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Research Article

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Statistical Analysis of Municipal Solid Waste Landfill Leachate Treatment by Electrochemical (EC) Method using Response Surface Methodology (RSM)

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Abstract

In the present study, the treatment of raw landfill leachate with emphasis on the COD, NH_4^+-N, total suspended solid (TSS), Cr, Cd and Ni removal efficiency was carried out by electrochemical (EC) method using aluminium electrodes. Central composite design (CCD) with three factors, namely current density, reaction time (t) and anionic polyelectrolyte concentration, with each factor at five levels, was applied to optimise the factors for higher landfill leachate treatment. The region of assessment for the process was chosen as the area enclosed by current density (0.5-1 A/cm^2), electrolysis times (20-100 min) and anionic polyelectrolyte concentrations (0-15 ppm) boundaries. The optimum current density, reaction time and polyelectrolyte concentration at which the removal efficiency of COD (89.5%) and TSS (99.7%) reached the maximum values were found to be 0.88 A/cm^2, 100 min and 15 mg/l, respectively. For the current density of 1 A/cm^2, N-NH_4, Ni, Cr and Cd removal efficiencies were 64.5, 92.5, 99.6 and 83.4%, respectively.

Keywords: Electrocoagulation; Wastewater treatment; Landfill leachate; Process optimisation; Response surface method

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INTRODUCTION

Landfill dumping widely used as an approach for the disposal of municipal solid waste due to such benefits as low price, simplicity, and landscape restoration of holes from mineral workings [1,2]. Municipal landfill leachate is produced during the municipal solid waste decomposition (MSW) in landfills. This leachate is considered by small amounts of biodegradable organics, high concentrations of ammonia, chemical oxygen demand (COD) and suspended solids (SS), low ratios of BOD/COD and COD/N, [3,4]. This fluid is exceedingly toxic and can contaminate the land, ground water. Thus, this hazardous and dark colour liquid with a strong smell before discharge to the environment to fulfill the discharge standards for its variable composition and high amount of refractory constituents should be collected and treated. The BOD/COD ratio of young landfills leachate was around 0.25 [5]. However, as the discharge becomes older, biodegradable organic materials in the landfill leachate decreases and the remaining portions almost are refractory organic matter, which can be degraded only by robust oxidising agents and not conventional biological treatment [6]. Also, the landfill leachate contains several types of harmful heavy metals that generate a severe discharge problem because of non-biodegradability, high toxicity and ecological features.

Therefore, the application of physicochemical treatment processes such as advanced oxidation processes (AOPs) [7], reverse osmosis [8], coagulation/flocculation [9,10], activated carbon (AC) adsorption [11,12], ion exchange, membrane-based technologies [13,14] and electrochemical treatment have been introduced in order to achieve the desirable decontamination level. Coagulation is the traditional technique for the metals removal from wastewater. But this technique has various disadvantages such as causing further contamination because of the undesired reactions and generating huge quantities of chemical sludge [15]. These boundaries encouraged many researchers to use other treatment approaches like electrocoagulation for heavy metals removal. In comparison with conventional methods for landfill leachate treatment, the electrochemical method has gained huge research attention due to easy operation and high efficiency, simple equipment necessity, no chemical use requirement, swift sedimentation and reduced quantity of sludge [16-18]. In electrocoagulation (EC) technique, the ions Fe^{3+} or Al^{3+} responsible for the coagulation, are in situ created by the anodic dissolution of iron or aluminium electrodes [19,20]. Simultaneously, the reduction of water, which arises on the cathode, participates in the elimination process owing to the production of hydroxide ions, and consequently to the increased pH of water at the surrounding area of the electrode, leading to metal hydroxide precipitation [16]. The electrocoagulation successfully has been applied for the treatment of different sorts of wastewater such as phenolic [21], electroplating [22], pulp and paper mill industries [23], latex particles [24], slaughterhouse wastewater [25] and pigments industries [26,27]. Also, several types of research have shown the high efficiency of electrocoagulation in the removal of heavy metal ions from industrial and synthesis wastewater [16,17,28]. Response surface methodology (RSM) as an assortment of mathematical and statistical methods can be employed for the calculation of both experimental and numerical responses [29]. The RSM application to optimisation is designed at decreasing the cost of expensive analysis approaches, assess the effects of numerous factors and attain the optimum conditions for desired responses. Recently, RSM has been used to optimise interactive effects of independent factors in several chemical and biochemical processes [30-32]. In routine experimentation, a single factor is varied while all other factors are kept constant for a particular experimental set. This method is time-consuming and unqualified of reaching the proper optimum as interaction among variables is not taken into consideration [33]. Therefore, it does not display what would happen if other factors are changed.

Based on the knowledge, there are few studies for the treatment of heavy metals removal from landfill leachate by electrochemical methods. Unlike the previous studies, the present work examined the simultaneous removal of COD, NH_4^+-N, chromium (Cr^{3+}), nickel (Ni^{2+}) and cadmium (Cd^{2+}) ions from landfill leachate using electrocoagulation (EC) method. Moreover, in the present work, to determine the best-operating conditions, achieving high COD, colour and heavy metals removal efficiency, the interaction effects of three practical variables (current density, reaction time and anionic polyelectrolyte concentration) as well as their direct impacts on the performance of the EC process were explored.

MATERIALS AND METHODS

Wastewater Characteristics

Leachate samples were collected twice with bottles made of polyethene materials from a landfill at Kermanshah city, Iran. Samples were conserved in a refrigerator at 4°C. The characteristics of the landfill leachate used in this study are provided in Table 1. Commercial anionic poly acrylamide (Magnafloc LT25, Medium Molecular Weight, Grade: A500) provided from Taha Kimia Tajhiz Co. (Iran).

