Optimization and Analysis of Zeolite Augmented Electrocoagulation Process in the Reduction of High-Strength Ammonia in Saline Landfill Leachate

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Abstract: This work examined the behavior of a novel zeolite augmented on the electrocoagulation process (ZAEP) using an aluminum electrode in the removal of high-strength concentration ammonia (3471 mg/L) from landfill leachate which was saline (15.36 ppt) in nature. For this, a response surfaces methodology (RSM) through central composite designs (CCD) was used to optimize the capability of the treatment process. Design-Expert software (version 11.0.3) was used to evaluate the influences of significant variables such as zeolite dosage (100–120 g), current density (540–660 A/m^2), electrolysis duration (55–65 min), and initial pH (8–10) as well as the percentage removal of ammonia. It is noted that the maximum reduction of ammonia was up to 71%, which estimated the optimum working conditions for the treatment process as follows: zeolite dosage of 105 g/L, the current density of 600 A/m^2, electrolysis duration of 60 min, and pH 8.20. Furthermore, the regression model indicated a strong relationship between the predicted values and the actual experimental results with a high R^2 of 0.9871. These results provide evidence of the ability of the ZAEP treatment as a viable alternative in removing high-strength landfill leachate of adequate salinity without the use of any supporting electrolyte.

Keywords: ammonia; zeolite; electrocoagulation; response surface methodology; stabilized; leachate

1. Introduction

In Malaysia, the rise in inhabitants, active urbanization development, and revolution of industrialization over the years has been causing fast economic growth. As a result, generation of municipal waste is increasing annually (6.2 million ton/year) and is linearly proportionate to the increase in population and migration of urbanization. Generally, in most developed countries, organic waste is the main contributor of about 40% to 60% of the total weight of municipal solid waste (MSW). In this sense, solid waste disposal due to rapid solid waste generation is one of the primary environmental concerns that must be addressed [1]. Presently, landfilling is the main option for waste disposal because of its low operation cost and simpler operating management [2]. Heterogeneous waste (municipal solid waste) deposited in landfills undergoes several physicochemical reactions, which result in an extremely polluted dark liquid with bad odor known as leachate [3]. Furthermore, as water passes over a landfill, most of the organic and inorganic contents such as ammoniacal nitrogen (NH$_3$-N) and heavy metals are transported into the leachates [4]. Lack of efficient leachate management

may lead to pollution of the water bodies resources and groundwater, which could harm human wellness and aquatic habitats [5].

A landfill is typically categorized into three major phases—acidogenic, intermediate, and methanogenic—according to their respective biodegradability ratios (BOD_5/COD); more than 0.5 (young, <5 years), between 0.1 and 0.5 (intermediate, 5 to 10 years), and less than 0.1 (stabilized, >10 years) [6,7]. Landfill leachate can be classified as a concentrated wastewater pollutant, which is very hard to be treated. Organic compounds such as ammonia, chemical oxygen demand (COD), and color are the most challenging soluble contaminants to be completely removed from landfill leachate [8]. Regrettably, conventional treatment techniques (single process) in normal operation are incapable to fully comply with the acceptable effluent limit as described accordingly in the Environmental Quality Act 1974. In contrast, an affiliation of multiple biological, chemical, and physical treatment techniques seems to be more effective for stabilized and high-strength landfill leachate [9].

A previous review by [10] had explained that a biological treatment includes aerobic and anaerobic processes as well as an efficient treatment of young leachate; meanwhile, physical and chemical treatments that involve several techniques such as ion exchange, adsorption, coagulation–flocculation, and oxidation are further effective in treating stabilized landfill leachate. Among advanced oxidation processes in physico-chemical treatment, the electrocoagulation (EC) technique offers an effective alternative method for treating various pollutants in water and wastewater [11]. In terms of simplicity of equipment, including reaction time, ease of operation, electro-generation of flocs, level of maintenance, supporting electrolyte requirement, and quantity of sludge, the EC method offers better advantages in comparison with other current processes [12]. Generally, an EC process consists of three essential mechanisms of coagulation, flotation, and electrochemistry [13]. In a landfill leachate treatment, electrocoagulation also includes the processes of ionization, electrolysis, hydrolysis, and free hydroxyl radicals, which lead to significant changes in the liquid properties as well as enhancement in the overall contaminant removal [14].

A prior review by [15] reported that the effectiveness of an EC process is subjected to several basic working parameters such as electrode type, current density, electrolyte concentration, pH, electrode distance, reaction time, and arrangement of the electrode. However, other researchers [16] with their study on a similar method claimed that the most vital factor affecting the overall efficiency of an electrocoagulation process is the type of electrode material used. Normally for an EC electrode, aluminum (Al) or iron (Fe) materials are mostly preferred as they are low priced, readily accessible, and effective in pollutant removal [17]. Several studies by [18–20] had proven that an aluminum electrode has a better performance in eliminating various contaminants in the treatments of landfill leachate. Moreover, in the removal of dissolved organic pollutants, for example, color, turbidity, chemical oxygen demand (COD), and so forth, aluminum electrodes prove to be more effective compared to other types of electrodes [1,21,22].

Despite the proven advantages and effectiveness of the EC method in landfill leachate treatment, current reviews have indicated that the removal of certain contaminants, particularly ammoniacal nitrogen (NH_3-N), is strictly ineffective and needs further attempts, and very limited studies were conducted in this case. There are various existing technologies focusing on the leachate treatment process that involve the removal of NH_3-N pollutants such as biological [23], air stripping [24], adsorption [25], chemical precipitation [26], and electro-oxidation [27] processes. In the physical treatment process, adsorption is a typical organic pollutant removal method used to transfer substances from catalysts to the solid surface. Since an adsorption process relates to the surface mechanism, the adsorbent surface area is the main affecting factor, where a high surface area provides more porosity for adsorbent interactions. A previous study by [28] revealed the effective application of activated carbon to mitigate COD and NH_3-N in landfill leachate by applying a fixed bed method.

Nevertheless, the preparation of activated carbon is costly and takes a longer time. As a comparison to this type of adsorbent for the reduction of NH_3-N, the mechanisms of adsorption and ion exchange displayed by zeolites are rather interesting, owing to their cost-effective and uncomplicated

approaches [29]. Zeolite adsorbent is also used in the aeration tank of a sludge process as an augmented medium. As a result, the removal of NH$_3$-N, in particular, is significantly improved [30]. In addition, the natural zeolite mineral also offers a strong ion exchange and good adsorption bonding in a mixed suspension of contaminants [31].

