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# Optimization of ammonia removal by ion-exchange resin using response surface methodology

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**Abstract** The ability of ion-exchange resin for ammonia removal from aqueous solution was studied. The results showed that Amberlite ion-exchange resin was effective in removing ammonia from aqueous solution. Factorial design and response surface methodology were applied to evaluate and optimize the effects of pH, resin dose, contact time, temperature and initial ammonia concentration. Low pH condition was preferred with the optimum pH found to be 6. High resin dose generated high removal rate and low exchange capacity. Results of factorial design and response surface methodology showed that temperature was not a significant parameter. The model prediction was in good agreement with observed data ( $R^2 = 0.957$ ). The optimum  $Q_e$  was 28.78 mg/ g achieved at pH = 6 and initial TAN concentration of 3000 mg/L. The kinetics followed the pseudo-second-order kinetic model ( $R^2 = 0.999$ ). Equilibrium data were fitted to Langmuir and Freundlich isotherm models with Langmuir model providing a slightly better predication ( $R^2 = 0.996$ ). The resin was completely regenerated by 2 N H<sub>2</sub>SO<sub>4</sub>.

**Keywords** Ammonia · Ion-exchange · Isotherm · Factorial design · Response surface methodology

# Introduction

In aqueous solution, ammonia exists in two forms: unionized ammonia ( $NH_3$ ) and ionized ammonia ( $NH_4^+$ ) with  $NH_3$  being the form that is toxic to most fish species even

M. Sartaj msartaj@uottawa.ca at low concentrations (0.53–22.8 mg/L) (Randall and Tsui 2002). The balance of these two types of ammonia is mainly a function of pH and temperature. It is common in aquatic chemistry to refer to and express the sum of the two as simply ammonia or total ammonia nitrogen (TAN) (Nair et al. 2014). The presence of excess ammonia can contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water bodies (Du et al. 2005). In addition, ammonia inhibition to the microorganism in biological treatments has been reported in the range of 1500–5000 mg/L as TAN (Lee et al. 2000; Liu et al. 2012).

Several treatment processes have been applied to remove ammonia from aqueous solution such as biological nitrification/denitrification, air stripping, adsorption and ion-exchange (Wang et al. 2007). Conventional aerobic and anaerobic biological degradation does not respond well to shock loads of ammonia (Karadag et al. 2006). Air stripping only provides satisfactory results in high pH conditions where most ammonia is in unionized form (NH<sub>3</sub>) (Marttinen et al. 2002). Adsorption by activated carbon was capable of eliminating ammonia from aqueous solution, but its adsorption capacity was reported to be relatively low (6.079 mg/g) compared to other adsorbent material that has high affinity for ammonia ion (Gotvajn et al. 2009). Hence, methods capable of efficient ammonia removal at reasonable cost are highly desired. Recently, ion-exchange has been applied in ammonia removal from aqueous solution due to the high removal efficiency and relatively simple operation (Bashir et al. 2010a; Lei et al. 2008; Lin and Wu 1996). Ion-exchange process involves a reversible interchange of ions between liquid and solid phase; i.e., the mobile ions of ion-exchange material can be replaced by similar charged ions from the surrounding medium (Bashir et al. 2010a).



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Solid ion exchanger can be classified as natural inorganic particles and synthetic organic resins. The first commercially used ion exchanger was natural zeolite (Bashir et al. 2010a). Zeolite was reported to have a classical aluminosilicate cage-like structure with high affinity for ammonium ion (Bernal and Lopez-Real 1993; Karadag et al. 2008; Lin et al. 2014; Rahmani et al. 2004). However, the development of synthetic ion-exchange resins has led to the replacement of natural zeolite in most modern applications due to the faster exchange rate, longer life and higher ion-exchange capacity (Letterman 1999). Synthetic organic resins are developed from high molecular weight polyelectrolytes and consist of a cross-linked polymer matrix where charged functional groups are attached by covalent bonding (Cheremisinoff 2001). Due to their controllable polymer matrices, functional groups, capacity and porosity during manufacturing process, resins can be made for a variety of applications (Letterman 1999).

Previous studies have confirmed the ability of different types of ion-exchange resins for removal of ammonia from aqueous solution. 100 % removal was achieved using Natype Dowex HCR-S strong acid cationic resin from synthetic ammonia solution of 20 mg/L at pH = 6 (Lin and Wu 1996). Approximately 39 and 29 mg/g of exchange capacity were achieved at initial TAN concentration of 200 mg/L by Dowex 50W-X8 and Purolite MN500 ion-exchange resins, respectively (Jorgensen and Weatherley 2003).

