New sequential treatment for mature landfill leachate by cationic/anionic and anionic/cationic processes: Optimization and comparative study

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ABSTRACT

Two new applications for sequence treatment of mature (stabilized) landfill leachate, that is, cationic resin followed by anionic resin (cationic/anionic) and anionic resin followed by cationic resin (anionic/cationic), are employed and documented for the first time in the literature. Response surface methodology (RSM) concerning central composite design (CCD) is used to optimize each treatment process, as well as evaluate the individual and interactive effects of operational cationic resin dosage and anionic resin dosage on the effectiveness of each application in terms of color, chemical oxygen demand (COD), and NH_3-N removal efficiency. A statistically significant model for color, COD, and NH_3-N removal was obtained with high coefficient of determination values ($R^2 > 0.8$). Under optimum operational conditions, the removal efficiency levels for color, COD, and NH_3-N are 96.8%, 87.9%, and 93.8% via cationic/anionic sequence, and 91.6%, 72.3%, and 92.5% via anionic/cationic sequence, respectively. The experimental results and the model predictions agree well with each other.

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1. Introduction

Landfilling is an important means of managing the increasing amount of solid wastes generated. However, the habitual disposal of municipal solid wastes in landfills presents the following problems: the contamination of surface and ground water through leachate; soil contamination through direct waste contact or leachate; air pollution through the burning of wastes and the uncontrolled release of methane by anaerobic decomposition of waste; spread of diseases by different vectors, such as birds and insects; and odor [1]. The presence of high concentrations of pollutants in municipal landfill leachate is one of the primary issues usually encountered by landfill operators. Because landfill leachate properties continue to be dangerous and poisonous over long periods, impurity removal (or at least reduction) has become an imperative concern in leachate treatment over recent decades [2–4].

Unfortunately, tropical countries, such as Malaysia, exhibit increased leachate production due to rainfall exceeding the amount that can be evaporated during the rainy season [5]. According to Trankler et al. [6], in hot and humid weathers, leachate production is considerably higher and varies more than in hot and arid regions because of intensive microbial activity.

Typically, the quality and quantity of landfill leachate can be influenced by several factors, including solid waste decomposition, landfill age, hydrology of landfill site, climatic condition, and moisture content [7].

Characteristically, landfills more than 10 years old are normally in the methanogenic phase, and the leachate produced is referred to as mature, "stabilized" leachate. According to Christensen et al. [8], many parameters change dramatically when a landfill becomes mature, in which the stabilized leachate normally contains a large quantity of non-biodegradable organic compounds, such as humic and fulvic substances. Moreover, the leachate contains considerable amounts of inorganic substances, particularly NH_3-N [9]. On account of its complicated characteristics, the application of biological treatment alone for stabilized leachate treatment is not a viable alternative [10]. Therefore, the common focus of research nowadays is on the treatment of stabilized leachate using physico-chemical techniques, such as adsorption, coagulation and flocculation, oxidation, air flotation, membrane filtration, and ion exchange processes [11–18]. Zagorodni [19] reported that ion exchange resins have been broadly employed in water and wastewater treatment for the extraction, separation, and purification of ion and organic substances.

According to the literature, however, the implementation of the ion exchange technique using cation and anion ion exchange resin for stabilized leachate treatment is still rare [4,20]. Recently, the removal efficiency of some ion substances from stabilized leachate using cation exchange resin has been advantageously employed by Bashir et al. [3] and Primo et al. [17]. Furthermore, anion exchange

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Table 1
Characteristics of raw leachate from PBLS.

Parameters	Units	Feb 2008–Jan 2010 (current study)		Sep 2007–Feb 2008 [15]		Standard discharge limit[a]
		Values	Average	Values	Average	
pH	–	8.30–9.17	8.58	7.76	8.2	6.0–9.0
COD	mg/L	1810–2850	2321	2270–2945	2667	400
NH$_3$–N	mg/L	1630–2200	1949	983–2170	1760	5
Color	Pt–Co	4250–5760	5094	3860–4248	4059	100
Turbidity	FAU	128–330	211	203–308	248	–
SS	mg/L	114–360	181	177–254	211	50
Conductivity	μS/cm	21,850–26,230	24,340	–	–	–

[a] Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Laws of Malaysia-Malaysia Environmental Quality Act 1974 [24].

resin has been employed for non-biodegradable organic compound [measured as chemical oxygen demand (COD)] removal [18,21].

To date, the application of the ion exchange process in landfill leachate treatment focuses on the use of a particular resin type (cation or anion) to treat a specific pollutant. In line with the above, this study is undertaken to examine, optimize, and compare the effectiveness of using two different sequential treatment systems for stabilized leachate [i.e., treatment by cationic exchanger followed by anionic exchanger (cationic/anionic), and treatment by anionic exchanger followed by cationic exchanger (anionic/cationic)]. The sequential utilization of both media for the simultaneous removal of color, COD, and NH$_3$-N from semi-aerobic stabilized landfill leachate is conducted and documented for the first time in the literature. Moreover, the experimental design and optimization for each process is carried out using response surface methodology (RSM) as an ideal statistical method for experimental design and data analysis. According to Montgomery [22], RSM is a technique used for modeling, designing experiments, evaluating the effects of process variables and their interactions, and searching for optimum conditions of variables to predict aim responses.

2. Materials and methods

2.1. Site characteristics and leachate sampling

Raw leachate was obtained from a leachate aeration pond at Pulau Burung Landfill Site (PBLS). PBLS is a semi-aerobic sanitary landfill situated within the Byram Forest Reserve at 5°24′ N Latitude, 100°24′ E Longitude in the northwest coast of Peninsular Malaysia (has a tropical climate), approximately 20 km southeast of Penang Island. PBLS has an area of 62.4 ha, of which 33 ha is currently operational and receives about 2200 t of municipal solid wastes daily. Pulau Burung's solid wastes are composed of 40.0% food, 22.0% plastic, 10.5% paper, 2.5% metal, 3.2% glass, 3.5% textile, and 18.2% other wastes. This site was developed in 1991 as a Level II semi-aerobic sanitary landfill by establishing a controlled tipping

technique. In PBLS, leachate is collected through a leachate collection pipe that flows into a detention pond. The site was chosen because it was developed semi-aerobically with leachate recirculation, and is one of only three sites of its kind in Malaysia [2]. These sites were developed consistently with the Fukuoka Landfill Method. PBLS is equipped with leachate collection and gas collection systems, as well as aeration for a leachate pond.

Leachate samples were taken from PBLS in accordance with the Standard Methods for the Examination of Water and Wastewater [23]. The samples were directly transported to the laboratory and stored in a cold room at 4 °C until analysis. The samples were characterized for color, COD, NH$_3$-N, SS, and turbidity concentrations and pH as illustrated in Table 1.

2.2. Materials

The strong cationic resin, INDION 225 Na, and the strong anionic resin, INDION FFIP MB, supplied by Ion Exchange (INDIA) Ltd. were used in this study. The resins and their physico-chemical properties are presented in Table 2. INDION 225 Na was chosen because of its known characteristics, such as its ability to work as a strong acid cation exchanger when used in the form of hydrogen; its possibility for use in hydrogen form and sodium form; and its application over a wide range of pH levels and temperatures. The same is true for INDION FFIP MB, which acts as a strong base anion exchanger. It can also be used in chloride form and hydroxide form [3,18]. The matrix is polystyre cross-linked divinylbenzene for both anion and cation which is the most popular matrix [25,26]. Typically, the strong acid cation exchangers have a greater affinity than weak resins for all ionized elements in water [26]. The strong base anion exchangers are principally effective for the removal of many synthetic and natural organic substances that contain weak acids, such as humic and fluvic substances [27–31].