Hence, in this work, a novel integrated treatment method was established to remove high-strength NH$_3$-H in saline landfill leachate using an electrocoagulation process with augmenting zeolite to enhance the efficiency of its performance. A preliminary experiment on the batch study of zeolite augmented on the electrocoagulation process (ZAEP) was rigorously conducted to evaluate its removal mechanism and the best fit of optimum conditions, where four vital variables affecting treatment capability were identified. The mechanisms of ammonia contaminant elimination from saline landfill leachate can be more complicated in ZAEP. According to [32], it was stated that the removal process mechanism for ammonia could be respectively distributed into four categories, namely direct oxidation by the anode, indirect oxidation of hydroxyl radicals, active chlorine sites, and adsorption by zeolite. The dissolution of aluminum particles (Al^{3+}) was directly reacted at the anode electrode when the electrical current was introduced. The bubbles produced indicate that the Al particles are being polarized. The reduced ammonia-forming nitrates are absorbed by zeolite through an ion exchange process with the aid of electrolysis and with synergistic effects of absorption. In addition, dissolved ammonia in electrolytes and zeolites can be oxidized via electro-generated HOCl/OCl$^-$. The electrical field generated by current facilitates the transition of ammonium towards the anode, speeding up the adsorption process of ammonium ions. The anode-generated hydroxyl radicals play a part in indirect ammonia oxidation [33] for the formation of flocs in the flotation process. Through the removal of ammonia using the EC process, organic pollutants are also removed by direct oxidation [16,27]. Considering this improvement mechanism, the main aim of this study was to achieve high removal contaminant efficiency of HN$_3$-H with the application of ZEAP in treating saline landfill leachate. Therefore, optimization of the ZAEP experiment using the four influential operating factor variables mentioned earlier, including current density, zeolite dosage, electrolysis time, and pH, on the elimination of NH$_3$-N was robustly investigated. A response surfaces methodology (RSM) based on central composite designs (CCDs) was applied to evaluate the interactions between the factors (variables) and response (removal). Experimental design by an analysis of variance (ANOVA) was performed to develop a statistical model of the second-order polynomial. Finally, a numerical optimization experiment based on the high desirability suggested by RSM was conducted to verify the correlation between the optimum conditions of operating variables and the predicted response values.

2. Materials and Methods

2.1. Leachate Sampling

The electrolytic landfill leachate, which was saline in nature, was taken from the Pulau Burung landfill site (PBLS) near the Byram forest reserve in Penang, Malaysia at the GPS location of 5°12'12.1" N latitude and 100°25'30.2" E longitude, which is situated next to the coastline. PBLS has an ordinary oceanic clay liner and receives around 2000 tons of municipal solid waste daily. On-site and laboratory testing were conducted using a multi-parameter instrument (YSI Pro Plus; YSI Incorporated, Yellow Springs, OH, USA) to determine the salinity value of the leachate. Approximately 15 sets of leachate sampling were done between January and September 2019 using a 30 L polyethylene container. The acquired samples were stored and immediately transferred into a refrigerator of 4 °C in accordance with the standard methods of the Examination of Water and Wastewater, American Public Health Association [34].

2.2. Characterization of Natural Zeolite

The granular of natural zeolite was purchased from the supplier by YM Multi trading company, Selangor, Malaysia. The mineral adsorbent size was provided in the range of 3–6 mm with a pH value

between 6.5 and 7.5. Before any experiment, the zeolites were washed thoroughly with deionized water four times to remove any impurities from their surface area altogether and were then dehydrated overnight in a furnace (Memmert, Schwabach, Germany) at 105 °C to eradicate water and moisture from the pores. The dried granular zeolites were crushed using crusher machines (Retsch, Haan, Germany) and sieved to obtain an average sample size of 75 to 150 μm. Next, the natural zeolite was characterized by BET, XRF and XRD analyses.

2.2.1. Brunner–Emmet–Teller Analysis

The particular area of the adsorbent surface (SA), size (PS), and volume (PV) of zeolite pores were investigated by using nitrogen gas involving a process of adsorption and followed by desorption to obtain isotherm data at 77 K. The zeolite was degassed at 200 °C and 145 min earlier than the N_2 adsorption measurement. The total pore volume was obtained by data from N_2 adsorption under saturation conditions. The specific surface area of zeolite was analyzed using Brunner–Emmet–Teller (BET). The SA, PV, and PS of zeolite were recorded as 49.3371 m^2/g, 0.0927 cm^3/g, and 7.5141 nm, respectively. According to [35], explained that the adsorbent media can be categorized based on pore diameter such as micropores (less than 2 nm), mesopores (2 nm to 50 nm) and macropores (more than 50 nm). Thus, zeolite used in this study can be classified as mesopores because of its PS between the range of 2.0 nm to 50 nm.

2.2.2. X-ray Fluorescence (XRF) Analysis

The chemical composition of natural zeolite was determined using XRF instrument and is depicted in Table 1. The composition and structure of zeolite was identified as crystalline aluminosilicate with pores of molecular dimensions. The common formula of zeolite is (Mx/n [(AlO$_2$) × (SiO$_2$) y]. mH$_2$O), where M is the metal or hydrogen cations of valence (n) occupying the transferrable cationic sites on the zeolite structure. AlO$_2$ and SiO$_2$ are the important compounds sharing oxygen ions to form tetrahedral AlO$_4$ and SiO$_4$ building blocks for zeolite unit cell since the silicon ion has +4 and the aluminum ion has +3 charges. The cationic charge of the metals or hydrogen ions balance the negative charge on the aluminosilicate framework. The XRF results demonstrated a silicon oxide content of 74.17%, whereas that of aluminum oxide was only 13.42% by weight. The Si/Al ratio of the natural zeolite structure was found to be 5.68. According to [36], if the ratio of natural zeolite is more than 4, indicating that the zeolite is at a higher temperature, the structure would not be easily broken.

Table 1. Chemical composition of natural zeolite.

