

**Statistical Analysis and Optimization of Ammonia Removal from  
Aqueous Solution by Zeolite and Ion-exchange Resin**

By  
**Yuanhao Ding**

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Under the supervision of Dr. Majid Sartaj

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Department of Civil Engineering  
University of Ottawa  
Ottawa-Carleton Institute for Environmental Engineering  
Ottawa, Ontario, Canada

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## ABSTRACT

The ability of natural zeolite and synthetic ion-exchange resin for ammonia removal from aqueous solution was studied through batch experiments. The results showed that both zeolite and ion-exchange resin were effective (up to 87% of removal) in eliminating ammonia from aqueous solution. Factorial design and response surface methodology were applied to evaluate and optimize the effects of pH, dose, contact time, temperature and initial ammonia concentration. Low pH condition was preferred with the optimum pH found to be 6 for both zeolite and ion-exchange resin. High 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 ( $R^2 = 0.969$  for zeolite and  $R^2 = 0.957$  for resin, respectively). For zeolite, the optimum  $Q_e$  was 22.90 mg/g achieved at pH=7 and initial ammonia concentration of 3000 mg/L. For ion-exchange resin,  $Q_e$  of 28.78 mg/g was achieved at pH=6 and initial TAN concentration of 3000 mg/L. The reaction kinetics for both of them followed the Pseudo-second order kinetic model ( $R^2=0.998$  and  $R^2=0.999$ , respectively). Equilibrium data were fitted to Langmuir and Freundlich isotherm models with Freundlich model providing a slightly better prediction for zeolite ( $R^2=0.992$ ) and Langmuir providing more accurate prediction for ion-exchange resin ( $R^2=0.996$ ). The ion-exchange resin can be completely regenerated by 2N  $H_2SO_4$ .

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## Table of Contents

ABSTRACT .....	i
ACKNOWLEDGEMENTS .....	ii
Table of Contents .....	iii
List of Figures .....	vi
List of Tables .....	viii
List of Abbreviations .....	ix
CHAPTER I .....	1
1.1 Background .....	1
1.2 Objectives .....	2
1.3 Methodology .....	3
1.4 Thesis layout .....	3
References .....	5
CHAPTER II .....	6
2.1 Ammonia .....	6
2.2 Issues of the excess ammonia .....	7
2.3 Ammonia toxicity .....	7
2.4 Ammonia Inhibition .....	8
2.5 Ammonia concentrations .....	9
2.6 Treatments for high concentration ammonia removal .....	11
2.6.1 Mixed with domestic wastewater .....	11
2.6.2 Biological treatment .....	12
2.6.3 Chemical precipitation .....	14
2.6.4 Air stripping .....	15
2.6.5 Adsorption by activated carbon .....	16
2.6.6 Ion-exchange resin .....	17
2.6.7 Zeolite .....	20
2.6.8 Membrane processes .....	24
2.6.9 Ultrasound .....	27
2.6.10 Microwave .....	28
2.7 Summary .....	29
References .....	31
CHAPTER III .....	41
3.1 Batch tests .....	41
3.2 Ion-exchange resin .....	42
3.3 Zeolite .....	44
3.4 Synthetic ammonia solution .....	46
3.5 Analytical methods .....	47
3.6 Effect of pH .....	49

3.7	Effect of dose .....	49
3.8	Kinetics.....	50
3.9	Adsorption isotherms .....	50
3.10	Factorial design and statistical analysis .....	51
3.11	Regeneration of ion-exchange resin .....	53
	References.....	54
CHAPTER IV .....		55
	Abstract.....	55
4.1	Introduction .....	57
4.2	Material and methods .....	58
4.2.1	Zeolite characteristics .....	58
4.2.2	Synthetic ammonia solution .....	59
4.2.3	Analytical methods .....	60
4.2.4	Batch adsorption experiments.....	60
4.2.5	Kinetics experiments .....	62
4.2.6	Statistical analysis.....	62
4.3	Results and discussion.....	63
4.3.1	Effect of pH .....	63
4.3.2	Effect of zeolite dose .....	64
4.3.3	Kinetics studies .....	65
4.3.4	Adsorption isotherms.....	67
4.3.5	Statistical analysis and modelling.....	71
4.3.6	Response surface methodology .....	75
4.4	Conclusion.....	77
	Acknowledgements.....	77
	References.....	78
CHAPTER V .....		81
	Abstract.....	81
5.1	Introduction .....	83
5.2	Material and methods .....	85
5.2.1	Ion-exchange resin characteristics .....	85
5.2.2	Synthetic ammonia solution .....	86
5.2.3	Analytical methods .....	86
5.2.4	Batch ion-exchange experiments .....	87
5.2.5	Kinetics experiments .....	88
5.2.6	Statistical analysis.....	89
5.2.7	Regeneration .....	89
5.3	Results and discussion.....	90
5.3.1	Effect of pH .....	90
5.3.2	Effect of resin dose .....	91
5.3.3	Kinetics studies.....	92

5.3.4	Isotherms.....	94
5.3.5	Statistical analysis and modelling.....	98
5.3.6	Response surface methodology .....	102
5.3.7	Regeneration .....	104
5.4	Conclusion.....	104
	Acknowledgements.....	105
	References.....	106
	CHAPTER VI .....	109
6.1	Effect of pH.....	109
6.2	Reaction rate.....	110
6.3	Isotherms .....	110
	CHAPTER VII .....	112
7.1.	Conclusions .....	112
7.2.	Future work .....	113
	APPENDIX .....	114

## List of Figures

Fig. 2.1 Percent of ionized ammonia in the aqueous solution as a function of pH and temperature (Lin and Wu, 1996).....	7
Fig. 2.2 Scheme of ion-exchange process.....	18
Fig. 2.3 Amberlite IR120 H synthetic ion-exchange resin .....	18
Fig. 2.4 Equilibrium exchange capacity of virgin and regenerated Na-type Dowex HCR-S ion-exchange resin (Lin and Wu, 1996).....	20
Fig. 2.5 Basic zeolite structure (IZA-SC, 2001) .....	21
Fig. 2.6 Granular natural zeolite .....	21
Fig. 2.7 Categories of membrane separation processes (Till and Mallia, 2001) .....	24
Fig. 2.8 RO process for complete desalination (Till and Mallia, 2001) .....	27
Fig. 2.9 Scheme of the ultrasound set-up (Wang et al., 2008).....	28
Fig. 3.1 50mL plastic centrifuge tube as the batch reactor.....	41
Fig. 3.2 Innova 2000 orbital shaker .....	42
Fig. 3.3 Amberlite IR120 H .....	43
Fig. 3.4 Natural zeolite .....	46
Fig. 3.5 Analytical grade ammonium chloride .....	47
Fig. 3.6 HACH TNT832 ammonia vial .....	48
Fig. 3.7 HACH DR6000 spectrophotometer .....	48
Fig. 4.1 The effect of pH on TAN removal from aqueous solution by using natural zeolite (initial TAN concentration of 1000 mg/L and a zeolite dose of 75 g/L).....	64
Fig. 4.2 The effect of adsorbent dose on $Q_e$ and removal efficiency (initial TAN concentration of 1000 mg/L) .....	65
Fig. 4.3 Effect of contact time on ammonia removal by zeolite and Pseudo-second order model prediction .....	67
Fig. 4.4 Linearized Langmuir isotherm plots for ammonia removal from aqueous solution by zeolite.....	68
Fig. 4.5 Linearized Freundlich isotherm plots for ammonia removal from aqueous solution by zeolite.....	69
Fig. 4.6 Equilibrium data of ammonia removal from aqueous solution by zeolite fitted to Langmuir and Freundlich isotherms .....	70
Fig. 4.7 Predicted versus observed experimental values for the reduced model .....	73

Fig. 4.8 Normal probability plot of the standardized residual for ammonia removal .....	74
Fig. 4.9 Diagnostic plots for ammonia removal (a) standardized residual versus runs, and (b) standardized residuals versus predicted .....	75
Fig. 4.10 Surface plot by response surface methodology .....	76
Fig. 4.11 Contour plot by response surface methodology .....	76
Fig. 5.1 The effect of pH on TAN removal from aqueous solution by using ion-exchange resin (initial TAN concentration of 1000 mg/L and a zeolite dose of 75 g/L).....	91
Fig. 5.2 The effect of adsorbent dose on $Q_e$ and removal efficiency (initial TAN concentration of 1000 mg/L).....	92
Fig. 5.3 Effect of contact time on ammonia removal by zeolite and Pseudo-second order model predication.....	94
Fig. 5.4 Linearized Langmuir isotherm plots for ammonia removal from aqueous solution by ion-exchange resin.....	95
Fig. 5.5 Linearized Freundlich isotherm plots for ammonia removal from aqueous solution by ion-exchange resin.....	96
Fig. 5.6 Equilibrium data of ammonia removal from aqueous solution by ion-exchange resin fitted to Langmuir and Freundlich isotherms.....	97
Fig. 5.7 Predicted versus observed experimental values for the reduced model.....	100
Fig. 5.8 Normal probability plot of the standardized residual for ammonia removal...	101
Fig. 5.9 Diagnostic plots for ammonia removal (a) standardized residual versus runs, and (b) standardized residuals versus predicted.....	102
Fig. 5.10 Surface plot by response surface methodology.....	103
Fig. 5.11 Contour plot by response surface methodology.....	103
Fig. 6.1 Comparison between zeolite and ion-exchange resin (pH).....	109
Fig. 6.2 Comparison between zeolite and ion-exchange resin (kinetics).....	110
Fig. 6.3 Comparison between zeolite and ion-exchange resin (isotherms).....	111

## List of Tables

Table 2.1 Ammonia concentrations in different landfill sites.....	10
Table 2.2 Air Stripping Process Efficiency.....	16
Table 2.3 Ammonia adsorption capacity of different zeolite.....	23
Table 3.1 Properties of Amberlite IR120 H.....	44
Table 3.2 Rock analysis of zeolite.....	45
Table 3.3 Independent variables of the experimental design (zeolite).....	52
Table 3.4 Independent variables of the experimental design (ion-exchange resin).....	52
Table 4.1 Rock analysis of zeolite.....	59
Table 4.2 Independent variables of the experimental design.....	61
Table 4.3 Kinetic modes for evaluating ammonia removal by zeolit.....	66
Table 4.4 Isotherm constants for zeolite.....	70
Table 4.5 ANOVA for quadratic model parameters.....	72
Table 4.6 Model coefficient and CI (zeolite).....	72
Table 5.1 Properties of Amberlite IR120 H.....	85
Table 5.2 Independent variables of the experimental design.....	88
Table 5.3 Kinetic modes for evaluating ammonia removal by ion-exchange resin.....	93
Table 5.4 Isotherm constants for ion-exchange resin.....	97
Table 5.5 ANOVA for quadratic model parameters.....	99
Table 5.6 Model coefficient and CI (IER).....	99
Table 6.1 Summary of isotherm models.....	111
Table A1 ANOVA of reduced model (zeolite).....	114
Table A2 ANOVA of reduced model (ion-exchange resin).....	114

## List of Abbreviations

AD: anaerobic digestion;

ANOVA: analysis of variance

AOXs: adsorbable organic halogens;

AS: activated sludge;

BOD: biochemical oxygen demand;

CI: confidence interval;

COD: chemical oxygen demand;

DF: degree of freedom;

DW: distilled water

IER: ion-exchange resin;

MAP: magnesium ammonium phosphate;

MF: microfiltration;

MLSS: mixed liquor suspended solids;

MS: mean square

NF: nanofiltration;

PAC: powdered activated carbon;

PAHs: polyaromatic hydrocarbons;

PCBs: polychlorinated biphenyls

RO: reverse osmosis;

RSM: response surface methodology;

SBR: sequencing batch reactor;

TAN: total ammonia nitrogen;

UASB: up-flow anaerobic sludge blanket;

UF: ultrafiltration;

VIF: Variance inflation factor;

VSS: volatile suspended solid.

# CHAPTER I

## INTRODUCTION

### 1.1 Background

Ammonia is considered the most commonly encountered nitrogen compound in the liquid phase and it is one of the most important pollutants in the aquatic environment because of its highly toxic nature as well as the ubiquity in surface water systems (Rand, 1995). In aqueous solution, ammonia exists in two forms: unionized ammonia ( $\text{NH}_3$ ) and ionized ammonia ( $\text{NH}_4^+$ ). 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). Ammonia can enter aquatic system via different means such as municipal effluent discharges, landfill leachate, run-off from agricultural activities, i.e. application of fertilizers and the excretion of nitrogenous wastes from animals (Metcalf and Eddy, 2003).

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 of microorganism in biological processes has been reported to occur in the range of 1500 to 5000 mg/L as TAN (Lee et al., 2000; Liu et al., 2012). USEPA has announced an updated fresh water quality criteria for ammonia of 17 mg/L (acute) and 1.9 mg/L (chronic), respectively as TAN at pH =7 and T= 20°C (USEPA, 2013). In Canada, the maximum concentration of un-ionized ammonia in the effluent has been set at 1.25 mg/L as  $\text{NH}_3\text{-N}$ , at 15°C  $\pm$ 1°C (Government of Canada, 2012).

Conventional treatment processes to remove ammonia from aqueous solution include biological nitrification/denitrification, air stripping, adsorption and ion-exchange (Wang et al., 2007). Application of different removal technologies at reasonable cost as a treatment or pre-treatment method has been one of the main research topics in recent years.

## **1.2 Objectives**

Sunflower seed, chitosan, coffee residual, activated carbon, natural zeolite and ion-exchange resin were first tested and among these materials, zeolite and ion-exchange resin were selected as potential adsorbents due to the high adsorption capacity of ammonia. The main objective of the present research was to study the ability and performance of natural zeolite and synthetic ion-exchange resin for removal of ammonia from high concentration aqueous solution.

Objectives specific to this research include:

- Evaluate and optimize ammonia removal using factorial design and response surface methodology (RSM) at different pH, temperature and initial ammonia concentration levels.
- Study and model the isotherms using existing common models.
- Investigate the reaction kinetics
- Determine the optimum pH and the effect of zeolite/ion-exchange resin dose.
- Study the regeneration ability of the synthetic ion-exchange resin.
- Compare the performance of zeolite and ion-exchange resin.

### **1.3 Methodology**

A preliminary comparison study was conducted to evaluate the equilibrium adsorption/ion-exchange capacity of zeolite, activated carbon, sunflower seed, chitosan, coffee residual and ion-exchange resin for removal of ammonia. Natural zeolite and synthetic ion-exchange resin were selected as their removal capacities were much higher than that of other materials.

Synthetic ammonia solution was used to simulate highly contaminated wastewater with high strength of ammonia. The zeolite and ion-exchange resin used in this study were both commercial products.

The research was carried out by batch adsorption/ion-exchange tests. Preliminary batch experiments were conducted to determine the effect of pH and dose. A factorial design with coded pH, temperature and initial ammonia concentration as independent variables was followed as the main phase of the study. In order to statistically analyze the results, each set up was run in triplicate. In addition, reaction kinetics was also studied to obtain the effect of contact time.

### **1.4 Thesis layout**

The thesis is presented in the form of technical papers, and divided into seven main chapters. Chapter I contains the introduction, the statement of the problem, the objectives of the research and the thesis organization. Chapter II is the literature review of the presence of high concentration ammonia in aqueous solution especially in landfill leachate and the treatment processes. Following Chapter III is the material and methods of this study. Chapter IV is the first technical paper entitled: “ Statistical Analysis and Optimization of Ammonia Removal from Aqueous Solution by Zeolite Using Factorial Design and Response Surface Methodology”. Chapter V is the second technical paper

entitled: “ Statistical analysis and optimization of ammonia removal from aqueous solution by an ion-exchange resin using factorial design and response surface methodology”. Chapter VI is the comparison between natural zeolite and ion-exchange resin. In the last chapter, a summary of important results and conclusions throughout the thesis are presented. Also, recommendations of future work on this research subject are included in the last chapter. It is necessary to mention that there could be some repeated information appearing in different chapters due to the paper based format.

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## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Ammonia

Ammonia ( $\text{NH}_3$ ) is the most commonly encountered nitrogen compound in liquid phase. It is considered one of the most important pollutants in the aquatic environment not only because of its high toxicity and ubiquity in surface water systems, but also because many effluents have to be treated extensively in order to keep the concentrations of ammonia in surface waters from being unacceptably high (Rand, 1995; USEPA, 2009). Ammonia can enter the aquatic system via direct ways such as municipal effluent discharges or indirect ways such as nitrogen fixation and run-off from animal raising operations. Moreover, effluents without proper ammonia removal treatments from industrial processes, agricultural run-off and migration of landfill leachate to the groundwater system also introduce large amounts of ammonia into aquatic environment (USEPA, 2009).

Chemically, ammonia is very soluble in water and it exists in liquid phase either in unionized form ( $\text{NH}_3$ ) or ionized form ( $\text{NH}_4^+$ ) depending on the pH and temperature. The balance of two types of ammonia is expressed by Eq. (2.1) and Fig. 2.1 below (Morel, 1993). The  $\text{pK}_a$  of ammonia at 25 °C is around 9.26 (Metcalf and Eddy, 2003). 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). Ammonia behaves as a moderately strong base with  $\text{pK}_a$  values to be within the range of approximately 9 to 10 depending on the temperature and ionic strength (Morel, 1993).

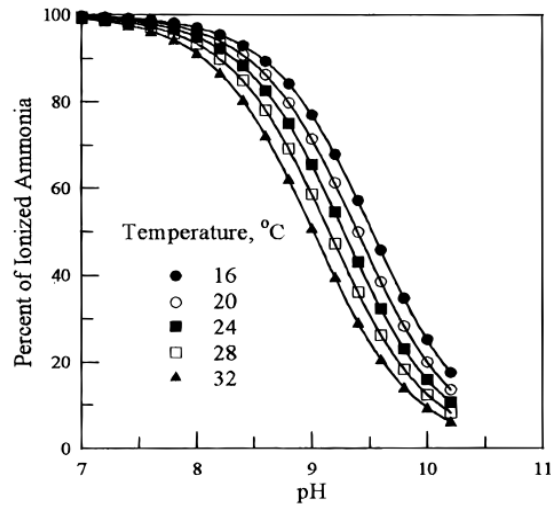


Fig. 2.1 Percent of ionized ammonia in the aqueous solution as a function of pH and temperature (Lin and Wu, 1996)

## 2.2 Issues of the excess ammonia

Ammonia is an important nitrogen compound in freshwater. However, excess ammonia can boost phytoplankton, exhibit toxicity to aquatic system and exert an oxygen demand in receiving water body (Beutel, 2006). The need to reduce ammonia inputs to aquatic ecosystem in order to protect drinking water resource as well as to reduce eutrophication including the proliferation of harmful algal blooms and dead zones in water ecosystems has widely received recognitions (Conley et al., 2009).

