion

The two-hour electrocoagulation was previously reported as optimal [7], therefore the results of present study are in accordance with the references. The obtained experimental results of EC process for Zn^{2+} and Cu^{2+} ions can be described with the first order kinetic model for batch reactor.

CONCLUSION

EC with Al electrodes was performed in order to remove metals and organic compounds from compost leachate. The results showed that Cu^{2+} and Zn^{2+} were efficiently removed from compost leachate using electrocoagulation. The results of experiments were attained with a 60 min electrocoagulation at U = 15 V, r = 3 cm and initial pH 5.4, where the removal efficiency of Cu^{2+} was 75 %, and Zn^{2+} 65 %. The organic compound (COD and BOD) of compost leachate was reduced by 36 % and 35 % respectively. Results of the first order kinetic model showed that 95 % heavy metal removal efficiency could be achieved in 120th min for Zn^{2+} and 102nd min for Cu^{2+}. Obtained experimental results of EC process for Zn^{2+} and Cu^{2+} can be described with the first order kinetic model for batch reactor.

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