



# Article Electrocoagulation Combined with Synthetic Zeolite—Does the Size of Zeolite Particles Matter?

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**Abstract:** Although electrocoagulation combined with zeolite (ECZ) shows higher efficiency in wastewater treatment, the actual contribution of zeolite particle size has not been fully explored. In this work, the influence of particle size of synthetic zeolite SZ (<90, 90–160, and 160–600  $\mu$ m) on ECZ treatment of compost leachate with very high organic load is investigated together with different electrode materials (Fe, Al, and Zn), current densities (0.003, 0.009 and 0.018 A/cm<sup>2</sup>), and contact times (10, 20 and 30 min). The results positively highlight that the largest particle size should be used in ECZ, as it leads to a lower increase in pH and temperature, a higher decrease of chemical oxygen demand (COD) and turbidity, and a lower electrode consumption, while causing more damage to the electrode surface. The estimated energy costs ranged from 3.960 kW/m<sup>3</sup>–1313.657 kW/m<sup>3</sup>. The Taguchi L9 orthogonal configuration showed the highest COD and turbidity decrease under the conditions of 160–600  $\mu$ m zeolite particles. The powder X-ray diffractometer (PXRD) analysis shows that interplanar spacing decreases when smaller and medium SZ particle sizes are used, while this effect was not observed with larger zeolite particle size. SEM-EDS shows that oxygen, silicon, and aluminium are the predominant elements in electrogenerated sludge coupled with zeolite.

**Keywords:** zeolite particle size; synthetic zeolite; electrocoagulation combine with zeolite; treatment efficiency; electrode surface analysis; zeolite and electrogenerate sludge analysis

# 1. Introduction

Zeolites are natural or synthetically produced hydrated aluminosilicates that are widely used as catalysts, ion exchangers, and molecular sieves due to their specific properties and characteristic structure of cavity channels [1,2]. Most technologies using zeolites for water purification are based on their ability to exchange and adsorb cations from the water solution, especially heavy metals [3–5], ammonium [6], and radioactive ions [7] with alkaline and alkaline–earth exchangeable cations from the zeolite structure. In addition to the removal of cations, modified zeolite forms are also efficient in the removal of various anionic and organic compounds [2,8–13]. After their use as adsorbents and ion exchangers, zeolites can be easily regenerated and reused without significantly losing their original capacity [14–16]. Moreover, natural zeolites are relatively cheap, environmentally friendly, and easy to use [17].

Although zeolites are recognized as minerals of natural origin, there are currently more than one hundred synthetic zeolite species produced under laboratory conditions [1,17]. Current research on zeolite synthesis is ecologically oriented, which implies the use of natural or already used raw materials for this purpose [18]. Compared to natural zeolites, synthetic zeolites have higher purity and more uniform quality [1,19]. Due to industrialization and the limitation of environmental standards, increasing amounts of wastewater with complex composition is generated, for which more complex treatment processes must be applied [20]. Therefore, the focus is on the development of hybrid processes that combine



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). or integrate two or more different physical, chemical, and biological processes [21–23]. In this paper, the hybrid process of electrocoagulation combined with zeolite addition is analysed.

Electrocoagulation is a sustainable alternative for the treatment of water and wastewater, in which an electric current is applied to the immersed metal electrode in the electrocoagulation cell and reactions occur at the anode and cathode [24–29]. At the anode, oxidation of the metal occurs in a short time, causing the metal anode to dissolve (or corrode). The resulting metal cations are immediately converted into various metal (oxy)hydroxides by further reactions. At the same time, an anodic oxygen evolution reaction takes place, while a hydrogen evolution reaction occurs at the cathode [24]. The pollutants from the solutions are mainly removed by the formed flocs of metal hydroxides through the sweep-floc mechanism. Thus, EC combines the advantages of coagulation, flocculation, flotation, and electrochemistry in one system [24–29].

Up to today, only few authors have combined electrocoagulation and zeolite (ECZ) in their studies (simultaneously or sequentially), and they include ammonia removal from landfill leachate [30–32], reduction in the bacterial content and turbidity in industrial wastewater treatment [33], remediation of phosphate from calcium phosphate solutions [34], ammonia removal from gold mine wastewater [35], reduction in the chemical oxygen demand (COD), total Kjeldahl nitrogen, electrical conductivity, and the turbidity of municipal wastewater with saltwater infiltrates [36], and COD and reduction in the turbidity of moderately polluted compost leachate [37–39].

Although the addition of zeolite in the EC process may increase treatment efficiency [36–39], the actual contribution of zeolite particle size has not been fully clarified. Zeolite is not only a good adsorbent and an ion exchanger [30–32,34,35], but also has an abrasive effect on the electrode surface and contributes to reducing the passivation effect [36–39]. Therefore, the focus of this work is to analyse the influence of different particle sizes of synthetic zeolite SZ on the efficiency of the hybrid ECZ treatment process of compost leachate with very high organic load. The studies are accompanied by microscopic electrode surface analyses, SEM and PXRD analyses of the zeolite used, and the electrogenerated sludge. Since the Taguchi method is known as a special orthogonal array design developed to study the effects of process parameters with a small number of experiments [40–44], it was used to optimize the ECZ process, and finally, the total electrode and power costs were compared for different experimental conditions.

# 2. Materials and Methods

**The compost leachate:** collected from composting of biowaste in the C-EcoForHome manual home composter using anaerobic microorganisms "Compost Help". After completion of composting, the collected leachate was mixed and the following indicators were determined according to the Standard Water and Wastewater Testing Methods [45]: pH of 4.03, electrical conductivity of 3.54 mS/cm, turbidity of 397 NTU, chemical oxygen consumption (COD) of 10427.6 mg O<sub>2</sub>/L, and total solids (TS) of TS = 10,330 mg/L.

**The synthetic zeolite (SZ):** purchased from the manufacturer Alfa Aesar, crushed and sieved to three different zeolite particle sizes ( $<90 \ \mu m$ , 90– $160 \ \mu m$ , 160– $600 \ \mu m$ ).

