

Original scientific paper

INFLUENCE OF CURRENT DENSITY ON LEACHATE TREATMENT EFFICIENCY BY ELECTROCOAGULATION WITH ZEOLITE ADDITION

Nediljka Vukojević Medvidović, Ladislav Vrsalović, Sandra Svilović and Mirjana Cestarić

University of Split, Faculty of Chemistry and Technology

ABSTRACT

The electrocoagulation with zeolite addition was used to treat compost leachate. The effects of different current densities and zeolite particle sizes on electrode dissolution, electrode surface condition, and removal efficiency were investigated. The surface of the electrodes was analysed by optical microscope, while the consumption of the aluminium electrodes was investigated by weighing. The results confirmed that the removal efficiency could be improved by conducting the experiment at higher current densities, but the electrodes used were significantly more damaged. Significant damage was also observed on the electrode used in the experiment with larger zeolite particles, which can be related to the stronger abrasion effect.

Keywords: current density, electrode surface, aluminium

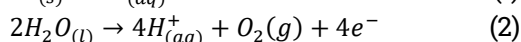
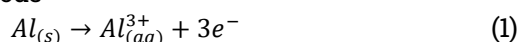
Corresponding Author:

Nediljka Vukojević Medvidović
Faculty of Chemistry and Technology in Split
Ruđer Bošković 35, 21000 Split, Croatia
Tel.: + 385 21 329 452; fax: + 385 21 329 461
E-mail address: nvukojev@ktf-split.hr

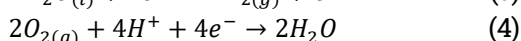
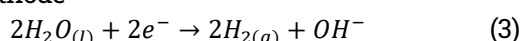
1. INTRODUCTION

Electrocoagulation (EC) is a process that combines coagulation, flocculation, flotation, and electrochemical anodic and cathodic reactions to remove pollutants from wastewater. It is based on the formation of flocs of metal hydroxides by dissolving the electrodes, which serve as flocculants on which pollutants can be removed by the *sweep flock* mechanism [1-7]. In general, the electrochemical reactions taking place in an EC reactor with immersed metal electrodes (M), and with aluminium electrode can be represented by the following equations [2,8]:

anode



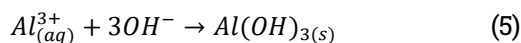
cathode



Oxidation of the aluminium occurs at the anode, causing the aluminium anode to dissolve (or corrode) and produces aluminium metal cations that instantly undergo further reactions to form different metal (oxy) hydroxides. At the same time, an anodic oxygen evolution reaction (OER) takes place (reaction 2), so there is competition between aluminium dissolution and OER. According to Teglada et al. [2], at low current density, aluminium dissolution mainly occurs, while at high current density, both processes compete. At the cathode, a hydrogen evolution reaction (HER) occurs (reaction 3), while under the condition of high dissolved oxygen content, an oxygen reduction reaction (ORR) also takes place (reaction 4) [2,8].

Corrosion product formation reaction of $Al(OH)_3$ which serves as flocculants is given by equation (5). Namely, the Al^{3+} ions generated at the anode and OH^{-} produced at

the cathode undergo several speciation reactions and generate intermediate species (such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, which are the precursors to the formation of the stable insoluble $Al(OH)_3$ flocs [8].



During EC processes, the appearance of passivation on the metal surface of the electrode causes an increase in potential [2]. Thus, passivation can reduce the dissolution process of metal cations from the electrodes and leads to increased electricity consumption. To prevent the occurrence of passivation, the addition of specific anions in the solution (so-called activators, like chloride ions), regular mechanical cleaning, and rinsing of the electrode surface or electrode polarity change are usually used [2, 9-12]. Therefore, further research is needed to provide a new solution that can contribute to better electrode dissolution. Our previous researches confirm that the zeolite addition in the EC process may enhance the EC treatment efficiency [13-16]. Moreover, the abrasive effect of zeolite particles on the electrode surface was also recorded, which can reduce the passivation effect.

The purpose of this paper is to investigate how changing the parameters of the EC experiments, such as different sizes of zeolite particles and different current densities, will affect the change in the surface of aluminium electrodes during the EC experiment, electrode consumption, and removal efficiency. The surfaces of the electrodes were analysed by optical microscope, while the consumption of the aluminium electrodes was investigated by weighing method. Treatment efficiency was evaluated by measuring pH, temperature, total solids, COD, and turbidity.