## 2.3 Ammonia toxicity

Most biological membranes are permeable to free ammonia ( $\text{NH}_3$ ) but relatively impermeable to ionized ammonia ( $\text{NH}_4^+$ ). Therefore, free ammonia is much more toxic

than ionized ammonia. Because the fraction of free ammonia in liquid phase increases with the increasing pH and temperature, the toxicity of ammonia to organisms also increases with those two parameters (Randall and Tsui, 2002). To aquatic life, in general, neither freshwater species nor seawater species are tolerant to ammonia with freshwater species has a slightly higher tolerance than the seawater species (2.79 compared to 1.86 mg/L as TAN) (USEPA, 2009). The nature of ammonia toxicity is similar in fish and mammals (Shingles et al., 2001).

A variety of deleterious effects of having high levels of ammonia in the body were have been reported (Ip and Chew, 2010). Severe ammonia toxicity is mainly because of its effect on the central nervous system of vertebrates, acute ammonia intoxication and convulsion (Rao et al., 1992). Some evidence has been found to indicate that the presence of high ammonia levels in the brain can lead to high levels of extracellular glutamate by increasing glutamate release and decreasing glutamate synaptic reuptake (Randall and Tusi, 2002). Based on the data available, it has been confirmed that elevated ammonium ion displaces potassium and depolarized neurons, which causes excessive activation of NMDA type glutamate receptor leading to subsequent cell death in the central nervous system because of the influx of excess calcium (Ip and Chew, 2001).

## **2.4 Ammonia inhibition**

In addition to being on the Canadian EPA (1999) toxic substance list, ammonia is regarded as a potential inhibitor during anaerobic digestion (AD) and activated sludge (AC) processes (Yenigün and Demirel, 2013). Ammonia inhibition has been reported to occur in the range of 1500 to 3000 mg/L as TAN (Liu et al., 2012). Aqueous solutions with high levels of ammonia are difficult to treat by conventional biological treatments due to ammonia inhibition to microbial activity in bioreactors. The effect of ammonia inhibition to total biomass activity is usually evaluated by methane production rate in AD,

volatile suspended solid (VSS) concentration, and dehydrogenase activity (Krylova et al., 1997).

Li and Zhao (1999) reported that chemical oxygen demand (COD) removal in landfill leachate declined from 95.1 to 79.1% and the dehydrogenase activity of the sludge decreased from 11.04 to 4.22  $\mu\text{g TF/mg}$  mixed liquor suspended solids (MLSS) with the ammonia concentration progressively increasing from 50 to 800 mg/L. It was reported by Lee et al. (2000) that when ammonia concentrations were beyond 5000 mg/L, decreases of more than 70% of dehydrogenase microbial activity were observed for both heterotrophs and nitrifiers. In addition, nitrifying bacteria was found to be more sensitive to high ammonia concentration than the heterotrophic bacteria (Lee et al., 2000).

In bioreactor landfill technology, leachate recirculation causes ammonia accumulation due to ammonification (Yenigün et al., 2013). When dealing with complex substrates such landfill leachate, high concentrations of ammonia in recirculated leachate could undermine the AD process performance by inhibiting microorganisms and result in low biogas production. Free ammonia was reported to inhibit anaerobic bacterial activity in doses as low as 1100 mg/L as  $\text{NH}_3\text{-N}$  at a pH of 8 (Hansen et al., 1998).

## **2.5 Ammonia concentrations**

Extremely high ammonia concentrations are mainly found in landfill leachate. Concentrations of ammonia in landfill leachate were reported to be in the range of 0.2 to 13000 mg/l depending on the age of the landfill and composition of the solid waste (Renou et al., 2008). Table 2.1 summarizes the range of TAN concentration from different landfill sites (Renou et al., 2008). Ammonia is mainly produced from the solid waste due to the decomposition of proteins. The only removal mechanism for ammonia is leaching as there is no mechanism for the degradation under methanogenic conditions (Burton and

Watson-Craik, 1998). A study was conducted in Germany based on 50 landfills. The results show that there was no significant decrease of ammonia concentration even 30 years after the closure (Ehrig, 1989). Thus, ammonia is considered to be the most significant long term pollutant within landfill leachate (Belevi and Baccini, 1989; Robinson et al., 1995).

Generally, high toxicity was observed in municipal landfill leachate (Cameron, 1980; Atwater et al., 1983; Plotkin et al., 1984; Schrab et al., 1993). Among all toxic substances, ammonia is reported to be the most probable factor that contribute to the observe toxicity and it was also found to be the main cause of the toxicity measured in the biotests (Cheung et al., 1993; Clément and Merlin, 1995; Bernard et al., 1997).

Table 2.1 Ammonia concentrations in different landfill sites (Renou et al., 2008)

Age	Landfill Site	TAN (mg/L)	Reference
Y	Canada	42	(Henry et al., 1987)
Y	Canada	10	
Y	China, Hong Kong	2260	(Lau et al., 2001)
Y	China, Hong Kong	3000	(Lo, 1996)
Y		11000	
Y		13000	
Y	China, Mainland	630-1800	(Wang and Shen, 2000)
Y	Greece	3100	(Tatsi et al., 2003)
Y	Italy	3917	(Di Palma et al., 2002)
Y	Italy	5210	(Lopez et al., 2004)
Y	South Korea	1682	(Im et al., 2001)
Y	Turkey	1120-2500	(Timur and Öztürk, 1999)
Y	Turkey	2020	(Ozturk et al., 2003)
Y	Turkey	1946-2002	(Çeçen and Aktaş, 2004)
MA	Germany	884	(Baumgarten and Seyfried, 1996)
MA	Germany	800	(van Dijk and Roncken, 1997)
MA	Greece	940	(Tatsi et al., 2003)
MA	Italy	1330	(Frasconi et al., 2004)
MA	Poland	743	(Bohdziewicz et al., 2001)
MA	Taiwan	5500	(Wu et al., 2004)
MA	Turkey	1270	(Kargi and Pamukoglu, 2003a)

O	Brazil	800	(Silva et al., 2004)
O	Finland	159	(Hoilijoki et al., 2000)
O	Finland	330-560	(Marttinen et al., 2002)
O	France	430	(Trebouet et al., 1999)
O	France	0.2	(Tabet et al., 2002)
O	France	295	(Gourdon et al., 1989)
O	South Korea	1522	(Cho et al., 2002)
O	Turkey	1590	(Uygur and Kargi, 2004)

Y: young; MA: mature; O: old

## 2.6 Treatments for high concentration ammonia removal

Highly contaminated wastewater with elevated levels of ammonia such as landfill leachate is usually accompanied by a mixture of high concentration organic and inorganic contaminants, heavy metals and xenobiotic organic compounds. Thus they need to be treated before discharging it into a sewer or a surface water due to their toxicities and adverse effects on the environment. Unfortunately, a universal solution for the treatment has not been yet established. The processes used currently often include a combination of different techniques (Wiszniewski et al., 2006).

Conventional treatments for high concentration ammonia removal from aqueous solution can be categorized into three main groups:

- 1) liquid transfer: mix highly contaminated aqueous solution with domestic sewerage and send to municipal wastewater treatment plant;
- 2) biological treatments: aerobic and anaerobic processes;
- 3) physical and chemical methods: chemical precipitation, adsorption, ion-exchange, air stripping, microwave and ultrasound (Renou et al., 2008).

### 2.6.1 Mixed with domestic wastewater

Many years ago, it was popular to treat landfill leachate along with municipal sewage in the wastewater treatment plant because of the low operating cost and easy maintenance (Ahn et al., 2002). The optimum ratio of leachate in the total wastewater was investigated by Diamadopoulos et al. using sequencing batch reactor (SBR) which undergoes filling, anoxic, aerobic and settling phase. The results indicated that nearly 95% BOD and 50% ammonia removal was achieved when the ration of sewage to leachate was 9/1 (Diamadopoulos et al., 1997). Another study also found that COD and ammonia reduction decreased with the increasing leachate to sewage ratio (Çeçen and Aktaş, 2001). However, this method has its own drawback due to the presence of heavy metals and high ammonia concentration that is toxic and inhibitory to the microorganism in the wastewater treatment plant. Also, low BOD/COD ratio indicates the poor biodegradability (Çeçen and Aktaş, 2004).

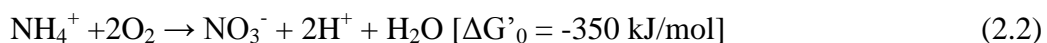
## **2.6.2 Biological treatment**

Biological treatment is widely used for the removal of ammonia with low to mid concentration due to the relatively simple operation and high cost-effectiveness. Biological processes have been proved to be effective in removing ammonia from aqueous solution with high BOD/COD ratio ( $>0.5$ ) (Renou et al., 2008). There are three major biological processes within biological nitrogen removal. These processes are ammonification, nitrification/denitrification and anammox (Metcalf and Eddy, 2003).

Ammonification allows the transformation of organic nitrogen into ammonia nitrogen which breaks down big molecule nitrogen into ammonia for further biological conversion.

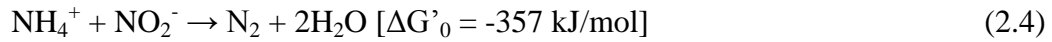
In nitrification, ammonia is firstly oxidized to nitrite in the presence of Nitrosomonas bacteria. Then further oxidization of nitrite to nitrate is accomplished by another group of bacteria including Nitrobacter. Overall, ammonia is converted into

nitrate under aerobic conditions as shown in Eq. (2.2) (Metcalf and Eddy, 2003). Denitrification is the second important step of integral nitrification/denitrification process. The complete process is displayed as Eq. (2.3) below. Nitrate is ultimately reduced into nitrogen gas by a great variety of bacteria called denitrifiers which includes *Pseudomonas*, *Alcaligenes*, *Acinetobacter*, *Hyphomicrobium*, *Thiobacillus*, *Lactobacillus* and *Spirillum* under anoxic condition (Metcalf and Eddy, 2003). Although the biological nitrification and denitrification are probably the most cost-effective process to remove ammonia nitrogen from aqueous solution, it is still hampered by several factors. The presence of PAHs (polyaromatic hydrocarbons), AOXs (adsorbable organic halogens), PCBs (polychlorinated biphenyls) and biorefractory organics such as humic substance severely restricts the performance of the process. Also the microbial inhibition due to high ammonia nitrogen concentration is an inevitable issue (Lema et al., 1988). Moreover, poor removal efficiency was reported for leachate generated from mature landfill due to the low level of biodegradable organic matter (Wiszniewski et al., 2006). Heterotrophic bacteria that consume the organic matter in aqueous solution, inhibit the growth and activity of nitrifying bacteria to biodegrade ammonia (Jorgensen and Weatherley, 2003).



The anaerobic ammonium oxidation process (anammox) is a promising and cost-effective alternative technology to conventional nitrification/denitrification process. The main advantage of anammox system is that ammonia nitrogen is directly oxidized to nitrogen gas under anaerobic condition following Eq. (2.4) so that it does not have any demand for oxygen which is a major part of the overall cost during the biological removal processes (Van de Graaf et al., 1995). However, the biochemistry of anammox

bacteria is not completely understood yet. One of the main drawbacks of this process is the slow bacteria grow rates. Typically, a 100 to 150 days set-up time is required for anammox reactor before it reaches maximum designed capacity (Strous et al., 1997).



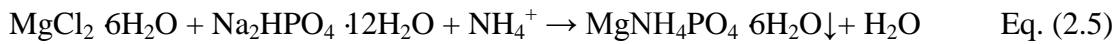
Successful removal of ammonia from the sludge digestion effluent by anammox process was achieved by Strous et al. (1997) using fluidized-bed reactor. A total of 82% of ammonia removal efficiency and 99% nitrite removal efficiency was reported during 150 days of operation. The maximum nitrogen conversion rate was as high as 0.7 kg/(m<sup>3</sup> day).

### 2.6.3 Chemical precipitation

Chemical precipitation has been used for treating wastewater with high ammonia concentration such as tannery effluents, digester supernatants, coke and nitrogen wastewater and also sludge liquor (Tünay et al., 1997). For highly contaminated wastewater with extremely high ammonia concentration such as landfill leachate, it is usually applied as a pretreatment stage prior to conventional biological treatment to remove high strength of ionized ammonia nitrogen, in other words, ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N) (Renou et al., 2008). Li and Zhao (1999) reported that conventional activated sludge process could be affected by high concentration of ammonium nitrogen due to the inhibition effect caused by ammonia toxicity. The COD removal efficiency decreased from 95 to 79% when NH<sub>4</sub><sup>+</sup>-N concentration increased from 50 to 800 mg/l.

Different types of precipitates were investigated for eliminating ammonium nitrogen. Li and Zhao (2001) reduced NH<sub>4</sub><sup>+</sup>-N concentration from 5600 mg/L to 110 mg/L by the

chemical addition of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  with a  $\text{Mg}/\text{NH}_4/\text{PO}_4$  ratio of 1/1/1 at a pH 8.5-9 within 15 minutes. The basic chemical reaction to form magnesium ammonium phosphate (MAP) is presented in Eq. (2.5).



MAP precipitation after anaerobic treatment of wastewater and landfill leachate mixture was studied by Yangin et al. (2002). Highest  $\text{NH}_4^+$ -N reduction was achieved as 66% at pH of 9.3 at the stoichiometric ratio while up to 86% of  $\text{NH}_4^+$ -N was removed at the same pH above the stoichiometric ratio. In the up-flow anaerobic sludge blanket (UASB) reactor,  $\text{NH}_4^+$ -N concentrations were reduced to 31 mg/L and 13 mg/L, respectively, at and above the stoichiometric ratio. The application of struvite precipitation ( $\text{Mg}:\text{NH}_4:\text{PO}_4 = 1:1:1$ ) to anaerobically treated effluents for ammonium removal was studied. The  $\text{NH}_4^+$ -N removals were reported to be 85% at pH of 9.2, 72% at pH of 12 and 20% at pH of 10 to 11 (Ozturk et al., 2003).

#### **2.6.4 Air stripping**

Air stripping is one of the most common approaches for eliminating high concentration of ammonia existing in wastewater (Marttinen et al., 2002). The principle of air stripping process is relatively simple. It transfers free ammonia which is a volatile component in liquid phase into an air stream (Metcalf and Eddy, 2003). In practice, air stripping process is operated in packed stripping towers. Satisfactory removal efficiency was achieved in high pH conditions where most ammonia is in unionized form (Emerson et al., 1975). The performance of this process also highly depends on the retention time. Table 2.2 is a summary of the ammonia removal efficiency by air stripping based on

several previous studies (Cheung et al., 1997; Marttinen et al., 2002; Kargi and Pamukoglu, 2003; Ozturk et al., 2003; Silva et al., 2004).

Table 2.2 Air Stripping Process Efficiency

Source	TAN (mg/L)	Stripping time (h)	Removal (%)	Reference
Landfill Leachate	556-705	24	76-93	(Cheung et al., 1997)
Landfill Leachate	72-220	24	89	(Marttinen et al., 2002)
Synthetic Wastewater	1270	0.75	45	(Kargi and Pamukoglu, 2003)
Synthetic Wastewater	1025	24	72	(Ozturk et al., 2003)
Landfill Leachate	750-800	96	99.5	(Silva et al., 2004)

Marttinen et al. (2002) reported 89% of ammonia removal at pH=11 and 20°C after 24h stripping time. Higher ammonia reduction with high initial ammonia concentration (500-700 mg/l as TAN) was reported by Cheung et al. (1997). Their results demonstrated over 93% of TAN were eliminated after a day retention time.

The major issue of ammonia air stripping process is the direct release of ammonia gas into atmosphere without any collection or further air treatment may led to severe air pollution problem. In order not to contaminate the air, ammonia gas released by air stripping process must be treated with either H<sub>2</sub>SO<sub>4</sub> or HCl. Other concerns of air stripping is the CaCO<sub>3</sub> scaling in the stripping tower due to the use of lime for pH adjustment and large tower is required to overcome foaming problem (Li et al., 1999).

### 2.6.5 Adsorption by activated carbon

Adsorption is a mass transfer operation in that a certain constituent in the liquid phase is transferred into the solid phase (Metcalf and Eddy, 2003). It is considered to be an efficient and promising approach in wastewater treatment. It is commonly used as the

advanced stage in the integrated chemical, physical and biological methods (Foo and Hameed, 2009). Powdered activated carbon (PAC) is the most commonly utilized adsorbent for water and wastewater treatments (Abbas et al., 2009). Langmuir and Freundlich adsorption isotherms are employed to model the adsorption characteristics of activated carbon applied in water and wastewater purification (Aziz et al., 2011).

Aziz et al. (2012) studied the equilibrium adsorption capacity ( $Q_e$ ) of PAC in terms of COD and ammonia removal from semi-aerobic landfill leachate. The solid phase concentrations of COD and ammonia were 37.88 mg/g and 6.08 mg/g, respectively (Halim et al., 2010). Similar results were reported in another study, with  $Q_e$  of 15.41 mg/g for COD and 6 mg/g for ammonia (Aziz et al., 2012). Although the ability of activated carbon regarding ammonia removal is reasonable, it is still considered to be more efficient for COD removal and the removal of organic molecules.

#### **2.6.6 Ion-exchange resin**

Ion-exchange resins (IER) are widely applied in different separation, purification, and decontamination processes. The most common examples in environmental are water softening and water purification. The 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 (see Fig. 2.4). (Bashir et al., 2010). Typically, the mobile ion is either in  $H^+$  or in  $Na^+$  form.

Solid ion-exchanger can be classified as natural-inorganic particles, such as zeolite, and synthetic-organic resins (Fig. 2.5). 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). In terms of ion-exchange performance, synthetic ion-exchange resins have several advantages over natural zeolite in most modern applications such as faster exchange rate, longer life and higher ion exchange capacity (Letterman, 1999).

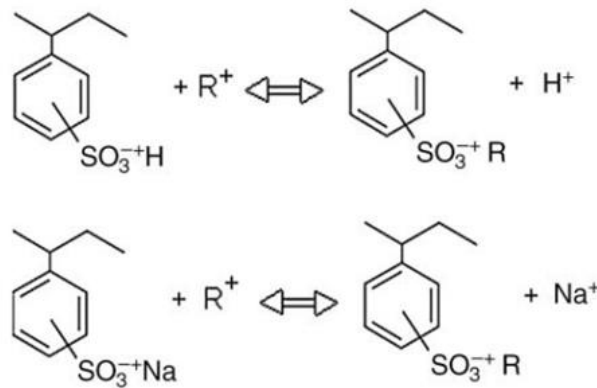


Fig. 2.2 Scheme of ion-exchange process



Fig. 2.3 Amberlite IR120 H synthetic ion-exchange resin

Cation resins and anion resins are the two most common resins used encountered in the ion exchange process. While cation resins attract positively charged ions such as  $\text{Ca}^{2+}$ ,

$Mg^{2+}$  and  $NH_4^+$ , anion resins attract negatively charged ions such as  $Cl^-$  and  $NO_3^-$ . Based on their different functional groups, ion-exchange resins are categorized into four main types (Hendershot et al., 2007):

- Strongly acidic, typically featuring sulfonic acid groups, e.g. sodium polystyrene sulfonate or polyAMPS.
- Weakly acidic, typically featuring carboxylic acid groups.
- Strongly basic, typically featuring quaternary amino groups, for example, trimethylammonium groups, e.g. polyAPTAC)
- Weakly basic, typically featuring primary, secondary, and/or ternary amino groups, e.g. polyethylene amine.