The main objective of this study was to evaluate and optimize ammonia removal by synthetic ion-exchange resin using factorial design and response surface methodology (RSM). The effect of different operational factors including pH, ion-exchange resin dose and temperature was also investigated. In addition, reaction kinetics and isotherms were modeled using existing common models.

## Materials and methods

## Ion-exchange resin characteristics

The synthetic ion-exchange resin used in this study was Amberlite IR120 H industrial-grade strong acid cation exchanger (obtained from Dow Chemical Co.). The resin had a total exchange capacity of  $\geq 1.80$  eq/L (H<sup>+</sup> form), moisture holding capacity of 53–58 %, a harmonic mean size in the range of 0.620–0.830 mm and a density of 800 g/L (Dow Chemical Co. 2013).

Ion-exchange resin was first washed with distilled water (DW) to remove adhering dirt and chemical impurities, and then, it was oven dried at 105 °C for 12 h. Then, based on results of preliminary tests, resin was pre-treated with different types of strong acids (HCl and  $H_2SO_4$ )



concentration at 0.1, 0.5, 1.0 normality (N) in sequence over 4 h to completely convert cation exchanger to their H<sup>+</sup> form (Bashir et al. 2010a). After that, resin was washed with DW again to remove all the acid and dried at room temperature ( $25 \pm 1$  °C).

#### Synthetic ammonia solution

Synthetic ammonia stock solution of 3000 mg/L as TAN was prepared by dissolving 5.72 g analytical-grade  $NH_4Cl$  into 500 mL distilled water. Then, the stock solution was diluted with DW to achieve desired concentration.

#### Analytical methods

The concentration of TAN in the liquid phase was determined by salicylate method (Method: 10205) TNTplus 832 test using a Hach DR6000 spectrophotometer. Solid phase concentration was calculated using a mass balance according to Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where  $Q_e$  is the mass of TAN exchanged per unit mass of resin (mg/g),  $C_0$  and  $C_e$  are initial and equilibrium concentration of TAN in the liquid phase (mg/L), respectively, V is the volume of solution (L) and m is the mass of resin (g).

The ammonia nitrogen removal efficiency was obtained by Eq. (2):

$$\Gamma \text{AN removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100\%$$
(2)

where  $C_0$  and  $C_e$  are initial and equilibrium concentration of TAN in the liquid phase (mg/L), respectively.

#### **Batch ion-exchange experiments**

Preliminary batch ion-exchange experiments were conducted to determine the effect of pH and optimum resin dose. Different amount of resin was added to 40 ml of synthetic ammonia solution with TAN concentration of 1000 mg/L in 50-ml centrifuge tubes. pH of the solution was adjusted by addition of 1 N NaOH or 1 N HCl. Samples were agitated by the shaker at 130 rpm for 24 h which was confirmed by another preliminary test that was more than enough to reach equilibrium. Then, solid phase and liquid phase were separated by centrifuging the sample at 8000 rpm for 10 min. TAN concentrations in the solution were then measured as explained above.

For the main phase of experiments, batch ion-exchange tests were conducted based on a factorial design at different pH, temperature and initial ammonia concentration. A  $3^2$ 

**Table 1** Independent variables

 of the experimental design

Independent variable	Symbol	Coded level					
		-1	-0.66	-0.11	+0.44	+1	
рН	рН	6	-	-	-	9.2	
Temperature (°C)	Т	26	-	-	-	32	
Initial TAN conc. (mg/L)	TAN	300	750	1500	2250	3000	

factorial design with pH (pH), temperature (T) and initial TAN concentration in the solution (TAN) as the independent variables was implemented. pH and temperature were coded at two levels at -1 and +1 at the designed ranges based on preliminary studies. pH = 6 was selected as the lower limit as it is the optimum pH while pH = 9.2 was chosen as the upper limit as it is close to the  $pK_a$  of ammonia. Room temperature of 26 °C and hot room temperature of 32 °C were coded as -1 and +1 level, respectively. In addition, initial TAN concentration was coded at five levels (-1, -0.11, -0.67, +0.44 and +1). The values of the independent variables are presented in Table 1. Initial TAN concentration of 300 mg/L was selected as the lower limit while 3000 mg/L was the upper limit. Each set of experiment was carried out in triplicate to ensure the reliability of the outcome response.