The electrode materials: Aluminium alloy AA2007 series 2000n with copper as the main alloying element (Al = 92.58%, Cu = 3.84%); carbon steel with main elements of iron and copper (Fe = 98.27%, Cu = 1.17%) and commercial zinc sacrificial anodes with main elements of zinc and aluminium (Zn = 99.31%–99.76%, Al = 0.1%–0.5%) [37]. The cube shaped electrodes are fabricated by cutting larger pieces of material with a band saw cooled with coolant, to prevent local overheating of the alloys during cutting. Electrical contact was made by drilling and making M3 threads in the centre of the electrode samples and inserting M3 threaded rods made of a copper alloy with high electrical conductivity. The threaded rods and the contacts between the rod and the alloy are insulated with a polyacrylate compound and a flexible polymer tube. The surface of the electrodes is ground with a Metkon Forcipol 1V grinder using sandpaper up to P800 and then ultrasonically

cleaned in 70% ethanol and deionized water. After drying and weighing on an analytical balance KERN ABS 320-4N, the electrodes were used in ECZ experiments.

Hybrid process of electrocoagulation and synthetic zeolite addition planned according to Taguchi L9 (3<sup>4</sup>) orthogonal array: The compost leachate treatment was performed using a hybrid process of electrocoagulation and addition of synthetic zeolite in three different particles sizes (<90  $\mu$ m, 90–160  $\mu$ m and 160–600  $\mu$ m). The experiments were carried out in a 350 mL capacity electrochemical cell, with the immersed cathode and anode made of the same material (AA2007 aluminium alloy or zinc or iron). The addition of SZ zeolite was 20 g/L, without changing the initial pH of the solution and without adding electrolyte, with an electrode distance of 3 cm and a mixing speed of 100 rpm. The current density varied in the range of *i* = 0.003–0.018 A/m<sup>2</sup>, and the contact time was 10–30 min. The experiments were planned according to the Taguchi orthogonal array L9 design. Nine experiments were conducted to test the influence of different SZ zeolite particle sizes Z (<90  $\mu$ m, 90–160  $\mu$ m or 160–600  $\mu$ m), current density *i* (0.003 A/cm<sup>2</sup>, 0.009 A/cm<sup>2</sup> or 0.018 A/cm<sup>2</sup>), electrode material M (Fe, Al or Zn), and contact time *t* (10, 20 or 30 min). Thus, each factor had three levels—represented by L1, L2, and L3, as shown in Table 1.

**Table 1.** Overview of the conducted ECZ experiments planned according to Taguchi L9 (3<sup>4</sup>) orthogonal array.

Exp. Label	Experiments Condition during Each ECZ	Zeolite Particle Size [Z], μm	Current Density [ <i>i</i> ], A/cm <sup>2</sup>	Electrode Material [M], -	Contact Time [t], min
C1	ECZ-Fe, SZ (<90 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 10 min	<90 (L1)	0.003 (L1)	Fe (L1)	10 (L1)
C2	ECZ-Al, SZ (<90 $\mu$ m), $i = 0.009 \text{ A/cm}^2$ , 20 min	<90	0.009 (L2)	Al (L2)	20 (L2)
C3	ECZ-Zn, SZ (<90 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 30 min	<90	0.018 (L3)	Zn (L3)	30 (L3)
C4	ECZ-Al, SZ (90–160 $\mu$ m), $i = 0.003 \text{ A/cm}^2$ , 30 min	90–160 (L2)	0.003	Al	30
C5	ECZ-Zn, SZ (90–160 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 10 min	90-160	0.009	Zn	10
C6	ECZ-Fe, SZ (90–160 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 20 min	90-160	0.018	Fe	20
C7	ECZ-Zn, SZ (160–600 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 20 min	160-600 (L3)	0.003	Zn	20
C8	ECZ-Fe, SZ (160–600 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 30 min	160-600	0.009	Fe	30
C9	ECZ-Al, SZ (160–600 $\mu$ m), $i = 0.018 \text{ A/cm}^2$ , 10 min	160-600	0.018	Al	10

After each ECZ experiment, a sedimentation test was performed according to Kynch's sedimentation theory and the physicochemical indicators of the wastewater were determined (pH, temperature, turbidity, COD).

In addition, both electrodes were ultrasonically cleaned in deionized water for 10 min after each experiment, dried in a dryer, and then weighed on an analytical balance to determine the change in mass of the electrodes during the ECZ experiment.

Analysis of electrode surface with an optical microscope: each electrode surface was examined after the ECZ experiment with an optical microscope MXFMS-BD, Ningbo Sunny Instruments Co. equipped with a Canon EOS 1300D digital camera, at a magnification of  $100 \times$ , illuminated with light through the objective lens (bright field microscopy).

Characterization of the zeolite and electrogenerated sludge: The mineral composition of parent zeolite and electrogenerated sludge coupled with zeolite of different particle sizes was determined by using a powder X-ray diffractometer (PXRD)—model Empyrean. Malvern Panalytical B.V., Netherlands. The X-ray source used was a tube with a Cu anode and the generator was set at the 45 kV and 40 mA. The detector used was a PIXcel<sup>3D</sup> detector with Medipix3. The diffraction patterns were collected using a gonio scan with a step size of 0.013° and a scan angle (°2Theta) from 2 to 80°. The collected patterns were corrected for systematic errors (external Si standard). Qualitative interpretation of XRD patterns was performed in comparison to standard patterns from the database PDF2 (ICDD, PDF2 Released 2020).

The morphology and elemental analysis of the parent zeolite and the electrogenerated sludge coupled with zeolite of different particle sizes were characterized using a scanning electron microscope (SEM) with energy dispersive analysis (EDS), type JEOL JSM -7610FPlus, and a Schottky field emission scanning electron microscope equipped with the Ultim Max 65 EDS detector from Oxford Instruments. The EDS spectra were analysed using Oxford Instruments Aztec v.5.1. software. For SEM/EDS analysis, the samples were prepared by grinding them in a grinding bowl and then glued to a brass stub with carbon paste. Due to this preparation method, the particle size does not provide any additional information about the samples studied.

