Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20116

68 (2017) 330–337
March

Pre-treatment of ammonia-nitrogen (NH_3–N) removal from scheduled waste leachate by air stripping

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Received 2 September 2015; Accepted 18 July 2016

ABSTRACT

The effect of lime dosage, pH and air flow rate on the removal process of NH_3–N from a scheduled waste landfill leachate was investigated by using a lab-scale air stripping column. The main objectives were to reduce NH_3–N concentration prior further biological treatment and to investigate factors affecting air stripping processes. A central composite design (CCD) of response surface methodology (RSM) was employed to optimize the parameters affecting NH_3–N removal from the leachate. It was observed that the optimal conditions obtained from desirable response (NH_3–N removal) were predicted at lime dosage of 9.8 g L^{-1}, pH = 11 and air flow rate of 2.25 L min^{-1}. Quadratic RSM predicted the maximum NH_3–N removal to be 96.5% at these optimal conditions and concurred with the experiments which successfully removed 96.3% of NH_3–N within 24 h. This study shows that the RSM could successfully predict the degree of NH_3–N removal. The findings suggest that RSM approach was feasible for optimizing the air stripping process for NH_3–N removal from scheduled waste landfill leachate in laboratory scale. Based on the obtained results, air stripping process can be used as an efficient pre-treatment for removal of NH_3–N in scheduled waste leachate.

Keywords: Air stripping; Ammonia-nitrogen removal; Leachate; Response surface methodology (RSM); Scheduled waste leachate

1. Introduction

The urbanization and rapid growth of world population greatly accelerates consumption rates, which leads to the increase of waste production and significantly contribute to the major environmental, economic and health problems worldwide [1,2]. Various alternative methods are available for controlling waste problem which include composting, incineration, recycling, hog feeding, anaerobic digestion and dumping. However, landfilling is still one of the predominant waste disposal methods especially in most developing countries, due to its simplicity and economic advantages [2,3]. Nevertheless, landfilling has a drawback, as it generates leachate, a high-strength wastewater or liquid that percolates through waste and extracts, dissolved or suspended materials, which contains a significant quantity of chemical constituents during the decomposition process in landfill [4]. Leachate contains biodegradable organic matter, recalcitrant organic matter (such as humic substances), heavy metals, inorganic salts and high concentration of ammonia–nitrogen [3,5–7]. The characteristic of leachate is highly complex which makes leachate treatment is one of the most important and difficult tasks in landfill management [4].

The treatment of leachate from sanitary or municipal solid waste landfill had been investigated. However, to date, a limited literature on the treatment of leachate from a scheduled waste or hazardous waste landfill is reported. The high content of ammonia-nitrogen (NH_3–N) is one

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of the main problems in the treatment of leachate. A high concentration of NH_3–N ranging from 800 to 5210 mg L^{-1} is toxic and threatens the life of living microbial and environment [5,6,8]. It was reported that total ammoniacal nitrogen (TAN) of approximately 1000 mg L^{-1} inhibits the activity of microorganisms and decreases the effectiveness of leachate treatments by biological processes [9,10].

Numerous methods are available to treat the problematic leachate including biological, chemical and physical methods. These include precipitation, magnetic field separation, adsorption, chemical oxidation, coagulation-flocculation, ammonia volatilization by air stripping and electrocoagulation (EC) [5,7,11]. Currently chemically enhanced leachate treatment was preferred, as it is difficult to be treated by conventional biological means. The difficulties are due to the waste content in the toxic leachate to biological growth. Microorganisms which degrade the waste in leachate could not survive in extreme condition such as high concentration of total ammoniacal nitrogen (TAN) and it may decrease the effectiveness of biological processes for leachate treatments, which results in low removals. As it is difficult to achieve high and reliable NH_3–N removal efficiencies alone, the combination of both biological and physical-chemical techniques are generally adopted [5,7]. Hence, it was suggested that chemical or physical pre-treatment could be introduced for reducing the concentration of NH_3–N before biological treatment takes place.