In the current study, anion resin was used in chloride form [18], whereas cation resin was used in hydrogen form [3]. Prior to use, the studied cation and anion resins were rinsed extensively with

Table 2
Physicochemical properties of the studied resins.

Property	INDION FFIP MB	INDION 225 Na
Type	Strongly base anion exchange resin	Strongly acid cation exchange resin
Matrix	Cross-linked polystyrene, isoporous type	Cross-linked polystyrene, gel type
Functional group	Quaternary amine (–N+R$_3$)	Sulfonic acid (–SO$_3$$^-$)
Ionic form (as supplied)	Chloride	Sodium form
Maximum operating temperature	60 °C (OH$^-$ form) 90 °C (Cl$^-$ form)	120 °C (H$^+$ form) 120 °C (Na$^+$ form)
Operating pH range	0–14	0–14
Particles size range	0.45–0.55 mm	0.3–1.2 mm
Total exchange capacity	1.2 meq/mL	2.0 meq/mL
Bulk density (g/cm^3)	0.611	0.81
Particle density (g/cm^3)	1.11	1.328
Porosity (%)	45.04	39.0
Surface area (m^2/g)	0.5419	0.0996
Appearance	Brown to dark brown	Yellow

distilled water to remove adhering dirt, followed by filtration using GC-50 filter papers (Advantec Toyo Kaisha Ltd., Japan) with 0.45 μm pore size. The resins were then dried at surrounding environmental temperature.

2.3. Analytical methods

All parameter measurements were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater [23]. Color concentration was measured as apparent color by a DR 2010 Hach spectrophotometer based on Method No. 2120C. COD concentration was determined using the closed reflux and colorimetric method of Method No. 5220D. The concentration of NH_3-N was measured by the Nessler method (Method: 8038, Hach) using a Hach DR2010 spectrophotometer. Suspended solids were determined by a DR 2010 Hach spectrophotometer based on Hach Method No. 8006. Turbidity was measured by DR/2010 according to Method No. 8237. The pH of the leachate was measured using a portable digital pH/mV meter (WITEG, W-100, Germany). Conductivity was measured as μS/cm by a portable multi-purpose meter (Multi 340i, Germany).

The removal efficiency of the studied parameters was obtained using the following equation:

$$\text{Removal} \ (\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final concentrations of parameters (mg L^{-1}), respectively.

2.4. Experimental design and analysis

Design-Expert 6.0.7 (Stat-Ease, Inc., Minneapolis, USA) was employed for the statistical design of the experiments and data analysis, whereas central composite design (CCD), the most widely used approach of RSM, was used to assess the relationship between response and process variables, as well as optimize the relevant conditions of the variables for the prediction of the best value of the responses.

Two sequence treatment systems for stabilized landfill leachate were optimized and compared. The sequence treatment systems are:

(i) Cationic resin (X_1, applied first) followed by anionic resin (X_2), in which the batch experiments were conducted by shaking 100 mL of the leachate sample in a 250 mL volumetric flask with different dosages of cationic resin (5–24 cm^3) at optimum operational conditions (contact time, 10 min; shaking speed, 150 rpm) [3]. Subsequently, 80 mL of the effluent was taken after filtration and treated with different dosages of anionic resin (5–28 cm^3) at a shaking speed of 150 rpm and a contact time of 75 min [18].

(ii) A reverse series system was also examined by first applying anionic resin (X_1) followed by cationic resin (X_2), in which 100 mL of leachate was agitated with different anionic dosages (5–35 cm^3) at a contact time of 75 min and a shaking speed of 150 rpm [18]. After this, 80 mL of the effluent was taken after filtration and treated with different dosages of anionic resin (5–20 cm^3) at a shaking speed of 150 rpm and a contact time of 10 min [3].

The narrower ranges of the process variables (i.e., anionic and cationic dosages) were selected based on the pre-determined results in previous work [3,18]. In each treatment sequence, the medium first used was X_1. The significant response parameters (dependent variables) considered in this study were color removal (%), COD removal (%), and NH_3-N removal (%). Table 3 illustrates the experimental conditions for each sequence based on CCD. The total number of experiments for each treatment process was 13 runs consisting of 3^k full factorial design with four additional experimental trials as replicates of the central point, where k is the number of variables ($k = 2$). Four replicates at the central points were employed to fit the second-order polynomial models and to obtain the experimental error for this study [32]. Each process variable was varied over three levels (i.e., −1, 0, +1) numerically. In Table 3, the independent variable levels are presented in terms of the actual values in addition to coded levels (in parentheses). Experimental results are shown as percent removal of color, COD, and NH_3-N.

Basically, the relationship between the response and the input is given in Eq. (2) as

$$Y = f(x_1, x_2, x_3 \ldots x_n) \pm \varepsilon \tag{2}$$

where Y is the response; f is the unknown function of the response; x_1, x_2, $x_3, \ldots x_n$ denote the input variables that can affect the response; n represents the number of independent variables; and ε is the statistical error that represents other sources of variability not accounted for by f [22]. Because there are only three levels for each factor, the appropriate model is the quadratic model (suggested by the software), expressed by Eq. (3). According to Bas and Boyaci

Table 3
CCD for the study of two experimental variables for both treatment sequence (*cationic/anionic and anionic/cationic*) and obtained results.

| Run no. | Treatment via cationic/anionic sequence | | | | | Treatment via anionic/cationic sequence | | | | |
| | Experimental design | | Response (removal) | | | Experimental design | | Response (removal) | | |
	X_1: cation dosage (code) (cm^3)	X_2: anion dosage (code) (cm^3)	1 Color (%)	2 COD (%)	3 NH_3-N (%)	X_1: anion dosage (code) (cm^3)	X_2: cation dosage (code) (cm^3)	1 Color (%)	2 COD (%)	3 NH_3-N (%)
1	14.5 (0)	28 (+1)	65.5	70.2	83.3	20 (0)	20 (+1)	90.8	66.8	92.4
2	14.5 (0)	16.5 (0)	57.1	62.9	82.7	20 (0)	12.5 (0)	90.3	68.4	80.8
3	14.5 (0)	5 (−1)	45.6	56.7	83.2	20 (0)	5 (−1)	60.5	55.6	64.4
4	14.5 (0)	16.5 (0)	58.7	63.4	82.9	20 (0)	12.5 (0)	91.5	67.7	80.55
5	14.5 (0)	16.5 (0)	59.6	62.9	84.1	20 (0)	12.5 (0)	91.1	67.9	82.1
6	14.5 (0)	16.5 (0)	59.2	63.4	84.7	20 (0)	12.5 (0)	91.4	67.2	81.5
7	5 (−1)	28 (+1)	62.2	62.9	50	5 (−1)	20 (+1)	85.7	57.4	92.5
8	14.5 (0)	16.5 (0)	78.6	63.5	82.9	20 (0)	12.5 (0)	91.2	67.9	82.1
9	24 (+1)	28 (+1)	98.1	88.3	93.5	35 (+1)	20 (+1)	91.5	71.4	92.6
10	5 (−1)	5 (−1)	44.7	50.7	49.3	5 (−1)	5 (−1)	44.4	41.3	54.3
11	24 (+1)	5 (−1)	93.7	76.24	92.5	35 (+1)	5 (−1)	91.3	70.4	61.8
12	24 (+1)	16.5 (0)	97.4	87.9	92.6	35 (+1)	12.5 (0)	91.5	73.9	79.4
13	5 (−1)	16.5 (0)	61.8	69.1	49.3	5 (−1)	12.5 (0)	83.1	50.7	81.3

