Application of Different Metals as Electrode Material in Compost Leachate Treatment

L. Vrsalović, N. Vukojević Medvidović,* S. Svilović, and J. Šarić

University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, 21 000 Split, Croatia

Abstract

In this paper, different metallic materials (alloys of Fe, Al, and Zn) were investigated as sacrificial anodes during electrocoagulation (EC) for the treatment of compost leachate. Taguchi's L9 orthogonal array design was applied to investigate the four controllable factors (different metallic material, initial pH value, stirring speed, and contact time) on decrease of chemical oxygen demand (COD) and electrodes mass loss. COD decrease reached values in the range of 75.72–92.97 %. The Taguchi optimisation results showed that the most effective factor for decrease of COD is the duration of the experiment, while the electrode material was for electrodes mass loss. The zinc electrode showed the lowest potential for use in the EC process for treatment of compost leachate, while the Al and Fe electrodes could be used in an acid or slightly acidic environment. The following decreasing order of energy consumption was recorded: Zn > Al > Fe. The measured values of metal electrode mass loss exceeded the theoretical values calculated using Faraday's law in EC experiments with Al electrodes, while in experiments with Fe and Zn electrodes, those differences were insignificant.

Keywords

Fe, Al, Zn, sacrificial anode, electrodes mass loss, Taguchi optimisation

1 Introduction

Although corrosion is generally a negative phenomenon in terms of the integrity of construction materials that causes great losses to the economies of the world,¹⁻³ if corrosion processes are applied in the treatment of contaminated water, anodic dissolution of metals can have a positive effect on the removal of contaminants. This process is called electrocoagulation (EC), which is by definition an electrochemical process, in which coagulant types are formed in situ by electrochemical oxidation (dissolution) of immersed metal anodes in a contaminated medium.⁴ The resulting metallic ions are subject to instantaneous and spontaneous hydrolysis reactions, which result in the formation of different monomeric and polymeric (oxy)hydroxy complexes that interact with dissolved pollutants to form stable flocs. This method of water purification is one of the advanced technologies that combine the principles of coagulation, flotation, and electrochemical principles.⁴⁻⁹ In general, metals with a lower standard electrode potential (such as Mg, Al, Zn, and Fe) have a higher affinity for corrosion, i.e., anodic dissolution, and thus are suitable for use as anodic materials in the electrocoagulation process. That is why the anodes made of aluminium and various types of its alloys, zinc, steel, etc., are most often used. The electrocoagulation process is influenced by a number of parameters, such as material and anode surface condition, characteristics of contaminated water such as the presence

Note: The investigations in this paper were presented at the 3rd International Convention of Scientists, Specialist Employees, and Students on the topic of Environmental Protection in the Republic of Croatia (3rd ZORH Convention), held on April 28–29, 2022, at the Faculty of Chemistry and Technology University of Split, Croatia.

of different ionic and organic species, their concentration, pH, electrolyte conductivity, temperature, electrolyte mixing, anode dissolution rate under electrical influence (optimal current density), etc.¹⁰⁻¹²

During electrocoagulation with Al, Fe, and Zn electrode, the generation of metallic ions occurs due to the anodic dissolution (Al³⁺ from the aluminium electrode, Fe²⁺ from the iron electrode, and Zn²⁺ from the zinc electrode), according to the general Eq. (1):^{13,14}

$$\mathcal{M}_{(s)} \to \mathcal{M}^{n+}_{(aq)} + ne^{-} \tag{1}$$

Metallic cations undergo further spontaneous reactions forming corresponding hydroxides $(Al(OH)_3 \text{ with } Al \text{ elec$ $trode, } Fe(OH)_2 \text{ and also } Fe(OH)_3 \text{ formed under the pres$ $ence of dissolved oxygen with Fe electrodes, while Zn(OH)_2$ with Zn electrode). In addition to these hydroxide species,Fe²⁺, Al³⁺ and Zn²⁺ also form monomeric, polymeric, andhydroxo- complexes with hydroxide ions, depending onthe pH range and removing pollutants by a sweep-flocmechanism.¹³ At the cathodes, the evolution of hydrogenusually occurs along with the hydroxide ions (Eq. (2)), influencing the increase in pH values. The evolution of H₂may promote the flotation of some portion of coagulatedpollutants to the surface:¹⁴

$$2H_2O_{(1)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$$
(2)

Anode oxygen evolution is also possible, Eq. (3):

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$$
 (3)

In addition, many authors have found that the actual anode dissolution is different from the anode dissolutions

KUI-26/2023

This work is licensed under a

Original scientific paper Received October 9, 2022

Accepted February 3, 2023

This work is licensed under a Creative Commons Attribution 4.0 International License

https://doi.org/10.15255/KUI.2022.066

3. ZORH SUSRET

^{*} Corresponding author: Professor Nediljka Vukojević Medvidović, PhD Email: nvukojev@ktf-split.hr

calculated using Faraday's law, which indicates that other electrochemical reactions might be taking place at the anode. Several authors have suggested that the evolution of oxygen at the anode that takes place at alkaline pH, and a sufficiently high anodic potential (see Eq. (3)), might be the reasons for the disparity between the theoretical and actual anodic dissolution.¹⁵