In most water and wastewater treatments, the transfer of material from the gas phase to water or from water to gas phase plays a vital role. Therefore, ammonia volatilization by air stripping or ammonium stripping had been widely practiced for removing NH_3–N in leachate [11]. Air stripping is the process of transferring NH_3 from liquid phase to the atmosphere across a water–air interface. Numerous studies have reported on the efficiency of using air stripping in removing NH_3–N from municipal but not on schedule waste leachate. The technique is successful in removing NH_3–N between 90 and 99% from wastewaters such as those from the fertilizer industry, pig slurry, anaerobic digestion effluent or source-segregated food waste [12]. Additionally, it is often easier and less expensive to remove ammonia–nitrogen (NH_3–N) in the form of ammonia gas (NH_3) rather than to convert it to nitrate-nitrogen before discharged to the environment. The removal process of free ammonia (NH_3) from the liquid form causes interruption of equilibrium in the direction of its formation. Ammonia in aqueous phase is found in two equilibrium forms, which are the ionic (NH_4^+) and the gaseous state (NH_3). The process of ammonia removal is based on the following Eq. (1):

$$NH_4^+ \text{ (aq)} + OH^- \rightleftharpoons NH_3 \text{ (g)} + H_2O \text{ (aq)} \qquad (1)$$

Based on Eq. (1), ammonium ion (NH_4^+) and free ammonia (NH_3) concentrations depend on pH. At lower pH, ammonium and hydrogen ions are dominant species. As the pH increases, the equation shifts to the right and consequently a higher elevation of the gaseous fraction. With a pKa of 9.25 of ammonium/ammonia equilibrium, ammonium nitrogen can be easily transferred from a liquid to dissolve ammonia gas [13]. As an alkaline agent such as lime added into the leachate, the pH of leachate will increase, hence more NH_4^+ will be converted to $NH_{3.}$

Efficiency and mechanism of air stripping process depend on numerous factors including air-liquid ratio, coagulant dosage and type, flocculants dosage and type, types and size of packing materials, temperature, alkalinity, pH, air flow rate, and operation time [14–16]. It was observed in previous studies that higher air-flow rate or air-liquid ratio gives higher volatile organic compounds (VOCs) and ammonia removal efficiency [17–19]. Hossini et al. (2015) concluded that ammonia stripping efficiency was strongly influenced by the air flow rate or air-to-water ratio. In their study, air flow rate of 1.8, 2 and 3 L min^{-1} were used for ammonia volatilization by air stripping, and the obtained results shows that air flow rate of 3 L min^{-1} was the best condition.

In the treatment of municipal waste leachate and sanitary leachate, ammonia transfer rate is enhanced by converting most ammonium ions (NH_4^+) to a gaseous form (NH_3), normally at pH ranged from 10.5 to 12 with the addition of chemical [20–22]. Lime powder ($Ca(OH)_2$), caustic soda (NaOH), aluminum sulphate ($Al_2(SO_4)_2$, calcium carbonate ($CaCO_3$), and calcium oxide (CaO) are commonly used in this case. Studies have investigated the role of such chemicals including magnesium hydroxide ($Mg(OH)_2$), and Polyaluminium Chloride (PaCl) for the treatment of wastewater and leachate [23–28]. However, $Ca(OH)_2$ was found to be the most effective in the removal of suspended solids, ammonia–nitrogen (NH_3–N), colour, heavy metals and other substances [23–26,29,30]. An appropriate dosage of chemical is crucial as to meet the effluent standards with minimum cost. The usage of $Ca(OH)_2$ as a pre-treatment stage may facilitate the applicability and efficiency in removing NH_3–N prior to air stripping. In the specific case of this study, the initial pH of the leachate was adjusted with NaOH in order to observe whether initial value of pH had an effect on NH_3–N removal efficiency as well as the amount of $Ca(OH)_2$ used in the study. Alkalinizing agent, $Ca(OH)_2$ was added to aid in NH_3–N removal [16].

The main objectives of this study were to reduce the NH_3–N concentration to improve the efficiency of the following biological treatment and to optimize the air stripping process and investigate the interactive effects of experimental factors such as lime dosage, effect of initial pH and air flow rate on the removal of ammonia. For this purpose, a scheduled waste landfill leachate was selected as the target to be treated by air stripping process which was optimized by response surface methodology (RSM). The removal of ammonia–nitrogen (NH_3–N) from leachate sample was selected as the dependent output variable. The experiment was carried out in a lab-scale air stripping column, and the removal of NH_3–N was determined by measuring the initial and final concentration of NH_3–N in scheduled waste leachate sample before and after air stripping treatment.