Component	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$
Weight (%)	71.8	0.13	12.63	1.43	0.03	0.61	2.11	0.93	2.56	0.02

2.2.3. X-ray Diffraction Analysis

The analysis results of XRD showed a raw clinoptilolite pattern, as illustrated in Figure 1. This identification of natural zeolite was done using X-pert High score Plus software (PANalytical, Almelo, The Netherlands). The sample exhibited crystalline structure elements that were confirmed to match with clinoptilolite characteristic peaks. The analyzed sample complied with the reference code 98-000-2606, and the density of zeolite was recorded at 2.151 g/cm^3. The finding also described that the chemical formula of clinoptilolite was recorded as [Na$_{1.66}$ K$_{2.56}$ Ca$_{1.9}$ (Al$_{5.48}$ Si$_{30.52}$ O$_{72}$).19.16 H$_2$O]. Although differing in practice, a similar clinoptilolite formula structure was also reported by [37] and revealed the Si/Al ratio was 5.569. Furthermore, this subfield of inorganic natural mineral also indicated a monoclinic structure type. The results were well in line with the literature [38], and the approximate overall raw mineral contents of clinoptilolite were 88% to 90%.
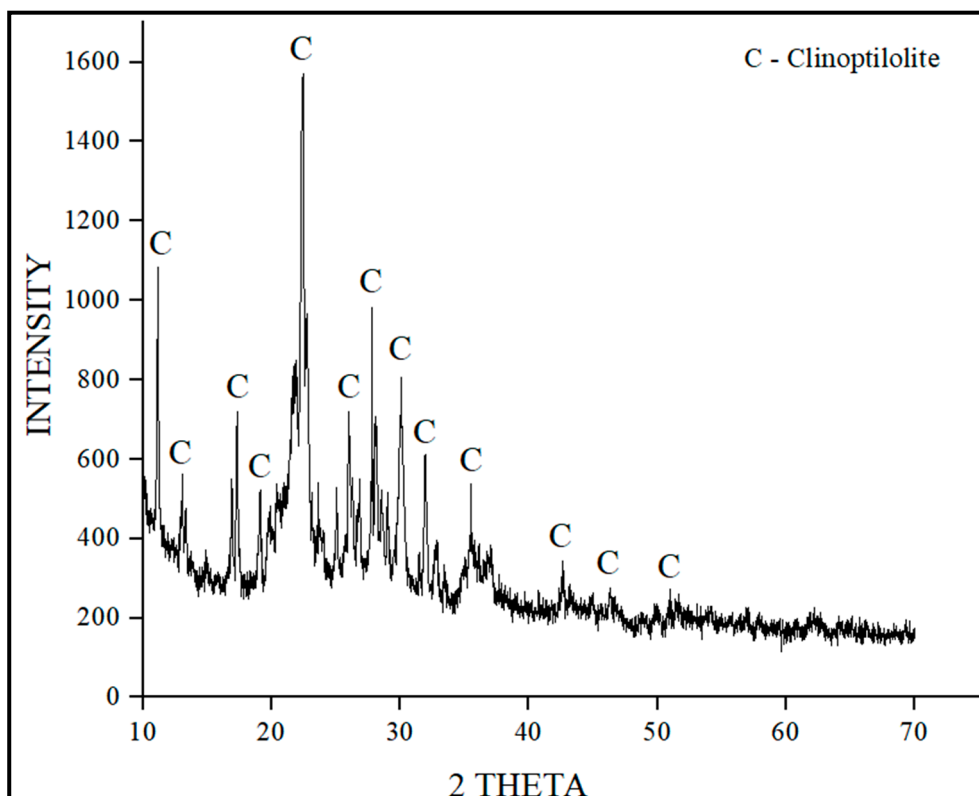
Figure 1. X-ray diffraction pattern of the natural zeolite (clinoptilolite) material.

2.3. Chemical Reagents and Instrument

The chemical reagents and instrument involved in this study were sulfuric acid, sodium hydroxide, pH meter (Eutech Instruments, Singapore), DR 2800 spectrometer (Hach Company, Loveland, CO, USA), measuring cylinder (NICE, London, UK), beaker (Fisher Scientific, Hampton, NH, USA), wired crocodile clip, laboratory film (Parafilm M; Bemis Company, Neenah, WI, USA), aluminum plate (grade 6061), DC power supply (OJE Model PS6005, 60 V/5 A, Suzhou, China), and stirrer (Heidolph MR Hei-Tec 220 V; Heidolph Instruments, Schwabach, Germany).

2.4. Analytical Methods

All experiments were conducted based on the standard methods 4500C (ammoniacal nitrogen) of the Examinations of Water and Wastewater [34]. The removal of pollutants of NH_3-N (mg/L) was tested via the Nessler Method 8038 using a Hach (Loveland, CO, USA) DR 2800 spectrometer. Meanwhile, salinity (ppt) was measured using a YSI Professional Plus multi-parameter probe (YSI Incorporated, Yellow Springs, OH, USA). All tests were done in triplicate.

2.5. Experimental Set-Up

The batch experiment of the zeolite augmented electrocoagulation process was conducted in the reduction of pollutants of NH_3-N, where the set-up is as shown in Figure 2. Landfill leachate electrolyte (750 mL) was firstly poured into a 1000 mL glass beaker. A DC power supply (OJE 60 V/5 A; Suzhou, China) was applied by connecting the positive and negative terminals to a pair of aluminum electrodes, which respectively acted as the anode and cathode.
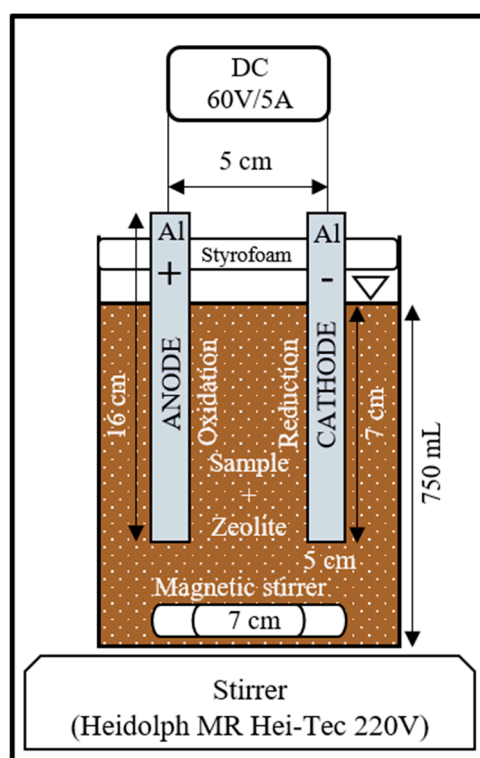
Figure 2. Experimental set-up for the zeolite augmented electrocoagulation treatment process.