# 3. Results and Discussion

#### 3.1. Analysis of the Physicochemical Parameters of the ECZ Process

The initial compost leachate solution is characterized by a low initial pH value (pH = 4.03), high electrical conductivity (3.54 mS/cm), high turbidity (397 NTU), and high value of the total solids (10.33 g/L), indicating the presence of salts, anions, and cations, as well as general contamination of the sample with suspended, dissolved, and settling matter. A significantly high value of COD (10,427.6 mg  $O_2/L$ ) confirms the high organic loading of initial compost leachate. The results for each ECZ experiment performed in terms of pH, temperature, COD, and turbidity are summarized in Table 2.

Table 2. Results of physicochemical parameters obtained for each ECZ process.

Exp. Label	Experiments Condition during Each ECZ	pH <sub>fin</sub>	$T_{fin'} \circ C$	COD Decrease, %	Turbidity Decrease, %
C1	ECZ-Fe, SZ (<90 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 10 min	5.52	24.2	9.54	83.32
C2	ECZ-Al, SZ (<90 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 20 min	6.20	27.6	6.87	94.58
C3	ECZ-Zn, SZ (<90 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 30 min	8.56	35.7	23.28	79.47
C4	ECZ-Al, SZ (90–160 $\mu$ m), $i = 0.003 \text{ A/cm}^2$ , 30 min	4.83	25.8	27.86	90.60
C5	ECZ-Zn, SZ (90–160 $\mu$ m), $i = 0.009 \text{ A/cm}^2$ , 10 min	5.24	27.0	9.54	93.68
C6	ECZ-Fe, SZ (90–160 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 20 min	5.25	27.1	9.92	86.45
C7	ECZ-Zn, SZ (160–600 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 20 min	4.81	26.0	21.76	91.18
C8	ECZ-Fe, SZ (160–600 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 30 min	4.95	25.5	23.66	90.00
C9	ECZ-Al, SZ (160–600 $\mu$ m), $i = 0.018 \text{ A/cm}^2$ , 10 min	4.63	28.5	35.11	90.65

# 3.1.1. pH Change

As expected, the initial pH of the solution (pH = 4.03) increased during the ECZ process up to a pH range of 4.63–8.56, depending on the experimental conditions, and is related to the water hydrolysis reaction, the formation of hydrogen gas and hydroxide ions [36–39], but also to the electrode type, the experimental duration, current density, and the properties of the initial compost leachate. When the influence of SZ zeolite particle size is analysed, it is evident that the higher pH increase is obtained with the smallest zeolite particle size (<90  $\mu$ m). Regardless of the other process conditions, the overall highest pH increase was obtained in the C3 experiment (pH = 8.56), at the highest current density of 0.018 A/cm<sup>2</sup>, the zinc electrode, and at a contact time of 30 min. According to Safwat (2020), a higher increase in pH for a Zn electrode is usually associated with a higher dissociation level of water molecules into  $OH^-$  and  $H_2$  [46]. However, in this experiment, the initial composition of the compost leachate has a significant effect on the increase in pH. Namely, the pH increase of the solution during ECZ usually reaches a higher pH value (at least 8) [36–39]. A lower increase in pH observed in this study can be related to the complex composition of the initial compost leachate solution, which acts as a buffer. This assumption was further confirmed by the addition of sodium hydroxide to the initial compost leachate solution.

# 3.1.2. Temperature Change

An increase in temperature is observed in all experiments (from the initial  $T_{in} = 22.8 \,^{\circ}$ C to the final value in the range of 24.2–35.7 °C), which is in accordance with references [36–39]. Taking into account the impact of SZ zeolite particle size, it is evident that the temperature increase is higher for smaller zeolite particles (<90 µm), leading to an increase in the temperature of the solution of up to 35.7 °C in experiment C3, which is the highest final temperature reached. In addition to the zeolite size, the current density has the highest impact on the electrolyte temperature, so that the highest temperature increase in already mentioned experiment C3 was obtained with the highest current density of 0.018 A/cm<sup>2</sup>, and the smallest zeolite particles used, and overlaps with the highest increase in pH.

#### 3.1.3. COD Decrease

Looking at the COD removal efficiency, we find that it is relatively low, which is due to the very high organic load of the wastewater. Nevertheless, the highest COD removal efficiency of 35.11% was obtained in the C9 experiment, which was performed with the largest zeolite particles and the shortest time. Although this value was obtained for the highest value of current density with the Al electrode, comparison of the COD removal with smaller particles shows that the current density (example experiment C6) and electrode material (example experiment C2) are less influential factors than particle size. Nevertheless, the results suggest that there is a complex mechanism associated with the COD removal efficiency that should be further investigated. According to Tegladza et al. (2021) [24], at low current density, metal dissolution mainly occurs, while at high current density, metal dissolution processes compete with the anodic oxygen evolution reaction and thus may influence COD decrease.

Regarding the final COD values determined in this study, additional treatment should be performed to comply with Croatian regulation for discharge of treated wastewater into the sewage system [47]. Obviously, the initial compost leachate has a very complex composition, it is loaded with a large amount of organic matter, which was not significantly removed in the one-step process of hybrid ECZ. Thus, further solutions can be found in two-step or multistep processes, or in the application of another pretreatment step, such as advanced oxidation processes.

#### 3.1.4. Turbidity Decrease

The turbidity decrease in results ranged from 79.47%–94.58%. The highest turbidity decrease was obtained in experiment C2, and the lowest in experiment C3. For the largest zeolite particle size (160–600  $\mu$ m), the turbidity decrease varies only slightly with electrode material, current density, and contact time. For smaller SZ particle sizes, the variations are more visible and depend on the experimental conditions. Except for the experiments with the highest particle size, the percentage of turbidity decrease was also very high (over 90%) for all experiments with Al electrodes.

#### 3.1.5. Settling Test

The results of the settling test (not given here) indicated poor sedimentation characteristics of the suspension after the application of ECZ. The reason for this was probably the complex composition of the original compost leachate solution and its very high organic load, which could not be efficiently processed in a single-stage ECZ. According to Smoczyńskia et al. (2017), insufficient electrocoagulant dosages can lead to the formation of residues of noncoagulated pollutants and residues of "unused" stable micelles or their destabilization products with very poor settling properties [48]. Even though the addition of zeolite had a positive effect on the settling properties of compost leachate with an organic load [36], this effect was not observed in this study when treating compost leachate with a high organic load. Thus, additional filtration will be necessary in the final application, since very poor separation of the formed precipitate from the solution was achieved.