Taking into account the increasing number of biowaste composting facilities, the availability of the process that can efficiently treat this leachate is a major concern, and electrocoagulation is recognised as a simple, cost-effective, and economic solution. However, there is a lack of published papers investigating the treatment of compost leachate by electrocoagulation, especially in comparing the efficiency of different electrode materials.¹⁶ Amani et al. investigated an electrocoagulation-flotation system for the treatment of high-load compost leachate in a batch reactor using various electrode configurations (Al-Al, Al-Fe, Fe-Al, Fe-Fe). They concluded that Al-Al was the best configuration based on the maximum decrease in COD and total suspended solids (TSS).17 Simonič et al. investigated the electrocoagulation efficiency of compost leachate using Al electrodes. They found removal efficiencies of Cu2+ and Zn²⁺ of 75 % and 65 %, respectively, after 60 min of experimentation at a voltage of 15 V, an electrode distance of 3 cm, and an initial pH of 5.4. In addition, the organic compound measured by chemical oxygen demand (COD) and biochemical oxygen demand (BOD) had reduced by 36 % and 35 %, respectively.18

To our knowledge, this is the first paper that investigates the electrocoagulation treatment efficiency of compost leachate using electrodes made from different metals (aluminium alloy, carbon steel, and zinc). Experiments were planned according to Taguchi method in order to perform the optimisation of compost leachate treatment by EC with different metallic materials (Fe, Al, and Zn), initial pH values (4, 6, and 8), stirring speeds (70, 170, and 270 rpm), and contact times (10, 20, and 30 min). In addition, electrode costs were evaluated from Faraday's law and from the measuring of mass changes in electrodes. Due to the obtained results, the electrodes used were compared.

2 Experimental

2.1 Samples

Compost leachate solutions were simulated from garden compost (Agro compost) using batch mode. The obtained leachate had a pH value of 5.8, electrical conductivity 594 μ S cm⁻¹, turbidity 167 NTU, COD 576.92 mgO₂l⁻¹, and total solids (TS) 1.07 gl⁻¹. Characterisation was performed according to Standard methods for examining water and wastewater.¹⁹

Electrode materials used in this study were: aluminium alloy AA2007 series 2000, in which the main alloying element is copper (w(AI) = 92.58 %, w(Cu) = 3.84 %); carbon steel in which the main elements are iron and copper (w(Fe) = 98.27 %, w(Cu) = 1.17 %); and commercial zinc electrodes in which the main elements are zinc and aluminium (w(Zn) = 99.31-99.76 %, w(AI) = 0.1-0.5 %).

2.2 Electrocoagulation study planned using Taguchi L9 (34) orthogonal array

Electrocoagulation (EC) experiments were performed in batch-type electrochemical cell of 400 ml, with immersed electrodes. Experiments were planned according to Taguchi's L9 orthogonal array design (Table 1). The aim of this study was to investigate the influence of different electrode materials (Fe, Al, and Zn), initial pH of suspensions (4, 6 and 8), stirring speeds (70, 170, and 270 rpm), and contact times (10, 20, and 30 min). Distance between electrodes was maintained at 3 cm. All experiments were performed with the addition of electrolyte NaCl in a concentration of 1 g l^{-1} , while the values of current and applied voltage were in the range of 0.32-1.00 A and 14.12-32.94 V (current density value $i = 0.018 \text{ A cm}^{-2}$). Table 1 gives an overview of experimental conditions during experiments. The L9 has nine rows representing the number of experiments, and four columns representing the controllable factors. The type of electrode material (E), initial pH (pH), stirring speed (S), and experiment duration (t) were chosen as controllable factors, and their impact on COD and electrodes

Table 1 – Overview of working conditions during EC experiments planned according to Taguchi L9 (3⁴) orthogonal array *Tablica 1* – Pregled radnih uvjeta tijekom EC eksperimenta planiranih prema Taguchi L9 (3⁴) ortogonalnom nizu

Exp. no. Eks. br.	Experiment label Oznaka eksperimenta	Electrode material Elektrodni materijal (E)	Solution initial pH adjustment Početno podešavanje pH otopine (pH)	Stirring speed Brzina okretaja miješala/okr min ⁻¹ (S)	Contact time Vrijeme kontakta/ min (t)
1	EC-Fe, pH = 4, 70 rpm, 10 min	Fe (L1)	4 (L1)	70 (L1)	10 (L1)
2	EC-Fe, pH = 6, 170 rpm, 20 min	Fe	6 (L2)	170 (L2)	20 (L2)
3	EC-Fe, pH = 8, 270 rpm, 30 min	Fe	8 (L3)	270 (L3)	30 (L3)
4	EC-Al, pH = 4, 170 rpm, 30 min	Al (L2)	4	170	30
5	EC-Al, pH = 6, 270 rpm, 10 min	Al	6	270	10
6	EC-Al, pH = 8, 70 rpm, 20 min	Al	8	70	20
7	EC-Zn, pH = 4, 270 rpm, 20 min	Zn (L3)	4	270	20
8	EC-Zn, pH = 6, 70 rpm, 30 min	Zn	6	70	30
9	EC-Zn, pH = 8, 170 rpm, 10 min	Zn	8	170	10