Zeolite was introduced into the electrolyte, and the mixture was mixed for a 1 min duration for homogeneous mixing of the electrolyte. At the end of the stir, the electrodes were submerged into the electrolyte, and the power supply of DC was promptly switched on. The concentration of NH_3-N in the electrolyte solution was examined before and after the EC process took place. The total active area of the single electrode was 35 cm^2 when being dipped 70 mm into the electrolyte solution, while the electrode size was $16 \times 5 \times 1$ cm. A stirrer (Heidolph MR Hei-Tec 220V; Heidolph Instruments, Schwabach, Germany) was set to produce a constant speed of 200 rpm, and a magnetic stirrer of 70 mm length was used for the stirring purpose. The spacing distance between both electrodes was set to 3 cm. At the beginning and end of each experiment, the electrodes were washed thoroughly with distilled water, dipped in 0.1 M HCl solution to remove impurities for 15 min, and again bathed with distilled water. At the end of the treatment process, the samples were undisturbed for 60 min [9]. The removal efficiencies of NH_3-N were determined based on Equation (1).

2.6. Concentration of Removed Pollutant

At designated intervals, samples were collected for analysis of the NH_3-N pollutant. The pollutant removal efficiency (Y%) was calculated based on Equation (1) below:

$$Y(\%) = \left(\frac{C_o - C}{C_o} \right) \times 100 \tag{1}$$

where, C_o is the initial concentration of the removed pollutant before the electrocoagulation process, and C is the concentration of the removed pollutant after t min of the electrocoagulation process.

2.7. Response Surface Methodology Design

Design of the ZAEP experiment and statistical modelling were performed using the Design-Expert software version 11.0.3 (StatEase, Minneapolis, MN, USA) for analysis purposes. The central composite designs (CCDs) through response surfaces methodology (RSM) were used to optimize variables and

investigate the correlation between the response and variable factors of ZAEP in the removal of NH$_3$-N contaminant. Four significant factorial variables were evaluated, including the zeolite dosage, current density, electrolysis duration, and pH. The coded variables and the second-order polynomial for response were determined, as shown in Equations (2) and (3). Table 2 tabulated the coded level of variables and their actual values (optimum values obtained from our previous experiment) involved in these studies

$$\text{Coded of variable } (X_i) = \frac{xi - Xcp}{\Delta x} \tag{2}$$

$$\text{Response } (Y\%) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i \neq 1j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

where, xi is the un-coded value, Xcp is the un-coded value at the center point, Δx is the value change between levels, β_0 is the constant-coefficient, β_i, β_{ii} and β_{ij} are the coefficients for the linear, quadratic and interaction effect respectively, x_i and x_j are the factors, and ε is the error.

Table 2. The coded and actual values of variables for the zeolite augmented on the electrocoagulation process (ZAEP) treatment.

Code	Factor	Unit	Coded Level of Variables		
			Low (−1)	Central (0)	High (+1)
A	Zeolite dosage	g	100	110	120
B	Current density	A/m^2	540	600	660
C	Electrolysis duration	Min	55	60	65
D	pH	-	8	9	10

3. Results and Discussion

3.1. Leachate Characteristics

The results of the compositions of the raw landfill leachate from PBLS are presented in Table 3. It is important to note that the biodegradability ratio (BOD$_5$/COD) of this landfill leachate was 0.051 < 0.1; thus, it can be considered as stabilized landfill leachate because of the high concentrated COD (4928 mg/L) and low concentration BOD$_5$ (254 mg/L). Furthermore, the raw leachate can be classified as alkaline since its average value of pH was 8.16, which was further categorized under the methanogenic phase because of a higher value than pH 7 [39]. A similar finding was also revealed by [40–42], which found alkaline conditions of landfill leachate in their studies on PBLS.

Table 3. Characteristics of Pulau Burung landfill leachate.

No.	Parameters	Value (January to June 2019)	Average	Standard Discharge Value from the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulation 2009
1.	BOD$_5$ (mg/L)	207–283	254	20
2.	COD (mg/L)	4266–6648	4928	400
3.	Ammonia (mg/L)	3125–3782	3471	5
4.	Color (Pt-Co)	4930–18,380	8240	100 ADMI
5.	pH	7.52–8.21	8.16	6–9
6.	Salinity (ppt)	15.01–17.2	15.36	-
7.	BOD$_5$/COD	0.043–0.049	0.051	-

According to [7], the increase in the pH value of leachate is ascribed to the higher NH$_3$-N concentration as well as the lower concentration of nitrate in the landfill leachate. Thus, these results indicated that high-strength compounds of ammonia were present and recorded to be 3471 mg/L, which are beyond the standard discharge value of 5 mg/L. The concentration of NH$_3$-N in this sample

was much higher than that reported by [43], which was only 2050 mg/L. The differentiation in the salinity value and concentration of ammonia may be the most vital indicator for microorganism survivability [6]. The development of bacteria has a strong correlation with the concentration of salinity and ammonia. The growth of microorganisms may be disturbed due to the high concentration levels of ammonia produced during the methanogenic phase [44]. Moreover, the landfill leachate produced from PBLS is aged and stabilized. Hence, biological treatment processes can hardly be fully employed.