[33], the model used in RSM is generally a full quadratic equation or the diminished form of the following equation:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i \qquad (3)$$

where Y is the response; X_i and X_j are the variables; β_0 denote a constant coefficient; β_j, β_{jj}, and β_{ij} represent the interaction coefficients of linear, quadratic, and second order terms, respectively; k is the number of studied factors; and e_i is the error. The matrix notation of the model is given in Eq. (4).

$$Y = X\beta + \varepsilon$$

$$\begin{bmatrix} Y_1 \\ Y_2 \\ \cdot \\ \cdot \\ \cdot \\ Y_n \end{bmatrix} = \begin{bmatrix} 1 & X_{11} & X_{12} & \cdot & \cdot & X_{1k} \\ 1 & X_{21} & X_{22} & \cdot & \cdot & X_{2k} \\ \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & & & \cdot \\ \cdot & \cdot & \cdot & & & \cdot \\ 1 & X_{n1} & X_{n2} & \cdot & \cdot & X_{nk} \end{bmatrix} \begin{bmatrix} \beta_0 \\ \beta_1 \\ \cdot \\ \cdot \\ \cdot \\ \beta_k \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \cdot \\ \cdot \\ \cdot \\ \varepsilon_n \end{bmatrix} \qquad (4)$$

$$\underbrace{\quad}_{Y} \quad \underbrace{\qquad\qquad\qquad}_{X} \quad \underbrace{\quad}_{\beta} \quad \underbrace{\quad}_{\varepsilon}$$

The system of equations given above is solved using least squares method, a multiple regression technique [33]. Analysis of variance (ANOVA) was used for graphical analyses of data to obtain the interaction between the independent (process) and dependent variables (responses). The quality of the fit polynomial model was expressed by R^2 (coefficient of determination), and its statistical significance was checked using the F-test. The probability (P-value) of the model terms was estimated with a 95% confidence level.

2.5. Media regeneration

Basically, ion exchange is a reversible process. Thus, once the medium becomes exhausted, it can be regenerated and the resin is returned to its original ionic form for reuse. Typically, regeneration involves pollutants desorption from the media using processes that drive the pollutants from the media without destroying it. In this study, the exhausted resins were washed and dried before subject to a solution containing a high concentration of the original ions. Later, the resin was subjected to rinsing with distilled water to remove loosely bound ions and traces of the regenerant solution [34]. In this study, several solvents were used for resins regeneration including 1 M H_2SO_4, and 1 M NaCl for cationic resin and 1 M NaOH and 1 M NaCl for anionic resin [34,35]. The dried exhausted media were introduced into 250 mL conical flasks each containing 200 mL of regenerate [36]. The flasks were agitated for 3 h using the orbital shaker. The media were separated from the regenerants via filter paper, washed and air dried for 24 h [36]. Later, the removal efficiencies of the fresh and regenerated media were tested by repeating the leachate treatment process with each type of resin separately.

2.6. Continuous flow study

Two columns connected in series were used in this study. The columns were made from Perspex tubing with an inner diameter of 2.5 cm, and bed depth of 29.0 cm. The best sequence treatment was selected based on the batch study results. Distilled water was pumped through the columns for cleaning prior to its use. The media were filed in the columns. Glass wool and wire mesh were placed at the inlet and outlet of the column in order to prevent the loss of the media. To avoid channeling, the raw leachate was pumped upward through the column at flow rate of 20.0 mL/min. The flow rate was controlled by a peristaltic pump [37]. The concentrations of color, COD and NH_3-N were checked by collecting 5 mL effluent for analysis at different times.

3. Results and discussion

3.1. Results and analysis of variance

A total of 13 runs of the CCD experimental design and response results, based on the experimental runs for each process, are illustrated in Table 3. The relationship linking the two independent variables (cationic dosage and anionic dosage) and the three important responses (dependent variables), that is, color, COD, and NH_3-N removal efficiencies for each sequence of treatment, were analyzed by RSM. CCD demonstrated in Table 3 is adequate for the development of mathematical equations where predicted responses (Y) are appraised as a function of cationic and anionic dosages according to Eq. (3). Subsequently, the results attained were analyzed by ANOVA to evaluate goodness of fit [32]. The empirical relationships between color, COD, and NH_3-N, and the independent variables were modified by neglecting the terms found statistically insignificant (Table 4). Table 4 demonstrates the modified quadratic models in terms of coded variables, and illustrates supplementary significant statistical parameters, as well. According to the data shown in Table 4, all the models for color, COD, and NH_3-N removal efficiencies are significant at a 5% confidence level ($P < 0.05$). Normally, the P-values for lack of fit are used to test the significance of the model correlation between the variables and process responses. However, the analysis of variance shows a consistent confidence in the evaluation of color, COD, and NH_3-N removal efficiency models ($R^2 > 0.80$). According to Myers and Montgomery [38], an R^2 value close to 1 is desirable and a realistic agreement with adjusted R^2 is needed. A high R^2 coefficient promises an appropriate adjustment of the quadratic model to the experimental data [22]. Typically, R^2 is used to express whether a regression model is appropriate. The R^2 gives an exact match if it is 1 and, if the residual increases, R^2 decreases in the range from 1 to 0. As the number of variables increases, the residual decreases which leads to an increase in R^2 value. Thus, to obtain a more precise regression model judgment, the coefficient of determination adjustment for the degree of freedom (R^2_{adj}) is used for comparing the residual per unit degree of freedom [39].

Table 4
Summary ANOVA results for response parameters.