Table 2 – TS and pH in final solutions, removal efficiency based on values of COD, and mass of electrodes consumed during the EC experiment

Tablica 2 – Ukupni isparı	ni ostatak i pH vrij	ednost u konačnir	n otopinama,	učinkovitost uklanjanja	organske tvari	izražena preko KPK
vrijednosti te	potrošnja elektrod	a tijekom EK ekspe	erimenta		0	

Exp. no.	Experiment label	TS	рН _{fin}	COD decrease	Electrode loss Potrošnja elektrode/g	
Eks. br.	Oznaka eksperimenta	Isparni ostatak/gl ⁻¹	$\dot{p}H_{kon}$	izraženo preko KPK/%	Anode Anoda	Cathode Katoda
1	EC-Fe, pH = 4, 70 rpm, 10 min	1.45	8.67	83.39	0.0601	-0.0016
2	EC-Fe, pH = 6, 170 rpm, 20 min	1.35	10.13	89.78	0.1340	-0.0017
3	EC-Fe, pH = 8, 270 rpm, 30 min	1.33	10.67	89.78	0.2047	-0.0041
4	EC-Al, pH = 4, 170 rpm, 30 min	1.33	8.80	90.42	0.1819	0.0869
5	EC-Al, pH = 6, 270 rpm, 10 min	1.22	8.58	85.94	0.0538	0.0006
6	EC-Al, pH = 8, 70 rpm, 20 min	1.57	9.12	91.05	0.0924	0.0518
7	EC-Zn, pH = 4, 270 rpm, 20 min	1.35	9.37	92.97	0.4280	-0.0118
8	EC-Zn, pH = 6, 70 rpm, 30 min	1.47	11.13	82.75	0.6469	-0.0305
9	EC-Zn, pH = 8, 170 rpm, 10 min	1.68	10.98	75.72	0.3300	0.2354

mass loss was studied. As seen in Table 1, each factor used had three testing conditions (levels – L1, L2, and L3).

Prior to each experiment, the electrodes were ground and polished with successive wet SiC emery papers (up to 800 grit), ultrasonically cleaned in 70 % ethanol, and deionised water. After the EC process, the final pH, TS, and COD were determined in the supernatant. Before and after the EC experiment, the electrodes were weighed on an analytical balance, and the electrodes mass loss was determined.

2.3 Taguchi optimisation

In this investigation, optimisation was performed for chemical oxygen demand and electrodes mass loss. The two quality characteristics, the *smaller-the-better* (SB) or the *larger-the-better* (LB) were used, depending on the parameter to be optimised. SB quality characteristic is represented by Eq. (4):²⁰

$$S / N_{\rm sB} = -10 \log \frac{\sum_{i=1}^{n} y_i^2}{n}$$
 (4)

S/*N* represents signal-to-noise ratio, *n* is the number of repetitions under the same experimental conditions, and *y* is a measured electrodes mass loss.

LB quality characteristic is represented by Eq. (5):^{21,22}

$$S / N_{\text{LB}} = -10 \log \frac{\sum_{i=1}^{n} \frac{1}{y_i^2}}{n}$$
 (5)

where *y* is a measured percentage of COD decrease.

As one of the aims of the study was to determine the optimal conditions for EC treatment of compost leachate, the average S/N ratio of each controllable factor at level *i* was calculated according to Eq. (6).

$$S / N_{FL} = \frac{\sum_{j=1}^{n_{Fi}} \left[\left(S / N \right)_{i}^{F} \right]_{j}}{n_{Fi}}$$
 (6)

 S/N_{FL} represents S/N ratio for factor F on level i, and the superscript j is the j^{th} appearance of the i^{th} level.²³ In this study, every level for the specific factor appears 3 times.^{21,22}

3 Results and discussion

3.1 Analysis of the efficiency of electrocoagulation with different electrode materials

Treatment efficiency during experiments was assessed from the COD, and is summarised in Table 2. TS results are also given. Before and after immersion, the electrodes were weighed on an analytical balance; the results of electrodes mass loss are given in Table 2.

TS in the initial compost solution equalled 1.07 gl⁻¹, indicating the presence of suspended, dissolved, and settleable solids in the composting leachate. Values of TS in final solutions were higher compared to the initial one, which can be associated with the addition of electrolyte NaCl in the concentration of 1 gl⁻¹ at the beginning of each experiment. It was also evident that TS values in the final solution oscillated depending on experimental conditions. The highest value was obtained in experiment no. 9 with Zn electrode, at pH 8, stirring speed of 170 rpm, and 10 min contact time, at which, interestingly, the lowest COD decrease was obtained, as was the highest increase in cathode mass.