Table 1: Characteristics of the raw wastewater (landfill leachate) used in this study

COD (mg/l)	61530 ± 5100
BOD_5 (mg/l)	29980 ± 6300
NH_4^+ (mg/l)	3122 ± 280
TSS (mg/l)	4500 ± 500
TDS(mg/l)	37940 ± 4550
Conductivity (ms/cm)	56.7 ± 5
SO_4^2 (mg/l)	2455 ± 250
Cl^-(mg/l)	3402 ± 150
Total alkalinity (mg $CaCO_3$/l)	3478 ± 180
pH	7 ± 0.5
Cr(mg/l)	37.6 ± 5.8
Ni(mg/l)	1.98 ± 0.6
Cd(mg/l)	7.6 ± 2.5

Experimental Setup

All electrochemical experiments were done with 1.5 L solution in a 2 L single-compartment electrolytic cell equipped with two parallel electrode plates. The commercial aluminium plate's electrodes with 98% purity were used. The electrodes gap was 6.5 cm. The plates have rectangular geometry with the dimensions of 15 cm × 5 mm × 3 mm. The total effective surface area of electrodes submerged in wastewater solution was 51.8 cm^2. Before electrolysis, the electrodes surface was scraped with sandpaper, then dipped in HCL solution (1 M), cleaned with water, dipped in acetone for 5 min and finally put in an oven at 100°C for 30 min to eliminate the alumina layer formed on the surface of the electrodes. The electrodes were fixed vertically in the middle of the reactor and connected to a DC power supply (ESCORT, 3060 TD Dual Tracking, Taiwan) with a controlled voltage up to 30 V. The reactor solution temperature was kept constant at 25 ± 2°C during electrocoagulation experiments, the solution was agitated incessantly using a Hitter stirrer (Heidolph MR-Hei) with rotational speed of about 500 RPM. The electrical conductivity of the solution was sufficient for electrolysis; no salt addition was used as supporting electrolyte.

Analytical Methods

The following parameters were analysed by the standard methods [34]: alkalinity, TSS, TDS, SO_4^{-2}, BOD, COD and NH_4^+-N. Heavy metals with the Perkin-Elmer Analyst 800 atomic absorption spectrophotometer were measured. Turbidity was measured by a turbidimeter model 2100P (Hach Co., USA).

Experimental Design and Mathematical Model

Experimental design:

There are various categories of response surface designs such as Central Composite design, Hybrid design, Box-Behnken design and Three-level Factorial design [33]. The design of experiments (DOE) reduces systematic errors with an approximation of the experimental error and diminishes the number of tests. The RSM used in the present study was a central composite face-centered design (CCFD) with three different factors, current density (A/cm^2), reaction time and anionic polyelectrolyte concentration (mg/l). The examined range of these variables is provided in Table 2. The electrocoagulation performance in COD, NH_4^+-N and metals (Cr, Ni and Cd) removal was assessed based on the full face-centered CCD experimental plan (Table 3). The design comprised of 2^k factorial points improved by 2k axial points and a centre point, where k is the variables number. The levels of three operating variables differ from a low to a high value which is statistically expressed or coded as -1 and 1. The intermediate level is coded as 0. Therefore, a total of 20 experiments were used in this work, containing 15 experiments designed in a factorial design (including 7 factorial points, 7 axial points and 1 centre point) and 5 replications at the centre point to get the best approximation of experimental error. Repetition experiments were carried out by order of runs designed by central composite design (CCD) as shown in Table 3. To carry out a widespread analysis of the reactor, 6 dependent parameters as COD, NH_4^+-N, TSS, Ni, Cr and Cd removal were measured.

Table 2: Experimental range and levels of the independent variables

Variables	Ranges and levels				
	-1	**-α**	**0**	**α+**	**1**
A: current density(A/cm^2)	0.5	0.625	0.75	0.875	1
B: Reaction time (min)	20	40	60	80	100
C:Anionic polyelectrolyte, mg/l	0	3.75	7.5	11.25	15

Table 3: Experimental conditions and results of central composite design

Run	Variables			Responses					
	Factor1: Current density	**Factor2: Reaction time**	**Factor3: Anionic polyelectrolyte**	**COD removal**	**NH_4^+ removal**	**TSS removal**	**Cr removal**	**Cd removal**	**Ni removal**
	A/cm^2	**min**	**mg/l**	**%**	**%**	**%**	**%**	**%**	**%**
1	0.5	20	15	31.1	20.5	65.1	28.6	50.81	26.7
2	1	20	15	46.3	35.1	86.4	45.4	43.44	49.5
3	0.75	60	7.5	53.3	33.5	88.2	48.7	55.3	52
4	1	20	0	18.3	17.3	72.5	37.3	29.51	34
5	0.63	60	7.5	30.1	27.2	68.8	58.2	62.37	51.6
6	1	100	0	60.5	45.8	85.8	66.4	42.62	72
7	0.75	60	7.5	49.2	30.5	88.7	47.3	61.31	48.9
8	0.5	20	0	7.7	6.5	53.3	17.7	64.75	12.4
9	0.5	100	0	33.4	25.5	68.1	28.3	72.13	32.6
10	1	100	15	89.4	66.5	99.8	79.6	65.57	87

11	0.75	40	7.5	46.7	25.2	83.4	41.4	57.38	41.3
12	0.75	60	3.75	42.6	24.5	82.6	50.4	55.74	47.1
13	0.88	60	7.5	62.2	43.4	96.5	61.4	54.09	57.3
14	0.75	60	11.25	60.5	39.6	89.1	55.2	56.8	53.9
15	0.5	100	15	58.9	43.8	77.3	48.2	90.16	46.4
16	0.75	60	7.5	54.2	34.2	85.4	48.7	55.3	52
17	0.75	80	7.5	63.3	43.9	93.7	46.2	52.9	49.3
18	0.75	60	7.5	49.7	36	82.3	51.2	55.1	50.2
19	0.75	60	7.5	52.4	34.5	87	48.9	50.1	54.7
20	0.75	60	7.5	46.9	32.8	80	49.4	49.9	48.7

Mathematical Modeling

Once the experiments were carried out, the polynomial model coefficients were calculated as follows, Khuri and Cornell [35].

$$Y = \beta_0 + \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^2 + \beta_{jj} X_j^2 + \beta_{ij} X_i X_j + \ldots \quad (1)$$

Where, i and j are the linear and quadratic coefficients, respectively, and ß is the regression coefficient. Model terms based on the P value with 95% confidence level were selected or rejected. The results were analysed by analysis of variance (ANOVA) (by Design Expert Software Stat-Ease Inc., version 6.0.6). The experimental conditions and results are presented in Table 3.