Bashir et al. (2010a) compared the performance of the same type of synthetic ion-exchange resin (INDION 225 Na) regarding ammonia removal by different mobile cation forms with the one in  $H^+$  form had a higher removal efficiency than the one in  $Na^+$  form (92.8% compared to 72%). Equilibrium exchange capacities were reported to be approximately 39 and 28 mg/g by using Dowex 50w-x8 and Purolite MN500, respectively, in another previous study (Jorgensen and Weatherley, 2003). 94.2% of ammonia was eliminated in only 6 minutes from the synthetic ammonia solution of approximately 1000 mg/L by INDION 225 Na strong acid cation exchanger (Bashir et al., 2010a).

Ion-exchange resins can be simply regenerated by acid, base or salt solutions at certain concentrations. Lin and Wu (1996) reported that less than 2.5% of the equilibrium exchange capacity was lost after each regeneration as can be seen from Fig. 2.6. Therefore, the lifespan of synthetic ion-exchange resin before completely exhausting should be long.

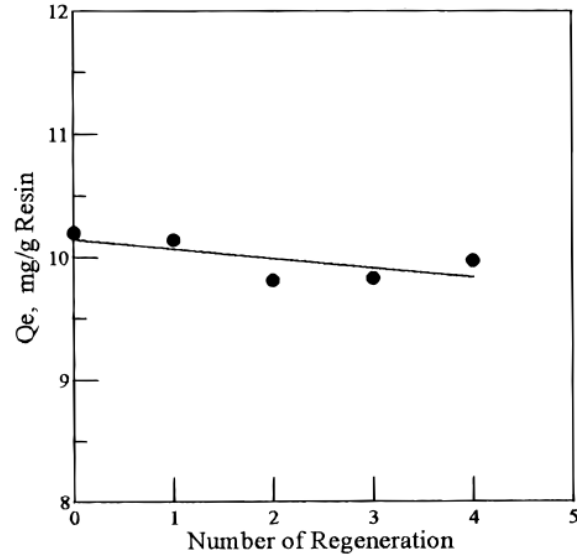
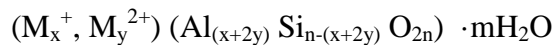


Fig. 2.4 Equilibrium exchange capacity of virgin and regenerated Na-type Dowex HCR-S ion-exchange resin (Lin and Wu, 1996)

### 2.6.7 Zeolite

Natural zeolite is a porous material with large surface area, high cation exchange capacity and cation selectivity. (Saltal et al., 2007). The cation exchange capacity was reported to reach 1.64 meq/g (as ammonium nitrogen) (Sarioglu, 2005). The major mineral component of natural zeolite is clinoptilolite which has a high affinity for ammonium nitrogen (Dixon and Weed, 1989). It has a classical three-dimensional alumina silicate structure. The basic zeolite structure and granular zeolite are shown in Fig. 2.2 and Fig. 2.3, respectively (Vassileva and Voikova, 2009). The general formula of a zeolite is as follows:



where  $Al^{3+}$  and  $Si^{4+}$  are known as the structural cations, and they make up the framework

if the structure with O, M<sup>+</sup> and M<sup>2+</sup>; the latter are monovalent and divalent cations such as Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, respectively. They are called exchangeable cations and can be easily replaced by same equivalent amount of other cations such as ammonium (NH<sub>4</sub><sup>+</sup>)(Saltali et al., 2007).

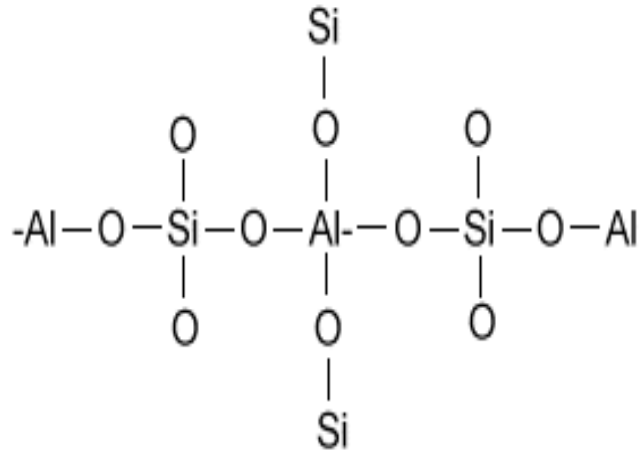
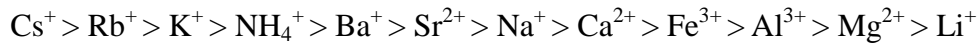


Fig. 2.5 Basic zeolite structure (IZA-SC, 2001)

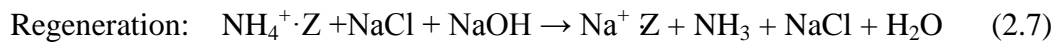
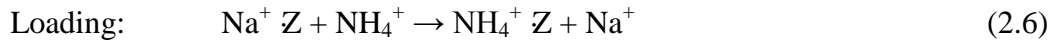


Fig. 2.6 Granular natural zeolite

The cation selectivity was different for each zeolite due to the size and charge of the hydrated cation, specific crystal structure of zeolite and the amount of exchange sites. Clinoptilolite was reported to be highly ammonium-ion selective (Maschmeyer and van der Water, 2006). The ion selectivity of clinoptilolite was reported as (Booker et al., 1996):



The loading of ammonia into zeolite and regeneration of the sodium form was expressed by Koon et al. (1975) as shown in Eq. (2.6) and Eq. (2.7), respectively, where Z represents the zeolite.



Zeolite is abundant and widely available in nature. It was the first commercially used exchanger in water and wastewater treatment (Bashir et al., 2010a). Due to the high cation exchange capacity and low cost, it could be used in ammonia removal process (Demir et al., 2002; Englert and Rubio, 2005). Previous studies have confirmed the ability of ammonia removal from aqueous solution by zeolite. Table 2.3 summarizes ammonia adsorption capacity achieved by some researchers by different kind of zeolite.

Several operating parameters are considered to have obvious impacts on the process. The effect of pH is significant. Du et al. (2005) reported that the optimum operating pH is 6, which is in great agreement with another earlier study by Koon and Kaufman (1975). pH can influence both the dominant species of ammonia in the solution and the characteristics of zeolite itself. Under low pH conditions, most ammonia is present in

ionized form, which is preferred by the exchange mechanism. However, at lower pH values, the ionized ammonia has to compete with hydrogen ions for the exchange sites. Moreover, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium carbonate, unaltered glass, etc., are possibly replaced by hydrogen ions at lower pH (Haggerty and Bowman, 1994).

Table 2.3 Ammonia adsorption capacity of different zeolite

Type of zeolite	Q <sub>e</sub> (mg/g)	Source
Natural Hungarian zeolite	11.72	(Hlavay et al., 1982)
New Zealand zeolite	7.39 – 7.43	(Nguyen and Tanner, 1998)
Natural Chinese clinoptilolite	14.42	(Wang et al., 2006)
Natural Turkish clinoptilolite	8.12	(Karadag et al., 2006)
Natural Akita clinoptilolite	16.06	(Jha and Hayashi, 2009)
Natural Iranian clinoptilolite	11.31-13.27	(Malekian et al., 2011)

The kinetics of ammonia uptake by zeolite has been usually described by Pseudo-second order rate expression as presented in Eq. (2.8) (Lei and Zhang, 2008; Malekian et al., 2011). It has been widely applied to describe kinetics of sorption and ion-exchange process (Ho and McKay, 1999; Bashir et al., 2010a).

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (2.8)$$

where  $q_t$  is the amount of ammonia adsorbed per unit mass of adsorbent at time  $t$  (mg/g);  $q_e$  is the amount of ammonia adsorbed per unit mass of adsorbent at equilibrium (mg/g);  $t$

is contact time (min) and  $k_2$  is the rate constant of Pseudo-second order expression (g/(mg h)).

Adsorption isotherm models are usually used to characterize the equilibrium behavior of zeolite at different initial ammonia concentrations. Langmuir and Freundlich isotherms were two most popular models applied to evaluate the experimental data (Saltali et al., 2007).

### 2.6.8 Membrane processes

Membrane technologies can be applied in landfill leachate treatment. These processes are classified as microfiltration (0.1-10 $\mu$ m), ultrafiltration (2-100 nm), nanofiltration (1-2 nm) and reverse osmosis (<1 nm) based on the pore size of the membrane (see Fig. 2.7) (Laitinen et al., 2006).

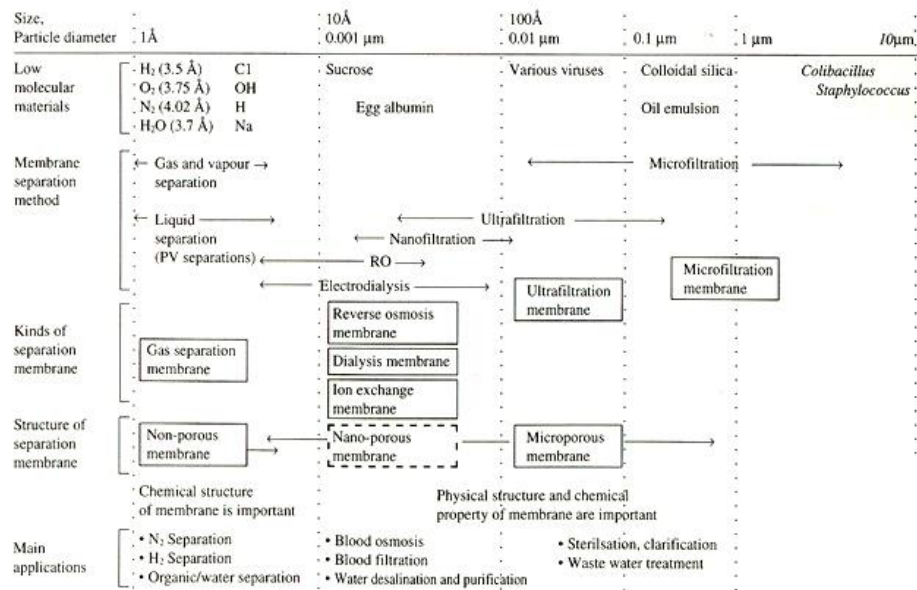


Fig. 2.7 Categories of membrane separation processes (Till and Mallia, 2001)

The application of microfiltration (MF) as the only treatment when dealing with wastewater of high ammonia concentration has its limitation. A research reported that only 25% to 35% of COD reduction was achieved by using MF as filtration stage (Piatkiewicz et al., 2001). MF is an effective method to remove colloids and suspended particles within aqueous solutions. It must be combined with other physical/chemical or biological processes or as a pretreatment of another membrane process (UF, NF or RO) (Renou et al., 2008).

Depending on the pore size of the membrane as well as the material that membrane is made of, ultrafiltration (UF) could be effective to eliminate the macromolecule pollutants. It is also used as a primary stage of treating highly contaminated wastewater such as landfill leachate (Tabet et al., 2002). It was suggested UF was an option as the pretreatment process prior to reverse osmosis due to its capability of eliminating large molecular weight components within landfill leachate that could possibly cause membrane fouling (Syzdek and Ahlert, 1984). The removal of UF process varies (10-75% in terms of COD) depending on the operational conditions and the types of membrane. And some authors reported that UF along can achieve 50% removal of organic compounds (Syzdek and Ahlert, 1984; Pirbazari et al., 1996; Bohdziewicz et al., 2001; Piatkiewicz et al., 2001).

Nanofiltration (NF) membranes are typically made of polymeric films with a molecular cut-off in the range of 200 to 2000 Da (Petersen, 1993). This makes it possible to remove multiple pollutants within aqueous phase such as organic, inorganic and microbial contaminants. The rejection rate for sulfate ions and for dissolved organic matter are high while the rejection of chloride and sodium is very low (Peters, 1998). Only few studies have been conducted on ammonia removal by NF. Nearly 50% of ammonia removal were achieved by NF regardless of the material of membrane and the geometry (flat, tubular or spiral wounded) with a driven pressure between 6 and 30 bar and an average velocity of 3 m/s (Rautenbach and Mellis, 1994; Trebouet et al., 1999;

Trebouet et al., 2001). When NF was used in combination of other physical processes, it was proved to be satisfactory for ammonia removal (50-60%) (Trebouet et al., 2001).

However, a variety of constituents in wastewater may lead to membrane fouling in NF process (Braghetta et al., 1998). These constituents include dissolved organic and inorganic matters, colloidal and suspended particles (Trebouet et al., 2001). Thus, the application of NF requires appropriate control of membrane fouling (Hong and Elimelech, 1997).

Reverse Osmosis (RO) membrane is capable of complete salt elimination from aqueous solution due to its extremely small pore size ( $< 1$  nm) as shown in Fig. 2.8. Several studies from both lab and industrial scale have reported that RO might be one of the most promising approaches among the new technologies for water and wastewater treatment (Bilstad and Madland, 1992; Linde et al., 1995). Previous studies demonstrated that over 98% and 99% of COD and heavy metal removal were achieved, respectively (Baumgarten and Seyfried, 1996; Chianese et al., 1999; Bohdziewicz et al., 2001). As for ammonia, comparable reductions of over 97% were observed in the optimal conditions of pH=6.4 using two different RO membranes (Di Palma et al., 2002). The introduction of disc-tube-module in 1988 by Pall-Exekia has led to the successful application of open channel membrane module in wastewater treatment. Due to the special surface characteristic, this membrane system can be cleaned with high efficiency with regard to membrane fouling, especially biofouling (Peters, 1998).

However, when dealing with wastewater, membrane fouling issues are still inevitable today. It is a major drawback for most pressure-driven processes and in particular for RO which requires very high transmembrane pressure (120 to 200 bars). Thus, extensive pretreatment and chemical cleaning for membrane is required. As a result, the lifecycle of the membrane and process productivity decrease. On the other hand, the generation of large amount of unusable concentrate has to be disposed or further treated

(Rautenbach et al., 2000).

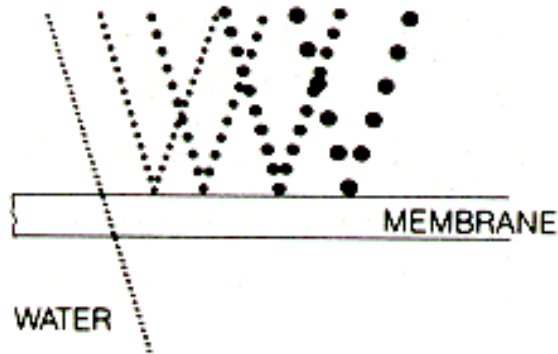


Fig. 2.8 RO process for complete desalination (Till and Mallia, 2001)

### 2.6.9 Ultrasound

Ultrasonication has been investigated to degrade organic compounds from wastewater for years. In recent years, several studies have been conducted to apply sono-chemical treatment in industrial wastewater and landfill leachate to eliminate organic matters and ammonia nitrogen of high concentrations (Gogate, 2008). The main mechanism of ammonia nitrogen reduction from aqueous solution by ultrasound irradiation appears to be the entry of ammonia molecules into the cavitation bubbles and the transformation into nitrogen molecules and hydrogen molecules via pyrolysis (Adewuyi, 2001) and the experimental set-up is relatively simple shown in Fig. 2.9 (Wang et al., 2008).

Up to 96% of ammonia removal was achieved after 180 min ultrasound irradiation time. The ultrasonic process was proved to be input power dependent. The removal rate increased with the increasing power input. It was also reported that high pH was favorable for ultrasound irradiation. The removal efficiency at pH 11 was approximately eight times as high that of pH 3. This could be explained the fact that at pH 11 almost all the ammonia is unionized ammonia rather than ionized ammonia which does not vaporize

into the cavitation bubbles. In molecular state, unionized ammonia can react inside by thermal cleavage after transforming into cavitation bubbles due to ultrasound irradiation (Wang et al., 2008).

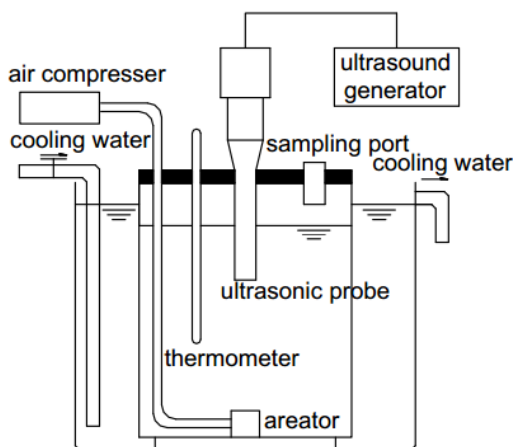


Fig. 2.9 Scheme of the ultrasound set-up (Wang et al., 2008)

The reactor design plays an important role in ultrasound irradiation process. Due to the limitation of ultrasound penetration ability, as the height of liquid increases, the ammonia removal efficiency decreases. Thus, a practical upper limit for the height of liquid needs to be properly designed to achieve optimum ammonia removal rate by ultrasound technology (Matouq and Al-Anber, 2007). Matouq reported that optimum liquid height was 0.0165 m and approximately 31% of ammonia removal was achieved within 90 minutes at a microwave radiation of 2.4 MHz (Matouq and Al-Anber, 2007).

### 2.6.10 Microwave

In recent years, microwave technology has become one of the research interests in wastewater treatment due to its high removal efficiency achieved by molecular-level

heating, which leads to homogeneous and quick thermal reactions (Menendez et al., 2002). Although neither chemical mechanism of microwave interaction with materials, nor microbial destruction mechanism of microwave in biological systems are fully understood, it has been widely applied to environmental remediation such as removal of dyes and heavy metals from wastewater (Gan, 2000; Quan et al., 2004). However, only few studies were conducted to remove ammonia by microwave radiation. According to the available literature, thermal and non-thermal effects could be two possible mechanisms for microwave process. Thermal effect is related to the heat generated by the absorption of microwave energy by water and other polar molecules. However, non-thermal effect affects the chemical, biochemical, or physical behaviors of systems (Lin et al., 2009a).

pH was found to be an important parameter of ammonia removal from wastewater by microwave radiation. High removal rate was reported at high pH level. The result could be explained by the pH dependent equilibrium between unionized and ionized ammonia. A 98% ammonia removal was achieved at pH 11 where most ammonia was in the form of  $\text{NH}_3$ , which indicated that microwave radiation was effective for removing volatile molecular ammonia from the solution. Another factor that could affect the removal efficiency was reported to be microwave radiation time. Heat was produced by microwave process and it results in the high temperature in the solution, which potentially benefits the free of unionized ammonia from the solution due to more impetuous and rapid molecular motion (Lin et al., 2009b).