3.2. Predicted Against Actual Values

　　　Figure 3 illustrates a diagnostic plot of the comparison between the results from actual experiments and the predicted values from a linear regression model by the indication of color point as minimum and maximum removal rates. This figure clearly shows that both data points in this plot matched to each other and were close to the diagonal line (R^2), which illustrates strong adequacy to satisfy both the actual experimental and prediction values by the established model [45]. Furthermore, if the value of R^2 is over 0.9 for a regression linear equation model, it indicates an excellent correlation between the laboratory findings and the values of prediction [46]. Thus, as can be noted in Table 4, the regression coefficient, the R^2 value, was equal to 0.9871, confirming the fact that a strong correlation response existed in this model.
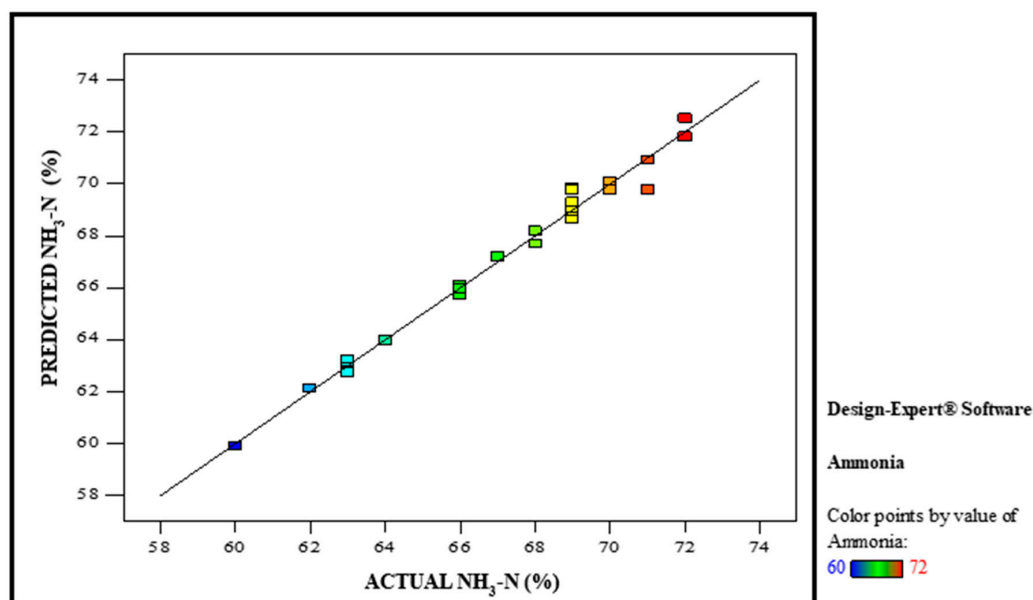

Figure 3. The plot of actual versus predicted values.

Table 4. Analysis of variance (ANOVA) and quadratic model validation on NH_3-N removal.

Final Equation of Actual Factor on Percentage Removal of NH_3-N					
% removal = 69.76 − 0.61A + 1.06B − 0.56C − 3.28D − 0.53A^2 − 1.53B^2 − 1.03C^2 − 0.53D^2 − 0.063AB − 0.69AC − 0.44AD + 0.31BC − 0.19BD + 0.44CD					
Analysis of Variance					
Source	**Sum^2**	**DF**	**Mean^2**	**F Value**	**Prob > F**
Model	317.06	14	22.65	82.06	<0.0001 (significant)
Lack of fit	2.14	10	0.21	0.53	0.8130 (not significant)
Model Validation					
R^2		**Adjusted R^2**		**Predicted R^2**	**Adequate Precision**
0.9871		0.9751		0.9633	33.938

3.3. Analysis of the Design of Experiments

Experimental validation was performed at an optimum condition of variables to study the interaction between the factors and response. The design matrix of independent variables as tabulated in Table 5 shows that a total of 30 runs of the experiment, with 16 factorial, 8 axial, and 6 centers, were suggested for ZAEP treatment in the reduction of NH_3-N.

Table 5. Design matrix and experimental results for optimized variables of ZAEP.

| Run | Point Type | Variable Factor | | | | Removal |
		Zeolite Dosage (g)	Current Density (A/m^2)	Electrolysis Duration (min)	pH	NH$_3$-N (%)
1	Center	110	2.10	60	9	69
2	Center	110	2.10	60	9	70
3	Center	110	2.10	60	9	72
4	Center	110	2.10	60	9	71
5	Center	110	2.10	60	9	71
6	Center	110	2.10	60	9	70
7	Axial	100	2.10	60	9	70
8	Axial	110	2.10	55	9	68
9	Axial	110	2.10	65	9	71
10	Axial	110	2.31	60	9	69
11	Axial	110	2.10	60	8	72
12	Axial	110	1.89	60	8	67
13	Axial	110	2.10	60	10	65
14	Axial	120	2.10	60	9	68
15	Fact	100	1.89	65	8	68
16	Fact	100	1.89	55	8	69
17	Fact	100	2.31	55	8	71
18	Fact	100	2.31	65	10	66
19	Fact	100	2.31	65	8	71
20	Fact	100	1.89	55	10	63
21	Fact	100	2.31	55	10	64
22	Fact	100	1.89	65	10	63
23	Fact	120	2.31	65	8	68
24	Fact	120	1.89	55	8	70
25	Fact	120	1.89	65	8	69
26	Fact	120	1.89	55	10	62
27	Fact	120	2.31	55	10	63
28	Fact	120	2.31	65	10	62
29	Fact	120	2.31	55	8	72
30	Fact	120	1.89	65	10	60

As shown in Table 5, the results from the present research revealed that the reduction of NH_3-N was in the spectrum between 60% (min) and 72% (max). From this experimental finding, statistical Equation in Table 4 based on the second-order polynomial modelling and the analysis of variance (ANOVA) of the respective variables A (zeolite dosage), B (current density), C (electrolysis duration), and D (pH) were established to examine the percentage removal efficiency of the treatment process (Table 4). In order to validate this empirical model, several parameters were considered, such as prob < 0.05 (significant), Lack of Fit (LOF) > 0.05 (not significant), adequate precision ≥ 4, R^2 ≥ 0.8, and $R^2 \approx R^2_{pre}$ [46,47]. Thus, according to the results shown in Table 4, justification is to be drawn that the mathematical equation of the second-order polynomial model has satisfied all the vital requirements and may be used to evaluate the effectiveness of a ZEAP treatment on the elimination of NH_3-N pollutant.