2. EXPERIMENT

2.1 Materials

Compost leachate was collected during the composting of biowaste in the "C-EcoForHome" composter with the use of "Compost Help" anaerobic microorganisms. Compost leachate is characterized by acidic pH (pH=4.03), very high organic load (initial

COD equals 10427.6 mg O_2/L), very high electrical conductivity of 3.54 mS/cm, turbidity of 397 NTU, and total solids (TS) of 10.33 g/L. All measured parameters are determined according to the Standard Water and Wastewater Testing Methods [17].

Electrode material: The aluminum alloy AA 2007 series 2000 was used as electrodes (anode and cathode), in which the main alloying element is copper (Al=92.58%, Cu=3.84%).

Synthetic zeolite: The synthetic zeolite NaX was purchased from Sigma-Aldrich (zeolite type with $r_{Si/Al} = 1.23$). Before use, the zeolite was crushed and sieved into two different granulations of NaX particles of 160-600 μm and < 90 μm .

2.2 Performance of the electrocoagulation process

Electrocoagulation (EC) was carried out in a 350 mL of electrochemical cell, with immersed aluminum electrodes and with the addition of 20 g/L NaX zeolite (particle zeolite size of <90 μm or 160-600 μm), without the addition of electrolyte. The initial pH of the solution was 4.03. Distance between electrodes was maintained at 3 cm and a mixing speed of 100 rpm and the working EC time was 30 min. The applied current density values were $i = 0.018$ A/cm² and 0.009 A/cm². Experiments labelling and working conditions are summarized in Table 1.

Table 1. Experiments labelling and working conditions

Experiments labelling	Working conditions
	Al electrode, $t = 30$ min, electrode distance = 3 cm, mixing speed = 100 rpm
A1	EC, NaX (< 90 μm), $i = 0.009$ A/cm ²
A2	EC, NaX (< 90 μm), $i = 0.018$ A/cm ²
A3	EC, NaX (160-600 μm), $i = 0.009$ A/cm ²
A4	EC, NaX (160-600 μm), $i = 0.018$ A/cm ²

For each EC process, pH, temperature, total solids, turbidity, and COD were measured

according to Standard Methods of Water and Wastewater Analysis [17].

2.3 Electrode surface preparation and consumption loss analysis

Before each measurement, the surfaces of the Al electrodes were ground with P240, P400, P600, and P800 grit water-based abrasive papers using Metkon Forcipol 1V metallographic grinding and polishing machine manufactured by Metkon, Turkey. After mechanical processing, the electrodes were ultrasonically degreased in ethanol, washed in deionized water, dried, and weighed on an analytical balance before use. The electrode consumption was determined by weighing both electrodes (anode and cathode) on analytical balance before and after each experiment.

2.4 Examination of the electrode surface with a light microscope

The electrode surface of the aluminum electrodes (anode and cathode) after the EC process was examined with a light microscope MXFMS-BD, Ningbo Sunny Instruments Co. with a magnification of 100 times. The is a trinocular microscope on which a Canon EOS 1300D digital camera is mounted and used to photograph the surface of the samples. The microscope is connected to the computer via a camera, and the image of the surface is projected on the computer monitor.

3. RESULTS AND DISCUSSION

3.1 Analysis of the electrode surface before and after the implementation of the electrocoagulation process using a light microscope

Electrochemical processes at the anode and cathode, as well as exposure of the electrodes to leachate produced by anaerobic composting, lead to significant changes on the surface of the electrodes. For this reason, it is important to examine the condition of the surface of the electrodes after carrying out the process in order to

determine the degree of wear and the form of corrosion attack on the electrodes. Therefore, the surfaces of the anodes and cathodes, before and after the implementation of the electrocoagulation process, were recorded using a light microscope with a magnification of 100 times and comparisons are given in Figure 1.

Despite the fact that polished Al alloy electrodes are shiny and smooth (image on the left side of Figure 1), microscopic pictures reveal surface inhomogeneity. Microscopic images of the electrodes after mechanical processing by grinding and before the EC process (image on the left side of Figure 1) show sandpaper "lines" which are clearly visible. The surface's small residual roughness aids in the dissolution of the electrodes, which is helpful in this situation, and no additional polishing is needed. Namely, the main alloying element of the 2000 series alloys is Cu, which improves the mechanical properties of the alloys of this series, but at the same time worsens their corrosion properties. Consequently, such alloys have significantly lower corrosion resistance compared to pure Al.

The image for anodes and cathodes on the right side of Figure 1 shows the appearance of the electrodes after the EC process. After each experiment, the anode and cathode lost their shine and smoothness, and damage and "roughness" of the surface caused by corrosion processes are visible. The surfaces of the anodes are significantly corroded due to the intensive dissolution process, whereby two dominant forms of corrosion are visible: general and pitting corrosion. Dots on the cathodes indicate the occurrence of pitting corrosion. The amount and size of the dots depend on the experimental conditions. In addition to dots, cracked surfaces are also present, indicating the existence of a layer of corrosion products.