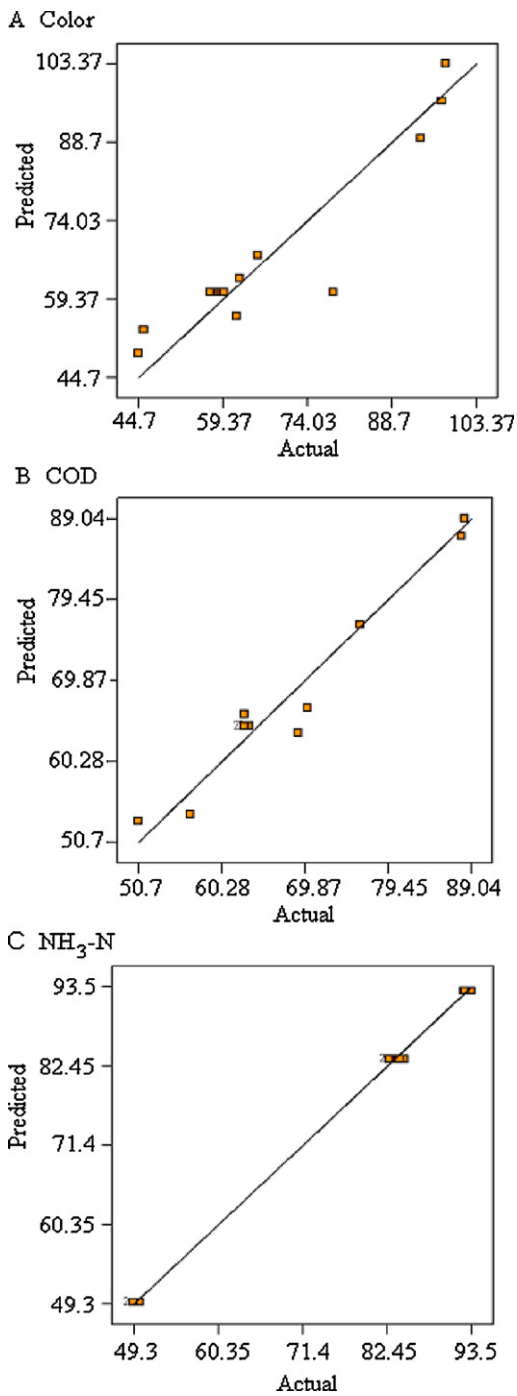| Response	Final equation in terms of code variables	P	PLOF	R^2	R^2_{adj}	AP	S.D.	CV	PRESS
Treatment via cationic/anionic sequence									
Color removal (%)	$60.61 + 20.08X_1 + 6.97X_2 + 15.70X_1^2$	0.0002	<0.0001	0.8727	0.8303	12.9	7.54	10.1	954.3
COD removal (%)	$64.49 + 11.62X_1 + 6.29X_2 + 10.84X_2^2 - 4.21X_2^2$	<0.0001	<0.0001	0.9487	0.9231	18.98	3.04	4.5	281.7
NH_3-N removal (%)	$83.40 + 21.67X_1 - 12.20X_1^2$	<0.0001	0.0337	0.9987	0.9985	140	0.6	0.828	6.48
Treatment via anionic/cationic sequence									
Color removal (%)	$90.01 + 10.18X_1 + 11.97X_2 - 12.65X_2^2 - 10.27X_1X_2$	<0.0001	<0.0001	0.9350	0.9025	19.43	4.58	5.44	1031.3
COD removal (%)	$67.21 + 11.05X_1 + 4.72X_2 - 3.37X_1^2 - 4.47X_2^2 - 3.77X_1X_2$	<0.0001	0.0033	0.9836	0.9720	32.53	1.58	2.5	127.04
NH_3-N removal (%)	$81.11 + 16.17X_2 - 4.77X_2^2$	<0.0001	0.0067	0.9644	0.9573	27.36	2.46	3.11	131.3

Fig. 1. Design-Expert plots; predicted versus actual values plot for (A) color, (B) COD, and (C) NH_3-N removal (cationic/anionic sequence).
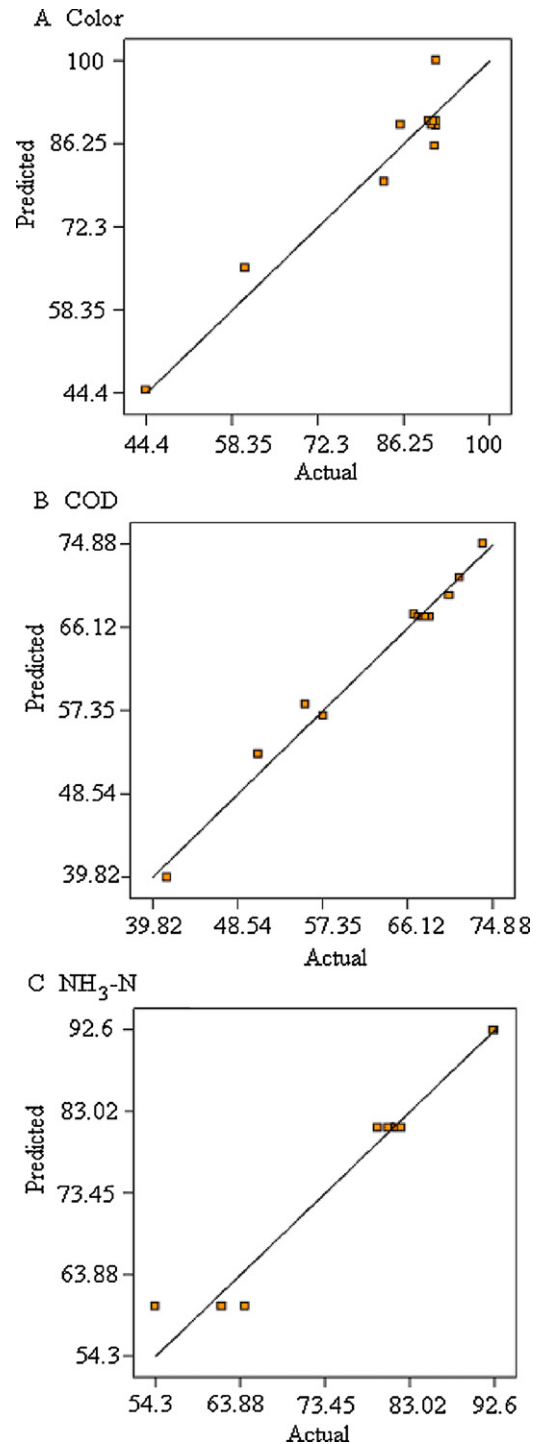

Fig. 2. Design-Expert plots; predicted versus actual values plot for (A) color, (B) COD, and (C) NH_3-N removal (anionic/cationic sequence).

The adequate precision (AP) ratio evaluates the signal-to-noise ratio. AP values >4 indicate adequate model favoritism [40]. Also, the coefficient of variance (CV) usually defines the reproducibility of the model. Table 4 demonstrates good model reproducibility; a model is normally considered reproducible if it's CV <10% [32]. Classically, the predicted versus the actual value plots of responses, as demonstrated in Figs. 1 and 2, facilitate the adequacy assessment of the model. The predicted versus the actual value plots of parameter removal are presented in Figs. 1 and 2 for the sequence treatment via cationic/anionic and anionic/cationic systems, respectively. As can be seen in Figs. 1 and 2, the predicted