2. Materials and method

2.1. Leachate sampling and characterization

Sample of leachate was collected from a collection sump of a scheduled waste leachate (SWL) treatment facility in Peninsular Malaysia. The main constituents of the scheduled waste are incinerated ashes of industrial and hazardous waste from factories and others. The sample was collected and preserved in accordance with the standard methods for the examination of water and wastewater [31]. The sample was collected in a 25 L plastic container, then transported to the laboratory and kept at 4ºC until used. The sample was removed and left in the ambient temperature for about three hours until it completely reached ambient temperature before the experiment was conducted [27,32]. The characterization of leachate was carried out immediately after it was taken to the laboratory.

2.2. Experimental set- up

Fig. 1 presents the experimental set-up of the lab-scale air stripping column made of PVC of 260 mm H × 100 mm D with a total capacity of 2.0 L and a working volume of 1.0 L. The upper part of the column was exposed to the atmosphere. The hydrated lime, $Ca(OH)_2$, was added into the column at varying dosage ranged from 0–10 g L^{-1} in each separate experiment as a pretreatment to enhance NH_3–N removal in scheduled waste landfill (SWL) leachate. The initial pH was adjusted to pH 10–12 by 0.1 M sodium hydroxide solutions [33]. Air was supplied through an air diffuser at the bottom of the column at various air flow rates ranging from 1.5–2.5 L min^{-1}. The leachate sample was aerated for 24 h and the concentrations of NH_3–N were measured on an hourly basis using ammonia ion selective electrode (HACH, Intellical). The NH_3–N removal (%) was calculated as;

$$\text{Removal (\%)} = 100 \times [(C_i - C_f)/C_i] \tag{2}$$

where C_i and C_f are the initial and final concentrations of NH_3–N in the leachate sample in mg L^{-1}, respectively [8,34].

2.3. Experimental design and optimization

The Design Expert Software (version 7.0) was used for the statistical design of experiments and data analysis. Central composite design (CCD) of the response surface methodology (RSM) was employed to optimize the removal of ammonia–nitrogen (NH_3–N) based on the lime dosage, initial pH and air flow rates. RSM is a statistical tool for designing experiments, evaluating the interactive effects of factors, reducing the number of experiments and searching optimal conditions. It has been widely used in biological optimizations in recent years [33]. Table 1 presents a summary of test conditions for the optimum removal of ammonia obtained from other studies. However, in this study, the following operating parameters were used; lime dosage 0–10 g L^{-1}, initial pH of 10–12, and air flow rate of 1.5–2.5 L min^{-1}.

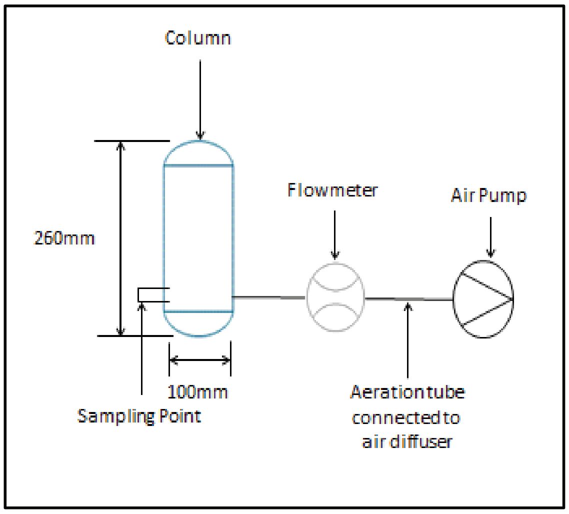

Fig. 1. The set up for air stripping column experiment.

The central composited design (CCD), which is the standard of RSM, was selected for the optimization of the parameters chosen. As different variables normally expressed in different units and/or have different limits variation, the significance of their effects on response can only be compared after they are coded. The variables were coded according to the following Eq. (3):

$$X_i = \frac{X_i - X_0}{\delta X} \tag{3}$$

where X_i is the coded value of the i^{th} independent variable, X_0 the value of X_i at the centre point of the investigated area and δX is the step change. Lime dosage (X_1), initial pH (X_2) and air flow rate (X_3) were chosen as three independent variables in NH_3–N removal. The range and level are given in Table 2.