Final pH values were higher compared to adjusted initial pH values in solution at the beginning of each experiment

(initial pH was adjusted at pH = 4, 6, or 8). The increase in final pH values is attributed to the hydrogen evolution reaction at the cathode, and the formation of hydroxide ions, as well as the speciation of the hydrolysis products.¹³ However, several other explanations in literature can also be found regarding the increase in pH, such as due to the release of CO₂, which is over-saturated in acidic solutions and enhanced by H_2 bubble evolution. Also, some anions, such as Cl⁻ and SO₄²⁻, may exchange partly with OH⁻ in metal hydroxide to free OH⁻, giving an increase in the solution pH.24,25 The lowest increase in solution pH was obtained with Al electrodes (in the range of 8.58–9.12), depending on the experimental conditions. According to Mansuri et al., the final pH near 9 observed in the presence of NaCl with Al electrode can be associated with buffering effects of aluminium hydroxides.²⁶ The highest increase in final pH was obtained with Zn electrodes (in the range of 9.37–11.13), while final pH with Fe electrodes was in the range of 8.67-10.67, depending on the experimental conditions.

Based on values of COD decrease, it was evident that electrocoagulation can easily remove both biodegradable and inorganic compounds susceptible to oxidation with dichromate from compost leachate, and suspension solids were easily removed from the solution with high efficiency. The final values of COD in all experiments were below the limit values prescribed by Croatian regulation²⁷ for discharge into natural surface water and public sewage system (125 mgO₂ l⁻¹). From the result given in Table 2, it is evident that the highest efficiency regarding the COD decrease was observed with Al electrodes under the conditions of experiments no. 6, and zinc electrode under the conditions of experiment no. 7.

Anode consumption was evident in all experiments, which confirmed anode sacrifice during EC. The highest consumption was evident in experiments with Zn electrode (experiments no. 7, 8, and 9, among which anode consumption was the highest at experiment no. 8.), followed by Fe anode consumption, while the lowest anode consumption was achieved in experiments with Al electrode (experiments no. 4, 5, and 6). However, cathode consumption was also evident in experiments with Al electrode (experiments no. 4, 5, and 6), and experiment no. 9 with Zn electrode. The chemical dissolution of the aluminium anode and cathode was due to the acidity and alkalinity produced in their vicinity during the process.²⁶ In other experiments, a slight increase in cathode mass was observed in all experiments with Fe electrode (experiments no. 1, 2, and 3), as well in experiments no. 7 and 8 with Zn electrode. Increased cathode mass is associated with a covering layer of corrosion product on electrode surfaces.

3.2 Taguchi optimisation

In order to find optimal experimental conditions, which provide the best COD decrease and the lowest anode and cathode mass loss, the LB and SB Taguchi characteristics were calculated, respectively. The values of S/N_{LB} or S/N_{SB} ratios determined using Eqs. (4) and (5) are presented in Table 3.

Table 3 $- S/N_{LB}$ and S/N_{SB} ratios Tablica 3 $- S/N_{LB}$ i S/N_{SB} omjeri

Exp. no. Eks. br.	S/N _{LB} ratio for COD decrease S/N _{LB} omjer za smanjenje KPK	S/N _{SB} ratio for electrode consumption S/N _{SB} omjer za potrošnju elektrode
1	38.42	24.66
2	39.06	17.57
3	39.03	13.95
4	39.13	11.41
5	38.68	25.29
6	39.19	16.82
7	39.37	7.61
8	38.36	4.20
9	37.58	4.95

Calculated S/N_{FL} values (Eq. (6)) are presented in Table 4. The range, i.e., the difference between the highest and lowest S/N_{FL} was also calculated and as a result, every factor was related to the rank. The most important factor, the factor whose change resulted in the highest change, was ranked as 1. In this study, the time is the most important factor for COD, while electrode material was for electrodes mass loss. In both cases, the initial pH was the least important.

Table 4	$-S/N_{FL}$ values and rank of factors for COD decrease and
	electrodes mass loss

*Tablica 4 – S/N*_{FL} vrijednosti i rangiranje faktora za smanjenje KPK-a te potrošnju elektroda

Parameter Parametar	(COD de Smanjer	ecrease nje KPk	e K	Electrode loss Potrošnja elektrode			
Factor Faktor	E	рН	S	t	E	рН	S	t
Level 1 Razina 1	38.84	38.97	38.65	38.23	18.73	14.56	15.23	18.30
Level 2 Razina 2	39.00	38.70	38.59	39.21	17.84	15.69	11.31	14.00
Level 3 Razina 3	38.44	38.60	39.03	38.84	5.59	11.91	15.62	9.86
Range Raspon	0.56	0.37	0.44	0.98	13.14	3.78	4.31	8.44
Rank Rang	2	4	3	1	1	4	3	2

Note: The optimal level for each tested factor is marked in bold numbers Napomena: Optimalna razina za svaki testirani faktor označena je podebljanim brojevima

The optimal electrode material for COD decrease was aluminium, while for electrodes mass loss it was steel, closely followed by aluminium. For both factors, the zinc electrode was the least preferable. The optimal initial pH for COD was 4, and for electrodes mass loss it was 6, showing that acidic or slightly acidic reaction mixture had a beneficial effect on EC. For both COD and electrode mass loss, the optimal stirring speed was the highest one used, *i.e.*, 270 rpm. The optimal experimental time most beneficial to COD decrease and electrode mass loss was 20 and 10 min, respectively. It may be seen that 10 min was not enough to sufficiently decrease the COD value, but longer experiments have no useful effect on the process examined. The lowest electrodes mass loss was, as expected, for the shortest experiments.