For each run, in order to obtain data to study isotherm, 1.0 g of resin was added into 40 mL of synthetic ammonia solution in 50-mL centrifuge tubes, containing concentrations in the range of 300–3000 mg/L as TAN. Samples were agitated in the shaker at 130 rpm for 24 h to achieve equilibrium. Then, samples were centrifuged at 8000 rpm for 10 min and concentrations of TAN in the solution were measured.

#### **Kinetics experiments**

4.0 g of resin was added to 400 mL synthetic ammonia solution with TAN concentration of 1000 mg/L in 1 L Erlenmeyer flask. The reactor was immediately subject to the agitation at 130 rpm. TAN concentrations were measured at 1, 2, 5, 10, 20, 30, 60, 120, 240 and 360 min after the shaking started.

#### Statistical analysis

The RSM is a combination of mathematical and statistical techniques commonly used in optimization of chemical reactions and industrial processes (Dong and Sartaj 2016; Ölmez 2009). In this study, RSM was used to evaluate the process of ammonia removal from aqueous solution using resin and to optimize the removal capacity ( $Y_1$ ) as the outcome response. The behavior of the system is usually described by the quadratic equation shown as Eq. (3) (Montgomery 2008).

$l=1$ $l=1$ $l\neq 1$	$Y_1 = A_0 +$	$\sum_{i=1}^{n} A_i X_i + 1$	$\sum_{i=1}^n A_{ii}X_i^2 +$	$\sum_{i\neq 1j=1}^n A_{ij}X_iX_j + \varepsilon$	(3)
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where  $Y_1$  is the outcome response;  $X_i$  and  $X_j$  are the independent variables;  $A_0$  is the value of the fixed response at the center point of the design;  $A_i$ ,  $A_{ii}$  and  $A_{ij}$  are the interaction coefficients of linear, quadratic and second-order terms, respectively; n is the number of independent variable; and  $\varepsilon$  is the random error. The accuracy of the model described above was evaluated by the correlation coefficient ( $R^2$ ). To judge the significance of the model as well as each model term, F value (Fisher variation ratio) and probability value (Prob > F) were applied (Montgomery 2008). Adequate precision ratio was checked to measure the signal-to-noise ratio. Also, lack of fit of the model was evaluated to check whether there is still some variation unaccounted in the model and the need to add additional terms to improve the model (Xu et al. 2014).

#### Regeneration

The regeneration of Amberlite IR120 H ion-exchange resin was also studied. Exhausted resin was regenerated by immersion in 2 N  $H_2SO_4$  for 12 h according to manufacturer's guide (Dow Chemical Co. 2013). The exchange capacities for both virgin and regenerated resin were evaluated to obtain the amount of exchange capacity lost due to the regeneration process.

## **Results and discussion**

## Effect of pH

As a preliminary set of experiment, the effect of pH on removing TAN from aqueous solution by using ion-exchange resin was studied within the range from pH = 4 to pH = 10 at room temperature ( $25 \pm 1 \,^{\circ}$ C). Maximum removal occurred at pH = 6, which was in good agreement with Ding and Sartaj (2015).  $Q_e$  slightly increased with the pH increase from 4 to 6 and then started to decrease as pH was further increased to 10. The decrease in  $Q_e$  may be explained by the fraction of ionized (NH<sub>4</sub><sup>+</sup>) and unionized ammonia (NH<sub>3</sub>) in aqueous solution. Under low pH conditions (pH < 7), the majority of ammonia is in the form of



 $NH_4^+$ , while under high pH conditions (pH > 7),  $NH_3$  starts to become the dominant species (Dong and Sartaj 2016). For optimum ion-exchange operation, it is preferred to keep ammonia in ionized form to enhance the main removal mechanism which is mainly cation exchange. Thus, pH = 6 was selected for subsequent kinetic. As stated before, the lower and upper limits for factorial design of main experiments were chosen pH = 6 and pH = 9.2, respectively.

# Effect of resin dose

The effect of resin dose on the removal efficiency and  $Q_e$ was evaluated by adding 0.5, 1.0, 2.0 and 4.0 g of ionexchange resin into 40 mL synthetic ammonia solution with initial TAN concentration of 1000 mg/L, which is equal to 12.5, 25, 50 and 100 g/L of dose. The removal efficiency increased from approximately 30 to 84 % with the increasing ion-exchange resin dose. However, an opposite trend was found in terms of the amount of TAN removed per gram of ion-exchange resin. It decreased from 23.49 mg/g at a dose of 12.5 g/L to only 8.43 mg/g at 100 g/L. Although 12.5 g/L was the optimum dose within the range studied in this set of experiment in terms of exchange capacity, from a practical point of view, a dose of 25 g/L was selected for subsequent experiments in order to achieve a higher removal rate and to keep the amount of resin used to a minimum and to keep the mix in a slurry form, and be able to collect adequate solution at the end.