RESULTS AND DISCUSSION

Statistical Analysis

In this study, the RSM along with CCD was used to optimise operating parameters involved in the experimental design, i.e., current density (0.5- 1 A/m^2), electrolysis times (20-100 min) and anionic polyelectrolyte concentrations (0-15 ppm) to find out the relationship between the variables and response function. The central composite design (CCD) permits the improvement of mathematical equations that predicted result Y (COD, NH_4^+, TSS, Cr, Cd and Ni removal (%)) were assessed as a function of A (current density (A/m^2)), B (electrolysis time (min)) and C (polyelectrolyte concentration (mg/l)) and calculated as the sum of a constant, three first-order effects (terms in A, B, and C), three second-order effects (A^2, B^2 and C^2) and three interaction effects (AB, AC and BC). As various responses were studied in this work and diverse degree polynomial models were applied for data fitting. The experimental conditions and results of the studied responses are shown in Tables 2 and 3 respectively. A total of 20 experiments was examined for three factors (Table 3) and the COD, NH_4^+, TSS, Cr, Cd and Ni removal were chosen as responses. The regression equations obtained are presented in Table 4. The model terms were achieved after the elimination of insignificant terms. To confirm the statistical model's significance employed in the experimental data at a 95% confidence level, the model was verified by analysis of variance (ANOVA) results. The ANOVA results for all responses are presented in Table 4. Lack-of-fit F-tests was used to test the model adequacy [36]. The lack of fit (LOF) F-test describes data variation around the modified model. According to statistical analysis, the models were significantly major with low probability values (from 0.03 to <0.0001) and high values of Fisher's test (from 4.51 to 103.6). The larger and smaller value of F and p respectively show that most of the variation in the response can be elucidated by the regression equation. Adequate precision measures the signal to noise ratio, and a ratio value greater than 4 is desirable. The obtained values (from 19.76 to 46.1) were found desirable for all models and also indicate a satisfactory signal for all the responses. Concurrently, low values of the variation coefficient (CV) (4.87-10%) pointed out good precision and reliability of the experiments as recommended by Khuri and Cornell [35] and Ahmad et al. [37]. A model generally can be deliberated reproducible if CV is not more than 10% [37]. The fittings of the models also were measured by the coefficient of determination R^2. According to the ANOVA results (Table 4), R^2 values were in the range of 0.9 to 0.98. The values of R^2 are close to 1.0, which are very high and express a robust correlation between the observed and predicted values. Also, an adequate agreement with the adjusted determination coefficient is essential. In this study, the values of adjusted R^2 were in the range of 0.84 and 0.97 that indicates the model's preference. Furthermore, the predicted R-squared values (0.8-0.92) are in reasonable agreement with the adjusted R-squared values.

Table 4: ANOVA results for the equations of the design expert 6.0.6 for studied response

Response	**Type of model**	**Modified equations with significant terms**	**Probability**	**F Value**	**R^2**	**Adj. R^2**	**Pred R^2**	**Adeq. Precision**	**SD**	**Mean**	**CV**	**PRESS**	**Probability for lack of fit**
COD removal	Quadratic	Y_1 =+51.41+11.70 A+17.30 B+13.50 C-8.40 A^2+3.98 AB	<0.03	4.51	0.95	0.93	0.92	32.2	4.82	47.84	10	509.88	0.07
NH_4^+ removal	Linear	+33.31+ 9.0 A+13.12 B+9.21 C	<0.0001	103.6	0.95	0.94	0.91	46.1	3	33.3	9.1	266.7	0.09
TSS removal, %	Quadratic	+85.92+11.12 A+6.92 B+6.13 C-9.93 A^2	0.0008	7.02	0.9	0.88	0.87	24.3	3.98	81.7	4.87	327.2	0.35
Cr removal, %	Quadratic	+50.79 +12.65A +11.28B +6.41C +28.63A^2 -35.37 B^2 + 4.14 AB	0.001	12.56	0.96	0.93	0.86	29.4	3.48	47.9	7.3	499	0.053
Cd removal, %	2FI	+56.27-11.87 A+9.38 B+4.88 C+4.10 AC+5.12 BC	<0.01	5.05	0.88	0.84	0.62	19.76	4.83	56.27	8.58	1082	0.34
Ni removal, %	Quadratic	+50.83+14.97A+14.05B+7.29C +15.41A^2-21.19 B^2+4.45 AB	<0.004	8.41	0.98	0.97	0.95	45.9	2.67	48.38	5.52	207.3	0.31

R^2: determination coefficient, Adj. R^2: adjusted R^2, Adeq. precision: adequate precision, SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares

COD Removal

To have a better understanding of the interactive relationships between independent variables and response, 3D response surface plots for the responses were prepared based on the model equation (Eq. (3)). As shown in Figure 1 in each plot, one variable was kept constant while the other two were varied within the experimental ranges. In Figure 1, the 3D response surface and contour plots for COD removal efficiency were introduced as a function of current density and reaction time, while the polyelectrolyte concentration was kept constant at three different levels (0, 7.5 and 15 mg/l). Almost the same trends were found as the polyelectrolyte concentration changed from 0 to 15 mg/l. As can be seen from Figure 1, COD removal efficiency, increased by simultaneous increasing of reaction time and current density in fixed polyelectrolyte concentration. An increase in current density would lead to a more rapid production of aluminium ion via anodic reaction, which improved the coagulation of organic molecules. Aluminum ions (Al^{3+}) generated by the dissolution of the anode electrode rapidly undergo spontaneous hydrolysis reactions which make various aluminum hydroxide compounds depending on the pH of the aqueous medium (Al (OH) $_2^{+}$, Al_2 (OH) $_2^{4+}$, Al (OH) $_4^{-}$, Al(OH) $_3$), Al_2 $(OH)_4$ $^{+2}$, Al(OH) $_{15}^{+3}$, $Al_7(OH)_{17}^{+4}$ and $Al_{13}(OH)_{34}^{+5}$). These hydroxides compounds have a large surface area as a coagulant, which is favourable for a fast absorption of soluble organic compounds and metal ions [27]. Also to adsorption and deposition of organic compounds, based on the pervious study [38], the organic pollutions also can be decomposed by direct or indirect oxidation method in the electrochemical process. In a direct anodic oxidation process, the organic materials are adsorbed on the anode surface and subsequently oxidised by the anodic electro-transfer reaction. While in an indirect oxidation process robust oxidants, such as active chlorine comprising hypochlorite and hypochlorous acid are in situ electrochemically produced. Therefore, the organic pollutants and NH_3–N by oxidation reactions of the generated oxidants are degraded in the bulk solution [38]. Chiang et al. [39] found that operational factors, such as anode material, current density, and chloride concentration, had similar effects on both chloride/hypochlorite production efficiency during electrolysis of saline water. Furthermore, they realised that COD and $NH4^+$-N removal efficiencies, improved with increasing current density, in electro-oxidation of leachate. Nevertheless, in a direct electrochemical oxidation, contaminant removal efficiency at the same charge loading was free of current density Murphy et al. Therefore, Chiang et al. [39] determined that indirect oxidation was the primary mechanism pathway in the electrochemical oxidation of leachate. The maximum COD removal efficiency in the polyelectrolyte concentration of 0, 5 and 15 mg/l were 62.5, 76 and 89.5% respectively. The effect of electrolysis time was investigated in the range 20 to 100 minutes. As can be seen in Figure 1 an increase in the time from 20 to 100 min yield an increase in the COD removal. When the electrolysis time increases, the concentration of aluminium ions and their hydroxide flocs increase, also the rate of organic compounds elimination in the wastewater increases.