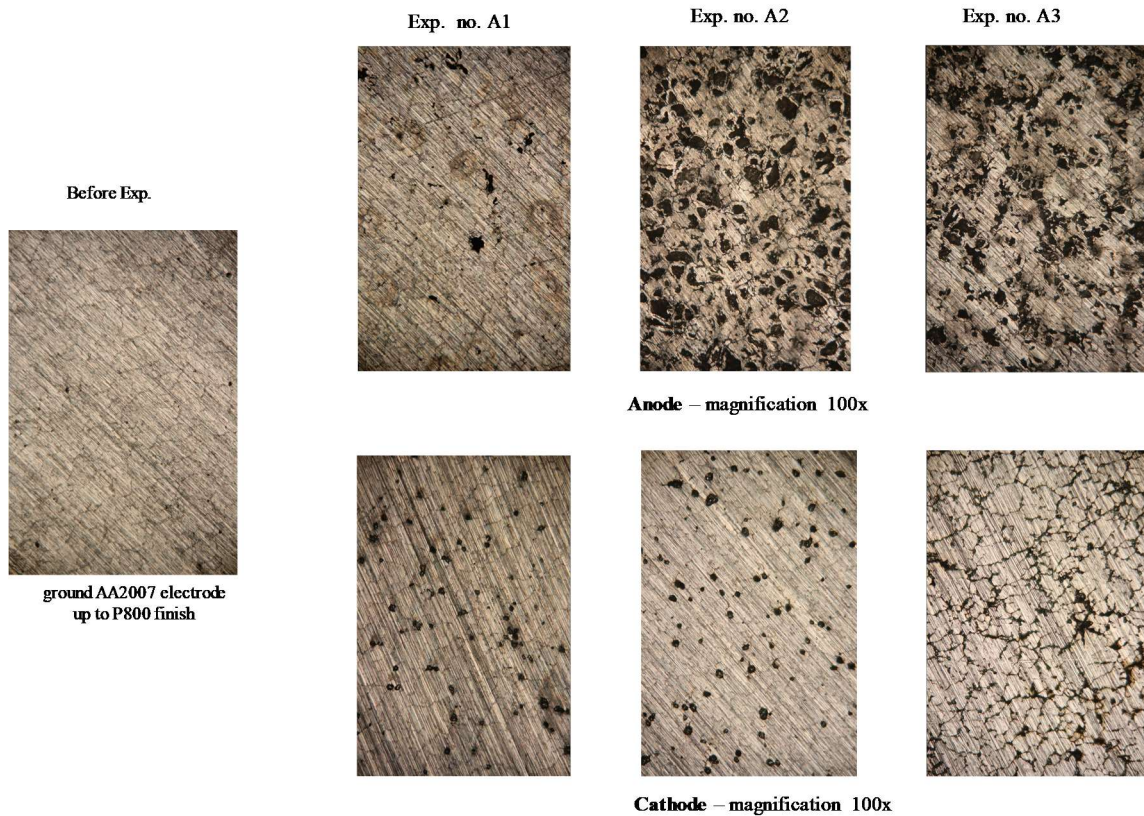


Figure 1. Comparison of Al electrode surface before and after EC process at experimental conditions of A1, A2, and A3

Comparing the surface of the electrodes after process A1 (with a current density of 0.009 A/cm^2) and A2 (with a current density of 0.018 A/cm^2), significantly greater damage is visible on the electrodes with higher values of current density. The difference in the surface appearance of the electrodes in experiment A1, in which zeolite with smaller particle sizes was used, and in experiment A3, in which zeolite with larger particle sizes was used, is also visible. The electrodes, used for experiment A3, were significantly damaged, which can be connected to the stronger abrasive effect of larger zeolite particles.

3.2 Electrode consumption analysis

Electrode consumption was determined during each experiment by weighing the anode and cathode before and after the EC process and the results are presented in Figure 2.

High anode consumption is observed in all EC experiments, but cathode consumption was also evident. Regarding the influence of

current densities, higher anode consumption was observed in experiments with higher current densities of 0.018 A/cm^2 , while at lower values of the current density of 0.009 A/cm^2 , the cathode consumption was higher. The impact of zeolite particle size was almost insignificant for lower current density (experiment A1/A3). However, at a higher current density, particle size affects cathode and anode consumption (experiment A2/A4).