## **2.7 Summary**

Methods for high concentration ammonia removal from aqueous solution include conventional biological nitrification/denitrition, physical adsorption, air stripping, chemical precipitation, ion-exchange and some new technology such as membrane,

ultrasound and microwave radiation. Biological processes do not response well to the shock loading of ammonia as well as the high ammonia levels. The main problems of air stripping, ultrasound and microwave technologies are the need of pH adjustment prior to the treatments and the energy input. Membrane fouling issue is inevitable. The costs for adsorption chemical precipitation and ion-exchange processes are relatively high. Thus, no single solution for high strength ammonia removal from aqueous has been found yet. Methods capable of reducing high levels of ammonia with high efficiency and relatively low cost are highly desired.

Although ammonia removal by natural zeolite has been widely studied, only few results regarding high ammonia concentration ( $> 1000$  mg/L as TAN) are available. Also, no data has been reported for the specific ion-exchange resin used in this study (Amberlite IR120 H). In this study, the factorial design and response surface methodology were applied to model and thus predict the potential of removing ammonia by zeolite and ion-exchange resin. This would provide a reference to other researches.

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## CHAPTER III

### MATERIAL AND METHODS

#### 3.1 Batch tests

Most of the experiment work in this study was conducted by batch tests. 50 mL plastic centrifuge tube was used as the reactor (Figure 3.1). Samples were agitated by a Innova 2000 orbital shaker (Figure 3.2).

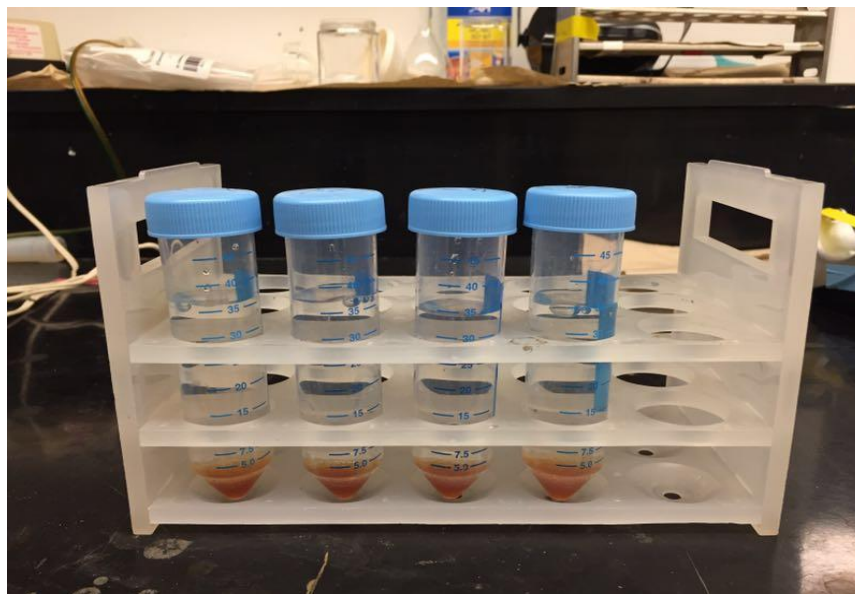


Fig. 3. 1 50 mL plastic centrifuge tube as the batch reactor

For quality control purpose, blanks and control samples were applied throughout the experiments. Blank sample contained only distilled water (DW) and underwent the same experimental conditions as other samples to check if there is any contamination occurring

within the process. Control sample was ammonia solution in the reactor without adsorbent and went through the same experimental conditions as other samples. This was to measure the amount of ammonia decreased due to some reasons such as volatilization other than adsorption or ion-exchange, and the amount obtained by controls was subtracted in the later data analysis to get an accurate estimation of ammonia removal by zeolite and ion-exchange resin.

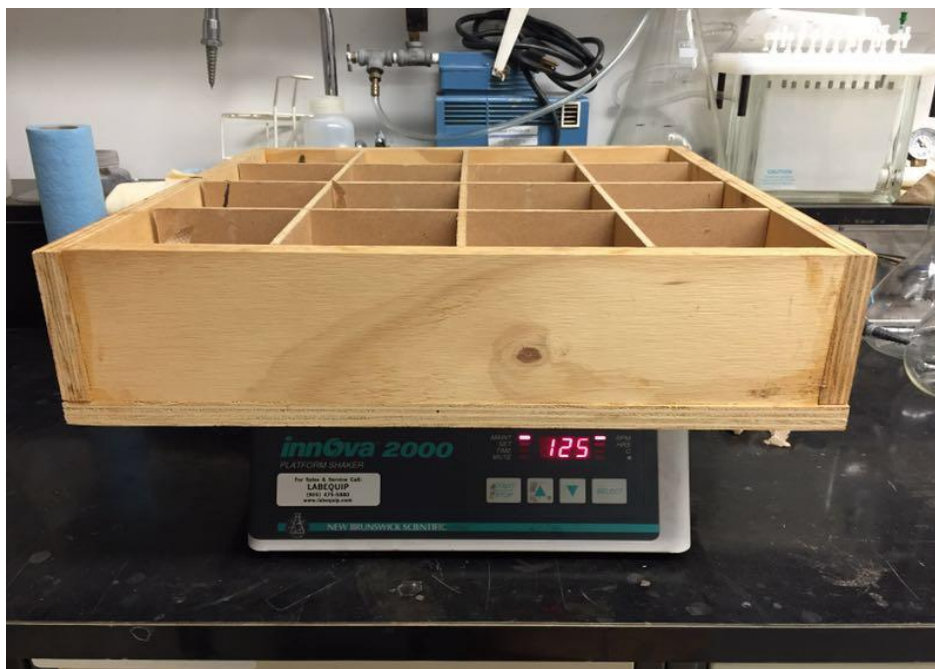


Fig. 3.2 Innova 2000 orbital shaker

### 3.2 Ion-exchange resin

A number of previous studies have been done on ammonia removal using other types of synthetic ion-exchange resin (eg., INDION 225 Na and Dowex HCR-S), and proved to be efficient. In this study, a relatively new synthetic ion-exchange resin product Amberlite IR120 H was investigated. Amberlite IR120 H is an industrial grade strong acid cation exchanger (obtained from Dow Chemical Co.). Properties of the resin were

provided by the manufacturer (Dow Chemical Co., 2013) (see Figure 3.3 and Table. 3.1).



Fig. 3.3 Amberlite IR120 H

Ion-exchange resin was first washed with DW to remove adhering dirt and chemical impurities, and then it was oven dried at  $105^{\circ}\text{C}$  for 12 h. Then, based on results of preliminary tests, resin was pretreated with different types of strong acids (HCl and  $\text{H}_2\text{SO}_4$ ) concentration at 0.1, 0.5, 1.0 normality (N) in sequence over 4 hours to completely convert cation exchanger to their  $\text{H}^+$  form (Bashir et al., 2010). After that, resin was washed with DW again to remove all the acid and dried at room temperature ( $25 \pm 1^{\circ}\text{C}$ ).

Table 3.1 Properties of Amberlite IR120 H

Properties	
Physical form	Amber spherical
Matrix	Styrene divinylbenzene copolymer
Ionic form as shipped	H <sup>+</sup>
Total exchange capacity	≥ 1.80 eq/L (H <sup>+</sup> form)
Moisture holding capacity	53 to 58 % (H <sup>+</sup> form)
Shipping weight	800 g/L
Uniformity coefficient	≤ 1.8
Harmonic mean size	0.620 to 0.830 mm < 0.300 mm 2 % max
Maximum reversible swelling	Na <sup>+</sup> → H <sup>+</sup> ≤ 11 %
Maximum operating temperature	135 °C
Regenerants	H <sub>2</sub> SO <sub>4</sub> HCl
Concentration	0.7 – 6 %                      5 – 8 %
Minimum contact time	30 minutes

### 3.3 Zeolite

The natural zeolite used in this study was a commercial product obtained from a fertilizer company. The reason why this specific zeolite was selected is that it was reported to have considerably high efficiency for ammonia. The selected zeolite type used in this study was clinoptilolite type which is the most common and abundant type of natural zeolite with widespread industrial and environmental applications. Both chemical and physical properties were provided by the producer. Rock analytical data (chemical

analysis) of the zeolite sample is summarized in Table 3.2 (The Raw Supply, 2014). 85% of the mineralogical content was clinoptilolite. The main components are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Bulk density and cation exchange capacity were reported to be 880-960 kg/m<sup>3</sup> and 1.4 to 1.65 meq/g, respectively. The natural zeolite sample was in granular form and particle size ranged within 0.3-2.0 mm (See Figure 3.4). The surface area of the natural zeolite, as reported by the producer, is 24.9 m<sup>2</sup>/g.

Table 3.2 Rock analysis of zeolite

Constituent	Value (%)
SiO <sub>2</sub>	67.40
Al <sub>2</sub> O <sub>3</sub>	10.60
FeO <sub>3</sub>	1.70
MgO	0.45
CaO	2.23
Na <sub>2</sub> O	0.59
K <sub>2</sub> O	4.19
TiO <sub>2</sub>	0.27
P <sub>2</sub> O <sub>5</sub>	0.10
MnO	<0.01
Loss of ignition (at 925°C)	11.40



Fig. 3.4 Natural zeolite

Zeolite sample was first washed with distilled water (DW) to remove fine dust and all water soluble residues, and then it was oven dried at  $105^{\circ}\text{C}$  for 12 h. Then, based on the results of preliminary tests, NaCl solution (2 Mol/L) was used to wash the zeolite for a second time and zeolite was dried for another 4 hours at  $25 \pm 1^{\circ}\text{C}$ . Zeolite was washed with DW one last time and dried (Klieve and Semmens, 1980).

### **3.4 Synthetic ammonia solution**

Synthetic ammonia stock solution of 3000 mg/L as TAN was prepared by dissolving 5.72g analytical grade  $\text{NH}_4\text{Cl}$  (Figure 3.5) into 500 mL distilled water. Then the stock solution was diluted with DW to achieve desired concentration.

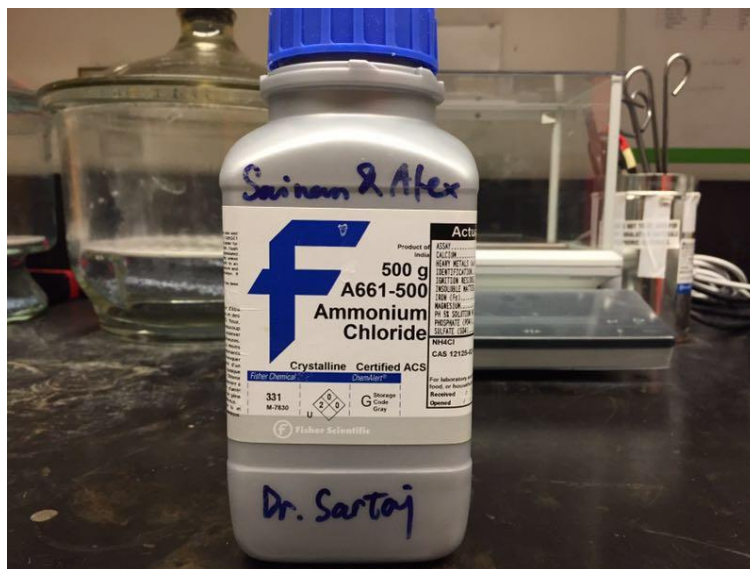


Fig. 3.5 Analytical grade ammonium chloride

### 3.5 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 (see Figure 3.6 and Figure 3.7, respectively). Solid phase concentration was calculated using the mass balance according to Eq. (3.1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (3.1)$$

where  $Q_e$  is the mass of TAN adsorbed per unit mass of zeolite (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 zeolite (g).



Fig. 3.6 HACH TNT832 ammonia vial



Fig. 3.7 HACH DR6000 spectrophotometer

The ammonia removal efficiency was obtained by Eq. (3.2):

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (3.2)$$

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

### 3.6 Effect of pH

Batch adsorption experiments were conducted to determine the effect of pH. 3.0 g of zeolite and 1.0 g of ion-exchange resin were added to 40 mL synthetic ammonia solution at 1000 mg/L as TAN, respectively. pH of the solution was adjusted by addition of 1N NaOH or 1N HCl. Samples were then agitated by the shaker at 130 rpm for 24 hours to reach equilibrium. After that, 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. All tests were conducted in duplicates and the average value was used.

### 3.7 Effect of dose

The effect of dose was evaluated by adding 0.5, 1.0, 2.0, 4.0 and 6.0 g of zeolite and 0.5, 1.0, 2.0 and 4.0 g of ion-exchange resin to 40 mL synthetic ammonia solution with initial TAN concentration of 1000 mg/L, respectively, which is equal to 12.5, 25, 50, 100 and 150 g/L of dose. pH of the solution was adjusted to 6 by 1N HCl and the temperature was set at 26 °C. Samples were then agitated by the shaker at 130 rpm for 24 hours to reach equilibrium. After that, solid phase and liquid phase were separated by centrifuging the sample at 8000 rpm for 10 min. Ammonia concentrations in liquid phase

were then measured and  $Q_e$  was thus obtained by the mass balance equation. Experiments were carried out in duplicates to ensure the accuracy.

### **3.8 Kinetics**

The kinetic studies were conducted at pH 6 and 26 °C. 4.0 g of zeolite and ion-exchange resin were added to 400 mL synthetic ammonia solution with TAN concentration of 1000 mg/L in 1L Erlenmeyer flask, respectively. Reactors were immediately subject to agitation in an orbital shaker at 130 rpm. The supernatant was taken from the solution at 1, 2, 5, 10, 20, 30, 60, 120, 240 and 360 minutes after the shaking started. Duplicates were achieved by repeating the kinetic experiment under the same conditions.

### **3.9 Adsorption isotherms**

In order to obtain data to model adsorption isotherms, 1.0 g of zeolite and ion-exchange resin were added to 40 mL of synthetic ammonia solution in 50 mL centrifuge tubes, containing concentrations in the range of 300-3000 mg/L as TAN at 26 °C. pH for zeolite and ion-exchange resin were set at 7 and 6, respectively. 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 ammonia in the solution were measured. Each set of test was triplicated.

### 3.10 Factorial design and statistical analysis

Batch adsorption tests were conducted based on a factorial design at different pH, temperature and initial ammonia concentration. A 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 of 7 was selected for zeolite as the lower limit as it is the neutral pH while pH of 9.2 was chosen as the upper limit as it is close to the  $pK_a$  of ammonia. For ion-exchange resin, the lower level of pH was 6. Due to the restriction of experimental condition, 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 of zeolite and ion-exchange resin are presented in Table 3.3 and 3.4, respectively. 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.

The response surface methodology (RSM) is a combination of mathematical and statistical techniques commonly used in optimization of chemical reactions and industrial processes (Ölmez, 2009; Sharma et al., 2009). In this study, RSM was used to evaluate the process of ammonia removal from aqueous solution and to optimize the removal capacity ( $Q_e$ ) as the outcome response. The behavior of the system is usually described by the quadratic equation shown as Eq. (3.3) (Montgomery, 2008).

$$Y_1 = A_0 + \sum_{i=1}^n A_i X_i + \sum_{i=1}^n A_{ii} X_i^2 + \sum_{i \neq j=1}^n A_{ij} X_i X_j + \varepsilon \quad (3.3)$$

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;  $A_i$ ,  $A_{ij}$  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 ( $\text{Prob} > F$ ) 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 if there is still some variation unaccounted in the model and the need to add additional terms to improve the model (Xu et al., 2014).

Table 3. 3 Independent variables of the experimental design (zeolite)

Independent variable	Symbol	Coded level				
		-1	-0.66	-0.11	+0.44	+1
pH	pH	7	-	-	-	9.2
Temperature (°C)	T	26	-	-	-	32
Initial TAN conc. (mg/L)	TAN	300	750	1500	2250	3000

Table 3. 4 Independent variables of the experimental design (ion-exchange resin)

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

### **3.11 Regeneration of ion-exchange resin**

The regeneration of Amberlite IR120 H ion-exchange resin was studied in duplicates at pH of 6 and 26 °C. Virgin ion-exchange resin was first loaded with ammonia solution with two different concentrations (1000 mg/L and 2000 mg/L as TAN). Then exhausted resin was regenerated by immersion in 2N H<sub>2</sub>SO<sub>4</sub> for 12 hours according to manufacturer's guide (Dow Chemical Company, 2013) and loaded with ammonia solution again. The exchange capacities for both virgin and regenerated resin were evaluated to obtain the amount of exchange capacity lost due to the regeneration process.

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## CHAPTER IV

### TECHNICAL PAPER I

#### **Statistical Analysis and Optimization of Ammonia Removal from Aqueous Solution by Zeolite Using Factorial Design and Response Surface Methodology**

**Yuanhao Ding, Majid Sartaj**

#### **Abstract**

The ability of zeolite as a low-cost adsorbent for ammonia removal from aqueous solution was studied through batch adsorption experiments. The results showed that zeolite was effective in eliminating ammonia from aqueous solution. Factorial design and response surface methodology were applied to evaluate and optimize the effects of pH, adsorbent dose, contact time, temperature and initial ammonia concentration. Low pH condition was preferred with the optimum pH found to be 6. High adsorbent dose generated high removal rate and low adsorption 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 ( $R^2=0.969$ ). The optimum  $Q_e$  was 22.90 mg/g achieved at pH=7 and initial TAN concentration of 3000 mg/L. The adsorption kinetics followed the Pseudo-second order kinetic model ( $R^2=0.998$ ). Equilibrium data were fitted to Langmuir and Freundlich isotherm models with Freundlich model ( $K_f= 2.24$  L/mg,  $1/n= 0.28$ ) providing a slightly better prediction ( $R^2=0.992$ ). The  $1/n$  value of less than 1 indicated that the removal process was favorable.

Keywords: Ammonia; zeolite; adsorption, kinetics, isotherm, factorial design, response surface methodology

## 4.1 Introduction

Ammonia ( $\text{NH}_3$ ) is the most commonly encountered nitrogen compound in liquid phase. Ammonia can exist in liquid phase either in unionized form ( $\text{NH}_3$ ) or ionized form ( $\text{NH}_4^+$ ) depending on the 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 high ammonia concentration can contribute to eutrophication in rivers and lakes, and dissolved oxygen depletion in receiving water bodies. Also, unionized ammonia is toxic to most fish species even at low concentrations (0.53 to 22.8 mg/L) (Randall et al., 2002). Extremely high ammonia concentrations (1500 to 5000 mg/L) can cause failure in wastewater treatment process due to the inhibition effect (Lee et al., 2000; Uygur and Kargi, 2004).