#### **Kinetics studies**

Figure 1 shows ammonia uptake by resin as a function of time.  $Q_t$  increased with increasing contact time in the first 30 min, and then, equilibrium was reached. After that, there was no significant increase in  $Q_e$ . This result was in good agreement with results reported by Lin and Wu (1996).



Fig. 1 Effect of contact time on ammonia removal by ion-exchange resin and pseudo-second-order model predication (initial TAN concentration of 1000 mg/L)



 Table 2 Kinetic modes for evaluating ammonia removal by ion-exchange resin

Model	Linearized equation	$R^2$
Pseudo-first order	$\ln \frac{q_e - q_t}{q_e} = -k_1 t$	0.419
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	0.999
First order	$\ln(q_t) = \ln(q_e) + k_1't$	0.215
Second order	$\frac{1}{q_t} = \frac{1}{q_e} + k_2' t$	0.173
Third order	$\frac{1}{q_t^2} = \frac{1}{q_e^2} + k_3' t$	0.136
Parabolic diffusion	$\ln(q_t) = \ln(k_d) + \frac{1}{2}\ln(t)$	0.725
Elovich's reaction	$q_t = q_e + \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$	0.787

Seven different kinetic models were applied to investigate the kinetics of ammonia removal by resin from aqueous solution. Linear regression was used to determine the best fit among those seven models. Table 2 summarizes the linearized equations of the selected seven kinetic models and their correlation coefficients ( $R^2$ ). According to the results, pseudo-second-order rate expression provided the best fit with the highest  $R^2$  (0.999). Pseudo-second-order model has been widely applied to describe kinetics of sorption and ionexchange process (Bashir et al. 2010a; Ho and McKay 1999; Zhang et al. 2013), as described mathematically below:

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where  $q_t$  is the amount of TAN exchanged per unit mass of resin at time t (mg/g);  $q_e$  is the amount of TAN exchanged per unit mass of resin at equilibrium (mg/g); t is contact time (min); and  $k_2$  is the rate constant of pseudo-secondorder expression (g/(mg h)). Linear regression was achieved by rearranging Eq. (4) into Eq. (5). The rate constant  $k_2$  was found from the intercept of Y axis  $\left(\frac{1}{k_2q_e^2}\right)$  by plotting  $t/q_t$  versus t. Figure 1 also shows the comparison of the actual experimental data and the predication from pseudo-second-order model.

# Isotherms

Isotherm models could be used to characterize the equilibrium behavior of ion-exchange resin at different ammonia concentrations. Therefore, two commonly used models (Langmuir and Freundlich isotherms) were applied to evaluate the experimental data. The equation of Langmuir isotherm is shown in Eq. (6).

$$Q_e = \frac{abC_e}{1+bC_e} \tag{6}$$



where  $Q_e$  is the mass of TAN exchanged into solid phase per unit mass of resin at equilibrium (mg/g); a (mg/g) and b (L/mg) are the constants; and  $C_e$  is equilibrium concentration of TAN in solution (mg/L). By rearranging the Langmuir equation into its linear form shown as Eq. (7), the constants *a* and *b* can be determined by plotting  $C_e/Q_e$  versus  $C_e$  (Fig. 2).

3.5

3.0

2.5

2.0

л

5

 $\ln Q_{\rm e}$ 

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \tag{7}$$

Freundlich isotherm is an empirical model widely used for the characterization adsorption behavior of mono layer binding with heterogeneous binding sites (Umpleby II et al. 2004). The Freundlich equation and the corresponding linearized form are mathematically illustrated as Eqs. (8) and (9), respectively. The constants  $K_f$  and 1/n can be determined by plotting  $\ln Q_e$  versus  $\ln C_e$  and the results are shown in Fig. 2.

$$Q_e = K_f C_e^{1/n} \tag{8}$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{9}$$

where  $Q_e$  is the mass of TAN exchanged into solid phase per unit mass of resin at equilibrium (mg/g);  $C_e$  is equilibrium concentration of TAN in solution (mg/L);  $K_f$  is Freundlich capacity factor (L/mg); and 1/n is Freundlich intensity parameter.