3.4. The Effects of Factor Variables on Pollutant Removal

Three-dimensional (3D) response surface plots for all factor variables were generated using CCD to examine the influence of each variable combination and the interaction between variables on the removal of ammonia pollutant after ZAEP treatment on natural saline landfill leachate. Figures 4–6

show higher removal percentages of NH$_3$-N yielded at lower pH and among the reactions of zeolite dosage, current density, and electrolysis duration variables. The surface charge of the particles may be affected by pH variability. A progressive response would change the pH of an electrolyte that, in turn, affects organic matter reduction [48]. As can be observed in Figure 4, the maximum reduction of NH$_3$-N was found at a lower pH range, between 8.0 and 8.5, and zeolite dosage range of 105–110 g. This can be explained by the transformation of NH$_3$-N into uncharged ammonia at higher pH (pH > 9) [49]. As a result, it would reduce the removal of NH$_3$-N. As reviewed by [47], they mentioned that, at a lower pH, neutralization of charges is encouraged as higher metal amounts are dissolved owing to the greater current density, which leads to floc formation and increases in the effectiveness of removal. High removal percentages of NH$_3$-N were observed at the current density peak of 600 A/m^2 and pH between 8.0 and 8.5 (Figure 5).
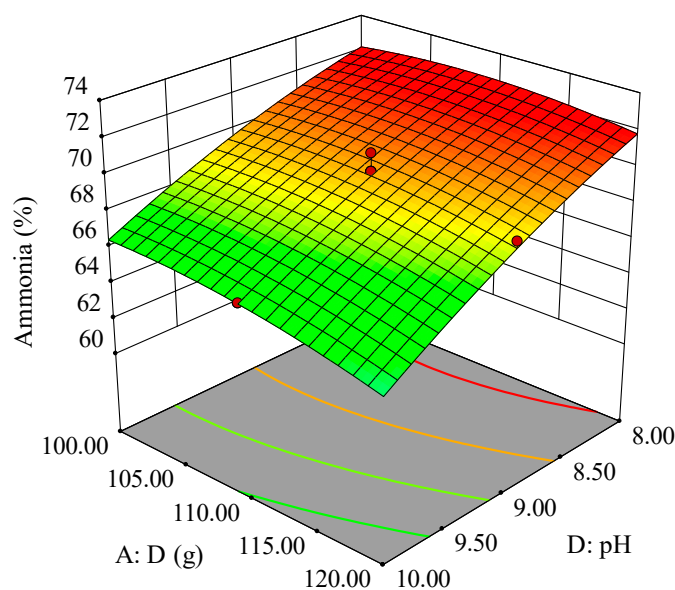

Figure 4. 3D surface plots for removal of ammonia on influences of dosage and pH.
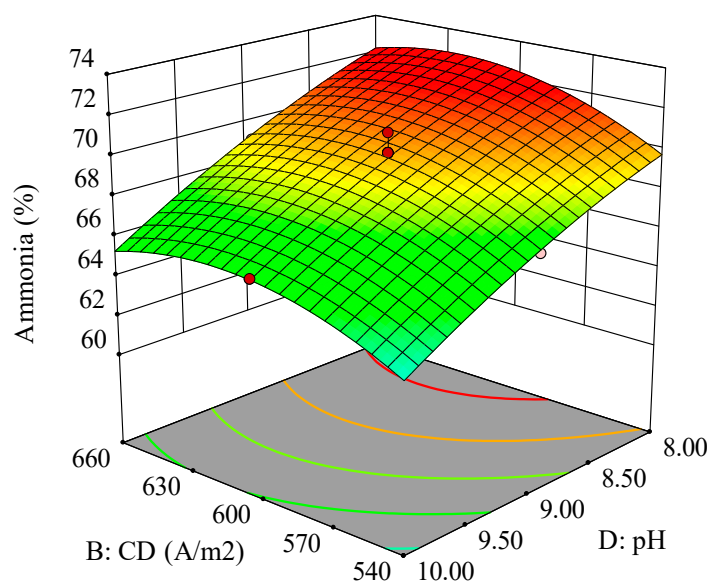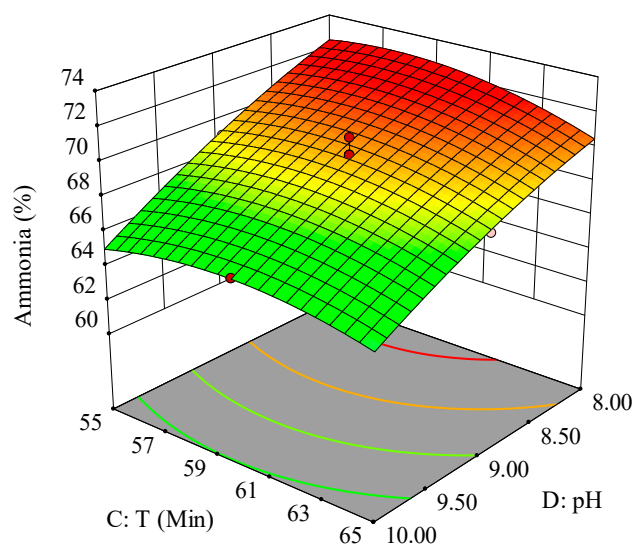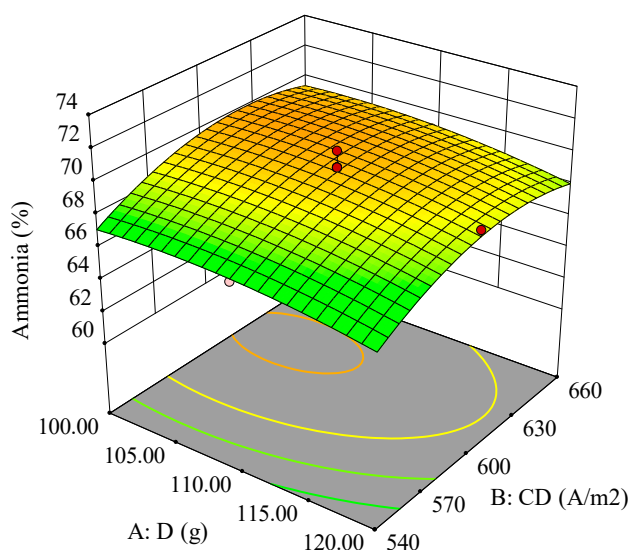