# 3.1.6. Electrode Consumption

Electrode consumptions during the ECZ experiments are compared in Figure 1. In addition to the expected decrease in the mass of sacrificial anodes, there is also a decrease in the mass of all cathodes. According to the literature [49], the decrease in cathode mass is mainly due to the attack of OH<sup>-</sup> ions produced during the hydrogen evolution reaction. However, the loss of cathode mass could also be due to the addition of zeolite and its abrasive effect [38,39].



**Figure 1.** Electrode consumption during ECZ experiments with different SZ particle sizes: (**a**) <90  $\mu$ m; (**b**) 90–160  $\mu$ m; (**c**) 160–600  $\mu$ m.

Considering the influence of SZ particle size, it can be seen that higher electrode consumptions were obtained in the experiments with smaller zeolite particle size (experiments C1, C2, and C3), with electrode consumption clearly dominating in the C3 experiment in amount of 0.6481 g, at condition of Zn electrode, highest current density of 0.018 A/cm<sup>2</sup>, and longest contact time of 30 min). At medium (SZ = 90–160  $\mu$ m) and largest zeolite particle size (SZ = 160–600  $\mu$ m), the highest electrode reductions were obtained with the Fe electrodes (at C6 and C8 experiments electrode consumptions equal to 0.1085 and 0.1002 g, respectively).

Compared to previous studies performed on compost leachate with medium organic loading [42,49], the changes in cathode mass for the Fe and Zn electrodes were different and varied between loss and gain, depending on the experimental conditions. In this study, only cathode mass loss was observed for all materials under all experimental conditions.

# 3.1.7. Stability of ECZ Experiments

Pourbaix diagrams (potential-pH diagrams) can provide information about the stability and corrosion of a particular metal as a function of pH and potential. However, they have limited explanatory power because they represent the thermodynamic considerations of pure metals immersed in pure water at 25 °C, without considering the presence of various ions that play an important role in corrosion processes [50,51].

According to the Pourbaix diagrams, aluminium shows passive behaviour in the pH range from about 4 to 8.5. However, this range can vary with temperature, the specific form of the film present, and in the presence of substances that can form soluble complexes or insoluble salts with aluminium. Beyond these limits, aluminium corrodes in aqueous solutions in the form of  $AI^{3+}$  ions or in the form of  $AIO_2^-$  because its oxides are soluble in many acids and bases, reflecting the amphoteric properties of aluminium oxide. The electrodes were made from the alloy AA 2007 (which belongs to the Al–Cu alloy series), which is known to have lower corrosion resistance compared to Al and other Al alloys, due

to the presence of Cu-rich precipitates [51–54]. In this context, the main anodic reaction will be:

$$Al \to Al^{3+} + 3e^{-} \tag{1}$$

If the anodic potential is sufficiently high, an oxygen evolution reaction can also occur (Equation (2)):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (2)

Like aluminium, Zn dissolves as a  $Zn^{2+}$  ion in the pH range from pH = 0 to pH  $\approx 8.5$  according to the reaction (3) [55,56]:

$$Zn \to Zn^{2+} + 2e^{-} \tag{3}$$

From pH  $\approx$  8.5 to pH  $\approx$  12 Zn is covered with the passive oxide film ZnO. In strongly alkaline solutions (above pH = 12), Zn corrodes and dissolves in the form of ZnO<sub>2</sub><sup>2-</sup>. Formed Zn<sup>2+</sup> ions react with the OH<sup>-</sup> ions in the solution to form Zn(OH)<sub>2</sub> [56,57].

Anodic reaction for the iron in solution with pH < 4 can be described with the reactions (4) and (5):

$$Fe \to Fe^{2+} + 2e^- \tag{4}$$

$$Fe \to Fe^{3+} + 3e^- \tag{5}$$

For the solutions with 4 < pH < 7, iron will be dissolved into Fe<sup>2+</sup> and Fe<sup>3+</sup> ions, with instant hydrolysis and the formation of hydroxides according to the reactions (6) and (7) [58,59]:

$$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2(aq)} + 2H^+ + 2e^-$$
 (6)

$$Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3(aq)} + 3H^+ + 3e^-$$
 (7)

Fe(III) hydroxide begins to precipitate floc with yellowish colour, together with precipitation of Fe(II) hydroxide with formation of a dark green floc.

Electrically generated metal ions form the corresponding hydroxides together with other monomeric, polymeric, and hydroxo complexes, which further destabilize the contaminants in the solution and allow their agglomeration and further separation from the solution by settling or flotation [60,61].

The formed hydroxocomplexes can contribute to the build-up of the electrode surface layers, which can lead to fouling and passivation [60]. The zeolite particles present in the solution impinge on the surface of the electrodes by mixing, thus cleaning the aforementioned surface layers, reducing these phenomena and contributing to the uniform dissolution of the anode.

# 3.2. Microscopic Electrode Surface Analysis

Figure 2 shows the surface of the electrodes before and after the ECZ experiments performed under different experimental conditions (labelled as C1–C9), which were examined with an optical microscope with  $100 \times$  magnification.

Before the ECZ process, the surfaces of all electrodes were relatively smooth, with flat lines that were the result of mechanical preparation of the surface using wet sanding with P800 grit sandpaper. After the ECZ process, both the anodes and cathodes of all the materials studied changed significantly as a result of the anodic and cathodic reactions that developed on their surfaces.

For the Al electrodes, the most severe damage is observed in experiment C9, which was performed with the highest corrosion current and the shortest time in the presence of the zeolite with the largest particle size, followed by experiment C2 (moderate current density, experimental duration of 20 min, and the smallest zeolite particles). The least



surface damage was observed in experiment C4 with the lowest corrosion current density and the longest experiment duration with the medium zeolite particle size.