Each variable in the CCD was studied at three different levels assigned as –1, 0, and +1. The removal of NH_3–N (mg L^{-1}) was used as the output or dependent variables. For optimal point prediction, a second order polynomial model function was fitted to the experimental results as in Eq. (4) below:

$$Y_m = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{i<j} \sum_{j} b_{i,j} X_i X_j \tag{4}$$

where Y_m is the response variable to be modelled; X_i and X_j are the independent variables which influence Y_m, b_0, b_i, b_{ii} and b_{ij} are the offset terms, the ith linear coefficient, the quadratic coefficient and the ijth interaction coefficient, respectively. The actual and predicted values of 20 designs of the experimental work with six replications of the centre points is presented in Table 3.

Table 1
Range of critical parameters obtained from literatures

Critical parameters	Range	Literature
Lime dosage (g L^{-1})	0–20	[21] [23] [35] [36]
Initial pH	7–12	[2] [16] [21] [23] [35]
Air flow rate (L min^{-1})	1–4	[36] [37]

Table 2
Experimental factors and levels used for optimization

Variables	Range and the levels		
	–1	0	1
X_1, Lime dosage (g L^{-1})	0	5	10
X_2, Initial pH	10	11	12
X_3, Air flow rate(L min^{-1})	1.5	2.0	2.5

Table 3
CCD for the study of three experimental variables in coded units and obtained results.

Run	Factors			NH_3–N removal efficiency (%)	
	Lime dosage (X_1)	pH (X_2)	Air flow rate (X_3)	Actual	Predicted
1	5 (0)	11 (0)	2.0 (0)	89.8	91.2
2	5 (0)	11 (0)	2.0 (0)	95.3	91.2
3	0 (–1)	10 (–1)	2.5 (1)	70.0	67.6
4	5 (0)	12 (1)	2.0 (0)	83.5	85.0
5	0 (–1)	11 (0)	2.0 (0)	90.6	90.8
6	5 (0)	11 (0)	2.0 (0)	91.5	91.2
7	5 (0)	11 (0)	2.0 (0)	87.8	91.2
8	10 (1)	10 (–1)	2.5 (1)	80.0	77.3
9	10 (1)	11 (0)	2.0 (0)	94.9	93.4
10	5 (0)	11 (0)	2.0 (0)	91.0	91.2
11	5 (0)	11 (0)	2.5 (1)	93.0	93.8
12	0 (–1)	12 (1)	2.5 (1)	90.2	85.9
13	10 (1)	10 (–1)	1.5 (–1)	61.0	65.6
14	10 (1)	12 (1)	1.5 (–1)	80.5	77.4
15	0 (–1)	10 (–1)	1.5 (–1)	70.0	73.5
16	10 (1)	12 (1)	2.5 (1)	90.4	93.1
17	5 (0)	11 (0)	2.0 (0)	89.1	91.2
18	5 (0)	10 (–1)	2.0 (0)	75.9	73.0
19	5 (0)	11 (0)	1.5 (–1)	85.2	83.0
20	0 (–1)	12 (1)	1.5 (–1)	72.9	76.0

The regression model was calculated by analysing the analysis of variance (ANOVA), *p*-and F-value. The adequacy of the model was expressed with the coefficient of determination, R^2. The model describes the interaction among the parameters influencing the response by varying them concurrently. The interactive effects of the independent variables on the dependent variables are illustrated by three and two-dimensional contour plots.

3. Results and discussion

3.1. Characteristics of scheduled waste leachate

Table 4 shows the general characteristics of raw leachate samples taken from the scheduled waste landfill compared to the permissible limit standards set by the Department of Environment, Malaysia (DOE) [38]. The pH of SWL was 10.1, much higher compared to municipal leachate which is between pH 5 and pH 8 [39]. Thus, a smaller quantity of lime is needed to enhance the volatilization of gaseous ammonia from SWL.

Furthermore, SWL contains a high concentration of BOD_5, COD, arsenic, boron, and ammonia–nitrogen(NH_3–N) compared to other municipal [39]. The BOD_5/COD ratio of SWL was 0.38. BOD_5/COD ratio gives the information about the degree of waste decomposition and landfill age. Generally, the low BOD_5/COD ratio shows the high concentration of non-biodegradable organic compounds, which makes the leachate difficult to be biologically degraded. Based on Table 4, the landfill was considered as young (<5 y) since the BOD_5/COD ratio value was more than 0.3 [8].