values of color, COD, and NH_3-N removal efficiency obtained from the models and the actual experimental data are in good conformity. The normal probability plots of the studentized residuals of all responses for cationic/anionic and anionic/cationic systems are shown in Figs. 3 and 4, respectively. A normal probability plot of residuals indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. Some scattering is expected even with normal data [13]. It can be observed from Figs. 3 and 4 that the data is normally distributed.
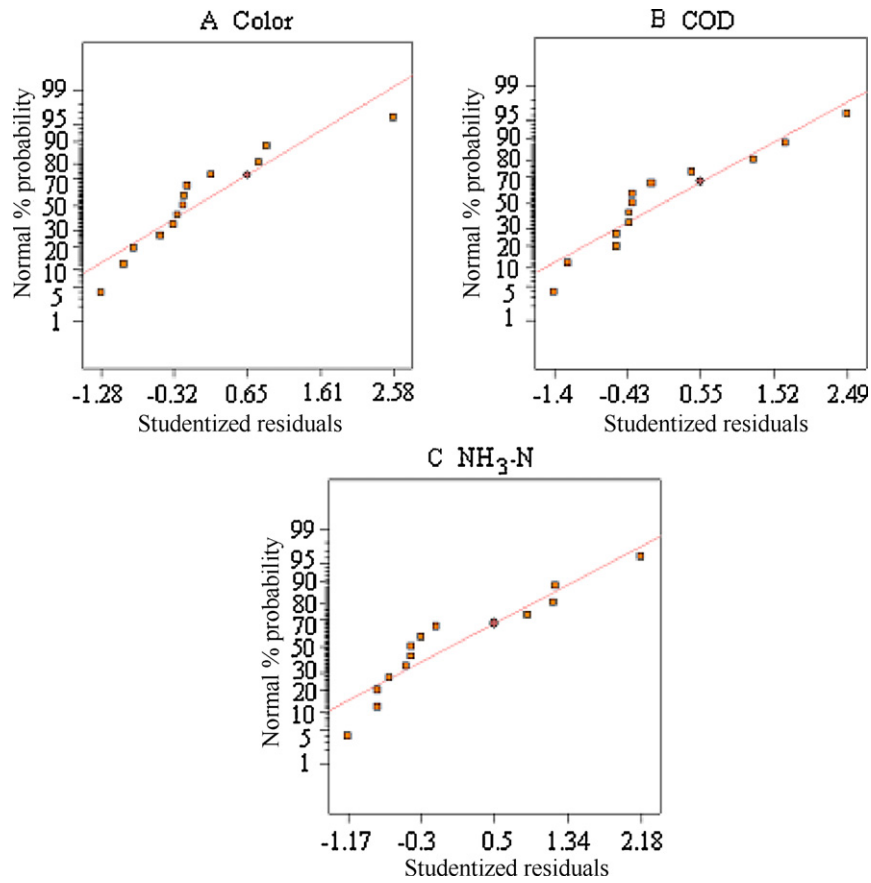
Fig. 3. Design-Expert plot; normal probability plot of studentized residuals for (A) color, (B) COD, and (C) NH_3-N removals (cationic/anionic sequence).
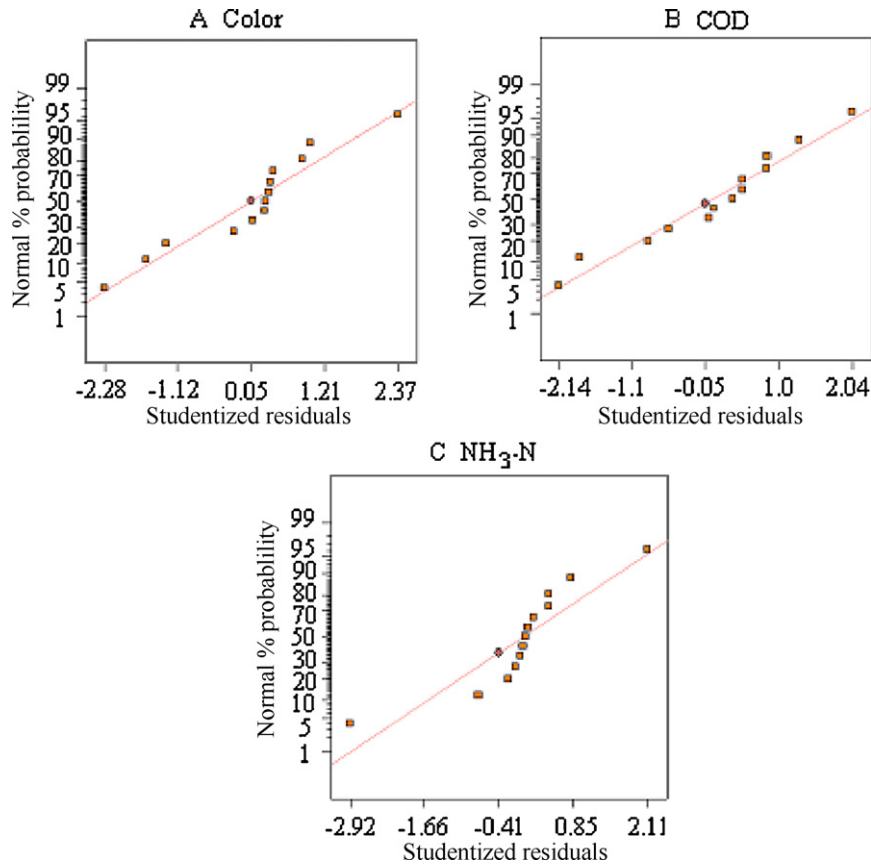

Fig. 4. Design-Expert plot; normal probability plot of studentized residuals for (A) color, (B) COD, and (C) NH_3-N removals (anionic/cationic sequence).
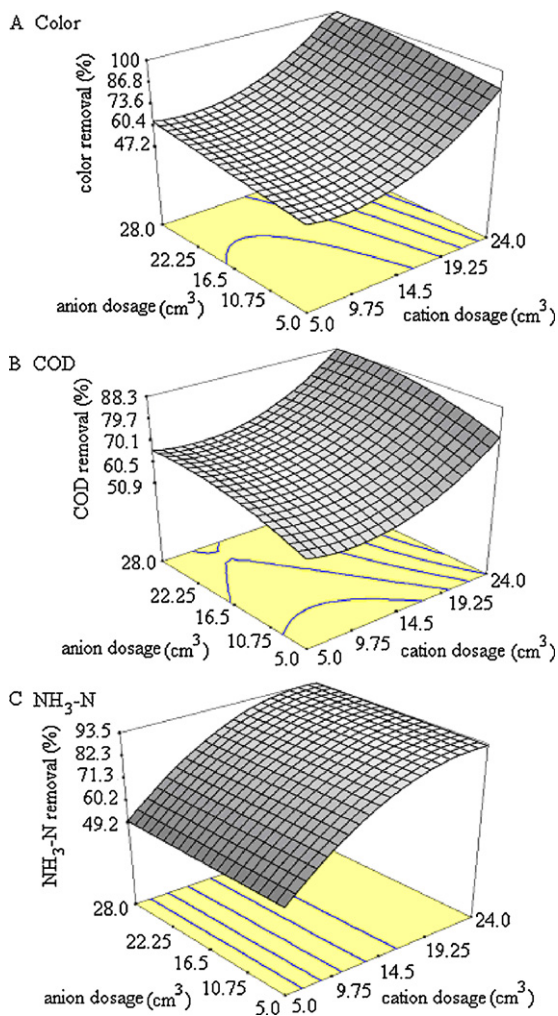
Fig. 5. Effect of process variables on color, COD, and NH$_3$-N removal efficiency (cationic/anionic sequence).

Fig. 6. Effect of process variables on color, COD, and NH$_3$-N removal efficiency (anionic/cationic sequence).

3.2. Process efficiency analysis

As demonstrated in Figs. 5 and 6, the three-dimensional response surface plots were generated by RSM based on the experimental results (Table 3) for color, COD, and NH$_3$-N removals via cationic/anionic and anionic/cationic systems, respectively. According to the predicted 3D graphs (Fig. 5A and B), about 100% and 88.3% removal of color and COD can be obtained when the stabilized leachate sample is treated via cation resin followed by anion resin. However, the maximum removal efficiency of NH$_3$-N via cation resin followed by anion resin is 93.5%. Fig. 5C demonstrates that NH$_3$-N removal efficiency appreciably increases when the cation dosage increases, whereas the effect of the anion dosage on NH$_3$-N removal efficiency is inconsequential. Conversely, Fig. 6 illustrates the effects of experimental conditions (i.e., anion and cation dosages) on color, COD, and NH$_3$-N removal efficiency as 3D surface plots. The figure shows an increase in color and COD removal efficiency when the cation and anion dosages increase. However, NH$_3$-N removal efficiency clearly increases when the cation dosage increases, whereas the effect of the anion dosage on NH$_3$-N removal efficiency is minimal. According to the predicted 3D surface plots, about 100%, 74.9%, and 92.6% removal of color, COD, and NH$_3$-N can be obtained when the stabilized leachate sample is treated via anionic/cationic sequence.