The effect of anionic polyelectrolyte concentration was studied in the range of 0 to 15 mg/l and shown in the Figure 1. This figure demonstrates that increasing the polyelectrolyte concentration prepare a more encouraging environment for sedimentation of organic contamination in wastewater. As polyelectrolyte concentration increased, the amount of free organic contamination decreased, and the amount of adsorption and deposition of pollution into polyelectrolyte increased, so the COD removal efficiency increased. At the current density of 0.5 A/m^2 and an experimental electrolysis time of 20 min (Table 3), when the polyelectrolyte concentration rose from 0 to 15 mg/l, COD removal % increased from 4.5% to 31.30%. It is important to note that at lower reaction time (20 min) and current density (0.5 A/m^2) the increase of polyelectrolyte concentration has a much larger effect on COD removal %, i.e., 7-fold increase (4.5 to 31.30%) when compared with high reaction time. At a lower current density (0.5 A/m^2) and higher reaction time (100 min), increasing the polyelectrolyte concentration from 0 to 15 mg/l increased the COD removal from 31.30 to 58.12% (1.85-fold). These results indicated that polyelectrolyte concentration had a more positive impact on the COD removal at a lower reaction time and current density.

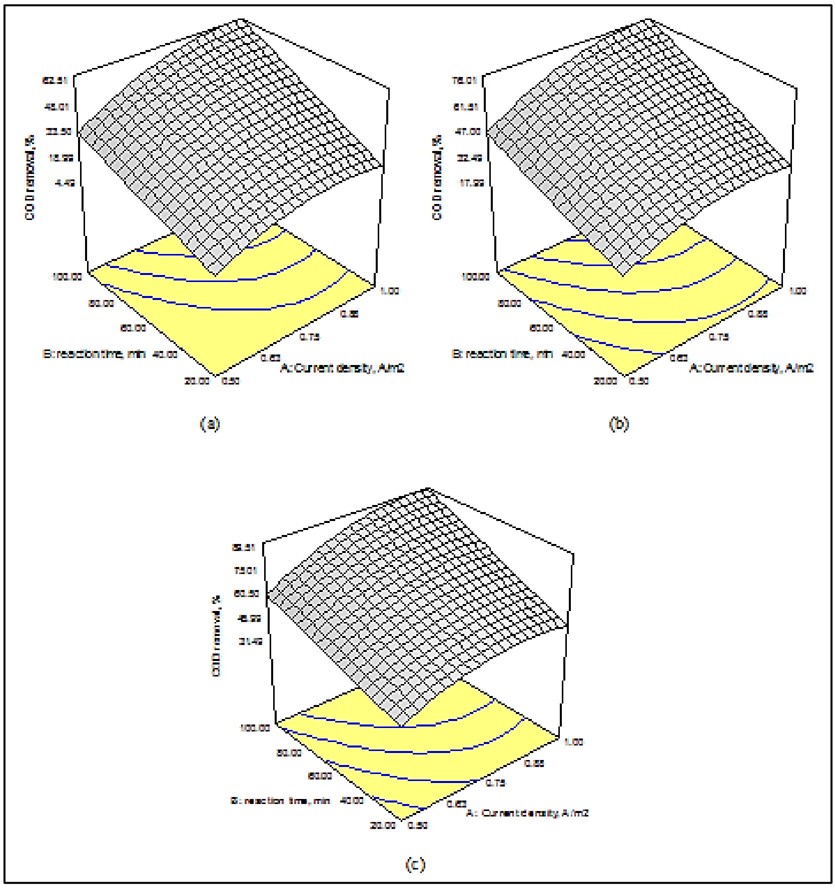

Figure 1: Response surface and counter plots for COD removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l and (c) 15 mg/l

Ammoniacal Nitrogen Removal

The existence of elevated levels of ammonia nitrogen in landfill leachate over a long span is one of the significant problems usually faced by landfill operators. The effects of operational variables, i.e., reaction time and current density on NH_4^+–N removal efficiency at three different polyelectrolyte concentration are illustrated in Figure 2. It is evident from these figures that all variables have positive effects on NH_4^+–N removal efficiency. At lower polyelectrolyte concentrations (<5mg/l) and current density (0.5 A/m^2), increasing the reaction time from 20 to 100 min increased the NH_4^+–N removal from 7.72 to 33.35 (4.31-fold). At higher polyelectrolyte concentrations (15 mg/l) and current density (1A/m^2), the same increase in reaction time increased the COD removal % from 31.15 to 64.65% (2.07-fold). Therefore, if reaction time is combined with higher values of polyelectrolyte concentration and current density, much higher NH_4^+–N removal rates can be observed. It is apparent from the perturbation plot (Figure 2) that in all cases the current density and polyelectrolyte concentration had a same positive effect on the process. Though, as presented in the perturbation plot (Figure 2), the influence of reaction time on $NH4^+$–N removal efficiency was greater than with current density and polyelectrolyte concentration, which had limited effects on NH_4–N removal. The maximum observed the removal of NH_4–N was 64.65% at a current density of 1 A/m^2, the polyelectrolyte concentration of 15 mg/l and reaction time of 100 min. Meanwhile, the minimum predicted NH3–N removal efficiency (6.5%) was obtained at a current density of 1 A/m^2, the polyelectrolyte concentration of 0 mg/l and reaction time of 20 min.