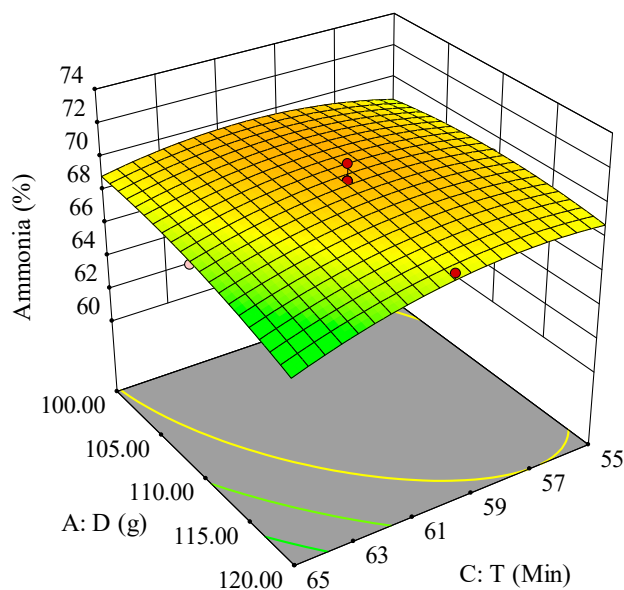**Figure 5.** 3D surface plots for removal of ammonia on influences of current density and pH.

Figure 6. 3D surface plots for removal of ammonia on influences of electrolysis time and pH.

A substantial effect on the reduction of NH_3-N from the interaction between electrolysis duration and electrolytic pH was observed, which is as shown in Figure 6. This finding indicates that the removal percentage increased when the process was operated at an electrolysis time of 60 min and at the pH range mentioned earlier. The improvement in the removal efficiency is due to the duration of electrolysis, which allows a longer catalytic reaction time resulting in an increase in contaminant degradation [50] and a higher number of hydroxyl radicals, which results in metal-polymer species formation for further increase in the efficiency of removal [51]. Meanwhile, Figures 7 and 8 portray a curve shape, which indicates an interaction between zeolite dosage and other factor variables of electrolysis time and current density. It is noted that the percentage reduction of NH_3-N in saline landfill leachate increased with increasing current density and zeolite dosage (Figure 7). The current density of the produced electrical field may enhance the rate of NH_3-N ion exchange with lateral movement to the anode and, thus, favor the NH_3-N adsorption on zeolite [52]. Other research by [53] had also reported that molecular structures, as well as high-capacity cation exchanges of zeolite, accommodate free surface ion exchange and absorption. However, at a current density of more than 630 A/m^2, a slight insignificant drop was seen from the maximum removal.
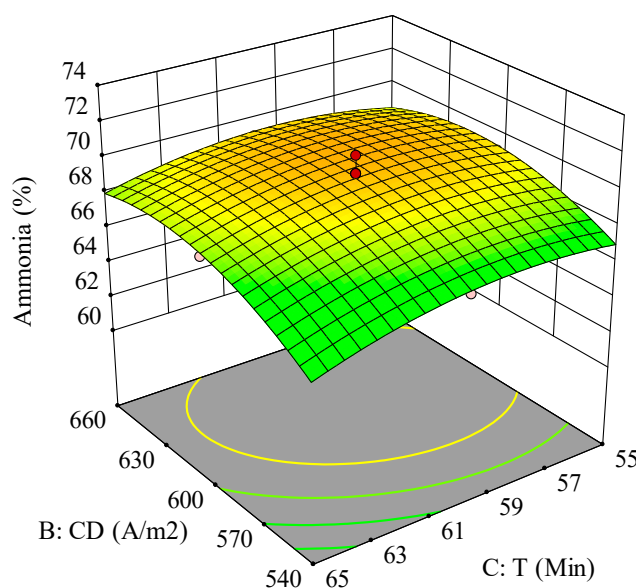

Figure 7. 3D surface plots for removal of ammonia on influences of dosage and current density.

Figure 8. 3D surface plots for removal of ammonia on influences of dosage and electrolysis time.

According to [54,55], the removal efficiency of adsorbents increase when increasing the adsorbent dosage, leading to the accessibility of the active surface area. This fact is in agreement with the results from this study, which exhibited that higher percentage removal of NH_3-N was achieved with increasing zeolite dosage in the range of 105–115 g versus electrolysis time of 57–61 min, as illustrated in Figure 8. Furthermore, Figure 9 clearly shows that the maximum reduction of NH_3-N occurred in the range of 600–630 A/m^2 current density and at electrolysis duration between 59 and 63 min. This phenomenon can be described by a rise in the Al^{3+} charged cations and thus releasing $Al(OH)_3$ particles by the anode when increasing the current density [56]. Therefore, this analysis leads to the conclusion that the maximum reduction of NH_3-N from saline landfill leachate was revealed to be 72%, obtained from the range of zeolite dosage of 105–115 g, current density of 600–630 A/m^2, electrolysis time of 59–61 min, and pH of 8–8.5.

Figure 9. 3D surface plots for removal of ammonia on influences of current density and electrolysis time.

3.5. Analysis of Variables Optimization

Optimizing operational variables is essential in the process development of a model in order to validate an experiment and maximize the removal of ammonia pollutant from high-strength landfill leachate. Simultaneous RSM optimization for the removal response based on the operating variables was carried out in an attempt to investigate the optimum working variables for this novel zeolite augmented electrocoagulation process. All the input variables, including the zeolite dosage (A), current density (B), electrolysis duration (C), and pH (D), were set between ranges during optimization, whereas the output response of variables was collected as the percentage ammonia removal. The effects of the chosen operating parameters were configured to achieve optimum removal performance based on the desirability suggested by CCD [57,58]. The scale of desirability ranged from 0 to 1, with 0 indicating an undesirable response and 1 being the most desirable reaction [59]. A high desirability of 0.9987 was obtained and chosen as it was the closest to 1. Experiments were conducted to verify the optimal conditions. The predicted results through an optimization process, which were computed by the RSM system and the actual experimental results on pollutant removal, are expressed in Table 6.

Table 6. Optimization between predicted and experimental results on NH_3-N removal.

Zeolite Dosage (g)	Current Density (A/m^2)	Electrolysis Duration (min)	pH	NH_3-N Removal (%)	
				Predicted	Experimental
105	600	60	8.20	72.51	71.01

The recommended operating variables are a zeolite dosage of 105 g, current density of 600 A/m^2, electrolysis duration of 60 min, and pH 8.20. It is noted from the verification experiment that the actual removal result of NH_3-N was very close to that of the predicted result, which were 71.01% and 72.51%, respectively. This proves a good correlation between both parameters and confirms the eligibility of the model on ZAEP treatment using the optimized conditions.