The concentration of TSS was 221 mg L^{-1} which indicates the presence of organic and inorganic solids. A greater concentration of colour was mainly contributed by the presence of dissolved organics in the form of recalcitrant material mainly composed of humic-like substances [40].

In this study, the value of NH_3–N is 1472.3 mg L^{-1}, which is relatively high to be treated directly by biological treatment. High concentration of NH_3–N ranges from 800 to 5210 mg L^{-1} is toxic to living microbial populations, especially on nitrifying bacteria (Nitrosomon as and Nitrobacter). This will cause the reduction in effectiveness of leachate treatments by biological processes and gives low removal [5,6,9]. Therefore, a chemical or physical treatment should be introduced first before biological treatment take place.

Table 4
Characteristics of raw leachate from scheduled waste landfill (SWL)

Parameter	Units	SWL leachate	DOE standard*
Temperature	°C	20.4	40
pH Value	–	10.1	5.5–9.0
Biochemical oxygen demand (BOD_5)	mg L^{-1}	1080	50
Chemical oxygen demand (COD)	mg L^{-1}	2840	200
Total suspended solids (TSS)	mg L^{-1}	221	100
Copper	mg L^{-1}	3.04	1.0
Arsenic	mg L^{-1}	15.40	0.10
Nickel	mg L^{-1}	0.73	1.0
Boron	mg L^{-1}	16.5	4.0
Phenols (total)	mg L^{-1}	6.48	1.0
Ammoniacal-nitrogen(NH_3–N)	mg L^{-1}	1472.3	20
Colour (pH natural)	ADMI	1130	200
Colour (pH adjusted to 7.6)	ADMI	1130	200

*Environmental Quality (Industrial Effluent or Mixed Effluent) Regulations 2009, Fifth Schedule (Standard B).

3.2. Statistical analysis

The relationship between the three variables (lime dosage, initial pH and air flow rate) and one response (NH_3–N removal) for the air stripping process was analyzed using response surface methodology (RSM). The value of NH_3–N removal was presented in Table 3. The following quadratic regression model for NH_3–N removal efficiency in terms of code factor was obtained:

$$\begin{aligned} Y_{NH_3\text{–}N} = {} & 91.21 + 1.31\,X_1 + 6.06\,X_2 + 5.40\,X_3 \\ & + 0.85\,X_1X_2 + 1.45\,X_1X_3 + 1.03\,X_2X_3 \\ & + 0.85\,X_1^2 - 12.20\,X_2^2 - 2.80\,X_3^2 \end{aligned} \tag{5}$$

where $Y_{NH_3\text{–}N}$ is the percentage of NH_3–N removal and X_1, X_2 and X_3 are lime dosage (g L^{-1}), initial pH and air flow rate (L min^{-1}), respectively. An empirical relationship was developed from the response surface analysis in which the response variable ($Y_{NH_3\text{–}N}$) was assessed as a function of lime dosage (X_1), initial pH (X_2) and air flow rate (X_3), three first-order effects (linear term in X_1, X_2 and X_3) three second-order effects (quadratic terms in X_1^2, X_2^2, and X_3^2), and three interaction effects (interactive terms in X_1X_2, X_1X_3, and X_2X_3). The result of Analysis of Variance (ANOVA) for NH_3–N removal is shown in Table 5.

ANOVA provides the statistical results and diagnostic checking tests which enable the adequacy of the models to be evaluated [41]. In fact, ANOVA assesses the "goodness of fit" of obtaining results. Significant model terms are preferred to obtain a good fit in a particular model. Based on the data given in Table 5, the model F-value of 12.42 implies the model is significant. There is only 0.02% chance that a "Model F-Value" could occur due to noise. It was demonstrated that the quadratic models were significant at the 5% confidence level since the probability of error (P) value was less than 0.05.

The value of the correlation coefficient ($R^2 = 0.92$) indicates that only 8.21% of the total variation could not be explained by the empirical model. The comparison of the range of predicted values at the design points to the average prediction error gives the value of adequate precision (AP). If the ratio is greater than 4, this indicates adequate model discrimination [42–44]. In this study, the AP value is 10.46 greater than 4. This shows that it is adequate and can be used to navigate the design space defined by the CCD. In ANOVA, the AP value proposes that most of the differences in the response can be explained using the regression equation. The associated P-value is used to predict, whether the AP value is large enough to show statistical significance. The model is statistically significant if the P-value is lower than 0.05. The low standard deviation (3.81) also demonstrates that the quadratic model is seemingly the best. The coefficient of variance (CV) is the ratio of the standard error of estimated to the mean value of the observed response which defines reproducibility of the model. The model is considered as reproducible if the CV value is not greater than 10% [44].