Figure 3 shows both Langmuir and Freundlich isotherm models along with experimental data. The constants and correlation coefficients for both Langmuir (a = 29.76 mg/g, b = 0.005 L/mg) and Freundlich ( $K_f = 3.3$  L/mg, 1/ n = 0.28) models were calculated. Both models performed well in describing the adsorption process; however, Langmuir isotherm model provided a better fit to the experimental data (higher  $R^2$  value of 0.996) compared to Freundlich isotherm model. The result was consistent with a previous study (Sharma et al. 2009). The Langmuir isotherm assumes only one solute molecule per site as well as a fixed number of sites, which provides a good prediction of ion-



Fig. 3 Equilibrium data of ammonia removal from aqueous solution by ion-exchange resin fitted to Langmuir and Freundlich isotherms

exchange process at equilibrium (Jorgensen and Weatherley 2003). The Langmuir constant a gave a measure of relative ammonia exchange capacity (Liu and Lo 2001). The value obtained in this study (29.76 mg/g) was higher than the one reported by Bashir et al. (2010a) using another ion-exchange resin (12.56 mg/g).

## Statistical analysis and modeling

Based on a factorial design of three independent variables. a total of 60 runs of the ammonia removal experimental results in terms of the exchange capacity  $(Q_e)$  were obtained. The response  $Q_e$  was predicted by a second-order polynomial equation shown as Eq. (10) below.

$$Q_e = 22.501 - 2.199 \text{pH} + 0.019 \text{T} + 7.434 \text{TAN} + 0.047 \text{pH} * \text{T} - 0.782 \text{pH} * \text{TAN} + 0.140 \text{T} * \text{TAN} - 5.442 \text{TAN}^2$$
(10)

Table 3 shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for  $Q_e$  (ammonia removal) using the results of all experiments performed. The model F value of 168.10 and the Prob > F value of < 0.0001 indicate that the model was statistically significant for ammonia removal.



Source	Full quadratic				Reduced			
	DF	Sum of squares	F value	$\operatorname{Prob} > F$	DF	Sum of squares	F value	$\operatorname{Prob} > F$
Model	7	2371.47	168.10	< 0.0001	4	2370.72	308.82	< 0.0001
pН	1	287.59	142.70	< 0.0001	1	287.59	149.85	< 0.0001
Т	1	0.022	0.011	0.9175	_	_	-	_
TAN	1	1743.86	865.30	< 0.0001	1	1743.86	908.64	< 0.0001
pH*T	1	0.13	0.066	0.7976	_	_	-	_
pH*TAN	1	19.33	9.59	0.0031	1	19.33	10.07	0.0025
T*TAN	1	0.62	0.31	0.5818	_	_	-	_
TAN <sup>2</sup>	1	294.70	146.23	< 0.0001	1	294.70	153.56	< 0.0001
Resid. error	52	104.80	_	_	55	105.56	_	_
Lack of fit	12	80.13	10.83	< 0.0001	15	80.89	8.74	< 0.0001
Pure error	40	24.67	_	_	40	24.67	_	_
Total	59	2476.27	_	_	59	2476.27	_	_
	$R^2 = 0.952$	$R_{\rm adj}^2 = 0.943,$		$R_{\rm pred}^2 = 0.952,$	$R^2 = 0.957,$	$R_{\rm adj}^2 = 0.950,$		$R_{\rm pred}^2 = 0.954,$
	Adequate precision $= 37.522$			Adequate precision $= 48.172$				

Table 3 ANOVA for quadratic model parameters

For parameters T, pH\*T and T\*TAN, the Prob > F value was greater than 0.050, indicating that these model terms were insignificant and hence could be eliminated from the model.