**Figure 2.** Microscopic electrodes surface analysis before and after the ECZ experiments performed under different experimental conditions (labelled as C1–C9). Note: with  $100 \times$  magnification.

On the other hand, the most severe damage to the Zn anode was observed in experiment C3 (highest current density, longest experimental duration, and smallest zeolite particle size) and in experiment C7 (lowest current density, moderate experimental duration, and largest zeolite particle size), while the least damage occurred in experiment C5 (moderate current density, shortest experimental duration, and moderate zeolite particle size). On the Zn anode surfaces in experiments C3 and C7, the pitting damage is clearly visible in contrast to experiment C5, while no pitting damage was observed during optical examination of the surface.

Regarding surface damage of the Fe electrodes, the most severe damage was observed on the Fe anode in experiment C8, where the entire surface was covered with a layer of corrosion products and black holes were observed, probably as a result of pitting. The Fe anodes in experiments C1 (lowest current density, experiment duration, and smallest zeolite particle size) and C6 (highest current density, average experiment duration, and average zeolite particle size) have visible corrosion products on their surface (which cannot be removed with ultrasonic cleaning in deionized water using the ECZ method), but without black holes on the surface. On the other hand, most changes in the cathode's surface were observed in the C6 experiment, followed by C8 (average current density, highest experimental duration, and largest zeolite particle size), while the cathode surface remained minimally damaged in the C1 experiment.

In general, the largest SZ zeolite particle size of 160–600  $\mu$ m causes greater damage to the electrode surface, although the greatest mass loss occurs with the smallest particles. An exception to this is experiment C3. In this experiment, the smallest zeolite particles are responsible for the highest anode mass loss, and at the same time, the most severe anode damage was observed, indicating that electrode type, current density, and contact time have a significant effect on the electrode surface.

The diffraction pattern of the parent SZ zeolite with a particle size of 90–160  $\mu$ m is shown in Figure 3 and Table 3. The most dominant structurally ordered phase belongs to the compound sodium potassium aluminium silicate hydrate, which belongs to the FAU-Faujasite family according to the zeolite classification.



**Figure 3.** PXRD pattern of the SZ zeolite with the particle size of 90–160  $\mu$ m.

Analysis of the diffraction pattern also indicates other mineral types of zeolites that are present in smaller quantities, namely zeolite-LTL (potassium silicon aluminium oxide), LTA, IFR(ITQ-4), ZZ1 and SFF(SSZ-44).

The faujasite type zeolites all have the same framework structure and they crystallize with cubic symmetry. The structure of the faujasite is microporous, characterized by channels and cavities accessible even to pollutants with a significant molecular size, such as toluene, cyclohexane etc.

**Table 3.** Identified the structural ordered phase which are present in the SZ zeolite with a particle size of 90–160  $\mu$ m.

Ref. Code	Compound Name	Chem. Formula
01-089-0770	Sodium Potassium Aluminium Silicate Hydrate	Na56K40Al96Si96O384(H2O)408.7
01-078-2453	Calcium Sodium Aluminium Silicate	Ca <sub>3.68</sub> Na <sub>4.64</sub> Al <sub>12</sub> Si <sub>12</sub> O <sub>48</sub>
01-086-5330	Potassium Aluminium Silicate	K <sub>9.8</sub> Si <sub>28</sub> Al <sub>8</sub> O <sub>72</sub>
01-087-2493	Silicon Oxide	SiO <sub>2</sub>
01-073-3447	Silicon Oxide	SiO <sub>2</sub>
00-052-0116	Sodium Aluminium Silicon Oxide	Na-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>

Figure 4 shows the simulated 3D structure of faujasite (FAU) prepared using the Mercury and the structure CIF file AMSD 0000128. The FAU framework is built on the basis of fused double six rings called hexagonal prisms and sodalite cages also called  $\beta$ -cages [62]. FAU crystalize in the space group Fd3m with the parameter of unite cell

a = b = c = 25.104 Å and  $\alpha$  =  $\beta$  =  $\gamma$  = 90°. The general composition of the faujasite is (Na<sub>2</sub>,Ca, Mg)<sub>29</sub>[Al<sub>58</sub>Si<sub>134</sub>O<sub>384</sub>]<sub>240</sub>H<sub>2</sub>O [63].



Figure 4. Structure of the Na-Faujasite (CIF file amcsd 0000128).

Figure 5 shows the PXRD patterns of the different zeolite fractions. From the comparison of the PXRD patterns of the different zeolite fractions, it is evident that the mineralogical composition is the same for all three granulations.



Figure 5. PXRD patterns of the SZ zeolite of three particle sizes: <90 µm, 90–160 µm, and 160–600 µm.

In this study, the analysis of the sludge electrolytically generated during the ECZ experiment and coupled with zeolite of different particle sizes was performed using PXRD and SEM/EDS. The diffraction patterns of mixtures of the electrogenerated sludge and zeolite (three different particle sizes SZ < 90  $\mu$ m, 90–160  $\mu$ m, and 160–600  $\mu$ m) compared to the untreated zeolites are shown in Figures 6–8.



**Figure 6.** Comparison of PXRD patterns of the zeolites SZ (<90 µm) before and after ECZ process marked as sludge (C1–C3).



Figure 7. PXRD patterns of the zeolites SZ (90–160  $\mu$ m) before and after ECZ process marked as sludge (C3–C6).



Figure 8. PXRD patterns of the zeolites SZ (160–600  $\mu$ m) before and after ECZ process marked as sludge (C7–C9).