Conventional methods for ammonia removal from aqueous solution include biological treatment, air stripping, ion-exchange and adsorption (Wang et al., 2007). Traditional biological processes incorporate nitrification and denitrification and they do not perform well to the shock ammonia loading (Karadag et al., 2006). Air stripping provides satisfactory results in high pH conditions where most ammonia is in unionized form ( $\text{NH}_3$ ) (Marttinen et al., 2002). Finding efficient and low-cost material for ammonia removal has become one of the research focuses in the field of ammonia removal from liquid phase. Recently, ion-exchange and adsorption processes have received more interests as possible treatments due to relatively simply operation and high removal efficiency (Huo et al., 2012). Previous studies have reported that natural zeolite could be a promising material as a means of ammonia removal from aqueous solution (Bernal and Lopez-Real, 1993; Du et al., 2005; Karadag et al., 2008; Malekian et al., 2011).

Natural zeolite is a porous material with large surface area, high adsorption and cation exchange capacity and cation selectivity (Beebe et al., 2013). The major mineral component of natural zeolite is clinoptilolite which has a high affinity for ammonium

nitrogen (Dixon and Weed, 1989). It has a classical three-dimensional alumina silicate structure (Vassileva and Voikova, 2009). Natural zeolite is abundant and widely available in nature at low-cost. As such, it could be an alternative material for the expensive ion-exchange resins or adsorption materials such as activated carbon and could be a promising material for ammonia removal in water and wastewater treatment (Demir et al., 2002; Englert and Rubio, 2005). Previous studies have confirmed the ability of removing ammonia from aqueous solution by zeolite. Du et al. (2005) reported that the adsorption capacity ( $Q_e$ ) of a Chinese natural zeolite was 14.50 mg/g at a pH=6 and initial ammonia concentration of 92.4 mg/L and a zeolite dose of 5 g/L. Higher  $Q_e$  (25.93 mg/g as ammonium nitrogen) was achieved by Sarioglu (2005) using natural Turkish zeolite at pH=4 and initial ammonia concentration of 885 mg/L with a zeolite dose of 10 g/L.

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

## **4.2 Material and methods**

### **4.2.1 Zeolite characteristics**

The natural zeolite used in this study was a commercial product obtained from a fertilizer company. Both chemical and physical properties were provided by the producer. Rock analytical data of the zeolite sample was summarized in Table 4.1 (The Raw Supply, 2014). 85% of the mineralogical content was clinoptilolite. Bulk density and cation exchange capacity were reported to be 880-960 kg/m<sup>3</sup> and 1.4 to 1.65 meq/g, respectively. The natural zeolite sample was in granular form and particle size ranged within 0.3-2.0

mm.

Zeolite sample was first washed with distilled water (DW) to remove fine dust and all water soluble residues, and then it was oven dried at 105 °C for 12 h. Then, based on the results of preliminary tests, 2N NaCl solution was used to wash the zeolite for a second time and zeolite was dried for another 4 hours at 25 ± 1 °C. Zeolite was washed with DW one last time and dried (Klieve and Semmens, 1980).

Table 4. 1 Rock analysis of zeolite

Constituent	Value (%)
SiO <sub>2</sub>	67.40
Al <sub>2</sub> O <sub>3</sub>	10.60
FeO <sub>3</sub>	1.70
MgO	0.45
CaO	2.23
Na <sub>2</sub> O	0.59
K <sub>2</sub> O	4.19
TiO <sub>2</sub>	0.27
P <sub>2</sub> O <sub>5</sub>	0.10
MnO	<0.01
Loss of ignition (at 925 °C)	11.40

#### 4.2.2 Synthetic ammonia solution

Synthetic ammonia stock solution of 3000 mg/L as TAN was prepared by dissolving 5.72g analytical grade NH<sub>4</sub>Cl into 500 mL distilled water. Then the stock solution was diluted with DW to achieve different desired concentrations.

### 4.2.3 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 the mass balance according to Eq. (4.1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (4.1)$$

where  $Q_e$  is the mass of TAN adsorbed per unit mass of zeolite (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 zeolite (g).

The ammonia removal efficiency was obtained by Eq. (4.2):

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (4.2)$$

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

### 4.2.4 Batch adsorption experiments

Preliminary batch adsorption experiments were conducted to determine the effect of pH and optimum zeolite dose. Different amounts of zeolite were added to 40 mL of synthetic ammonia solution with TAN concentration of 1000 mg/L in 50 mL plastic centrifuge tubes. pH of the solution was adjusted by addition of 1N NaOH or 1N HCl.

Samples were agitated by the shaker at 130 rpm for 24 hours 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.

Table 4.2 Independent variables of the experimental design

Independent variable	Symbol	Coded level				
		-1	-0.66	-0.11	+0.44	+1
pH	pH	7	-	-	-	9.2
Temperature (°C)	T	26	-	-	-	32
Initial TAN conc. (mg/L)	TAN	300	750	1500	2250	3000

For the main phase of experiments, batch adsorption tests were conducted based on a factorial design at different pH, temperature and initial ammonia concentration. A 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=7 was selected as the lower limit as it is the neutral 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 4.2. 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 isotherms, 1.0 g of zeolite 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 the concentrations of TAN in the solution were measured.

#### 4.2.5 Kinetics experiments

4.0 g of zeolite was added to 400 mL synthetic ammonia solution with TAN concentration of 1000 mg/L in 1L Erlenmeyer flask. The reactor was immediately subjected to agitation in an orbital shaker at 130 rpm. The supernatant was taken from the solution at 1, 2, 5, 10, 20, 30, 60, 120, 240 and 360 minutes after the shaking started. Duplicates were achieved by repeating the kinetic experiment under the same conditions.

#### 4.2.6 Statistical analysis

Response surface methodology (RSM) is a combination of mathematical and statistical techniques commonly used in optimization of chemical reactions and industrial processes (Ölmez, 2009; Sharma et al., 2009). In this study, RSM was used to evaluate the process of ammonia removal from aqueous solution using zeolite and to optimize the removal capacity ( $Q_e$ ) as the outcome response. The behavior of the system is usually described by the quadratic equation shown as Eq. (4.3) (Montgomery, 2008).

$$Y_1 = A_0 + \sum_{i=1}^n A_i X_i + \sum_{i=1}^n A_{ii} X_i^2 + \sum_{i \neq j}^n A_{ij} X_i X_j + \varepsilon \quad (4.3)$$

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 evaluate the significance of the model terms, F-value (Fisher variation ratio) and probability value ( $\text{Prob} > F$ ) were applied (Montgomery, 2008).

## 4.3 Results and discussion

### 4.3.1 Effect of pH

As a preliminary set of experiment, the effect of pH on removing TAN from aqueous solution by using natural zeolite was studied within the range from pH=3 to pH=11 at room temperature ( $25 \pm 1^\circ\text{C}$ ) and the results are shown in Fig. 4.1. Although the maximum  $Q_e$  occurred at pH=6, there is no considerable difference as pH increases from 3 to 7. The adsorption capacity ( $Q_e$ ) started to decrease as pH was further increased from 7 to 11. The decrease of  $Q_e$  may be explained by the fraction of ionized ( $\text{NH}_4^+$ ) and unionized ammonia ( $\text{NH}_3$ ) in aqueous solution. Under low pH conditions ( $\text{pH} < 7$ ), the majority of ammonia is in the form of  $\text{NH}_4^+$ , while under high pH conditions ( $\text{pH} > 7$ ),  $\text{NH}_3$  starts to become the dominant species (Nair et al., 2014). For ammonia removal using zeolite, it is preferred to keep ammonia in ionized form to enhance the main removal mechanism which is adsorption/ion exchange. Thus, pH=6 was selected for the kinetic studies. As stated before, the lower and upper limit for factorial design of main experiments were chosen pH=7 and pH=9.2, respectively.

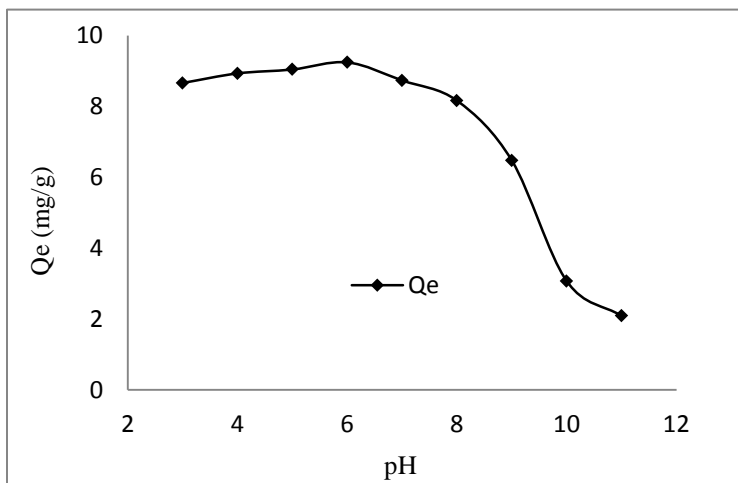


Fig. 4.1 The effect of pH on TAN removal from aqueous solution by using natural zeolite (initial TAN concentration of 1000 mg/L and a zeolite dose of 75 g/L)

#### 4.3.2 Effect of zeolite dose

The effect of zeolite dose on the removal efficiency and  $Q_e$  was evaluated by adding 0.5, 1.0, 2.0, 4.0 and 6.0 g of natural zeolite into 40 mL synthetic ammonia solution with initial TAN concentration of 1000 mg/L, which is equal to 12.5, 25, 50, 100 and 150 g/L of dose. Results in terms of removal efficiency and  $Q_e$  are illustrated in Fig. 4.2. The removal efficiency increased from approximately 21% to 87% with increasing zeolite dose. However, a decreasing trend was found for the ammonia solid phase concentration. It decreased from 17.56 mg/g at a dose of 12.5 g/L to only 5.94 mg/g at 150 g/L. Although 12.5 g/L was the optimum dose within the range studied in this experiment in terms of adsorption 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 zeolite used to a minimum to keep the mix in a slurry form, and be able to collect adequate solution at the end.

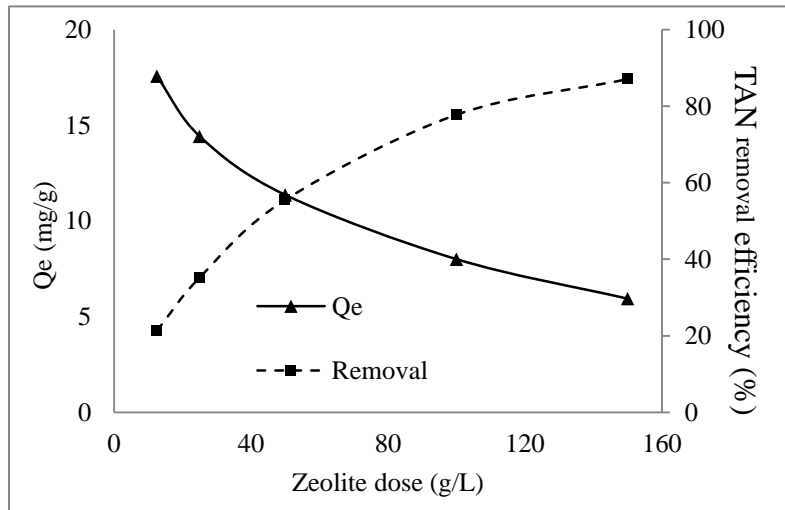


Fig. 4.2 The effect of adsorbent dose on  $Q_e$  and removal efficiency (initial TAN concentration of 1000 mg/L)

### 4.3.3 Kinetics studies

Fig. 4.3 shows ammonia uptake by zeolite as a function of time.  $q_t$  increased with increasing contact time in the first 4 h and then equilibrium was reached. After 4 hours, there was no significant increase in  $q_t$ . This result was in good agreement with Du et al. (2005).

Seven different sorption kinetic models were applied to investigate the kinetics of ammonia removal by zeolite from aqueous solution. Linear regression was used to determine the best fit among those seven models. Table 4.3 summarizes the linearized equations of the selected seven kinetic models and their correlation coefficients ( $R^2$ ). According to the results, the Pseudo-second order rate expression provided the best fit with the highest  $R^2$  (0.998). The Pseudo-second order model has been widely applied to describe kinetics of sorption process (Ho et al., 1999), as described mathematically below:

Table 4.3 Kinetic modes for evaluating ammonia removal by zeolite

Model	Linearized Equation	R <sup>2</sup>
Pseudo-first order	$\ln \frac{q_e - q_t}{q_e} = -k_1 t$	0.976
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	0.998
First order	$\ln(q_t) = \ln(q_e) + k_1 t$	0.714
Second order	$\frac{1}{q_t} = \frac{1}{q_e} + k_2' t$	0.630
Third order	$\frac{1}{q_t^2} = \frac{1}{q_e^2} + k_3' t$	0.548
Parabolic diffusion	$\ln(q_t) = \ln(k_d) + \frac{1}{2} \ln(t)$	0.918
Elovich's reaction	$q_t = q_e + \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	0.879

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (4.3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.4)$$

where  $q_t$  is the amount of TAN adsorbed per unit mass of zeolite at time  $t$  (mg/g);  $q_e$  is the amount of TAN adsorbed per unit mass of zeolite at equilibrium (mg/g);  $t$  is contact time (min) and  $k_2$  is the rate constant of Pseudo-second order expression (g/ (mg h)). Linear regression was achieved by rearranging Eq (4.3) into Eq (4.4). The rate constant  $k_2$  was found from the intercept of Y axis ( $\frac{1}{k_2 q_e^2}$ ) by plotting  $t/q_t$  versus  $t$ . Fig. 4.3 also demonstrates the comparison of the actual experimental data and the predication from the Pseudo-second order model.

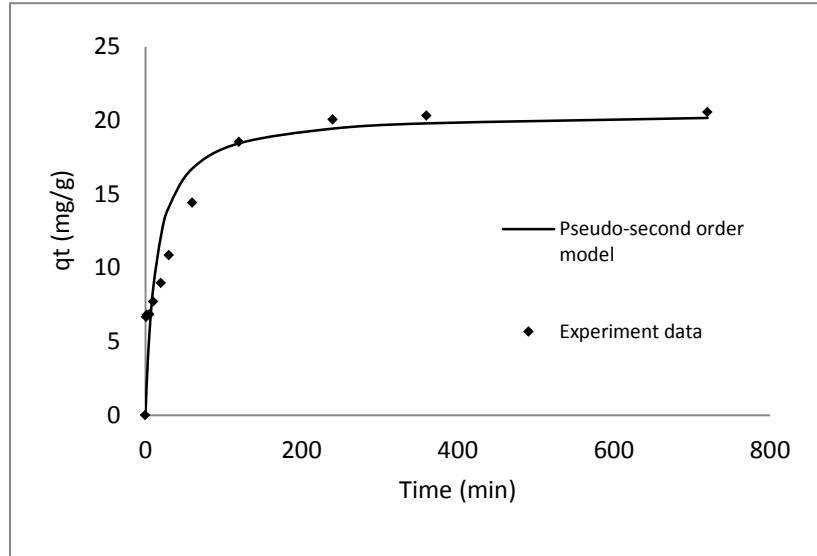


Fig. 4.3 Effect of contact time on ammonia removal by zeolite and Pseudo-second order model predication

#### 4.3.4 Adsorption isotherms

Adsorption isotherm could be used to characterize the equilibrium behavior of zeolite at different ammonia concentrations. Therefore, two commonly used adsorption models (Langmuir and Freundlich isotherms) were applied to evaluate the experimental data. The equation of Langmuir isotherm is shown in Eq. (4.5).

$$Q_e = \frac{abC_e}{1+bC_e} \quad (4.5)$$

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (4.6)$$

Where  $Q_e$  is the mass of TAN adsorbed in solid phase per unit mass of zeolite at equilibrium (mg/g);  $a$  (mg/g) and  $b$  (L/mg) are the constants;  $C_e$  is equilibrium

concentration of TAN in solution (mg/L). By rearranging the Langmuir equation into its linear form shown as Eq. (4.6), the constants a and b can be determined by plotting  $C_e/Q_e$  versus  $C_e$  (Fig. 4.4).

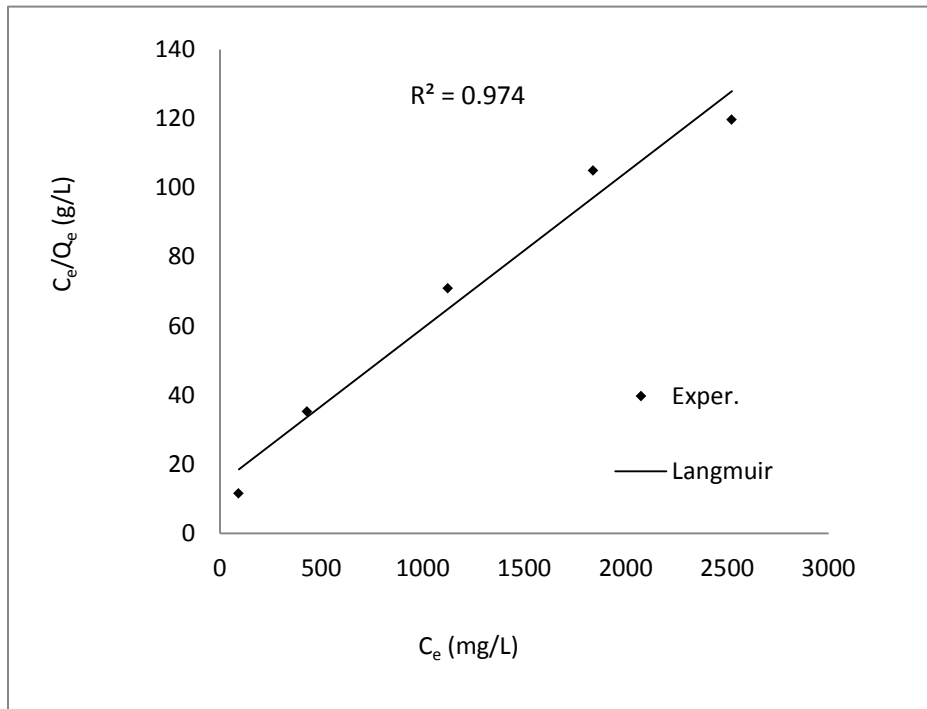


Fig. 4.4 Linearized Langmuir isotherm plots for ammonia removal from aqueous solution by zeolite

Freundlich isotherm is 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 Eq. (4.7) and Eq. (4.8), respectively. The constants  $K_f$  and  $1/n$  can be determined by plotting  $\ln Q_e$  versus  $\ln C_e$  and the results were demonstrated in Fig. 4.5.

$$Q_e = K_f C_e^{1/n} \quad (4.7)$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4.8)$$

where  $Q_e$  is the mass of TAN adsorbed in solid phase per unit mass of zeolite 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.