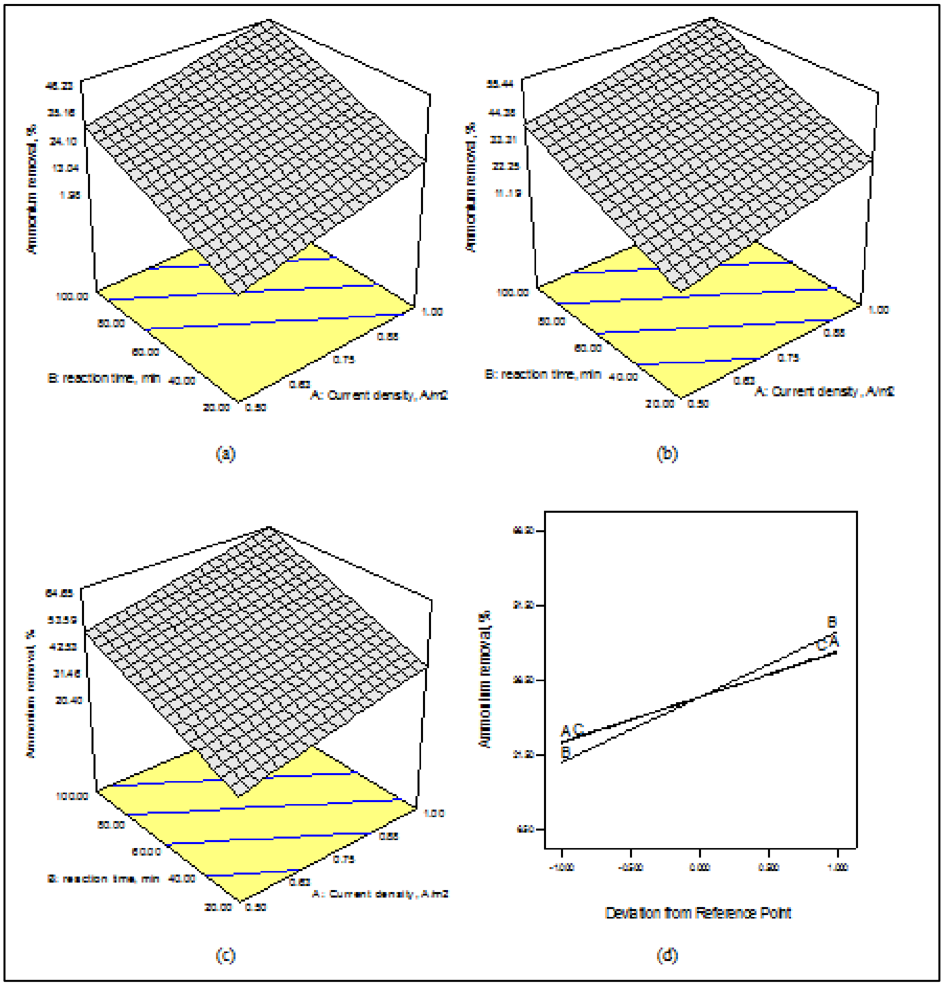

Figure 2: Response surface and counter plots for ammonical nitrogen removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l, (c) 15 mg/l and (d) Perturbation plot

TSS Removal

Total suspended solids (TSS) are a water quality factor used to evaluate the quality of wastewater after treatment. It prepares a definite weight of the particulate material present in the wastewater and gives a measure of the turbidity. Suspended solids, decrease visibility and absorb light, which can raise temperatures and reduce photosynthesis. Thus, reduction in the TSS is a key factor in wastewater treatment.

The effects of changing current density and reaction time on the removal efficiency of total suspended solids (TSS) at three different polyelectrolyte concentration in the EC reactor are plotted in Figure 3. The removal efficiency of TSS increases with increasing current density from 51.8% at 0.5 A/cm^2 till it reaches 99% at 1.0 A/cm^2 with a reaction time of 20 min and polyelectrolyte concentration of 0. As shown in the Figure 3 the current density has a negligible effect on TSS removal after 0.88 A/cm^{2,} and there is no benefit of increasing the current density after this value. The same is true for the effect of increasing current density on the efficiency of COD removal. Figures 1 and 3 clearly show that COD removal is dependent on the TSS removal as both trends are relatively similar. Removal of the TSS might automatically reduce the COD to the lower level accordingly. The increase in removal efficiency of TSS and COD as a result of an increase in current density can be described by an increase in anodic dissolution of the aluminium electrode and thus in floc formation at high current densities. The relationship between the TSS removal efficiency and the reaction time is shown in Figure 3. The figure indicates that as the reaction time increased from 20 to 100 min, removal efficiencies rose from 51.8% to 65.7% and from 74.5% to 87.9% for the currents of 0.5 and 1 A/cm^2 as a function of time, respectively. It is evident that Al^{+3} made at the electrode is responsible for the damaging particles destabilising in water. The amount of Al^{3+} irons is small at the start in the EC reactor so Al^{3+} is not sufficient to precipitate all colloids from the water. Hence, the efficiency of removing turbidity and TSS is little at small reaction times. As can also be seen from Figure 3, polyelectrolyte concentration had a positive effect on the TSS removal efficiency. As the polyelectrolyte concentration increased from 0 to 7.5 mg/l, the removal efficiency for the current density of 0.88A/cm^2 and reaction time of 100 min increased from 89.8% to 95.9%, respectively. In this condition, as the polyelectrolyte concentration rose from 7.5 to 15 mg/l the removal efficiency improved from 95.9% to 99.9%, respectively.