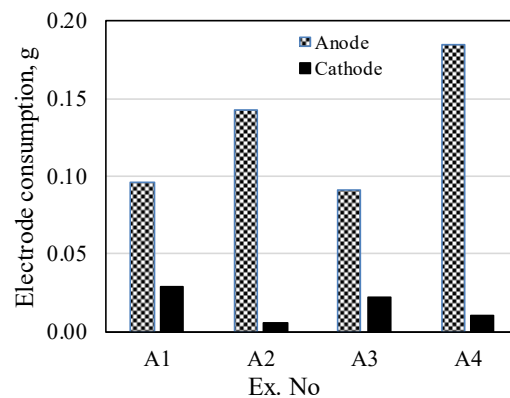


Figure 2. Comparison of anode and cathode electrode consumption

The corrosion of the anode was expected, however, the corrosion of the cathode confirms the occurrence of a different mechanism of electrode dissolution in the EC process, which is characteristic of Al electrodes [13-16].

3.3 Efficiency analysis

During each EC experiment, the pH, temperature, total solids, and COD were determined and the results are summarised in Table 2.

Table 2. Results of pH in final solutions, initial and final temperature values, the total solids, turbidity, and COD for each EC experiment

Exp. no.	Experiment mark	pH _{fin} , -	T _{in} , °C	T _{fin} , °C	TS, g/L	Turbidity decrease, %	COD decrease, %
A1	EC-NaX (< 90 µm), <i>i</i> =0.009 A/cm ²	6.76	23.2	28.9	11.45	87.88	17.56
A2	EC-NaX (< 90 µm), <i>i</i> =0.018 A/cm ²	7.14	22.8	34.1	11.99	70.28	32.82
A3	EC- NaX (160-600 µm), <i>i</i> =0.009 A/cm ²	5.76	22.8	29.6	11.03	88.94	31.30
A4	EC-NaX (160-600 µm), <i>i</i> =0.018 A/cm ²	5.83	23.5	41.6	10.19	97.00	51.91

An increase of initial pH values from 4.03 to pH in the range of 5.76-7.14 is evident in all experiments, which is mainly associated with the formation of OH⁻ ions at the cathode (reaction 3) [2]. The slightly higher increase is observed with a smaller zeolite particle size of < 90 µm (pH is in the range of 6.76-7.14), compared to the larger zeolite particle size (pH is in the range of 5.76-5.83). Also, higher current density values result in a slightly higher increase in pH values. Even a rise in pH is observed in all experiments, this rise is lower than it is expected according to literature (pH ≈ 8) [13-16], which can be attributed to the complex composition of the initial compost leachate solution, which practically acts like a buffer. During each experiment, a significant increase in temperature is observed (final temperature is in the range of 28.9-41.6 °C), which is connected with higher electrode consumption (see Figure 2). A similar was observed previously [13-16]. Values of TS oscillate around initial TS values of 10.33 g/L, in dependence on experimental conditions. Namely, the initial TS values are significantly high, and thus no significant reduction was observed in the final solution.

Turbidity and COD decrease was observed. The turbidity decrease was significant (in the range 70.28-97.00 %) compare to the COD decrease (in the range of 17.56-51.91%). The best turbidity and COD removal was observed at experiment A4 (at higher zeolite particle and higher current density). This indicates that larger zeolite particle size and

higher current density enhance Al electrode dissolution and formation of Al flock, thus removal of a higher amount of soluble and colloidal species from compost leachate is observed.

Even significant turbidity reduction was achieved with the application of the EC process, final values of COD in all experiments significantly exceed the limit values prescribed by Croatian regulation for discharge into natural surface water and public sewage system (125 mg O₂/L) [18], thus additional treatment process needs to be performed before final discharge.

4. CONCLUSION

Microscopic images of the electrodes after the electrocoagulation process indicate significant damage to the electrode surface. The surfaces of the anodes were severely corroded due to the intense dissolution process, with general and pitting corrosion observed. The appearance of pitting corrosion is visible on the cathodes, along with the presence of a cracked surface indicates the existence of a layer of corrosion products. Increased values of current density induced higher electrode damage. Also, significant damage was observed on the electrode that was used in the experiment with larger zeolite particles, which can be associated with its stronger abrasive effect. Anode consumption was more pronounced at higher values of current density and higher zeolite particle size, with the highest turbidity and COD decrease observed.

Conflict of interest

The authors declare that they have no competing interests.