Table 5
ANOVA for response surface quadratic model

Response	NH_3–N removal
F	12.42
P	0.0002
R^2	0.9179
Adequate precision	10.455
Standard deviation	3.81
Coefficient of variance	4.53

Based on results in Table 5, the regression, linear, interaction and quadratic terms are significant and the model is considered being adequate in terms of reproducibility with CV = 4.53. The graph plot of predicted versus experimental NH_3–N removal efficiency of scheduled waste leachate (SWL) is close to $y = x$, indicating the prediction of experimental data is rather satisfying (Fig. 2). According to regression equation, the optimal conditions for NH_3–N removal were obtained as follows: coagulant dosage = 9.8 g L^{-1}, initial pH = 11 and air flow rate = 2.25 L min^{-1}. With NH_3–N removal as the response, the response surfaces of the quadratic model are shown in Figs. 2–4. The surface graphs demonstrate that the optimal condition exactly located inside the design boundary. The curves with noticeable bend indicate that there are significant interactions between the NH_3–N removal efficiency and the process variables.

As shown in Fig. 3, lime dosage and initial pH have strong effects on NH_3–N removal efficiency. The optimum domain identified was $Ca(OH)_2$ dosage of 5 to 10 g L^{-1} and at an initial pH of 11–11.5. As the pH increases, the fraction of gaseous NH_3 is also increased and more NH_3 will be released to the air, thus reducing the concentration of NH_3–N in the leachate. $Ca(OH)_2$ was chosen as chemical to enhance the volatilization of gaseous ammonia in this study based on previous preliminary study as it was more effective compared to caustic soda (NaOH) [29,30]. Previous researches also demonstrated the usage of $Ca(OH)_2$ as an added alkali aids in removal of suspended solids, ammonia–nitrogen (NH_3–N), colour, heavy metals and

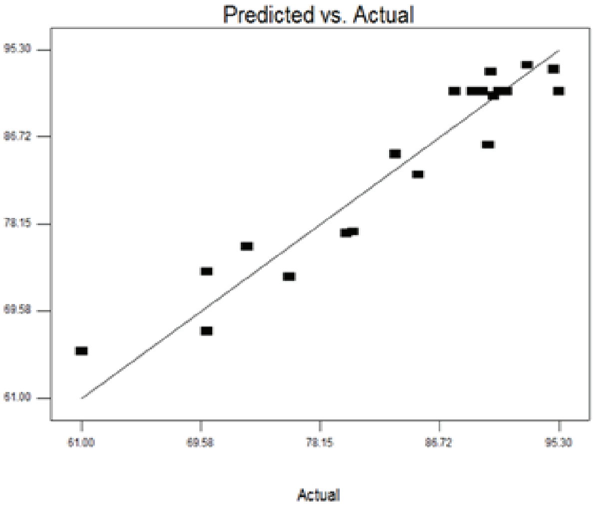

Fig. 2. Predicted vs. actual data for SWL NH_3–N removal efficiency.

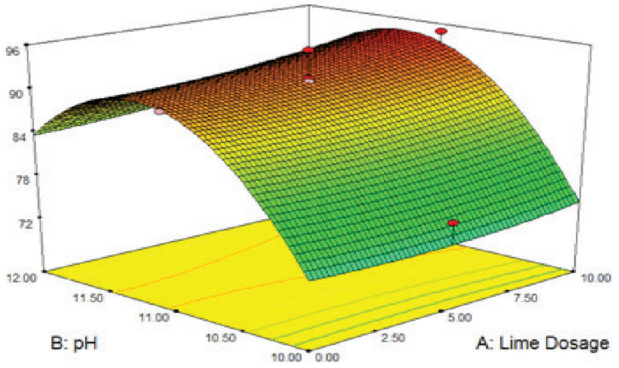

Fig. 3. Design-expert plot; response surface plot for NH_3–N removal at different lime dosage and initial pH.