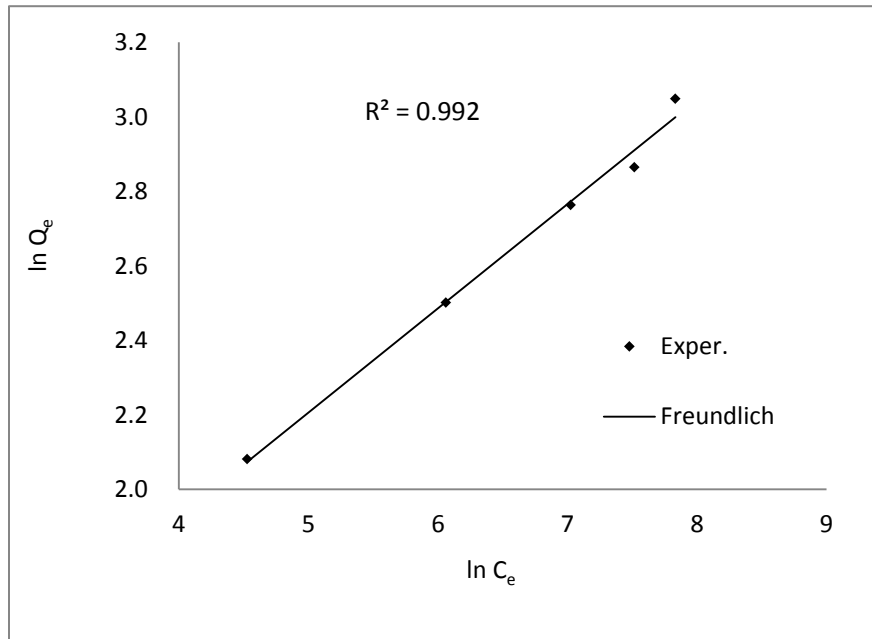


Fig. 4.5 Linearized Freundlich isotherm plots for ammonia removal from aqueous solution by zeolite

Fig. 4.6 shows both Langmuir and Freundlich isotherm models along with experimental data. The constants and correlation coefficients for both Langmuir and Freundlich model were calculated. The values are given in Table 4.4. Both models performed well in describing the adsorption process, however, Freundlich isotherm

model provided a better fit to the experimental (higher  $R^2$  value of 0.992) compared to Langmuir isotherm model. The Freundlich intensity parameter ( $1/n$ ) is an indicator of surface heterogeneity or exchange intensity. An  $1/n$  value of 0.28 was close to the result ( $1/n = 0.279$ ) obtained by Du et al. (2005) and in the range of 0.1 to 1.0, which suggested that the process of ammonia removal from aqueous solution by zeolite was under favorable conditions (Acar and Malkoc, 2004).

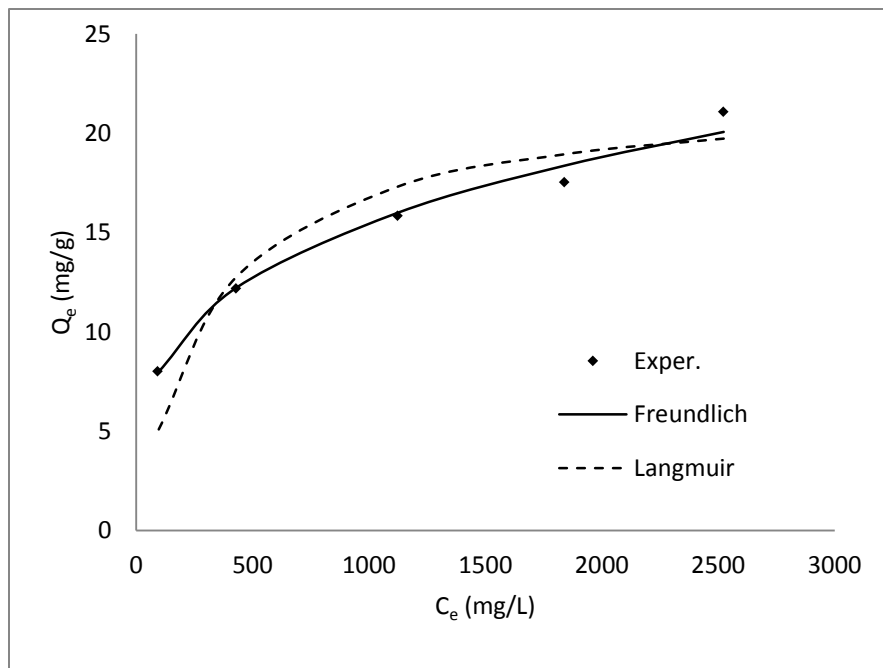


Fig. 4.6 Equilibrium data of ammonia removal from aqueous solution by zeolite fitted to Langmuir and Freundlich isotherms

Table 4.4 Isotherm constants for zeolite

Langmuir			Freundlich		
a (mg/g)	b (L/mg)	$R^2$	$K_f$ (L/mg)	$1/n$	$R^2$
22.22	0.003	0.974	2.24	0.280	0.992

#### 4.3.5 Statistical analysis and modelling

Based on a factorial design of three independent variables at two levels in triplicates, a total of 60 runs of the ammonia removal experimental results in terms of the adsorption capacity ( $Q_e$ ) were obtained. The response  $Q_e$  was predicted by a second order polynomial equation shown as Eq. (4.9) below.

$$Q_e = 14.143 - 2.671 \text{ pH} + 0.076T + 5.430 \text{ TAN} - 1.255TAN^2 + 0.009\text{pH} * T - 1.086 \text{ pH} * T + 1.115 T * \text{TAN} \quad \text{Eq. (4.9)}$$

Table 4.5 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 230.50 and the Prob > F value of < 0.0001 indicate that the model was statistically significant for ammonia removal. For parameters T, pH\*T and T\*TAN the Prob > F value was greater than 0.1 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. (4.10) and presented in Table 4.5. The confidence interval as well as the standard error of the coefficient is also presented in Table 4.6. As can be seen from Table 4.5, the reduced quadratic model was significant with a model F-value of 430.73 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  $R^2$  ( $R^2_{adj.}$ ) value of the reduced model was 0.966 compared to a value of 0.965 for the full model showing a slight improvement after eliminating insignificant terms (Sapsford and Jupp, 2006). An adequate precision ratio of 61.769 indicates an adequate signal (adequate precision > 4) (Bashir et al., 2010). The mean square values for the model as well as each model term are presented in Appendix (Table A1).

Table 4. 5 ANOVA for quadratic model parameters

Source	Full quadratic model				Reduced model			
	DF	Sum of squares	F-value	Prob > F	DF	Sum of squares	F-value	Prob > F
Model	7	1380.15	230.50	< 0.0001	4	1394.55	430.73	< 0.0001
pH	1	417.48	488.06	< 0.0001	1	424.17	524.05	< 0.0001
T	1	0.18	0.21	0.6496	-	-	-	-
TAN	1	924.31	1080.59	< 0.0001	1	930.56	1149.69	< 0.0001
pH*T	1	0.052	0.061	0.8060	-	-	-	-
pH*TAN	1	35.92	41.99	< 0.0001	1	37.24	46.01	< 0.0001
T*TAN	1	0.29	0.34	0.5611	-	-	-	-
TAN <sup>2</sup>	1	14.72	17.21	0.0001	1	15.66	19.35	< 0.0001
Resid. error	52	44.48	-	-	55	44.52	-	-
Lack-of-fit	12	27.92	5.62	< 0.0001	15	27.68	4.39	< 0.0001
Pure error	40	16.56	-	-	40	16.83	-	-
Total	59	1424.63	-	-	59	1439.07	-	-
R <sup>2</sup> = 0.969, R <sup>2</sup> <sub>adj</sub> = 0.965, R <sup>2</sup> <sub>pred</sub> = 0.958, Adequate precision = 48.136				R <sup>2</sup> = 0.969, R <sup>2</sup> <sub>adj</sub> = 0.966, R <sup>2</sup> <sub>pred</sub> = 0.963, Adequate precision = 61.769				

$$Y_1 = 14.143 - 2.671\text{pH} + 5.430\text{TAN} - 1.255\text{TAN}^2 - 1.086\text{pH} * \text{TAN} \quad \text{Eq. (4.10)}$$

Table 4.6 Model coefficient and CI (zeolite)

Factor	Coefficient estimate	DF	Standard error	95% low	CI	95% high	CI	VIF
Intercept	14.14	1	0.19	13.76		14.53	-	
pH	-2.67	1	0.12	-2.90		-2.44		1.01
TAN	5.43	1	0.16	5.11		5.75		1.00
pH*TAN	-1.09	1	0.16	-1.41		-0.77		1.01
TAN <sup>2</sup>	-1.25	1	0.29	-1.83		-0.68		1.00

The results of ANOVA showed that the lack-of-fit was significant ( $P < 0.0001$ ). This means that there might be some systematic variation 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., 2010). Introducing a higher order term to the model could result in a more complicated model, with higher number of terms and insignificant lack-of-fit. In fact in this case a quartic model showed no significant lack-of-fit ( $P > 0.1$ ), 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.  $R^2_{adj.} = 0.966$  indicates that only less than 4% of the total variation could not be explained by the empirical model.

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 0.969 ( $R^2_{adj.} = 0.966$ ), indicating a very good agreement between the predicted response and observed results. Fig. 4.7 illustrates the plot of calculated outcomes by the model versus observed experimental data for ammonia removal. All points were distributed close to the straight line in the model, confirming a reasonable good fit of the reduced model.

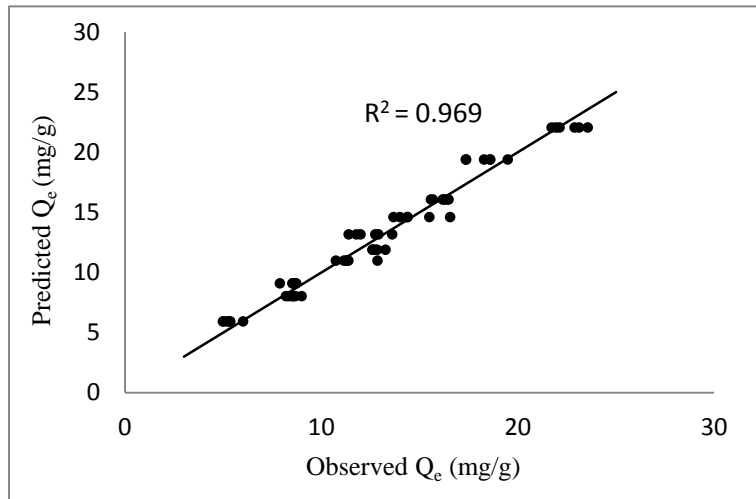


Fig. 4.7 Predicted versus observed experimental values for the reduced model

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 real system, diagnostic plots of residuals were produced and evaluated. Fig. 4.8 presents 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. 4.8, 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. Figs. 4.9a and 4.9b are 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 across the graph confirming the model was accurate and there was no need to suspect any violation of the independence or constant variance assumption in all runs.

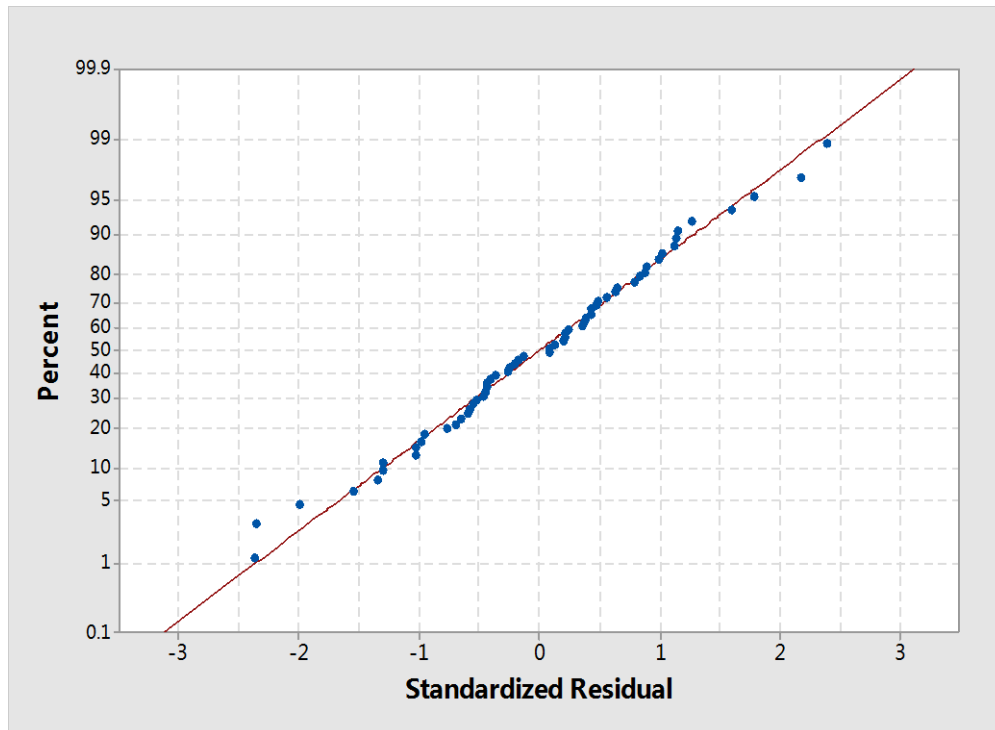


Fig. 4.8 Normal probability plot of the standardized residual for ammonia removal

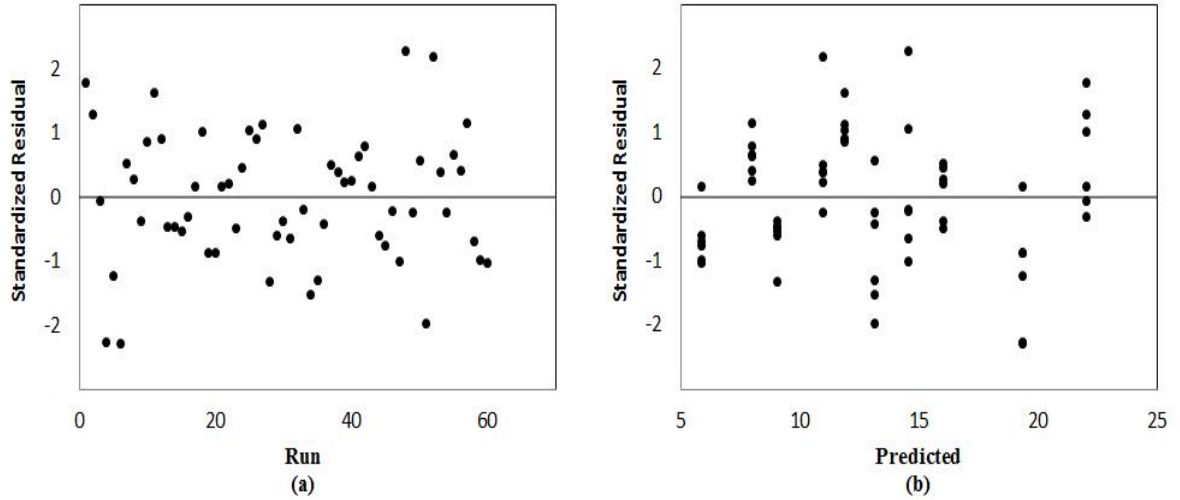


Fig. 4.9 Diagnostic plots for ammonia removal (a) standardized residual versus runs, and (b) standardized residuals versus predicted

#### 4.3.6 Response surface methodology

As temperature was found not to be a significant model parameter and was excluded from Eq. (4.9), response surface methodology 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. 4.10 and Fig. 4.11, respectively. It is obvious from the figures 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 pH of 7 and initial TAN concentration of 3000 mg/L (Fig. 4.10), and the maximum  $Q_e$  predicted within the range of experiment is 21.89 mg/g.

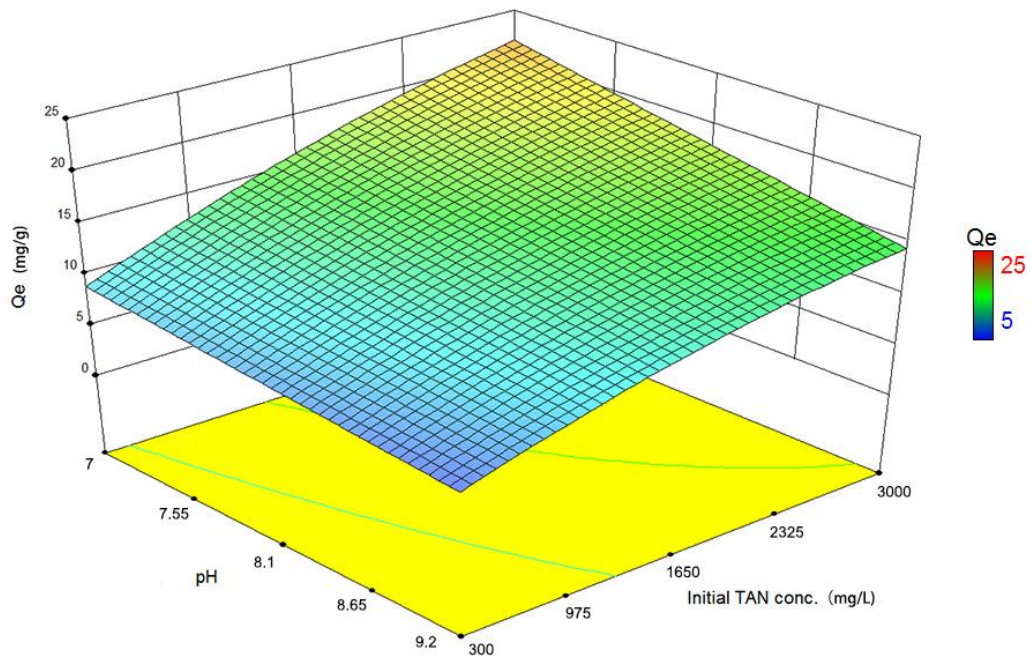


Fig. 4.10 Surface plot by response surface methodology

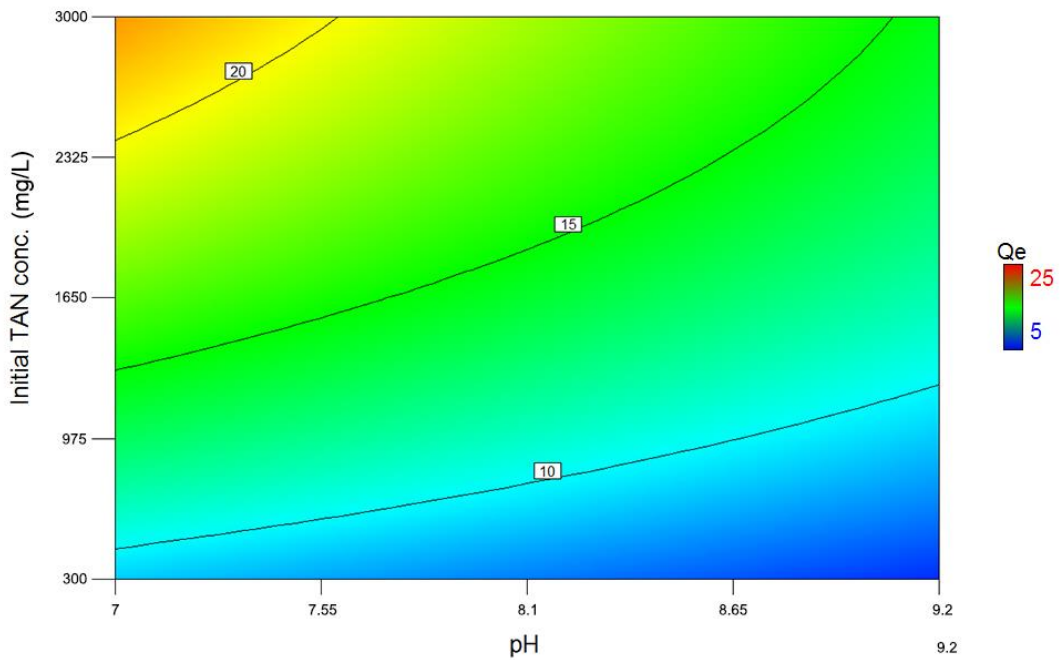


Fig. 4.11 Contour plot by response surface methodology

## 4.4 Conclusion

Experimental results indicated that zeolite can be an alternative low-cost material for ammonia removal from aqueous solution and can be used to treat or pre-treat any wastewater containing high ammonia concentration such as landfill leachate.