5. References

- [1] S. Sen, A. K. Prajapati, A. Bannatwala, D. Pal, Electrocoagulation treatment of industrial wastewater including textile dyeing effluent – a review, *Desalination Water Treat.*, 161(2019), p. 21–34, doi: 10.5004/dwt.2019.24302
- [2] I. D. Tegladza, Q. Xu, K. Xu, G. Lv, J. Lu, Electrocoagulation processes: a general review about the role of electro-generated floc in pollutant removal, *Process Saf. Environ. Prot.*, 146(2021), p. 169–189, doi.org/10.1016/j.psep.2020.08.048
- [3] I. Kabdaşlı, I. Arslan-Alaton, T. Ölmez-Hancı, O. Tünay, Electrocoagulation applications for industrial wastewaters: a critical review, *Environ. Technol. Rev.*, (2012), p. 1–44, doi.org/10.1080/21622515.2012.715390
- [4] D. T. Moussa, M. H. El-Naas, M. Nasser, M. J. Al-Marri, A comprehensive review of electrocoagulation for water treatment: Potentials and challenges, *J. Environ. Manage.*, 186(2017), p. 24–41, doi:10.1016/j.jenvman.2016.10.032
- [5] M. Bharath, B. M. Krishna, B. M. Kumar, A Review of electrocoagulation process for wastewater treatment, *Int. J. Chem. Tech. Res.*, 11(2018), p. 289–302, doi.org/10.20902/IJCTR.2018.110333
- [6] A. Tahreen, M. S. Jami, F. Ali, Role of electrocoagulation in wastewater treatment: A developmental review, *J. Water Process Eng.*, 37(2020), p. 101440, doi.org/10.1016/j.jwpe.2020.101440
- [7] 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), p. 43143–43172, doi.org/10.1007/s11356-021-14631-w
- [8] K. S. Hashim, A. Shaw, R. Al Khaddar, M. O. Pedrola, D. Phipps, Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor, *J. Environ. Manage.*, 189(2017), p. 98–108, doi:10.1016/j.jenvman.2016.12.035
- [9] C. Vargel, *Corrosion of Aluminium*, Elsevier LTd., Netherlands, 2004, p. 96–101
- [10] J. Tao, *Surface composition and corrosion behavior of an Al-Cu alloy*, [doctoral thesis], Université Pierre et Marie Curie, Paris VI, 2016, <https://tel.archives-ouvertes.fr/tel-01412882>
- [11] G. Mouedhen, M. Feki, W. De Petris Wery, H. F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, *J. Hazard. Mater.*, 150 (2008) p. 124–135, doi:10.1016/j.hazmat.2007.04.090
- [12] M. Ingelson, N. Yasri, E. P. L. Roberts, Electrode passivation, faradaic efficiency, and performance enhancement strategies in electrocoagulation – a review, *Water Res.*, 180(2020) p. 116433, doi.org/10.1016/j.watres.2020.116433
- [13] N. Vukojević Medvidović, L. Vrsalović, T. Brozinčević, S. Svilović, Treatment of municipal wastewater by electrocoagulation and natural zeolite – influence of initial pH values, In: K. Szramowiat-Sala, M. Karczewski, K. Sornek, R. Figaj, (eds.), Book of Abstracts of the 4th International Conference on the Sustainable Energy and Environmental Development, Krakov, Institute of Sustainable Energy, 2021, p. 11
- [14] N. Vukojević Medvidović, L. Vrsalović, T. Ugrina, I. Jukić, *Electrocoagulation augmented with natural zeolite—the new hybrid process for treatment of leachate from composting of biowaste*, In: N. Dolić, Z. Zovko Brodarac, S. Brajčinović, (eds.), Proceedings of the 19th International Foundrymen Conference: Humans—Valuable Resource for Foundry Industry Development, Split, Croatia, 16–18 June 2021; Faculty of Metallurgy, University of Zagreb, Zagreb, Croatia, 2021, p. 489–498. https://ifc.simet.hr/?page_id=2518
- [15] N. Vukojević Medvidović, L. Vrsalović, S. Svilović, A. Bobanović, Electrocoagulation vs. Integrate Electrocoagulation-Natural Zeolite for Treatment of Biowaste Compost Leachate—Whether the Optimum Is Truly Optimal, *Minerals*, 12(2022), p. 442, doi.org/10.3390/min12040442
- [16] S. Svilović, N. Vukojević Medvidović, L. Vrsalović, A. Kulić, Combining Natural Zeolite and Electrocoagulation with Different Electrode Materials – Electrode Surface Analysis and Taguchi Optimization, *App. Surf. Sci. Adv.*, 12(2022), p. 100330, doi.org/10.1016/j.apsadv.2022.100330
- [17] 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); Water Environment Federation (WEF): Washington, DC, USA, 2005
- [18] Regulation on emission limit values in wastewater, NN 26/2020 (in Croatian)