3.3 Comparison of energy and electrode consumption during electrocoagulation

Electrode consumption was evaluated from Faraday's law and by measuring of electrodes mass loss before and after EC process. Consumption of electrical energy (C_{energy} ; kW m⁻³) and mass consumption of electrode ($C_{\text{electrode}}$; kg m⁻³) were calculated by Eqs. (7) and (8):²⁸

$$C_{\text{energy}} = \frac{U \cdot I \cdot t}{V}$$
(7)

$$C_{\text{electrode}} = \frac{I \cdot t \cdot M}{z \cdot F \cdot V} \tag{8}$$

where U is cell voltage (V), t is operating time (s), V is volume of the treated leachate (m^3) , z is number of electron

Table 5– Comparison of electrode and energy consumptionTablica 5– Usporedba potrošnje elektroda i energije

transfers (2 or 3), *F* is Faraday constant (96 485.33 C mol⁻¹), and *M* is molecular mass of metal (g mol⁻¹).

 $C_{\text{electrode}}$ from the mass consumption was calculated according to Eq. (9).²⁹

$$C_{\text{electrode}} = \frac{m}{V} \tag{9}$$

 $C_{\text{electrode}}$ is the electrode consumption measured by electrodes mass loss before and after EC process (mg l⁻¹), *m* is the total mass of released metal obtained from electrodes mass loss (mg), and *V* is total volume of solution in the electrocoagulation cell (l).

The difference between the electrodes mass loss obtained by calculation according to Faraday's law and from actual electrodes mass loss were analysed, and the results compared in Table 5.

From the results shown in Table 5, the highest voltage was applied in experiment no. 5 (32.94 V), while the lowest was in experiment no. 3 (14.12 V). The lowest current consumption was in the experiments with Fe electrode, followed by Al electrode, and the significantly highest with Zn electrode. The highest energy consumption was in experiment no. 4, while the lowest was in experiment no. 1.

The measured values of aluminium electrode mass loss by weighing of electrode significantly exceeded theoretical values calculated using Faraday's law. This phenomenon has been called "super-faradaic efficiency".³⁰ According to

Exp. no. Eks. br.	Experiment label Oznaka eksperimenta	U/V	I/A	C_{energy} / kWh m ⁻³	Calculation based on Faraday's law Izračun temeljem Faradayeva zakona	Calculation based on electrode loss Izračun temeljem potrošnje elektroda		
					$C_{ m electrode}/ m kgm^{-3}$	$C_{\rm anode}/{\rm kg}{\rm m}^{-3}$	$C_{\rm cathode}/{\rm kg}{\rm m}^{-3}$	$C_{anode + cathode} / \text{kg} \text{m}^{-3}$
1	EC-Fe, pH = 4, 70 rpm, 10 min	14.80	0.320	1.973	0.139	0.150	-0.004	0.146
2	EC-Fe, pH = 6, 170 rpm, 20 min	18.12	0.382	5.768	0.332	0.335	-0.004	0.331
3	EC-Fe, pH = 8, 270 rpm, 30 min	14.12	0.382	6.742	0.497	0.512	-0.010	0.502
4	EC-Al, pH = 4, 170 rpm, 30 min	31.00	0.910	35.263	0.382	0.455	0.217	0.672
5	EC-Al, pH = 6, 270 rpm, 10 min	32.94	0.750	10.294	0.105	0.135	0.002	0.136
6	EC-Al, pH = 8, 70 rpm, 20 min	23.09	0.700	13.469	0.196	0.231	0.130	0.361
7	EC-Zn, pH = 4, 270 rpm, 20 min	25.78	1.000	21.483	1.017	1.070	-0.030	1.041
8	EC-Zn, pH = 6, 70 rpm, 30 min	27.92	1.000	34.900	1.525	1.617	-0.076	1.541
9	EC-Zn, pH = 8, 170 rpm, 10 min	25.30	1.000	10.542	0.508	0.589	0.825	1.414

Mansuri et al., the excess in dissolved aluminium is primarily due to the chemical dissolution of aluminium.²⁶ In addition, aluminium dissolution occurs not only at the anode but also at the cathode, which is in agreement with the finding obtained by *Ghernaouta et al.*³¹ The residual amount of aluminium in the final solution may have a negative influence on living organisms if these effluents are discharged into the natural recipient without additional treatment.

In experiments with Fe and Zn electrodes, the measured values of metal electrode consumptions were almost equal to theoretical values calculated using Faraday's law, except in experiment no. 9, were those differences were high. In addition, in experiments with Fe, only cathode increase was observed, while for Zn electrodes both cathode consumption and cathode increase were observed.

4 Conclusions

Due to the increased number of biowaste composting facilities, a high amount of compost leachate with a very complex composition is produced and requires additional processing. Thus, the application of a simple and economically feasible process of electrocoagulation with different electrode materials is encouraged to investigate the treatment of compost leachate. In this paper, Taguchi's L9 orthogonal array design was applied to investigate the effect of different metallic materials (Fe, Al, and Zn), initial pH values (4, 6, and 8), stirring speeds (70, 170, and 270 rpm), and contact times (10, 20, and 30 min) on COD decrease and electrodes mass loss during compost leachate treatment.