The PXRD patterns (Figure 6) of the SZ zeolite specimens where particle size was <90  $\mu$ m in experiments C1 (ECZ-Fe), C2 (ECZ-Al), and C3 (ECZ-Zn) after the ECZ process compared to the untreated SZ zeolite show that interplanar spacing between (111) planes (d<sub>111</sub>) decreases from 14.35 Å (SZ < 90  $\mu$ m) to values of 14.07, 14.34, and 14.20 Å, respectively. In the PXRD patterns (Figure 7) for the specimens C4 (ECZ-Al), C5 (ECZ-Zn), and C6 (ECZ-Fe), where the particle size of the zeolite was 90–160  $\mu$ m, interplanar spacing between the same plane d<sub>111</sub> decreases from 14.35 Å (SZ 90–160  $\mu$ m) to values of 14.24, 14.29, and 14.19 Å, respectively. However, the PXRD patterns (Figure 8) of specimens C7 (ECZ-Zn), C8 (ECZ-Fe), and C9 (ECZ-Al), where particle size of the zeolite was in the range of 160–600  $\mu$ m, do not show a change in interplanar distances d<sub>111</sub>, suggesting that in the stabile structure of SZ the particle size was in the range of 160–600  $\mu$ m. According to Castaldi et al. (2008), structural changes of zeolite samples may occur due to different interactions between the zeolite framework and ions in solutions that change the interplanar spacing [64].

In order to obtain a better insight into the elemental composition, Figure 9 and Table 4 compare the SEM/EDS mapping with the elemental distribution and map sum spectrum of untreated SZ zeolite and electrogenerated sludge mixed with zeolite after ECZ experiments.



**Figure 9.** The SEM/EDS mapping with the elemental distribution of untreated SZ zeolite and electrogenerated sludge mixed with zeolite after ECZ experiments.

	SZ		C1-	Fe	C2-	Al	C3-	Zn	C4-	·Al	C5-	Zn	C6-	·Fe	C7-	Zn	C8-	·Fe	C9-	·Al
Map Sum Spec.	Wt%	Wt% Sig.																		
0	43.36	0.09	40.19	0.06	38.24	0.06	40.64	0.11	43.64	0.07	41.29	0.08	47.26	0.08	36.01	0.07	43.07	0.06	44.42	0.03
Si	26.21	0.06	22.29	0.04	14.28	0.03	17.69	0.05	25.10	0.05	18.13	0.05	22.01	0.05	20.49	0.04	19.67	0.04	17.23	0.02
Al	12.15	0.04	10.39	0.03	10.44	0.02	12.19	0.04	17.42	0.04	12.56	0.04	15.20	0.04	13.72	0.03	10.38	0.03	11.80	0.02
С	4.76	0.09	15.09	0.00	30.77	0.07	15.26	0.00	3.60	0.09	15.50	0.00	4.22	0.11	13.52	0.00	16.17	0.00	16.68	0.00
Mg	4.74	0.02	4.06	0.02	1.27	0.01	1.55	0.01	1.98	0.01	1.56	0.02	1.88	0.02	1.66	0.01	2.01	0.01	1.74	0.01
Fe	2.86	0.11	2.92	0.09	0.95	0.06	1.80	0.11	1.69	0.06	1.99	0.07	1.85	0.05	3.79	0.06	3.48	0.08	0.98	0.02
Na	2.40	0.02	2.06	0.02	1.88	0.01	3.24	0.03	3.36	0.02	3.02	0.03	4.70	0.02	3.74	0.02	3.31	0.02	4.94	0.01
Κ	1.51	0.03	1.30	0.02	0.83	0.01	1.06	0.02	1.61	0.02	2.48	0.03	1.53	0.02	4.36	0.03	0.96	0.02	1.25	0.01
Ca	1.18	0.03	1.01	0.02	0.68	0.01	0.86	0.02	1.31	0.02	1.12	0.02	0.93	0.02	1.43	0.02	0.43	0.02	0.66	0.01
Р	0.60	0.02	0.50	0.01	0.52	0.01	0.54	0.01	0.26	0.01	0.37	0.01	0.21	0.01	0.24	0.01	0.29	0.01	0.16	0.01
Ti	0.15	0.04	0.13	0.03	0.03	0.02	0.07	0.03	-	-	0.11	0.03	0.08	0.02	0.27	0.03	-	-	0.06	0.01
S	0.08	0.01	0.07	0.01	0.04	0.01	0.06	0.01	0.03	0.01	0.01	0.01	0.03	0.01	0.03	0.01	-	-	0.02	0.01
Cu	0.01	0.03	0.00	0.03	0.06	0.02	-	-	-	-	0.16	0.05	0.11	0.04	0.24	0.04	-	-	0.02	0.02
Zn	-	-	-	-	-	-	4.18	0.04	-	-	1.70	0.07	-	-	0.46	0.06	-	-	-	-
Cl	-	-	-	-	-	-	0.04	0.01	-	-	-	-	-	-	0.05	0.01	-	-	0.04	0.01
Mn	-	-	-	-	-	-	0.82	0.22	-	-	-	-	-	-	-	-	-	-	-	-
Ν	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.24	0.07	-	-
Total	100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00	

Table 4. SEM/EDS map sum spectrum of the untreated SZ zeolite and the electrogenerated sludge mixed with zeolite after ECZ experiments.

The results show that the elemental distribution and map sum spectrum of electrogenerated sludge mixed with zeolite after ECZ treatment differ slightly in elemental composition. Oxygen (O), silicon (Si), and aluminium (Al) are the dominant elements. The elemental distribution of carbon (C) is also significant but cannot be considered due to the overlap with the carbon pasta used in the SEM /EDS analysis. Other elements present in lower amounts are magnesium (Mg), iron (Fe), sodium (Na), potassium (K), calcium (Ca), and phosphorus (P). However, some elements such as titanium (Ti), sulphur (S), copper (Cu), zinc (Zn), chloride (Cl), manganese (Mn), and nitrogen (N) are present only in certain samples, which depends on the experimental conditions of each ECZ process. In comparison with elemental distribution and the map sum spectrum of electrogenerated sludge obtained in our previous study [37] with Al electrode but without zeolite addition performed, it is evident that sludge contains mainly oxygen (O) and aluminium (Al). In the experiment with the Fe and Zn electrodes, the main elements are iron and oxygen, and zinc and oxygen, respectively. In this study, the amount of zeolite significantly dominates in the total amount of sludge after the ECZ process, indicating that oxygen, silicon, and aluminium are mainly from the zeolite used.