Removal strongly depended on pH and ammonia concentration with the optimum pH found to be around 6. The removal efficiency also increased with the increasing zeolite dose while  $Q_e$  decreased with the increasing zeolite dose. Statistical analysis of experimental data based on a factorial design and RSM showed that temperature was not a significant parameter in the process. The correlation coefficient of determination  $R^2$  was 0.969, indicating that the observed results fitted well with the model prediction. Surface plot and contour plot showed the optimum  $Q_e$  was achieved within the range of experiment is 21.89 mg/g at a pH of 7 and initial TAN concentration of 3000 mg/L TAN.

Equilibrium was achieved in 4 hours. The Pseudo-second order kinetic model provided the best prediction for the ammonia removal process among seven selected kinetic models. Both Freundlich and Langmuir isotherm models were able to describe the results well ( $R^2=0.992$  and  $R^2=0.974$ , respectively).

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**CHAPTER V**  
**TECHNICAL PAPER II**

**Statistical Analysis and Optimization of Ammonia Removal from Aqueous Solution  
by an Ion-exchange Resin Using Factorial Design and Response Surface  
Methodology**

**Yuanhao Ding, Majid Sartaj**

**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 a high removal rate (83.60%) and low exchange capacity (8.43 mg/g). Results of factorial design and response surface methodology showed that temperature was not a significant parameter. The reduced 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 reaction 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 provides a slightly better simulation ( $R^2=0.996$ ).

Keywords: Ammonia; ion-exchange; isotherm; factorial design; response surface

methodology

## 5.1 Introduction

In aqueous solutions, ammonia exists in two forms: unionized ammonia ( $\text{NH}_3$ ) and ionized ammonia ( $\text{NH}_4^+$ ) with  $\text{NH}_3$  being the form that is toxic to most fish species even at low concentrations (0.53 to 22.8 mg/L) (Randall et al., 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 to 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 ( $\text{NH}_3$ ) (Martinen et al., 2002). Adsorption by activated carbon adsorption 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 (Lin and Wu, 1996; Lei and Zhange, 2008; Bashir et al., 2010). 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., 2010).

Solid ion-exchangers can be classified as natural-inorganic particles and synthetic-organic resins. The first commercially used ion exchanger was natural zeolite (Bashir et al., 2010). 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). 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 Na type 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, zeolite dose and temperature were also investigated. In addition, reaction kinetics and isotherms were modeled using existing common models.

## 5.2 Material and methods

### 5.2.1 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.). Properties of the resin were provided by the manufactory (Dow Chemical Co., 2013) (see Table. 5.1).

Table 5. 1 Properties of Amberlite IR120 H

Properties		
Physical form	Amber spherical	
Matrix	Styrene divinylbenzene copolymer	
Ionic form as shipped	H <sup>+</sup>	
Total exchange capacity	≥ 1.80 eq/L (H <sup>+</sup> form)	
Moisture holding capacity	53 to 58 % (H <sup>+</sup> form)	
Shipping weight	800 g/L	
Uniformity coefficient	≤ 1.8	
Harmonic mean size	0.620 to 0.830 mm	
	< 0.300 mm	
	2 % max	
Maximum reversible swelling	Na <sup>+</sup> → H <sup>+</sup> ≤ 11 %	
Maximum operating temperature	135 °C	
Regenerants	H <sub>2</sub> SO <sub>4</sub>	HCl
Concentration	0.7 – 6 %	5 – 8 %
Minimum contact time	30 minutes	

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 pretreated with different types of strong acids (HCl and H<sub>2</sub>SO<sub>4</sub>) concentration at 0.1, 0.5, 1.0 normality (N) in sequence over 4 hours to completely convert cation exchanger to their H<sup>+</sup> form. Previous study has reported that cation exchanger has higher removal efficiency in H<sup>+</sup> form than in Na<sup>+</sup> form (Bashir et al., 2010). After that, resin was washed with DW again to remove all the acid and dried at room temperature (25±1 °C).

### 5.2.2 Synthetic ammonia solution

Synthetic ammonia stock solution of 3000 mg/L as TAN was prepared by dissolving 5.72g analytical grade NH<sub>4</sub>Cl into 500 mL distilled water. Then the stock solution was diluted with DW to achieve desired concentration.

### 5.2.3 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. (5.1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (5.1)$$

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 removal efficiency was obtained by Eq. (5.2):

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (5.2)$$

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

#### 5.2.4 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 1N NaOH or 1N HCl. Samples were agitated by the shaker at 130 rpm for 24 hours. A separate test confirmed that 24 hours 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. The 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 factorial design was implemented with pH (pH), temperature (T) and initial TAN concentration in the solution (TAN) as the independent variables. 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 5.2. 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.

Table 5. 2 Independent variables of the experimental design

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

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 orbital shaker at 130 rpm for 24 h to achieve equilibrium. Then samples were centrifuged at 8000 rpm for 10 min and the supernatant TAN concentration were measured.

### 5.2.5 Kinetics experiments

4.0 g of ion-exchange resin was added to 400 mL synthetic ammonia solution with TAN concentration of 1000 mg/L in 1L Erlenmeyer flask. The reactor was immediately subjected to agitation in an orbital shaker at 130 rpm. The supernatant was taken from the solution at 1, 2, 5, 10, 20, 30, 60, 120, 240 and 360 minutes after the shaking started.

Duplicates were achieved by repeating the kinetic experiment under the same conditions.

### 5.2.6 Statistical analysis

The response surface methodology (RSM) is a combination of mathematical and statistical techniques commonly used in optimization of chemical reactions and industrial processes (Ölmez, 2009; Sharma et al., 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 ( $Q_e$ ) as the outcome response. The behavior of the system is usually described by the quadratic equation shown as Eq. (5.3) (Montgomery, 2008).

$$Y_1 = A_0 + \sum_{i=1}^n A_i X_i + \sum_{i=1}^n A_{ii} X_i^2 + \sum_{i \neq j=1}^n A_{ij} X_i X_j + \varepsilon \quad (5.3)$$

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 if there is still some variation unaccounted in the model and the need to add additional terms to improve the model (Xu et al., 2014).

### 5.2.7 Regeneration

The regeneration of Amberlite IR120 H ion-exchange resin was also studied. Exhausted resin was regenerated by immersion in 2N H<sub>2</sub>SO<sub>4</sub> for 12 hours according to manufacturer's guide (Dow Chemical Company, 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.

## 5.3 Results and discussion

### 5.3.1 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±1 °C) and the results are shown in Fig. 5.1. Maximum removal occurred at pH=6, which was in good agreement with Lin and Wu, (1996).  $Q_e$  slightly increased with the pH increase from 4 to 6 and then started to decrease as pH was increased to 10. The decrease of  $Q_e$  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<sub>4</sub><sup>+</sup>, while under high pH conditions (pH > 7), NH<sub>3</sub> starts to become the dominant species (Nair et al., 2014). For optimum ion-exchange operation, it is preferred to keep ammonia in the ionized form to enhance the main removal mechanism which is mainly cation exchange. Thus, pH=6 was selected for subsequent kinetic tests. As stated before, the lower and upper limit for factorial design of main experiments were chosen pH=6 and pH=9.2, respectively.

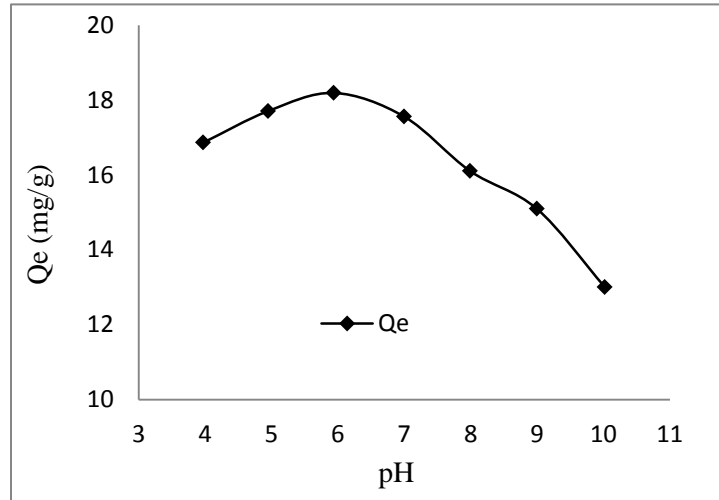


Fig. 5. 1 The effect of pH on TAN removal from aqueous solution using ion-exchange resin (initial TAN concentration of 100 mg/L and a resin dose of 25 g/L)

### 5.3.2 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 ion-exchange resin into 40 mL synthetic ammonia solution with an initial TAN concentration of 1000 mg/L, which is equal to 12.5, 25, 50 and 100 g/L of dose. Results in terms of removal efficiency and  $Q_e$  are illustrated in Fig. 5.2. The removal efficiency increased from approximately 30% to 84% with the increasing zeolite 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.

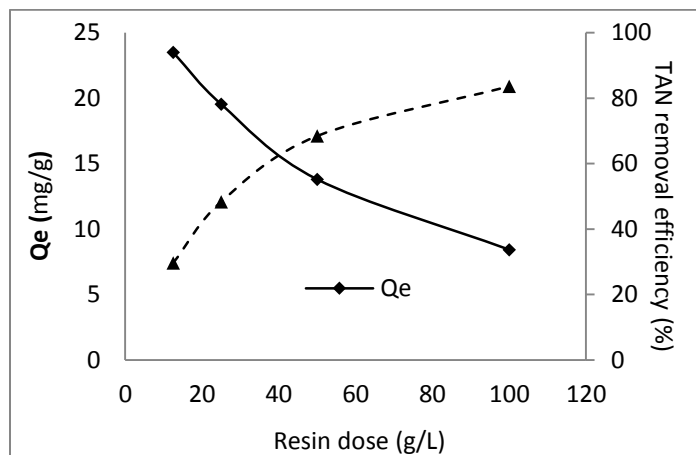


Fig. 5.2 The effect of resin dose on  $Q_e$  and removal efficiency (initial TAN concentration of 1000 mg/L)

### 5.3.3 Kinetics studies

Fig. 5.3 shows ammonia uptake by resin as a function of time.  $q_t$  increased with increasing contact time in the first 30 minutes and then equilibrium was reached. After that there was no significant increase in  $q_t$ . This result was in good agreement with results reported by Lin et al. (Lin and Wu, 1996).

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 5.3 summarizes the linearized equations of the selected seven kinetic models and their correlation coefficients ( $R^2$ ). According to the results, the Pseudo-second order rate expression provided the best fit with the highest  $R^2$  (0.999). The Pseudo-second order model has been widely applied to describe kinetics of sorption and ion-exchange process (Ho and Mckay, 1999; Bashir et al., 2010). It described mathematically below:

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (5.3)$$

and the linear version is :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5.4)$$

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-second order expression (g/ (mg h)).

Table 5.3 Kinetic modes for evaluating ammonia removal by ion-exchange resin

Model	Linearized Equation	R <sup>2</sup>
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

Linear regression was achieved by rearranging Eq (5.3) into Eq (5.4). The rate constant  $k_2$  was found from the intercept of Y axis ( $\frac{1}{k_2 q_e^2}$ ) by plotting  $t/q_t$  versus  $t$ . Fig. 5.3 also demonstrated the comparison of the actual experimental data and the predication

from the Pseudo-second order model.

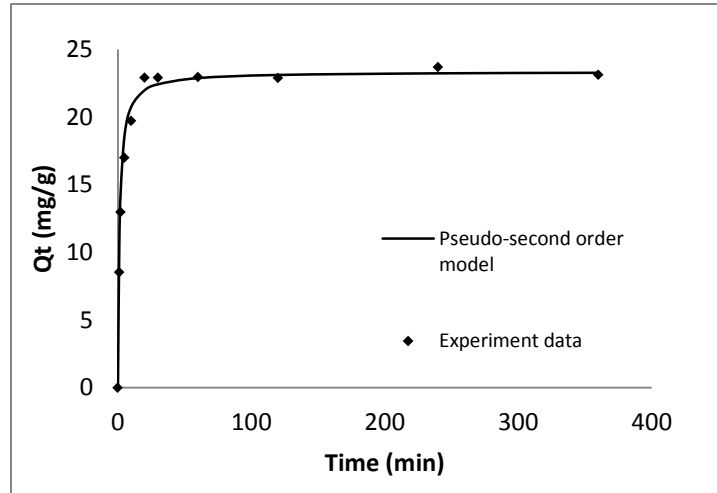


Fig. 5.3 Effect of contact time on ammonia removal by ion-exchange resin and the Pseudo-second order model prediction (initial TAN concentration of 1000 mg/L)

#### 5.3.4 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 the Langmuir isotherm is shown in Eq. (5.5).

$$Q_e = \frac{abC_e}{1+bC_e} \quad (5.5)$$

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;  $C_e$  is equilibrium concentration of TAN in solution (mg/L). By rearranging the Langmuir equation into its

linear form shown as Eq. (5.6), the constants a and b can be determined by plotting  $C_e/Q_e$  versus  $C_e$  (Fig. 5.4).

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (5.6)$$

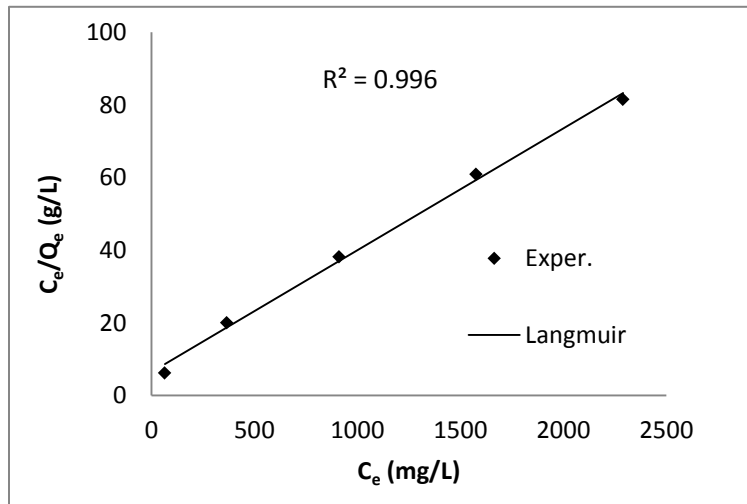


Fig. 5.4 Linearized Langmuir isotherm plots for ammonia removal from aqueous phase by ion-exchange resin

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 Eq. (5.7) and Eq. (5.8), respectively. The constants  $K_f$  and  $1/n$  can be determined by plotting  $\ln Q_e$  versus  $\ln C_e$  and the results were demonstrated in Fig. 5.5.

$$Q_e = K_f C_e^{1/n} \quad (5.7)$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5.8)$$

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.

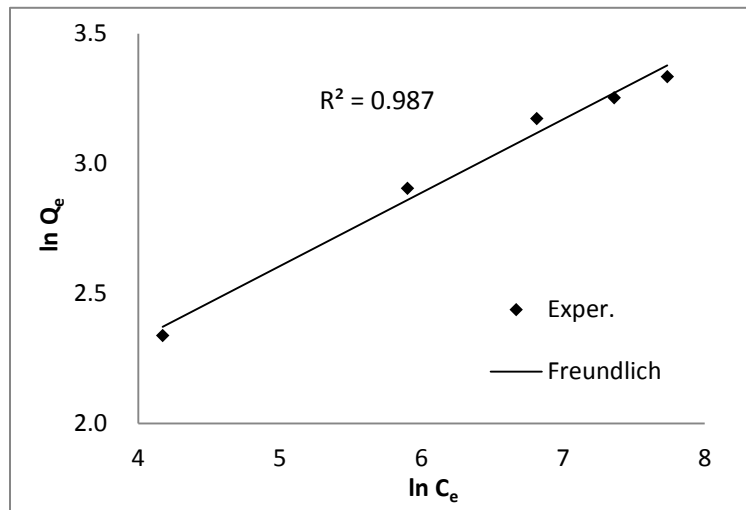


Fig. 5.5 Linearized Freundlich isotherm plots for ammonia removal from aqueous phase by ion-exchange resin

Fig. 5.6 shows the both Langmuir and Freundlich isotherm models along with experimental data. The constants and correlation coefficients for both Langmuir and Freundlich model were calculated. The values are given in Table 5.4. 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-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 Mohammed et al. (2010) using another ion-exchange resin (12.56 mg/g) (Bashir et al., 2010).