The results showed that addition of electrolyte increased the TS and pH values in final effluent, while COD values decreased. The lowest increase in final pH was obtained with Al electrodes. The highest efficiency regarding the COD decrease was observed with Al electrodes, under experimental conditions no. 6, and with Zn electrode under experimental conditions no. 7. However, the final values of COD in all experiments were below the limit prescribed by Croatian regulation.

The highest anode mass loss was achieved in experiments with the Zn electrode, followed by Fe, and the lowest anode mass loss was achieved in experiments with the Al electrode. In addition, anode and cathode mass loss occurred in experiments with Al electrodes. In experiments with Fe and Zn electrodes, the measured values of metal electrodes mass loss were almost equal to theoretical values calculated using Faraday's law, while in experiments with Al electrodes, those differences were significant.

Taguchi optimisation showed that the most effective factor for the decrease in COD was the duration of the experiment, while for electrodes mass loss it was the electrode material. The optimal conditions for the decrease in COD determined by Taguchi include: aluminium electrode, pH of 4, stirring speed of 270 rpm, and contact time of 20 min. The optimal conditions for mass loss of electrodes include: steel electrode, pH of 6, stirring speed of 270 rpm, and contact time of 10 min. Thus, the optimum conditions must take into account both effects, COD decrease and electrode mass loss. Zinc electrodes showed no potential for use in the EC process when treating compost leachate, while Al and Fe electrodes could be used in an acidic or slightly acidic environment with agitation.

However, the total operating cost of the EC process will depend on the market price of each metal, as well as the electricity cost. The price of metal has increased drastically recently, which will negatively influence the total EC operating cost. Thus, the use of waste metal materials as electrodes is highly encouraged in the EC process. Electricity costs can be reduced by implementing renewable energy sources. Special accent should be focused on the determination of the residual amount of metals in the final solution, as it is known that a higher amount will negatively influence living organisms. In this regard, some other materials should be investigated to make the electrocoagulation process more applicable in compost leachate treatment.

ACKNOWLEDGEMENTS

The results in this paper were funded from the institutional funds of the Faculty of Chemical Technology University of Split, Croatia, and by project "Development of a new hybrid process for wastewater treatment based on electrocoagulation and natural zeolite" partially supported by HAZU Foundation (Foundation of the Croatian Academy of Sciences and Arts).

List of abbreviations and symbols Popis kratica i simbola

BOD/BPK - biochemical oxygen demand biokemijska potrošnja kisika COD/KPK - chemical oxygen demand - kemijska potrošnja kisika Ε - electrode materials - elektrodni materijal EC/EK - electrocoagulation - elektrokoagulacija - controllable factor at level L FL - kontrolirani faktor na razini L LB - larger-the-better veće je bolje NTU - nephelometric turbidity units - nefelometrijska jedinica mutnoće S stirring speed brzina vrtnje miješala SB - smaller-the-better manje je bolje TS - total solids – ukupni isparni ostatak TSS - total suspended solids – ukupne raspršene tvari - signal-to-noise ratio S/N - omjer signal-šum

$C_{\text{electrode}}$	– electrode consumption – potrošnja elektrode
C_{energy}	– energy consumption – potrošnja energije
F	– Faraday constant – Faradayeva konstanta
i	– current density – gustoća struje
т	 total mass of released metal obtained from electrodes mass loss ukupna masa otopljenog metala temeljem potrošnje mase elektroda
М	– molecular mass of metal – molekulska masa metala
n	 number of repetitions under the same experimental conditions broj ponavljanja pod istim eksperimentalnim uvjetima
t	– experiment duration time or contact time – vrijeme trajanja eksperimenta ili vrijeme kontakta
U	– cell voltage – napon ćelije
V	 volume of treated leachate volumen obradene procjedne vode
Ζ	– number of electron transfers – broj prijenosa elektrona
У	 measurement value of electrodes mass loss or COD decrease mjerna vrijednost gubitka mase elektroda ili smanjenja KPK