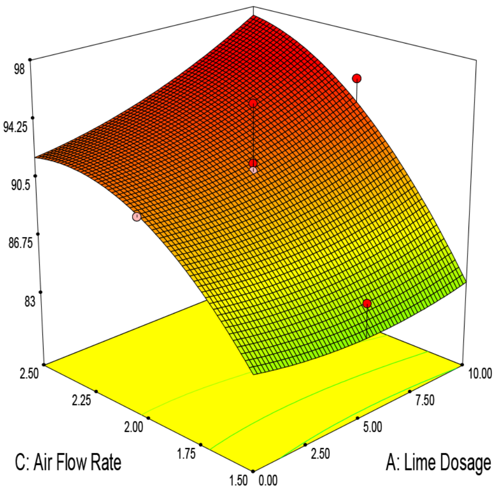

Fig. 4. Design-expert plot; response surface plot for NH_3–N removal at different lime dosage an air flow rate.

other substances [23–26,29,30,45]. When the $Ca(OH)_2$ is added as precipitant into the leachate, the following reactions occur [20]:

$$Ca(OH)_2 + H_2CO_3 \rightleftharpoons CaCO_3 + 2H_2O \tag{6}$$

$$OH^- + NH_4^+ \rightleftharpoons NH_3 + H_2O \tag{7}$$

In this study, lime ($Ca(OH)_2$) reacts with carbonic acid (H_2CO_3) in leachate, producing water (H_2O) and form a white insoluble precipitate of calcium carbonate ($CaCO_3$), at the end of a chemical reaction as described in Eq. (6). Lime also reacts with sulphates in the wastewater producing hard precipitates. Simultaneously, hydroxide ion (OH^-) from $Ca(OH)_2$ reacts with ammonium ion (NH_4^+) in the leachate to form ammonia (NH_3) gas. Lime in excess prevented the pH from dropping and to limit the concentration of free ammonia in leachate. The recarbonation process of the limed leachate by absorption of carbon dioxide from the atmosphere or air bubbles leads to lower pH as hydroxides were converted to carbonates until there was no excess dissolution of lime to compensate the loss of hydroxide ions.

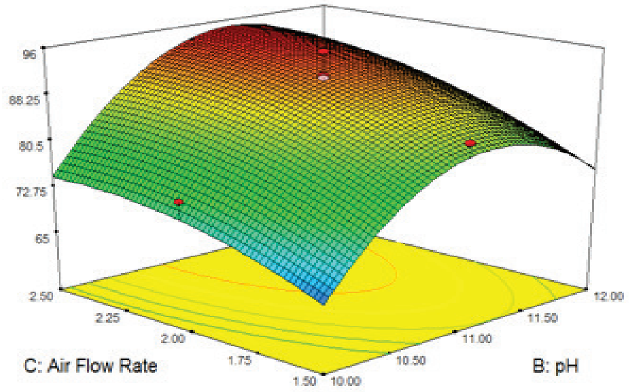

Fig. 5. Design-expert plot; response surface plot for NH_3–N removal at different initial pH and air flow rate.

In the case of ammonia, an increase in hydroxide ion concentration through the addition of lime will aid in ammonia removal. The process of ammonia removal is based on the mass transfer as described in Eq. (7). In the aqueous phase (liquid leachate), two principal forms of inorganic ammonia existed, namely free ammonia (NH_3) and ammonium ion (NH_4^+) [12]. As lime is an alkaline, the additions of lime increase the pH of leachate. Hence, the reaction is shifted to the right, forming the ammonia (NH_3) gas. Generally, at pH 10.5 to 12, most ammonium ions (NH_4^+) are in the form of NH_3 gas, thus resulting in a higher removal of ammonia [20–22]. Hence, pH 11 to 11.5 was reasonably optimal and effective range of maximum NH_3–N removal efficiencies which was up to 96.3%.

The response surface plots for NH_3–N removal at different lime dosage and an air flow rate, and different initial pH and air flow rate are shown in Figs. 4 and 5, respectively. The plot show the optimum points to be at lime dosage ranged from 5 to 10 g L^{-1}, initial pH ranged from 11 to 11.5 and air flow rate 2 to 2.5 L min^{-1}. It was observed that the value of removal efficiencies is reduced when moving away from these optimum points, meaning that either increase or decrease in any of the tested variable results in the decline of the responses. Besides, an increase in air flow rate may enhance the NH_3–N removal performances for scheduled waste landfill leachate, which agrees with previous findings [23,36,37].