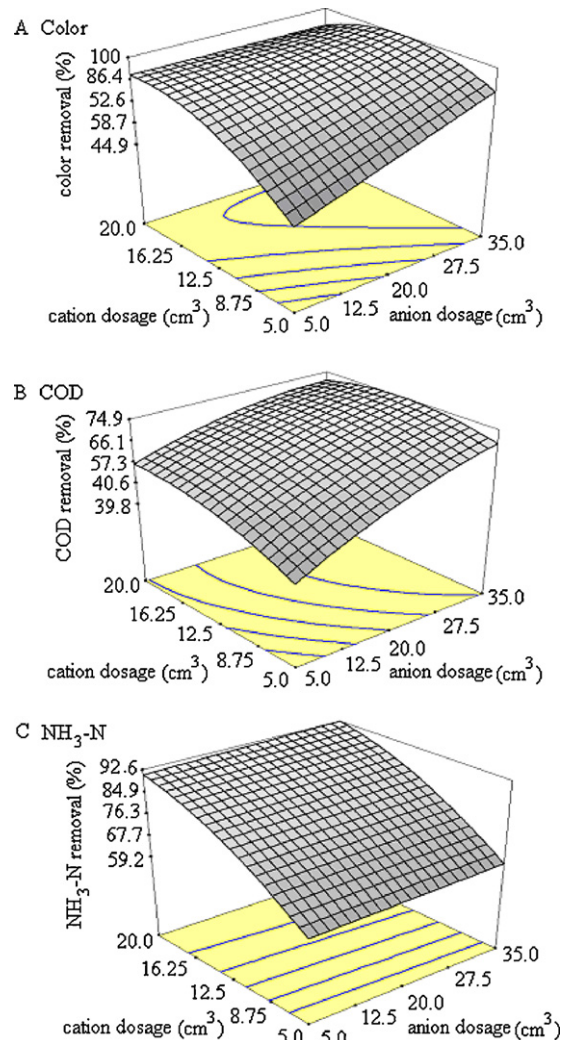### 3.3. Process sensitivity to cationic and anionic dosage

The sensitivity of color, COD, and NH$_3$-N removal efficiency to the operational variables (cationic and anionic dosages at cationic/anionic and anionic/cationic sequences) were demonstrated via Perturbation plots (Figs. 7 and 8) obtained by RSM. The two variables valued range from −1 to +1, as shown in Figs. 7 and 8.

Fig. 7 demonstrates the proportional effects of operational variables on the responses when the leachate is treated via the cationic/anionic system. In the case of color and COD removal, a sharp curvature in cation and anion dosages demonstrates that color and COD removal are sensitive to cation and anion dosages. However, in the case of NH$_3$-N removal, the semi-flat anion dosage curve displays an insignificant effect of the anion dosage on NH$_3$-N removal. By contrast, NH$_3$-N removal is very sensitive to the cation resin. As can be seen from Fig. 8 (treatment via anionic/cationic system), a curvature in anionic and cation dosages demonstrates that color and COD removal efficiencies are sensitive to these operational variables. To some extent, a curvature in anion dosage seems sharper than the cation dosage curve, indicating that color and COD removal efficiencies are more sensitive to anion dosage in this treatment process. However, in the case of NH$_3$-N removal (Fig. 8C), the cation dosage curvature seems extremely sharper than the anion dosage curvature, indicating that the anionic dosage has negligible
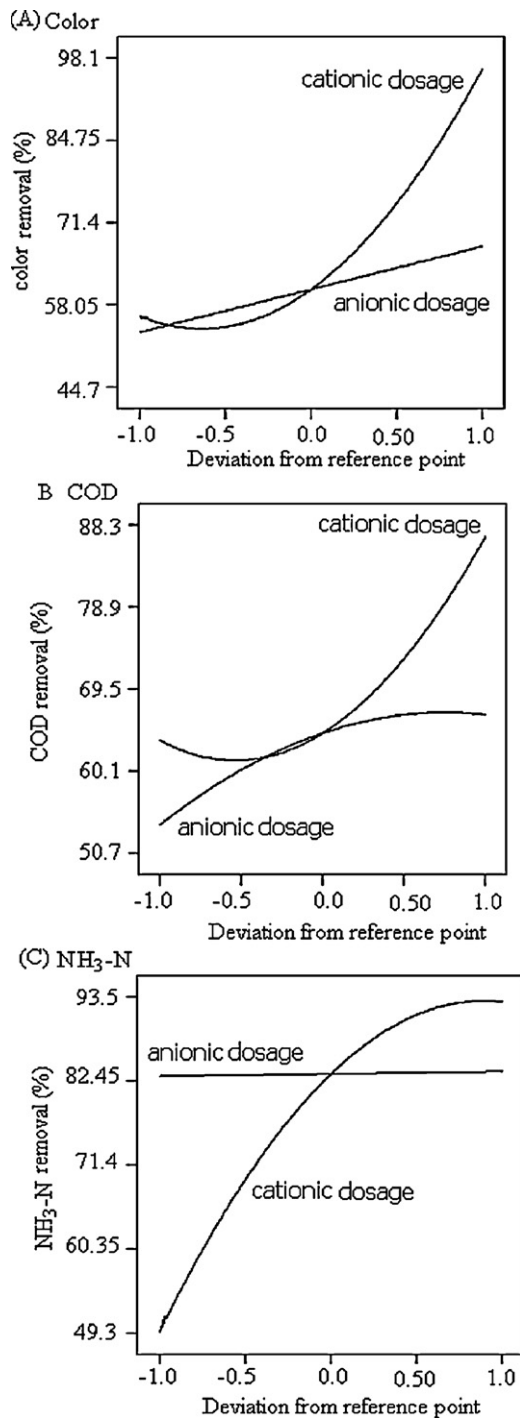
Fig. 7. Perturbation plots for (A) color, (B) COD, and (C) NH$_3$-N removal (cationic/anionic sequence).

effects on NH$_3$-N removal efficiency compared with the cationic dosage.