# 3.4. Taguchi Optimization

The influence of the selected controllable parameters on chemical oxygen demand (COD) and turbidity decrease was investigated. These controllable parameters were zeolite SZ particle size (Z), current density (i), electrode materials (M), and contact time (t). As already stated, each parameter employed had three testing levels (L1, L2, and L3), as shown in Table 1. In this study, the larger-the-better quality characteristic Equation (8) was used:

$$S/N_{LB} = -10 \log \frac{\sum_{i=1}^{n} \frac{1}{y_i^2}}{n}$$
 (8)

where, *S/N* represents the signal-to-noise ratio, subscript LB represents larger-the-better, n is the number of repetitions under the same experimental conditions, and y is an experimental value [37,39].

The average  $S/N_{LB}$  ratio of each controllable factor at level "i" was calculated and results are given in Table 5.

Experiment	S/N <sub>LB</sub> for COD Decrease	S/N <sub>LB</sub> for Turbidity Decrease
C1	19.59	38.42
C2	16.74	39.52
C3	27.34	38.00
C4	28.90	39.14
C5	19.59	39.43
C6	19.93	38.74
C7	26.57	39.20
C8	27.48	39.08
C9	30.91	39.15

Table 5. Taguchi design of experiments L9.

Statistical analysis employing the sum of squares (SS), mean square (MF), percentage of contribution (pC), and range was performed in order to evaluate the significance of all parameters employed. The formula for the calculation methodology is available elsewhere [40].

Analysis of the data shows, as can be seen in Figure 10, that for the following values: Z3, *i*3, M2; and *t*3, i.e., the largest zeolite SZ particles used, the highest current density used, Al electrodes, and after 30 min the highest COD decrease should be achieved. The highest turbidity removal should be achieved at the following values: Z3, *i*2, M2; and *t*2, i.e., the largest zeolite SZ particles used, the medium current density used, Al electrodes, and after

20 min. The analysis of the optimal values for both results shows the following: the highest COD and turbidity decrease is achieved with a zeolite particle size of 160–600  $\mu$ m and with Al electrodes. In addition to analysing the optimal level of the factors, their effect on the mean values and SN ratios was also investigated. As can be seen from Tables 6 and 7, the effects of the studied parameters on COD and the reduction in turbidity are completely opposite. The results show that in the optimization of two responses, the final selection of the optimal parameters cannot be based only on the Taguchi results. Regarding current density and contact time, some other factors, such as energy and electrode costs, must be considered before a final decision is made.



Figure 10. Main effect plot for *S/N* ratios (red dot—optimal level).

	COD decrease								
Factor	Z	i	М	t					
DoF	2	2	2	2					
SS	314.34	138.41	119.79	220.38					
MF	157.17	69.20	59.89	110.19					
pC (%)	39.64	17.46	15.11	27.79					
Rank	nk 1 3		4	2					
		Turbidity decrease							
Factor	Z	i	М	t					
DoF	2	2	2	2					
SS	43.20	79.60	45.66	25.07					
MF	21.60	39.80	22.83	12.54					
pC (%)	22.32	41.13	23.59	12.95					
Rank	3	1	2	4					

Table 6. Effect of controllable factors on means.

where: DoF—degree of freedom for selected controllable factor, SS—sum of squares, MF—mean square, pC—percentage of contribution.

**Table 7.** Effect of controllable factors on *S/N* ratio.

	COD decrease								
Factor	Z	i	М	t					
DoF	2	2	2	2					
SS	84.80	38.42	15.99	71.35					
MF	42.40	19.21	8.00	35.68					
pC (%)	bC (%) 40.27	18.25	7.60	33.89					
Rank	1	3	4	2					
		Turbidity	decrease						
Factor	Z	i	М	t					
DoF	2	2	2	2					
SS	0.46	0.78	0.44	0.25					
MF	0.23	0.39	0.22	0.13					
pC (%)	23.79	40.19	22.96	13.05					
Rank	3	1	2	4					

where: DoF-degree of freedom for selected controllable factor, SS-sum of squares, MF-mean square, pC-percentage of contribution.

# 3.5. Energy and Electrode Consumption during ECZ Process

The electrode cost was calculated using Faraday's law and mass loss measurements before and after the ECZ experiments, while the energy cost was calculated using only Faraday's law [39]. The results are compared in Table 8.

Table 8. Comparison of electrode and energy consumption.

Exp.	Experiments Condition during ECZ	U,	Ι,	C <sub>energy,</sub> kWh/m <sup>3</sup>	Based on Faraday Low	Based on Electrode Mass Consumption			
Label		v	Α		C <sub>electrode</sub> , kg/m <sup>3</sup>	C <sub>anode,</sub> kg/m <sup>3</sup>	C <sub>cathode</sub> , kg/m <sup>3</sup>	C <sub>anode+cathode</sub> , kg/m <sup>3</sup>	
C1	ECZ-Fe, SZ (<90 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 10 min	3.08	0.045	3.960	0.022	0.499	0.013	0.512	
C2	ECZ-Al, SZ (<90 μm), <i>i</i> = 0.009 A/cm <sup>2</sup> , 20 min	8.05	0.435	200.100	0.139	0.200	0.087	0.288	
C3	ECZ-Zn, SZ (<90 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 30 min	15.80	0.970	1313.657	1.690	1.848	0.004	1.852	

Exp.	Experiments Condition during ECZ	U,	I, A	C <sub>energy,</sub> kWh/m <sup>3</sup>	Based on Faraday Low	Based on Electrode Mass Consumption			
Label		V			C <sub>electrode,</sub> kg/m <sup>3</sup>	C <sub>anode,</sub> kg/m <sup>3</sup>	C <sub>cathode,</sub> kg/m <sup>3</sup>	C <sub>anode+cathode,</sub> kg/m <sup>3</sup>	
C4	ECZ-Al, SZ (90–160 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 30 min	4.21	0.108	38.973	0.052	0.103	0.016	0.119	
C5	ECZ-Zn, SZ (90–160 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 10 min	8.41	0.534	128.313	0.310	0.242	0.006	0.248	
C6	ECZ-Fe, SZ (90–160 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 20 min	10.41	0.270	160.611	0.268	0.010	0.010	0.310	
C7	ECZ-Zn, SZ (160–600 $\mu$ m), <i>i</i> = 0.003 A/cm <sup>2</sup> , 20 min	4.36	0.160	39.863	0.186	0.168	0.030	0.198	
C8	ECZ-Fe, SZ (160–600 $\mu$ m), <i>i</i> = 0.009 A/cm <sup>2</sup> , 30 min	6.38	0.189	103.356	0.281	0.280	0.007	0.286	
C9	ECZ-Al, SZ (160–600 $\mu$ m), <i>i</i> = 0.018 A/cm <sup>2</sup> , 10 min	17.00	0.696	338.057	0.111	0.145	0.005	0.150	