3.3. Experimental condition optimization

Based on the factorial experiment results, the second order polynomial model was used in this study to confirm the validity of the statistical experimental strategies at optimum conditions for lime dosage, initial pH and air flow rate determined from RSM previously. In addition, once the models have been developed and checked for adequacy, optimization criteria can be selected to find out the operating conditions. The results suggest that the optimal conditions for maximum removal of NH_3–N were at lime dosage of 9.8 g L^{-1}, initial pH 11 and air flow rate of 2.25 L min^{-1}

Table 6
The optimum parameters and NH_3–N removal obtained by RSM

Lime dosage (g L^{-1})	pH	Air flow rate	RSM (%)	
			Actual	Predicted
9.8	11	2.25	96.3	96.5

(Table 6). The maximum value for NH_3–N removal via air stripping was estimated as 96.5%. To validate the optimum combination of the process variables, confirmatory experiments were carried out. The selected combinations of the three variables resulted in 96.3% NH_3–N removal (influent = 1347 mg L^{-1}, effluent = 49.5 mg L^{-1}). Ozturk et al. (2003) found that 8 g L^{-1} of $Ca(OH)_2$ was sufficient to bring the pH of young municipal landfill leachates to 12 and obtained good ammonia removal efficiency of 85% after 17 h of aeration treatment at a rate of 7.6 L min^{-1} [45].

In another study by Cheung et al. (1997), it was observed an air flow rate of 5 L min^{-1} with 10 g L^{-1} $Ca(OH)_2$ removed up to 90% of NH_3–N after 24 h of treatment [23]. However, in this study, 96.4% of NH_3–N were successfully removed from scheduled waste leachate at an initial pH of 11, 9.8 g L^{-1} of $Ca(OH)_2$ dosage and aeration treatment at a rate of 2.25 L min^{-1} for 24 h. Similarly, Marttinen et al. reported 89% ammonia removal at pH 11 at 20°C after 24 h [11]. The model prediction from the regression equation agreed well with the data from validation experiments. This verified that RSM approach was appropriate to optimize the operational conditions of the air stripping process in NH_3–N removal efficiency of scheduled waste leachate.

Therefore, the optimum values of the process variables were with lime dosage at 9.8 g L^{-1}, initial pH = 11 and air flow rate of 2.25 L min^{-1}. The pH after the addition of Ca $(OH)_2$ at this optimum condition is 11.89, which is in the range of favourable condition for ammonia removal (pH 10.5–12) as been discussed in previous study [20–22]. The permissible limit standard of NH_3–N is 20 mg L^{-1} and pH 9 as stated in Environmental Quality (Industrial Effluent or Mixed Effluent) Regulations 2009, Fifth Schedule (Standard B) [38]. However, the effluent after current treatment process still did not meet the discharge requirements. Air stripping method successfully reduced NH_3–N by 96.3% with the effluent and final pH of 49.5 mg L^{-1} and 10.21, respectively, after 24 h of treatment. Hence, further treatment should be carried out. The NH_3–N concentration in the effluent after air stripping process was low and suitable enough for biological treatment to take place effectively until the permissible limit standards was achieved.

4. Conclusions

It was proven in this study that optimization of air stripping process, including lime dosage ($Ca(OH)_2$), initial pH adjustment and air flow rates can significantly enhance the ammonia–nitrogen (NH_3–N) removal. Data analysis result by using response surface methodology (RSM) showed that the most suitable treatment of NH_3–N removal in this study was at an initial pH of 11 with a lime dosage of 9.8 g L^{-1} and air flow rate of 2.25 L min^{-1}, where up to 96.3% of NH_3–N had been successfully removed after 24 h of treatment. The results showed good agreement between experimental and model predictions. The verification experiments prove that RSM approach was appropriate for optimizing the air stripping process for NH_3–N removal of scheduled waste landfill leachate in laboratory scale.

Acknowledgement

This work were supported by Universiti Putra Malaysia (Vot No.: 9393400) and MyBrain15-MyPhD. The authors also wish to acknowledge their gratitude to the waste management centre for providing the leachate sample in this study.

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