References Literatura

- 1. C. M. Hansson, The impact of corrosion on society, Metall. Mater. Trans. A 42A (2011) 2952-2962, doi: https://doi. org/10.1007/s11661-011-0703-2.
- 2. G. H. Koch, M. P.H. Brongers, N. G. Thompson, Y. P. Virmani, J.H. Payer, Corrosion Costs and Preventive Strategies in the United States, Publication No. FHWA-RD-01-156, 2002, url: http://impact.nace.org/documents/ccsupp.pdf.
- 3. V. S. Sastri, Challenges in corrosion, costs, causes, consequences and control, Willey, New Jersey, USA, 2015.
- 4. M. Mousazadeh, E. K. Niaragh, M. Usman, S. U. Khan, M. A. Sandoval, Z. Al-Qodah, Z. B. Khalid, V. Gilhotra, M. M. *Emamjomeh* A critical review of state-of-the-art electrocoagulation technique applied to COD-rich industrial wastewaters, Environ. Sci. Pollut. Res. 28 (2021) 43143-43172, doi: https://doi.org/10.1007/s11356-021-14631-w.
- 5. D. Sharma, P. A. K. Chaudhari, S. Dubey, A. K. Prajapati, Electrocoagulation treatment of electroplating wastewater: A review, J. Environ. Eng. 146 (10) (2020) 03120009, doi: https://doi.org/10.1061/(ASCE)EE.1943-7870.0001790.
- 6. D. S. Babu, T. S. A. Singh, P. V. Nidheesh, M. S. Kumar, Industrial wastewater treatment by electrocoagulation process, Sep. Sci. Technol. 55 (17) (2020) 1-33, doi: https://doi.org/1 0.1080/01496395.2019.1671866.
- 7. B. N. Malinović, M. G. Pavlović, T. Djurićić, Electrocoagulation of textile wastewater containing a mixture of organic dyes by iron electrode, J. Electrochem. Sci. Eng. 7 (2017)

103-110, doi: https://doi.org/10.5599/jese.366.

- 8. H. A. Petersen, T. H. T. Myren, S. J. O Sulivan, O. R. Luca, Electrochemical methods for materials recycling, Mater. Adv. 2 (2021) 1113–1138, doi: https://doi.org/10.1039/ D0MA00689K.
- 9. E. Magnisali, Q. Yan, D. Vayenas, Electrocoagulation as a revived wastewater treatment method-practical aproaches: a review, J. Chem. Technol. Biotechnol. 97 (2022) 9-25, doi: https://doi.org/10.1002/jctb.6880.
- 10. T. S. A. Singh, S. T. Ramesh, An experimental study of Cl Reactive Blue 25 removal from aqueous solution by electrocoagulation using aluminium sacrificial electrode: kinetics and influence of parameters on electrocoagulation performance, Desalin. Water Treat. 52 (2014) 2634-2642, doi: https://doi. org/10.1080/19443994.2013.794714.
- 11. C. H. Hung, S. Y. Shen, C. W. Chen, C.-D. Dong, M. Kumar, B. Dakshinamoorthy, J.-H. Chang, Effect of chloride ions on electrocoagulation to treat industrial wastewater containing Cu and Ni, Sustainability 12 (2020) 7693, doi: https://doi. org/10.3390/su12187693.
- 12. K. Oguzie, E. Oguzie, S. Nwanonenyi, J. Edozeim, L. Vrsalović, Electrochemical decolorization of disperse blue-1 dye in aqueous solution, Environ. Eng. Manage. J. 20 (2021) 1467-1476, https://eemj.eu/index.php/EEMJ/article/view/4387.
- 13. A. Dura, Electrocoagulation for water treatment: the removal of pollutants using aluminium alloys, stainless steels and iron anodes, PhD thesis, National University of Ireland, 2013. https://core.ac.uk/download/pdf/297020266.pdf.
- 14. I. D. Tegladza, Q. Xu, K. Hu, G. Lv, J. Lu, Electrocoagulation processes: A general review about role of electro-generated flocs in pollutant removal, Process Saf. Environ. Prot. 146 (2021) 169-189, doi: https://doi.org/10.1016/j. psep.2020.08.048.
- 15. N. A. Fayad, The application of electrocoagulation process for wastewater treatment and for the separation and purification of biological media, PhD thesis, Université Clermont Auvergne, 2017, url: https://theses.hal.science/tel-01719756/file/2017 CLFAC024 FAYAD.pdf.
- 16. D. Roy, A. Azaïs, S. Benkaraache, P. Drogni, R. D. Tvagi, Composting leachate: characterization, treatment, and future perspectives, Rev. Environ. Sci. Biotechnol 17 (2018) 323-349, doi. https://doi.org/10.1007/s11157-018-9462-5.
- 17. T. Amani, K. Veysi, S. Elyasi, W. Dastyar, A precise experimental study of various affecting operational parameters in electrocoagulation-flotation process of high-load compost leachate in a batch reactor, Water Sci. Technol. 70 (8) (2014) 1314-1321, doi: https://doi.org/10.2166/wst.2014.374.
- 18. M. Simonič, M. Čurlin, L. Zemljič, Analysis of electrocoagulation process efficiency of compost leachate with the first order kinetic model, Holistic Approach Environ. 10 (2) (2020) 35-40, doi: https://doi.org/10.33765/thate.10.2.2.
- 19. A. D Eaton, L. S. Clesceri, E. W. Rice, A. E. Greenberg, M. A. H. Franson (Eds.), Standard methods for the examination of water and wastewater, 21st ed.; American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington DC, 2005.
- 20. Y.-P. Zeng, C.-L. Lin, H.-M. Dai, Y.-C. Lin, J.-C. Hung, Multi-Performance Optimization in Electrical Discharge Machining of Al_2O_3 Ceramics Using Taguchi Base AHP Weighted TOPSIS Method, Processes 9 (2021) 1647, doi: https://doi. org/10.3390/pr9091647.
- 21. S. Svilović, M.N. Mužek, I. Nuić, P. Vučenović, Taguchi design of optimum process parameters for sorption of copper ions using different sorbents, Water Sci. Technol. 80 (2019) 98-108, doi: https://doi.org/10.2166/wst.2019.249.