3.6. Comparison of Treatment Performance

Numerous past studies reported the ability and effectiveness of the electrocoagulation system in the reduction of various organic and inorganic pollutants from landfill leachate. Although various literature exists on the treatment of landfill leachate in batch mode or continuous operation of the EC process, only a few studies reported on the reduction of ammonia pollutants. Current literature revealed that there are limitations in the conventional EC process on the treatment performances of specific parameters in leachate treatment, especially ammoniacal nitrogen [60,61]. In most cases, previous literature, as presented in Table 7, was in agreement with the mentioned fact of the ineffective ammonia pollutant removal performance in the treatment of landfill leachate.

As noted in Table 6, most of the works dealt with low concentrations of ammonia (50–2240 mg/L) as compared to the current study with a much higher concentration of 3471 mg/L. Ammonia removal efficiencies of 14% to 37% were reported in most studies, except by [65] where 80 removal efficiency of ammonia was reported at longer electrolysis time (2 hours) by using dual-electrode anode and much lower ammonia concentration (50–110 mg/L). Whereas, this current research uses more economical operating parameters (Al anode) and less treatment duration (60 min).

There have been a few studies on the removal of organic and inorganic pollutants using zeolite and other combination/coupling treatment processes in previous literature, as revealed by [33] and [32]. Nonetheless, they focused on the synthetic solution and soluble dye in pure water, in addition to municipal wastewater of concentrations between 30 and 50 mg/L. This is in contrast with the present study, which used natural high-strength ammonia through the novel ZAEP treatment. In addition, water matrix landfill leachate was also utilized as the electrolyte to evaluate the effectiveness of this process, which is known as the real wastewater that is difficult to be treated due to the various contents of complex organic compounds, heavy metals, and other contaminants [66,67]. Therefore,

this present research produced a high-performance ammonia removal of up to 71%, without any required ancillary processes for further efficiency enhancement, owing to its ability and effectiveness in contaminant removal.

Table 7. The summary of studies on the treatment of landfill leachate using the electrocoagulation process.

No.	Water Matrix	Pollutant	Concentration	Experimental	Performance	References
1	Leachate	COD Ammonia	12,860 mg/L 2240 mg/L	Current density: 631 A/m^2, Time: 45 min, electrode: Al	59% 14%	[62]
2	Leachate	COD Ammonia	2566 mg/L 386 mg/L	Current density: 29.8 A/m^2, Time 30 min, pH 6	21% 20%	[63]
3	Leachate	COD Ammonia Color Turbidity Suspended solids	1992 mg/L 982 mg/L 3500 Pt–Co 181 NTU 330 mg/L	Current density: 200 A/m^2, pH: 4, Time: 20 min	60% 37% 94% 88% 89%	[61]
4	Leachate	Color Ammonia	2660 mg/L 577.04 mg/L	Current density: 150 A/m^2, Time: 60 min, Electrode: Al/Fe, Coagulant: 0.3 g/L, pH: 5	88% 25%	[64]
5	Leachate	COD Ammonia	167–180 mg/L 50–110 mg/L	Current: 1.6, Time: 120 min, Electrode: Dual anode, Type: TiO$_2$/IrO$_2$	75% 80%	[65]

3.7. The Economic Aspect of the ZAEP Treatment

Despite an enormous number of publications on coupling/combination with the EC method, very few studies have taken the optimization of processes and their cost efficiency into consideration. According to [68], they mentioned that the total cost estimation typically includes the chemical reagents, cost of electricity, sludge handlings, operators, and maintenance and equipment used in the EC system. However, in laboratory research, the electrode, consumption of electrical energy, and chemicals are the main parameters of the operating expenditure [69,70]. Also, the consumption of zeolite is also revealed in this analysis using Equation (4) as follows:

$$\text{Overall operating cost } (\$/m^3) = aEEC + bEMC + cCC + dNZ \qquad (4)$$

where EEC is the energy of electrical consumption (kWh/m^3), EMC is the electrode material consumption (kg/m^3), CC is the chemical consumption (kg/m^3), and NZ is the natural zeolite consumption (kg/m^3). Meanwhile, the coefficients of a, b, c, and d respectively represent the ratios for electrical energy, Al electrode, chemical, and natural zeolites. For the Malaysian commercial market in 2019, the prices were 0.05 \$/kWh, 0.96 \$/kg for Al, 0.10 \$/m^3, and 0.25 \$/kg for NZ. These rates are similar to those of the international market. Based on the optimization of the ZAEP, the operation cost is computed to be approximately 36.46 \$/m^3. Currently, no literature provides the operational cost calculation for this type of treatment process. However, it was found that in other wastewater treatments and combined/coupled EC processes, the operational cost study is much more significant, especially based on the studies by [71–73]. Although these studies had portrayed excellent results, which can provide assessments on the combined processes as cost-effective and more efficient than the process of electrocoagulation alone, further studies are strongly recommended to investigate the cost-saving aspect in this combined treatment method.

4. Conclusions

In this work, the treatment efficiency of the zeolite augmented electrocoagulation process (ZAEP) was evaluated for the ammonia reduction from high-strength landfill leachate, which was saline in nature. The process of condition optimization investigated the influences of interactions between the significant variables, including current density, zeolite dosage, electrolysis duration, and pH, using the experimental design of RSM. The results revealed that the most vital operating parameter affecting ammonia removal through the ZAEP treatment was pH. Based on the analysis of CCD, the

actual experiment yielded a removal of ammonia of up to 71% at the optimal operating variables of zeolite dosage of 140 g/L, current density of 600 A/m^2, electrolysis duration of 60 min, and pH 8.20. The second-order polynomial model developed in this research was used to evaluate the percentage removal of ammonia with a strong correlation between the data points of experimental and prediction. Under these optimization conditions, the overall reasonable operating cost of the current treatment process was recorded as \$36.46/m^2. The outcomes of various experiments lead to the conclusion that the treatment of concentrated landfill leachate using a ZAEP reactor is an effective process in the elimination of soluble organic pollutants.

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