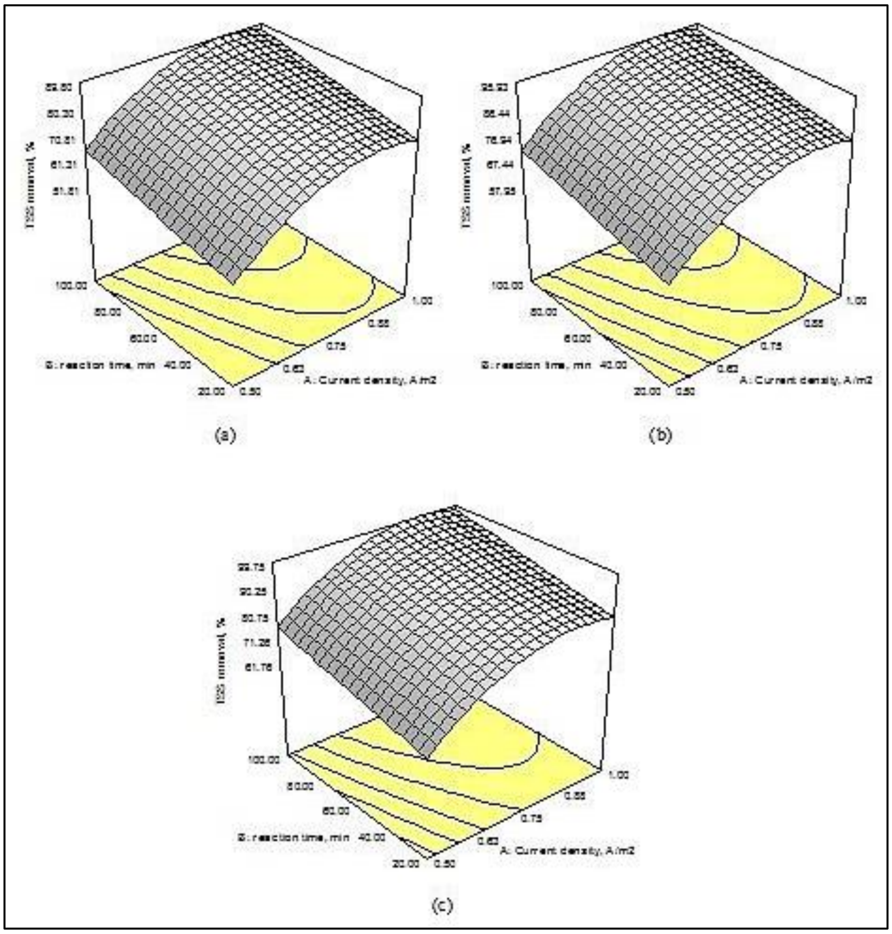

Figure 3: Response surface and counter plots for TSS removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l and (c) 15 mg/l

Metals Removal

As mentioned above, in the electrocoagulation process, the Fe^{3+} or Al^{3+}ions that are responsible for the coagulation, in situ produced by the anodic dissolution of iron or aluminium electrodes. At the same time, the reduction process of water, which take place on the cathode surface, participates to the removal process owing to the production of hydroxide ions at the vicinity of the electrode, leading to increasing of water pH and metal hydroxides precipitation [18]. The electrolytic oxidation of the aluminium anode generated Al^{3+} ions which are immediately transformed into solid particles of Al(OH)$_3$ or other ionic species [27]. These species have a large surface area as coagulant agents who are useful for quick adsorption of soluble organic materials and metal ions [27].

The effect of reaction time and current density on the removal efficiency of Ni, Cr and Cd at three different polyelectrolyte concentrations is shown in Figures 4-6. These figures indicated that the removal efficiency of nickel, chrome and cadmium are increased with increasing the reaction time. This is because of the higher Al and OH$^-$ species concentration in the EC cell. Because based on Faraday's law when a rise is occurred in the reaction time, more Al^{3+} and OH^- form monomeric and polymeric aluminium hydroxides by hydrolysis reactions on the anode and cathode surface respectively. Thus, the EC process yield is improved [25,27].