3.4. Process optimization and verification

The optimization of both cationic/anionic and anionic/cationic treatment processes for simultaneous color, COD, and NH$_3$-N removal was carried out using the trial version of Design-Expert 6.0.7. In Design-Expert, the optimization module searches for a combination of operational variable levels that simultaneously gratify the prerequisites placed on each of the independent (fac-
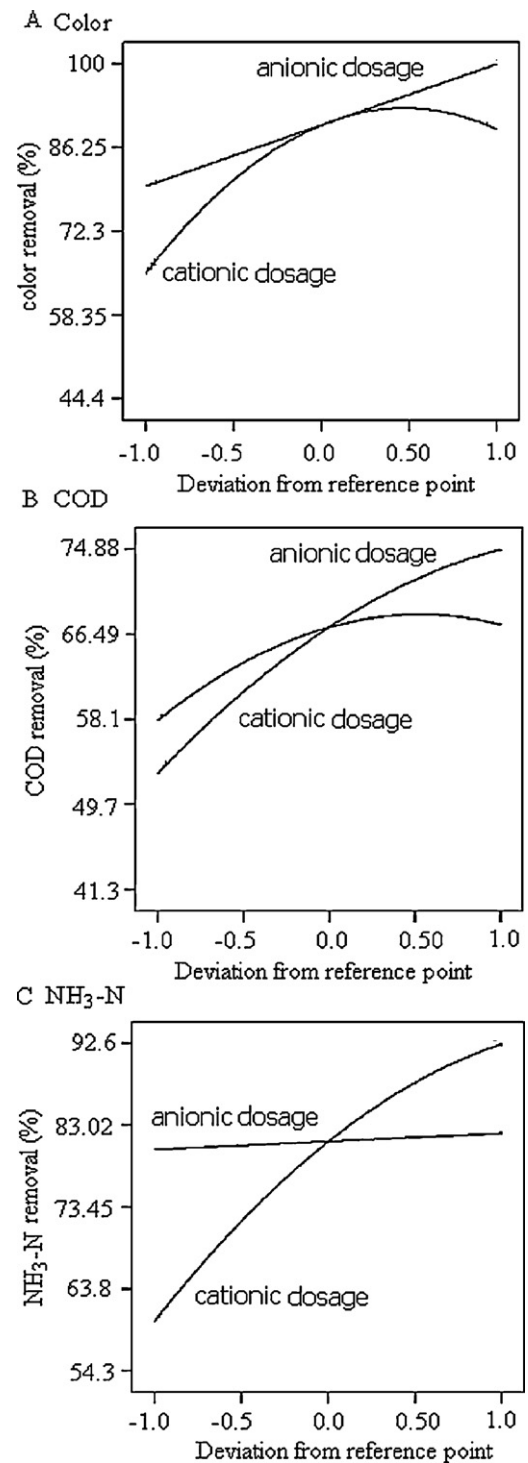

Fig. 8. Perturbation plots for (A) color, (B) COD, and (C) NH$_3$-N removal (anionic/cationic sequence).

tors) and dependent variables (responses) [41]. The desired goal for each independent variable (cationic and anionic dosages) and the responses were conventionally selected using the optimization step of the program. In this study, the responses (color removal, COD removal, and NH$_3$-N removal) of each process were chosen to be maximized, and the operational variables were selected to be within range.

In the cationic/anionic treatment case, the optimum removals occur at a cation dosage of 23.3 cm^3 and an anion dosage of 25.3 cm^3. According to the model, this should result in 98.0%,

Table 5
Optimum response results from model prediction and laboratory.

Conditions	Response (removal (%))		
	Color	COD	NH$_3$-N
Treatment via cationic/anionic sequence			
Model results	98	86.86	93
Laboratory results	96.8	87.9	93.8
Treatment via anionic/cationic sequence			
Model results	90.16	70.73	92.17
Laboratory results	91.6	72.3	92.5.

86.8%, and 93.0% removal of color, COD, and NH$_3$-N, respectively. However, in the anionic/cationic treatment case, the optimized conditions occur by applying the anion dosage (28.3 cm^3) followed by the cation dosage (19.6 cm^3). Based on the model, this should result in 90.1%, 70.7%, and 92.1% removal of color, COD, and NH$_3$-N, respectively. Two additional experiments were then performed under the estimated optimal conditions to confirm the model's satisfactoriness and the soundness of the optimization procedure. As illustrated in Table 5, the removal efficiencies for all response parameters obtained from model prediction and the laboratory experiment are in close agreement. Table 5 also shows that the performance generated by the cationic/anionic process was better than that when the anionic/cationic process was applied. Furthermore, the application of cationic/anionic (sequential treatment) proved to be more efficient when compared with treatment by cationic or anionic alone particularly for color and COD removals. Whereas, treatment of stabilized landfill leachate by utilizing the optimum dosage (24.6 cm^3) of anionic resin [3] resulted in 68.9%, 38.0%, and 92.0% removal of color, COD, and NH$_3$-N, respectively. However, only 67.8%, 60.9%, and 15.8% removal of color, COD, and NH$_3$-N were obtained, respectively, when stabilized landfill leacahte was treated by the optimum dosage of anionic resin (30.9 cm^3) [18].

3.5. Regeneration efficiency

The effects of sulfuric acid (1 M), and sodium chloride (1 M) as regenerants on the recovery efficiency of cationic resin are illustrated in Table 6. The results showed that the cation resin generated by H$_2$SO$_4$ gave a high degree of color, COD and NH$_3$-N removals than the cationic resin generated by NaCl. The high influence of H$_2$SO$_4$ in cation resin regeneration confirmed the result obtained from previous study, where cation resin in H$^+$ form gave better removal efficiencies of color, COD and NH$_3$-N than those obtained via cation resin in Na$^+$ form [42]. In case of anion resin regeneration, Table 6 illustrates the effectiveness of using NaOH (1 M), and NaCl (1 M) as regenerants. A relatively higher removal efficiency of color and COD was achieved when anion resin was regenerated by NaCl. Unalike, the removal efficiency of NH$_3$-N obtained using cation resin generated by NaOH was better. It can be observed from Table 6 that the performances of reused cation resin (regenerated by H$_2$SO$_4$) and reused anion resin (regenerated by NaCl) in terms of parameters removal were almost same as the fresh media. The results indicated

Table 6
The performance of fresh and regenerated media in leachate treatment.

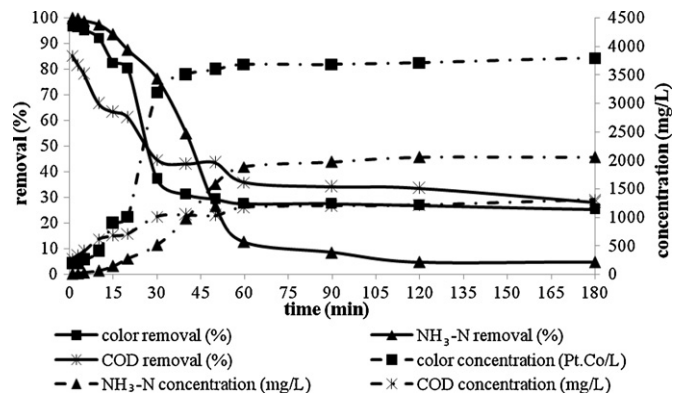| Media	Regenerant	Removal efficiency (%)		
		Color	COD	NH$_3$-N
Cationic	Fresh media	68.9	38.0	92.0
	NaCl (1 M)	9.0	19.5	82.7
	H$_2$SO$_4$ (1 M)	74.3	42.0	90.3
Anionic	Fresh media	67.8	60.9	15.8
	NaCl (1 M)	61.5	57.2	13.2
	NaOH (1 M)	60.4	54.8	18.7

Fig. 9. Breakthrough curve of color, COD, and NH$_3$-N onto cationic- anionic resin at flow rate of 20 mL/min.

that a high recovery efficiency of cation and anion exchangers can be obtained by regeneration. According to Grote and Schumacher [43], in most cases, the ion exchangers can be reused many times in cyclic operations. Thus, the regeneration and ruse of the resin is often cost-effective.

3.6. Continuous flow tests

In this study, leachate was continuously treated by passing through cation resin column followed by anion resin column (the best sequence based on the batch study). The breakthrough curves of color, COD, and NH$_3$-N onto cationic/anionic resin at flow rate of 20 mL/min are shown in Fig. 9. Also, Fig. 9 demonstrates the effect of continuous flow rate on color, COD, and NH$_3$-N removal efficiencies. The result show that the removal of color, COD and NH$_3$-N could reach up to 96%, 85% and 100%, respectively, in the first 1 min of experiments. On the other hand, 92%, 97% and 66% removals of color, COD and NH$_3$-N, respectively, were achieved after 10 min. It can be noticed from Fig. 9 that a significant reduction in the removal efficiency of color, COD and NH$_3$-N occurred in the first 60 min of the experiments. According to the results, the exhausted time in case of color and COD was 60 min while it was about 120 min in case of NH$_3$-N.