The reduced form of the model is shown in Eq. (11) and presented in Table 3. As given in Table 3, the reduced quadratic model was significant with a model *F* value of 308.82 and the Prob > *F* value of <0.0001. This showed that there was only a 0.01 % chance that an *F* value this large could occur due to the noise. The adjusted  $R^2 (R_{adj}^2)$ value of the reduced model was 0.950 compared to a value of 0.943 for the full model showing a slight improvement after eliminating insignificant terms (Sapsford and Jupp 2006). An adequate precision ratio of 48.172 indicates an adequate signal (adequate precision >4) (Bashir et al. 2010b).

$$Q_e = 21.50 - 2.20 \text{pH} + 7.43 \text{TAN} - 0.78 \text{pH} \\ * \text{TAN} - 5.44 \text{TAN}^2$$
(11)

The correlation coefficient  $(R^2)$  provides a measure of the goodness of the fit for the predicted outcomes by the model and the observed data within the range of experiment. The  $R^2$  obtained in this study was 0.957 ( $R^2_{adj} = 0.950$ ), indicating a very good agreement between the predicted response and observed results. Figure 4 illustrates the plot of calculated outcomes by the model versus observed experimental data for ammonia removal. The results of ANOVA showed that the lack of fit was significant. This means that there might be some systematic variation



Fig. 4 Predicted versus observed experimental values for  $Q_e$ 

unaccounted for in the model (Xu et al. 2014). This may also due to the close replicate values that provide an estimate of pure error (Bashir et al. 2010b). Introducing a higher-order term to the model could result in a more complicated model, with higher number of terms, with insignificant lack of fit. In fact, in this case a quartic model showed no significant lack of fit; however, the reduced quadratic model was considered to be appropriate to navigate the design space due to the high  $R^2$  value and adequate precision ratio.  $R_{adj}^2 = 0.950$  indicates that only 5 % of the total variation could not be explained by the empirical model.

Analysis of residuals is necessary to confirm that the assumptions for the ANOVA are met. To ensure that adequate approximation is provided by this model to the







Fig. 6 Diagnostic plots for ammonia removal a standardized residual versus runs and b standardized residuals versus predicted

real system, diagnostic plots of residuals were produced and evaluated. Figure 5 shows the normal probability plots of standardized residual. If the residuals follow a normal distribution without any obvious pattern, all the points will follow a straight line. From Fig. 5, it shows a reasonable good fit of the normal probability percentage versus standardized residuals, which represents that the model prediction statistically fits the observed results. Figure 6a, b is standardized residual versus runs and predicted values, respectively. As can be seen, no obvious patterns were shown in both plots. All the standardized residuals were randomly scattered within the range (-2 to +2) across the graph, confirming that the model was accurate and there was no need to suspect any violation of the independence or constant variance assumption in all runs.

#### **Response surface methodology**

As temperature (T) was found not to be a significant model parameter and was excluded from Eq. (11), RSM was utilized to evaluate the interaction between two independent variables (pH and initial TAN conc.) and the response ( $Q_e$ ). A three-dimensional surface plot and a two-dimensional contour plot of the quadratic model are shown in Fig. 7. It is obvious from the figure that  $Q_e$ increased significantly as the initial TAN concentration increased and the pH decreased. The impact of initial







TAN was greater than that of pH. The optimum pH and initial TAN concentration for ammonia removal in terms of  $Q_e$  were found to be -1.0 for pH (pH = 6) and +1.0for initial TAN concentration (3000 mg/L), and the maximum  $Q_e$  predicted within the range of experiment is 27.47 mg/g.

# Regeneration

The equilibrium exchange capacities of virgin and regenerated ion-exchange resins were compared. There appeared to be no noticeable difference in virgin and regenerated resin in terms of  $Q_e$ . Thus, the ion-exchange resin used in this study can be almost completely regenerated by 2 N  $H_2SO_4$ .

# Conclusion

Experimental results indicated that the Amberlite ion-exchange resin can be effectively used to remove ammonia from aqueous solution and can be used to treat or pre-treat any wastewater containing high ammonia concentration such as landfill leachate.



Removal strongly depends on pH and ammonia concentration with the optimum pH found to be around 6. The removal efficiency also increased with the increasing resin dose while  $Q_{\rho}$  decreased with the increasing resin dose.

Statistical analysis of experimental data based on a factorial design and RSM showed that temperature was not a significant parameter in this process. The correlation coefficient of determination  $R^2$  was 0.957, indicating that the observed results fitted well with the model prediction. Surface plot and contour plot showed the optimum  $Q_e$  achieved within the range of experiment was 27.47 mg/g at pH of 6 and initial TAN concentration of 3000 mg/L.

The pseudo-second-order kinetic model provided the best predication ( $R^2 = 0.999$ ) for the ammonia removal process among seven selected kinetic models. Both Freundlich and Langmuir isotherm models were able to describe the results well ( $R^2 = 0.996$  and  $R^2 = 0.987$ , respectively).

The ion-exchange resin used in this study can be completely regenerated by proper procedures.

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