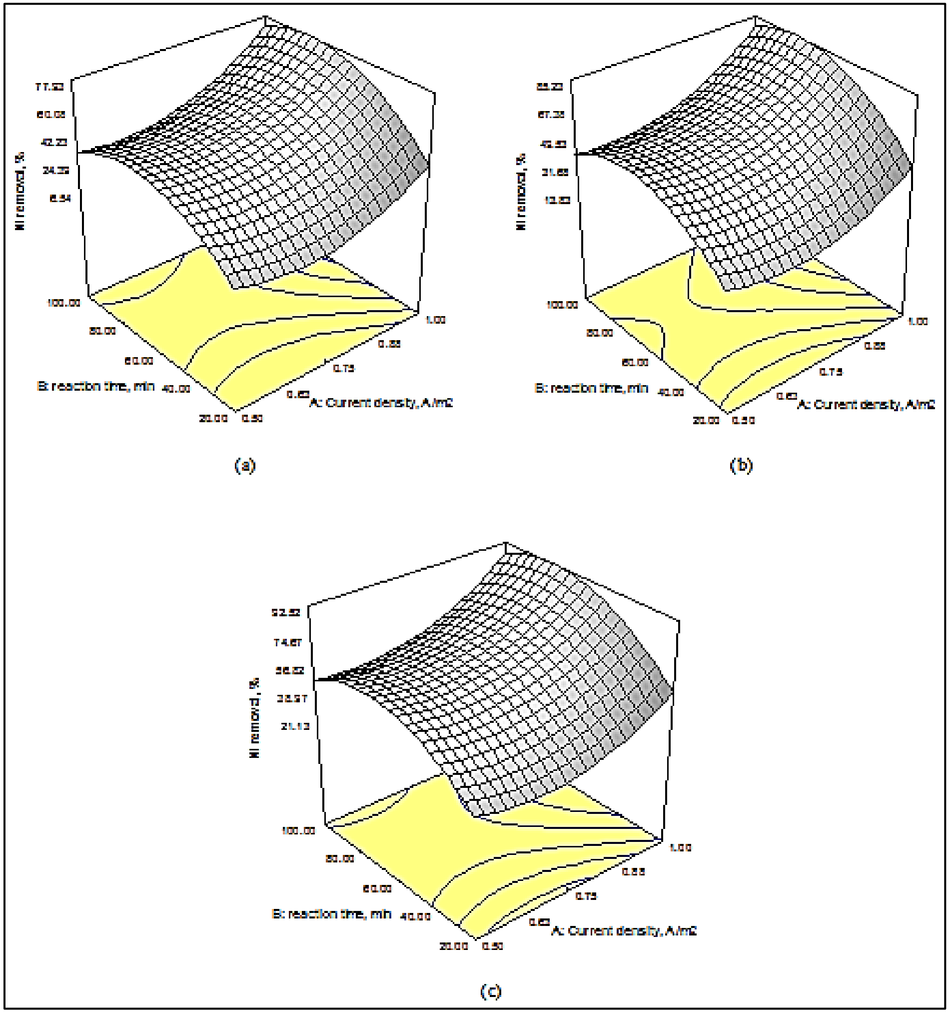

Figure 4: Response surface and counter plots for Ni removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l and (c) 15 mg/l

Based on the literature [18], two mechanisms can be used to explain the removal of heavy metals like Ni^{2+}, Cr^{3+} and Cd^{2+}: (1) Adsorption of the metallic ions on the surface of the $Al(OH)_3$ particles and aluminium ionic species produced. (2) Precipitation of the metallic ions as the corresponding hydroxides $Ni(OH)_2$, $Cr(OH)_3$ and $Cd(OH)_2$, particularly at the vicinity of the cathode where pH is higher owing to the hydroxide ions formation. Furthermore, adsorption of the aluminium ionic species can be done on the hydroxide particles surface and neutralise the surface charge, lead to coagulation and incorporation in the aluminium hydroxide precipitate to form large flocs which decantation is rapidly gained. As shown in these figures, the influence of reaction time is stronger on the removal efficiency of nickel and chrome than cadmium.

The control of current density in the range of 0.5-1 A/m^2 on the removal efficiency of Ni, Cr and Cd is shown in Figures 4-6. The current density is expected to exhibit a strong effect on the removal effectiveness and determines the reaction rate of the anode and cathode electrodes [40-42]. Therefore, the current density will determine the generation rate of metal hydroxides and the growth of flocs for absorbing the heavy metal ions. An increase in current density from 0.5 to 1 A/m^2 yields an increase in the removal efficiency of Ni (Figure 4), Cr (Figure 5) and Cd (Figure 6). This can be related to the fact that the amounts of dissolved Al ions at high values of current density increases, resulting in a greater amount of precipitate and removal of Ni, Cr and Cd [40]. According to the obtained results, the highest Ni removal efficiency (>90%) was obtained after 80 min under the condition of 1 A/m^2 of current density and polyelectrolyte concentration of 15 mg/l (Figure 4). The Cr removal efficiency (>99%) was obtained after 75 min by using a current density of 1 A/m^2 and polyelectrolyte concentration of 15 mg/l (Figure 5).

In the case of Cd, the highest removal efficiency (>83%) was achieved at a current density of 1A/m^2 and polyelectrolyte concentration of 15 mg/l after 100 min (Figure 6).

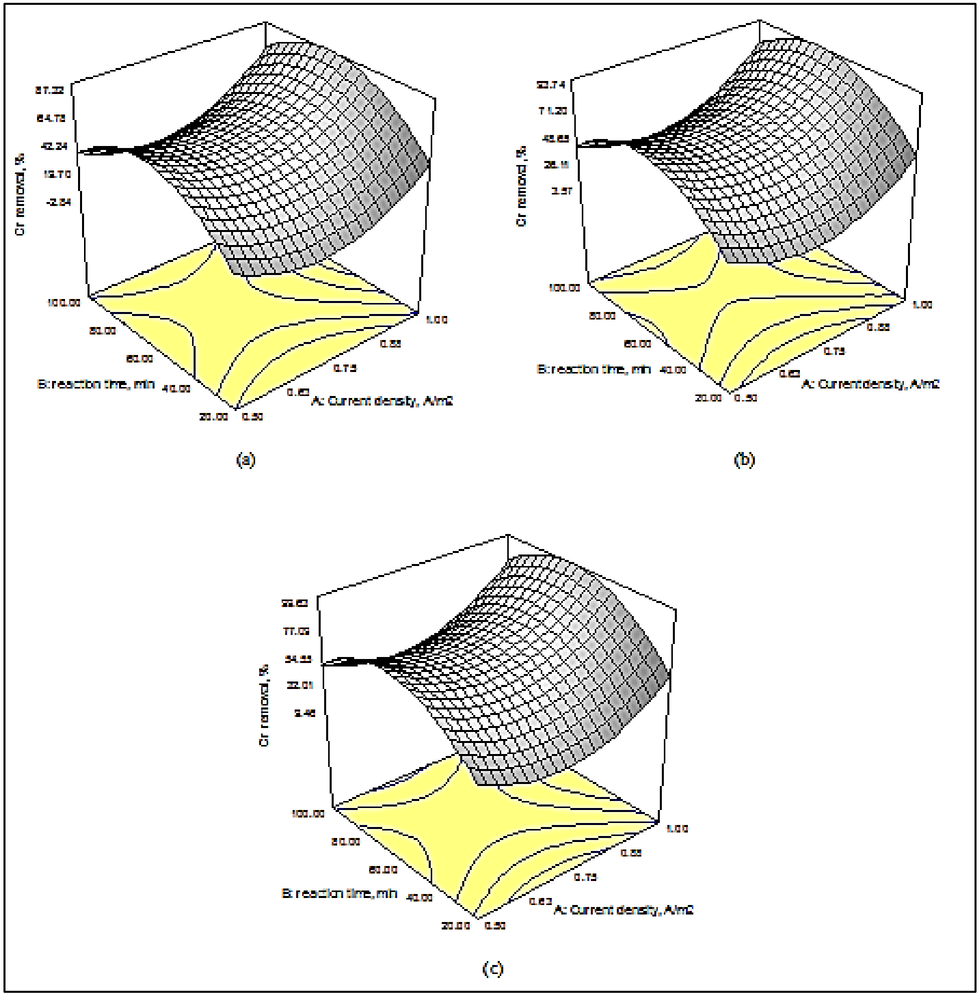

Figure 5: Response surface and counter plots for Cr removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l and (c) 15 mg/l