3.7. Removal mechanism discussion

The performance difference between two various sequences can be caused by the presence of high amounts of different ion substances, such as NH$_3$-N, in leachate. The application of the cationic exchanger resin first results in a considerable amount of removal of NH$_3$-N that is replaced by H$^+$ ions. Accordingly, the alkalinity weakens, which later enhances the effectiveness of the anionic resin. In addition, the released H$^+$ ions can react with chloride, sulfide, or nitrite, and create acidic conditions inside the solution. In acidic conditions, a more considerable removal of COD and color is observed [21]. Rodriguez et al. [21] indicated that at lower pH values, the precipitation of solids will increase, which improves the efficiency in removing COD and color. This is due to the positive charge dominating the surface of the adsorbent, which slightly increases the electrostatic attraction between the negatively charged substances and the positively charged surface of the adsorbent [44]. On the other hand, applying the anionic/cationic process has resulted in slightly less efficient color and COD removal, indicating less reduction efficiency for organic substances.

Principally, ion exchange resins are insoluble materials that contain exchangeable mobile ions. Once the resin comes in contact with the solution, the ion separates and becomes mobile. The ions on the exchanger can be replaced via dissolved ions in the aque-

ous phase and thus maintain overall neutral charge [19]. Therefore, in this study, the removal of positive ions substances, such as NH_3-N, basically occur because of strong exchangeability with the cationic resin mobile ion (H^+). This chemical exchange process can be described by the following equation:

$$(5)$$
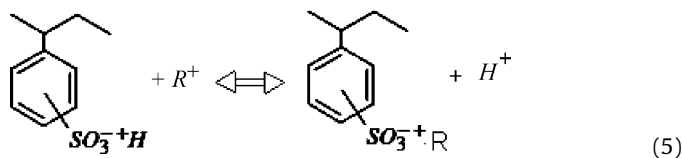
According to Eq. (5), the cationic resin with a stationary functional group (sulfonate group ($-SO_3^-$)) and H^+ mobile ions is highly capable of replacing its mobile ions with an equivalent amount of other positive counter ions (R^+), such as ammonia from the solution [19]. Nevertheless, the description of the interactions between the organic substances (mainly humic and fluvic substances), the main contributor to COD in stabilized leachate and anionic resin (carrying negative mobile ions), is complicated.

According to Zagorodni [19], when an ion exchanger sorbs an organic ion, the hydrocarbon radical of the ion can be engaged in hydrophobic interactions with the matrix of exchangers. This occurrence is particularly marked if the matrix is a hydrophobic polymer (for instance, styrene–divinylbenzene). As a result, hydrophobic interaction plays a vital role in offering high ion exchange selectivity in favor of aromatic and other hydrophobic ions [45]. The process mechanism of attraction between the

exchanger hydrophobic matrix and hydrophobic parts of sorbed ions can be described in two steps, as illustrated in Fig. 10 [19,29,45]. In general, the polarity of media has an important influence on the interactions of the non-polar portion of the organic ion and molecules of the solvent. The hydrophobic part of the aromatic ion dissolved in aqueous media is surrounded by highly structured clusters of water molecules. When such ion is moved from the solutions in the ion exchanger phase, these structured water clusters break down, causing an increase of the overall entropy [19]. In the second step of the sorption process, the aromatic ions bind to the ion exchanger via (i) electrostatic interaction between the ion charge and functional group charge, and (ii) the interaction between the non-polar part of the organic ion and the hydrophobic matrix of the ion exchanger. According to Streat and Sweetland [46], the interactions between organic compounds and ion exchange resin matrixes are normal behavior. However, they showed that the interaction follows the surface sorption mechanism rather than the stoichiometric ion exchange.

4. Conclusions

Mature, stabilized landfill leachate is characteristically non-biodegradable and contains high quantities of color, COD, and NH_3-N, which can cause serious toxicological effects on the receiving water bodies if not treated adequately. In the current study, two new applications for sequence treatment of mature leachate (cationic/anionic and anionic/cationic) were investigated and documented for the first time in the literature. The optimum effectiveness of each application in terms of color, COD, and NH_3-N removal efficiencies was appraised by employing RSM concerning CCD. In the cationic/anionic treatment case, the experimentally achieved optimum removal levels of color, COD, and NH_3-N are 96.8%, 87.9%, and 93.8%, respectively. However, the application of the anionic/cationic treatment results in 91.6%, 72.3%, and 92.5% removal, respectively. Consequently, we can conclude that the application of the cationic/anionic sequence for the treatment of mature stabilized landfill leachate is more effective than the employment of the anionic/cationic sequence; thus, the cationic/anionic sequence is recommended. In addition to that, the regeneration results indicated that ion exchangers can be reused productively which can significantly reduce the overall operation cost.

Fig. 10. A schematic illustrating the interactions between non-polar part of organic (NPM) and solvent, NPM and anion exchanger resin matrix, and electrostatics interactions (EL) during sorption of the organic anion from the aqueous phase [45].

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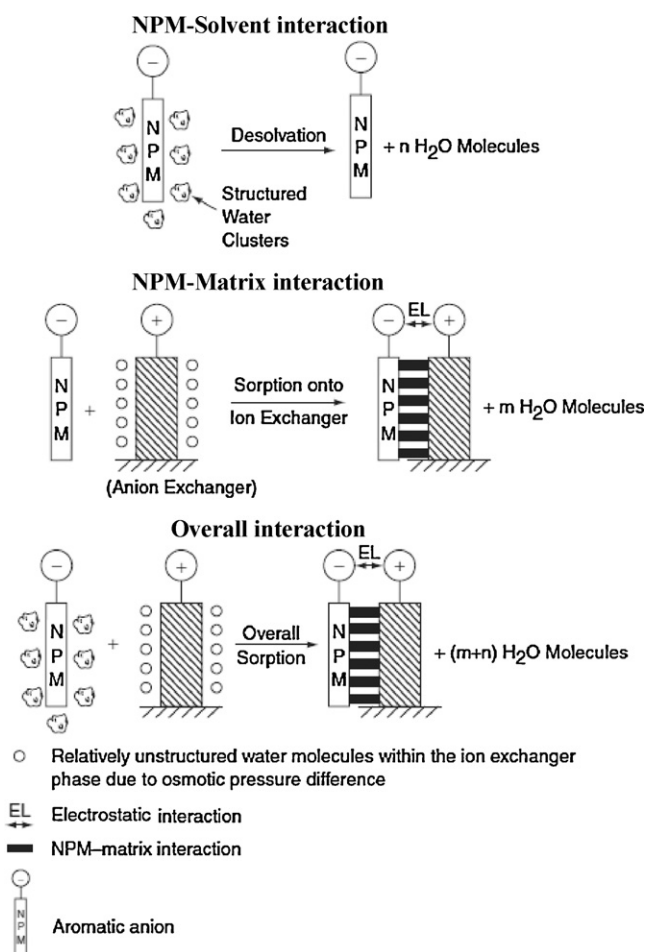
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