- S. Svilović, D. Rušić, R. Stipišić, N. Kuzmanić, Process optimization for copper sorption on synthetic zeolite NaX, Bulg. Chem. Commun. 52 (2020) 189–196, doi: https://doi. org/10.34049/bcc.52.2.4620.
- S. Anhreya, Y. D. Vankatesh, Application of Taguchi Method for Optimization of Process Parameters in Improving the Surface Roughness of Lathe Facing Operation, Int. Ref. J. Eng. Sci. (IRJES) 1 (3) (2012) 13–19, url: http://irjes.com/Papers/ vol1-issue3/Version%201/C131319.pdf.
- S. F. Weiss, M. L. Christensen, M. K. Jorgensen, Mechanisms behind pH changes during electrocoagulation, AIChE J. 67 (2021) e17384, doi: https://doi.org/10.1002/aic.17384.
- G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41, doi: https://doi. org/10.1016/j.seppur.2003.10.006.
- K. Mansouri, K. Ibrik, N. Bensalah, A. Abdel-Wahab, Anodic Dissolution of Pure Aluminum during Electrocoagulation Process: Influence of Supporting Electrolyte, Initial pH, and Current Density, Ind. Eng. Chem. Res. **50** (2011) 13362– 13372, doi: https://doi.org/10.1021/ie201206d.
- 27. Croatian Regulation on Emission Limits Values in Wastewater, NN 26/2020. (In Croatian). Available online: https://nar-

odne-novine.nn.hr/clanci/sluzbeni/2020_03_26_622.html (29. 8. 2022.).

- C.-D. Dong, C.-W. Chen, M. Raj, Effect of Chloride Ions on Electro-Coagulation to Treat Industrial Wastewater Containing Cu and Ni, Sustainability **12** (2020) 7693, doi: https:// doi.org/10.3390/su12187693.
- C.-J. Lin, S.-L. Lo, C.-Y. Kuo, & C.-H. Wu, Pilot-Scale Electrocoagulation with Bipolar Aluminum Electrodes for On-Site Domestic Greywater Reuse, J. Environ. Eng. 131 (3) (2005) 491–495, doi: https://doi.org/10.1061/(asce)0733-9372(2005)131:3(491).
- C. E. Barrera-Díaz, P. Balderas-Hernández, B. Bilyeu, Electrocoagulation: Fundamentals and Prospectives, in: C. A. Martínez-Huitle, M. A. Rodrigo, O. Scialdone (Eds.), Electrochemical Water and Wastewater Treatment, Elsevier Inc., Oxford, UK, 2018, pp. 61–76, doi: https://doi.org/10.1016/b978-0-12-813160-2.00003-1.
- D. Ghernaouta, B. Ghernaoutb, A. Boucherita, M. W. Naceura, A. Khelifaa, A. Kelli, Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, Desalin. Water Treat. 8 (2009) 91–99, doi: https://doi.org/10.5004/dwt.2009.668.

SAŽETAK

Primjene različitih metala kao elektrodnog materijala u obradi kompostne procjedne vode

Ladislav Vrsalović, Nediljka Vukojević Medvidović,* Sandra Svilović i Josipa Šarić

U ovom radu različiti metalni materijali (legure Fe, Al, Zn) ispitivali su se kao žrtvene anode tijekom elektrokoagulacije (EK) za obradu kompostne procjedne vode. Taguchijev L9 ortogonalni niz primijenjen je za ispitivanje četiriju kontroliranih čimbenika (različiti metalni materijali, početne pH vrijednosti, brzine vrtnje miješala i vremena kontakta) na uklanjanje organske tvari izražene preko kemijske potrošnje kisika (KPK) i gubitak mase elektroda. Učinkovitost uklanjanja organske tvari izražene preko KPK-a dosegla je vrijednosti u rasponu od 75,72 do 92,97 %. Rezultati optimizacije Taguchi pokazali su da je najučinkovitiji čimbenik za uklanjanje organske tvari, izražene preko vrijednosti KPK-a, trajanje eksperimenta, dok je gubitak mase elektroda za materijal elektrode. Cinkova elektroda pokazala je najmanji potencijal za uporabu u EK procesu za pročišćavanje kompostne procjedne vode, dok se Al i Fe elektroda mogu upotrebljavati u kiselom ili blago kiselom području. Zabilježen je sljedeći opadajući redoslijed potrošnje energije: Zn > Al > Fe. Izmjerene vrijednosti gubitka mase metalne elektrode premašuju teorijske vrijednosti izračunate Faradayevim zakonom u EK eksperimentima s Al elektrodama, dok su u eksperimentima s Fe i Zn elektrodama te razlike manje.

Ključne riječi

Fe, Al, Zn, žrtvovana anoda, potrošnja elektrode, Taguchi optimizacija

Sveučilište u Splitu, Kemijsko-tehnološki fakultet, Ruđera Boškovića 35, 21 000 Split

Izvorni znanstveni rad Prispjelo 9. listopada 2022. Prihvaćeno 3. veljače 2023.