The effect of anionic polyelectrolyte concentration on the removal of Ni^{2+}, Cr^{3+} and Cd^{2+} has been studied in the range of 0 to 15 mgL^{-1}. As presented in Figures 4 and 5 the removal efficiency of Ni and Cr ions increased as the initial concentration of polyelectrolyte rose from 0 to 15 mg/l. However, the effect of this variable on the Cd removal was negligible. The positive metals ion attends to make a link among the anionic polyelectrolyte and negatively charged functional groups on the surface of colloidal particle. The polyelectrolyte is used to produce a tougher and denser floc, which grows to an enormous size and settles more rapidly than is possible using a primary coagulant alone. This is due to the action of the long chain molecules which, form bridges of cross-links between colloidal particles. Figures 4-6 and data in Table 3 have shown that the removal of constituents is useful in the presence of polyelectrolyte as coagulant aid, except for the Cd. Increased in the removal is significant for Ni and Cr. It can be noted from Figure 4 that at a current density of 0.5 A/m^2 and reaction time of 20 min the removal of Ni without the presence of the polyelectrolyte is 13.20%. The removal improves to above 27.8%, in the presence of 15 mg/l polyelectrolyte in this condition (Figure 4). Similarly, the removal of Cr in the presence of 15 mg/l of the polyelectrolyte is 30.87%, as compared to 17.87% removal without the polyelectrolyte (Figure 5). As depicted in these figures the Cr and Ni have been fully removed after 80 min of electrocoagulation at a current density of 1A/m^2 and polyelectrolyte concentration of 15 mg/l.

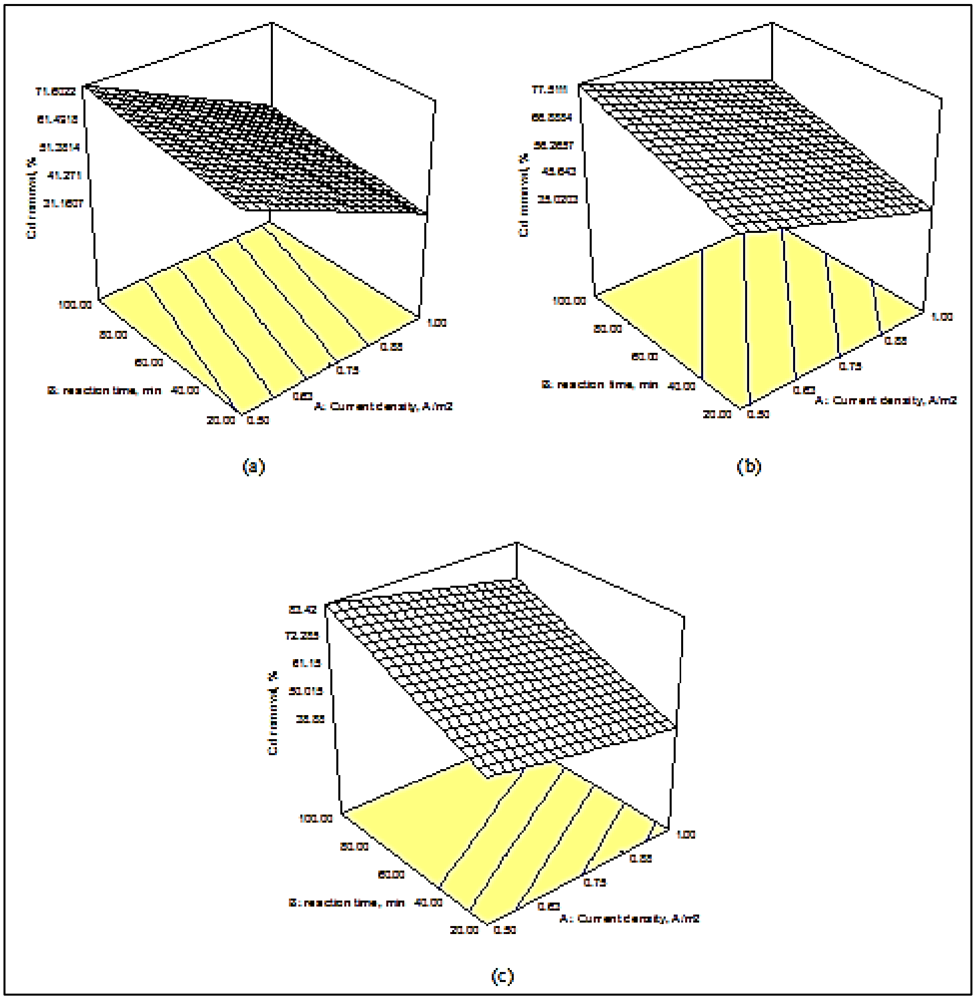

Figure 6: Response surface and counter plots for Cd removal efficiency with respect to current density and reaction time at constant value of poly electrolyte concentration; (a) 0, (b) 7.5 mg/l and (c) 15 mg/l

CONCLUSION

The present study investigated the applicability of an electrocoagulation technique in the landfill leachate treatment with the aim of simultaneous removal of COD, N-NH_4, TSS and heavy metals (Ni, Cr and Cd). Treatment process optimisation focused on the effect of operating variables, such as current density, reaction time, and anionic polyelectrolyte concentration using RSM with CCD. Furthermore, interaction among all the operating variables was explored by employing RSM. An increase in current density and reaction time would lead to rapid and more regeneration of aluminium ion via an anodic reduction reaction, which improved the precipitation of metals and organic compounds as hydroxides by the hydroxyl ions formed at the cathode. The optimum current density, reaction time and polyelectrolyte concentration at which the removal efficiency of COD (89.5%) and TSS (99.7%) reached the maximum values were found to be 0.88 A/cm^2, 100 min and 15 mg/l, respectively. For the current density of 1 A/cm^2, N-NH_4, Ni, Cr and Cd removal efficiencies were 64.5, 92.5, 99.6 and 83.4%, respectively. The results show that electrocoagulation can efficiently decrease COD, TSS and metal ions to a very low concentration.

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