Table 8. Cont.

where: *U*—cell voltage (V), *I*—current (A),  $C_{\text{energy}} = (U \cdot I \cdot t)/V$ —cost of electrical energy calculated from Faraday Low (kW/m<sup>3</sup>),  $C_{\text{electrode}} = (I \cdot t \cdot M)/(z \cdot F \cdot V)$ —cost of electrode calculated from Faraday Low (kg/m<sup>3</sup>), *t*—operating time (s), *V*—volume of the treated leachate (m<sup>3</sup>), *z*—number of electron transfers (*z* = 2 or 3), *F*—Faraday constant (96 485.33 C/mol), *M*—molecular mass of metal (g/mol),  $C_{\text{electrode}} = m/V$ —cost of electrode calculated from electrode mass consumption, *m*—mass of released metal obtained from electrodes mass loss (g).

Applied voltages ranged from 3.08-17.00 V, while applied currents ranged from 0.045-0.970 A. The highest energy cost was obtained in experiment C3 with the Zn electrode (1313.657 kW/m<sup>3</sup>), while the lowest was obtained in C1 with the Fe electrode (3.960 kW/m<sup>3</sup>), indicating a very high oscillation depending on the experimental conditions. Considering the influence of the zeolite particle size, a tendency towards lower power costs can be observed for the largest zeolite particle size.

The electrode costs calculated from the electrode mass consumption mostly exceeded the theoretical values calculated using Faraday's law, which is known as "superfaradiac efficiency" [65]. These are the result of two effects: dissolution of the cathode, which occurs during EC, and electrochemical oxidation and reduction of water, which can change the solution pH in vicinity of the anode and cathode, thus contributing to their dissolution. However, these differences are less pronounced at the largest zeolite particle size. As electrode distance and mixing speed were constant in all experiments, this suggests that even the largest zeolite particle size causes greater surface damage, which has a positive effect on lower electrode consumption and contributes to higher COD and turbidity decrease (see Table 2).

However, the final values of electrode and power costs will depend on the market price. These fluctuations are even more pronounced today, as we face extremely increasing costs of electrical energy and market prices of metals. Thus, a possible solution to reduce the electricity cost during the ECZ process should consider the application of renewable energy sources, while decreasing metal electrode costs can be compensated using waste material as electrodes for ECZ.

In the context of limiting environmental standards, it is necessary to determine the residual amount of metal in the final solution, especially if the effluents are discharged into the natural receiving water without additional treatment, as they may have a negative impact on living organisms. The management of the electrosludge generated during the ECZ process can still be a problem as it can contain organic matter, metals, and nonmetallic compounds. A solution needs to be found on how to convert the EC sludge into a valuable resource to achieve sustainability. Furthermore, spent zeolite can be regenerated and reused in a later cycle, ensuring its recyclability.

# 4. Conclusions

Electrocoagulation coupled with zeolite (ECZ) is used to treat compost leachate with a very high organic load and to investigate the influence of SZ zeolite particle size on the efficiency of the ECZ process. The results show that with the largest zeolite particle size of 160-600 µm generally obtains a lower increase in pH and temperature and a higher COD and turbidity decrease. However, the electrode type, current density, and contact time also have a significant effect on the measured parameters, but their changes are less pronounced with the largest zeolite particle size. Consumption of anode and cathode electrodes is observed in all experiments. Higher electrode consumption in amount of 0.6481 g was obtained in experiments with the smallest zeolite particle size of  $<90 \ \mu m$ and with the Zn electrode, while with medium (SZ =  $90-160 \mu m$ ) and large zeolite particle size (SZ =  $160-600 \mu m$ ), the highest electrodes consumptions were obtained with the Fe electrode (in range 0.1002–0.1085 g). Microscopic images of the electrode surface before and after the ECZ process generally show more damage on the electrode surface with the largest zeolite particle size of 160–600  $\mu$ m, but the influence of electrode type, current density, and contact time cannot be neglected. The diffraction pattern of the SZ zeolite used shows the most dominant structurally ordered phase of the sodium potassium aluminium silicate hydrate and belongs to the FAU-Faujasite family. The diffraction patterns of electrogenerated sludge mixed with zeolite show only small changes in interplanar spacing at low and medium particle size, while this effect was not observed at higher zeolite particle size. SEM/EDS analysis of electrogenerated sludge mixed with zeolite after ECZ treatment differ slightly in elemental composition, but oxygen, silicon, and aluminium are dominant elements. Taguchi L9 orthogonal array was applied to analyse the effects of synthetic SZ zeolite particle size, electrode materials, current density, and contact time on COD and turbidity decrease. The highest COD and turbidity decrease is achieved with the largest zeolite particle size of 160–600  $\mu$ m, and with Al electrodes. For current density and contact time, the obtained results differ, and for the final decision, the energy and electrode costs should be considered before making a final selection. The energy costs estimated by Faraday's law ranged from 3.960 kW/m<sup>3</sup> to 1313.657 kW/m<sup>3</sup>, but in general, the lower energy costs and the smaller difference between the electrode costs calculated from the electrode mass consumption and the theoretical values calculated by Faraday's law were obtained for the experiments with the largest zeolite particle size of 160–600  $\mu$ m.

Although electrocoagulation with zeolite (ECZ) was efficiently used to treat compost leachate with a very high organic load, the final COD values are significantly higher than the Croatian regulations for the discharge of treated wastewater into the sewer system. This means that for the treatment of compost leachate with very high organic load additional processes, such as two-stage or multistage ECZ processes, the application of another pretreatment stage such as advanced oxidation processes must be considered.

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