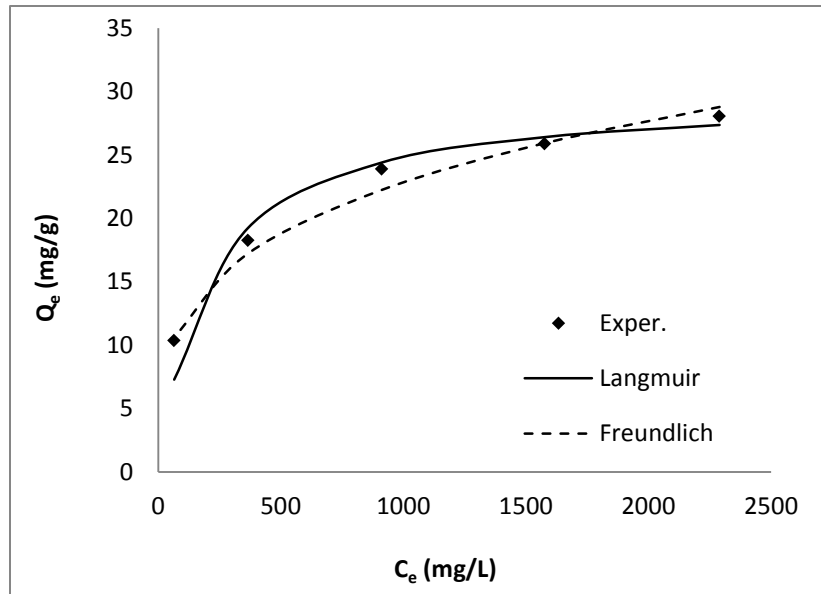


Fig. 5.6 Equilibrium data of ammonia removal from aqueous solution by ion-exchange resin fitted to Langmuir and Freundlich isotherms

Table 5.4 Isotherm constants for zeolite

Langmuir			Freundlich		
$a$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$ (L/mg)	$1/n$	$R^2$
29.76	0.005	0.996	3.30	0.28	0.987

### 5.3.5 Statistical analysis and modelling

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. (5.9) below.

$$Q_e = 22.501 - 2.199 \text{pH} + 0.019T + 7.434 \text{TAN} + 0.047\text{pH} * T - 0.782 \text{pH} * \text{TAN} + 0.140 T * \text{TAN} - 5.442 \text{TAN}^2 \quad \text{Eq. (5.9)}$$

Table 5.5 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. For parameters T, pH\*T and T\*TAN the Prob > F values were 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. (5.10) and the statistical analysis for this model is presented in Table 5.5. The confidence interval as well as the standard error of the coefficient is also shown in Table 5.6. As can be seen from Table 5.5, 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  $R^2$  ( $R^2_{\text{adj}}$ ) 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., 2010). The mean square values for the model as well as each model term are presented in Appendix (Table A2).

Table 5.5 ANOVA for quadratic model parameters

Source	Full quadratic model				Reduced model			
	DF	Sum of squares	F-value	Prob > F	DF	Sum of squares	F-value	Prob > F
Model	7	2371.47	168.10	< 0.0001	4	2370.72	308.82	< 0.0001
pH	1	287.59	142.70	< 0.0001	1	287.59	149.85	< 0.0001
T	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 <sup>2</sup> = 0.952    R <sup>2</sup> <sub>adj</sub> = 0.943,    R <sup>2</sup> <sub>pred</sub> = 0.952, Adequate precision = 37.522					R <sup>2</sup> = 0.957,    R <sup>2</sup> <sub>adj</sub> = 0.950,    R <sup>2</sup> <sub>pred</sub> = 0.954, Adequate precision = 48.172			

$$Q_e = 21.50 - 2.20 \text{ pH} + 7.43 \text{ TAN} - 0.78 \text{ pH} * \text{TAN} - 5.44 \text{ TAN}^2 \quad \text{Eq. (5.10)}$$

Table 5.6 Model coefficient and CI (IER)

Factor	Coefficient estimate	DF	Standard error	95% low	CI	95% high	CI	VIF
Intercept	14.14	1	0.19	13.76		14.53		-
pH	-2.67	1	0.12	-2.90		-2.44		1.01
TAN	5.43	1	0.16	5.11		5.75		1.00
pH*TAN	-1.09	1	0.16	-1.41		-0.77		1.01
TAN <sup>2</sup>	-1.25	1	0.29	-1.83		-0.68		1.00

The results of ANOVA showed that the lack-of-fit was significant ( $P < 0.0001$ ). This means that there might be some systematic variation unaccounted for in the model (Xu et

al., 2014). This may also be due to the close replicate values that provide an estimate of pure error (Bashir et al., 2010). Introducing a higher order term to the model could result in a more complicated model, with a 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.  $R^2_{adj.}=0.950$  indicates that only 5% of the total variation could not be explained by the empirical model.

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. Fig. 5.7 illustrates the plot of calculated outcomes by the model versus observed experimental data for ammonia removal.

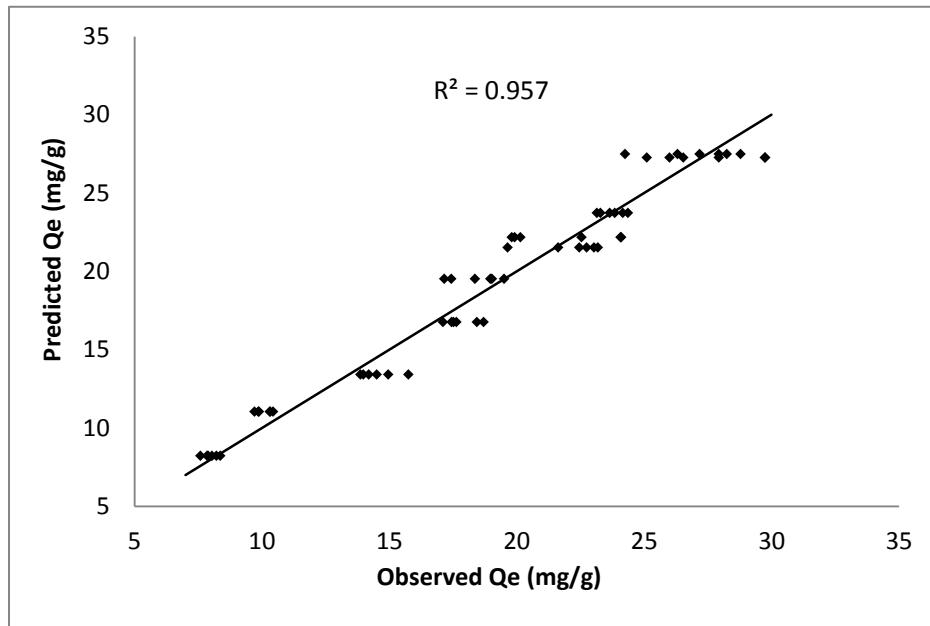


Fig. 5.7 Predicted versus observed experimental values for Qe

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 real system, diagnostic plots of residuals were produced and evaluated. Fig. 5.8 presents 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. 5.8, 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. Figs. 5.9a and 5.9b are 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 the model was accurate and there was no need to suspect any violation of the independence or constant variance assumption in all runs.

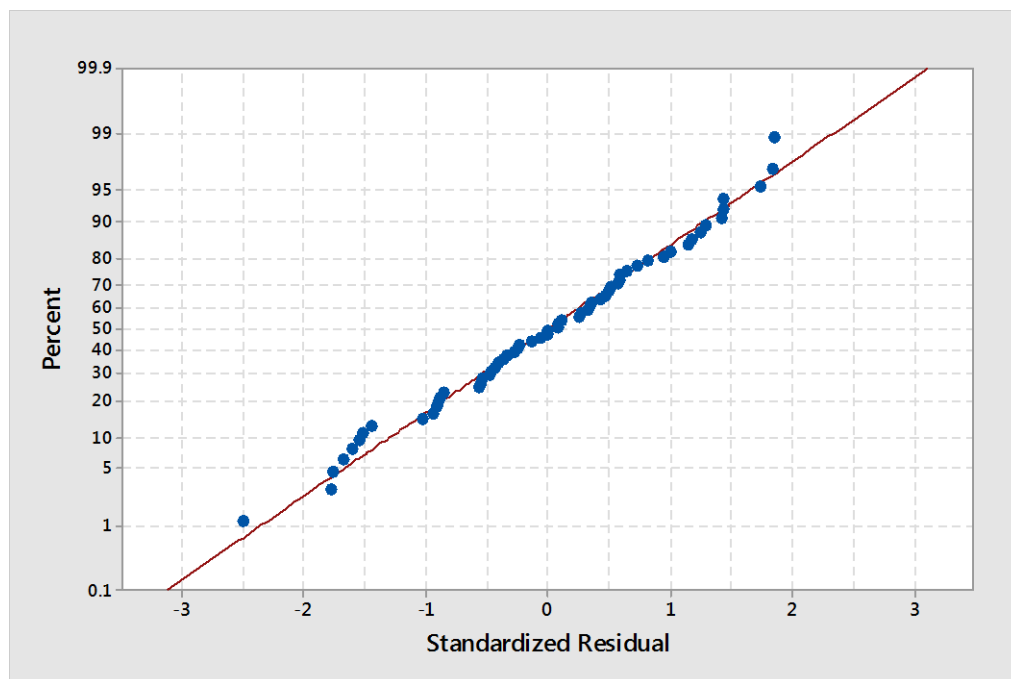


Fig. 5.8 Normal probability plot of the standardized residual for ammonia removal

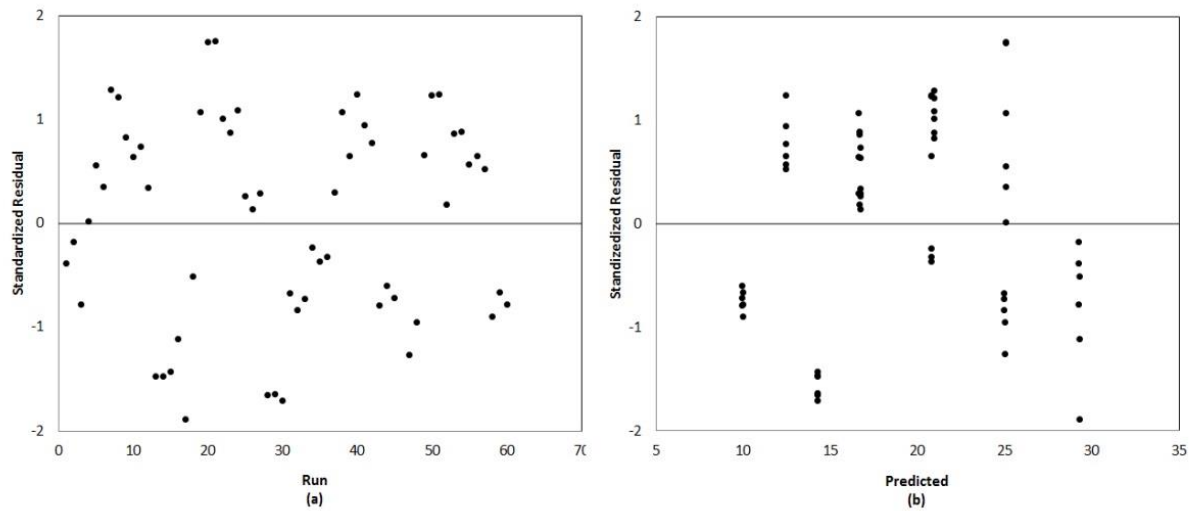


Fig. 5. 9 Diagnostic plots for ammonia removal (a) standardized residual versus runs, and (b) standardized residuals versus predicted

### 5.3.6 Response surface methodology

As temperature (T) was found not to be a significant model parameter and was excluded from Eq. (5.9), response surface methodology 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. 5.10 and Fig. 5.11, respectively. It is obvious from the figures 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 +1.0 for initial TAN concentration (3000 mg/L) (see Fig. 5.10), and the maximum  $Q_e$  predicted within the range of experiment is 27.47 mg/g.

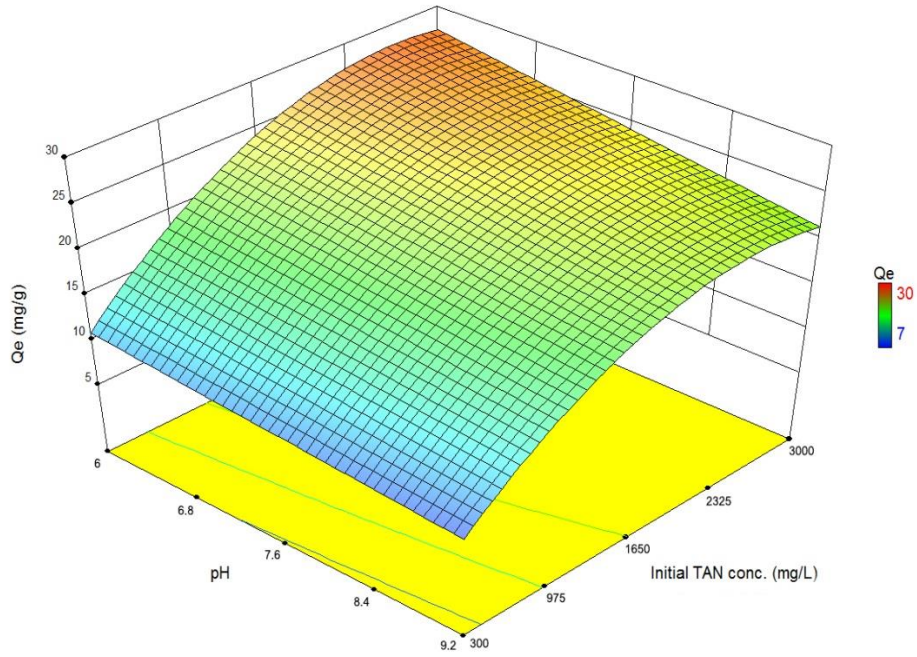


Fig. 5. 10 Surface plot by response surface methodology

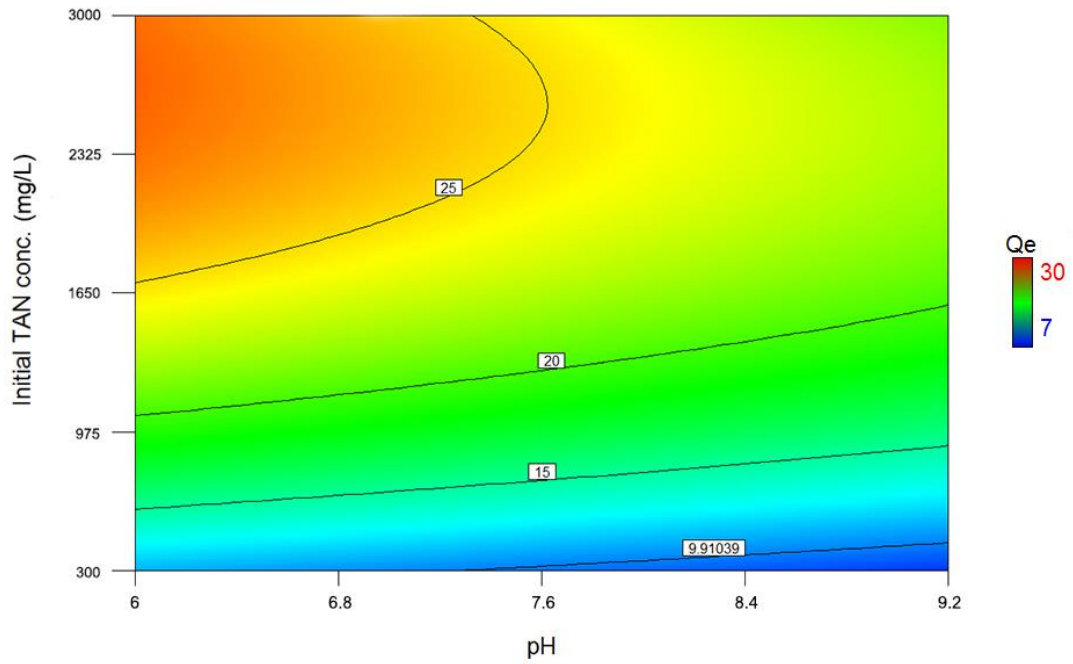


Fig. 5. 11 Contour plot by response surface methodology

### 5.3.7 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 2N  $H_2SO_4$ .

## 5.4 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 depended 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  $Q_e$  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  $Q_e$  was achieved within the range of experiment is 27.47 mg/g at pH of 6 and initial TAN concentration of 3000 mg/L.

Equilibrium was reached within 30 minutes. The Pseudo-second order kinetic model provided the best prediction ( $R^2=0.999$ ) 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.

## **Acknowledgements**

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## CHAPTER VI

### COMPARISON BETWEEN ZEOLITE AND ION-EXCHANGE RESIN

#### 6.1 Effect of pH

$Q_e$  of both zeolite and ion-exchange resin started to decrease from pH of 6 as illustrated in Fig. 6.1. This can be explained by the balance of ionized and unionized ammonia in the aqueous solution. In addition, at any pH,  $Q_e$  of ion-exchange resin is much higher than that of zeolite which indicates a better exchange ability (zeolite dose of 75 g/L and IER dose of 25 g/L, respectively).

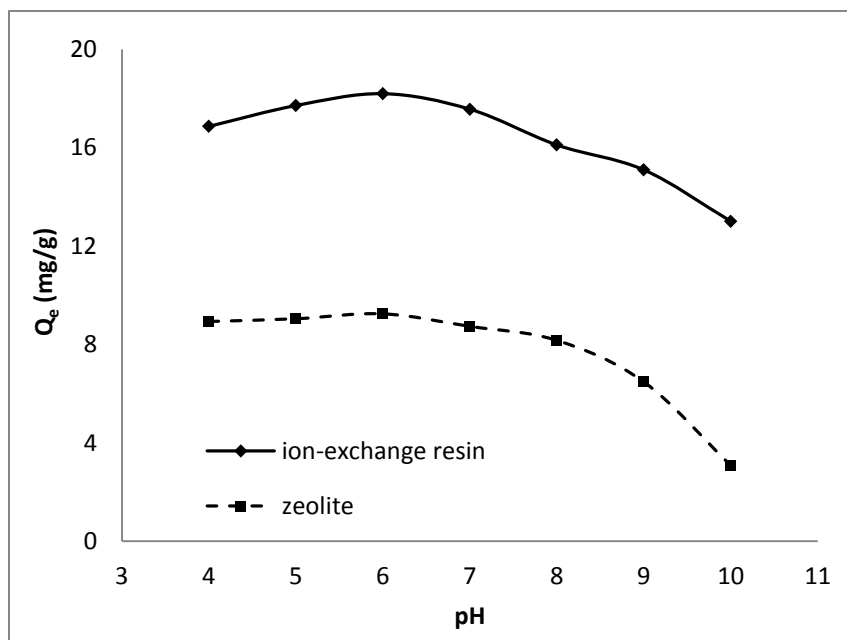


Fig. 6.1 Comparison between zeolite and ion-exchange resin (pH)

## 6.2 Reaction rate

As can be seen from Fig. 6.2, the reaction rate of ion-exchange resin is much faster than that of zeolite. For zeolite, it takes approximately 240 min to reach equilibrium while for ion-exchange resin it takes only 30 min. The adsorption capacity of ion-exchange resin at any time is about 30-60% higher than that of zeolite.

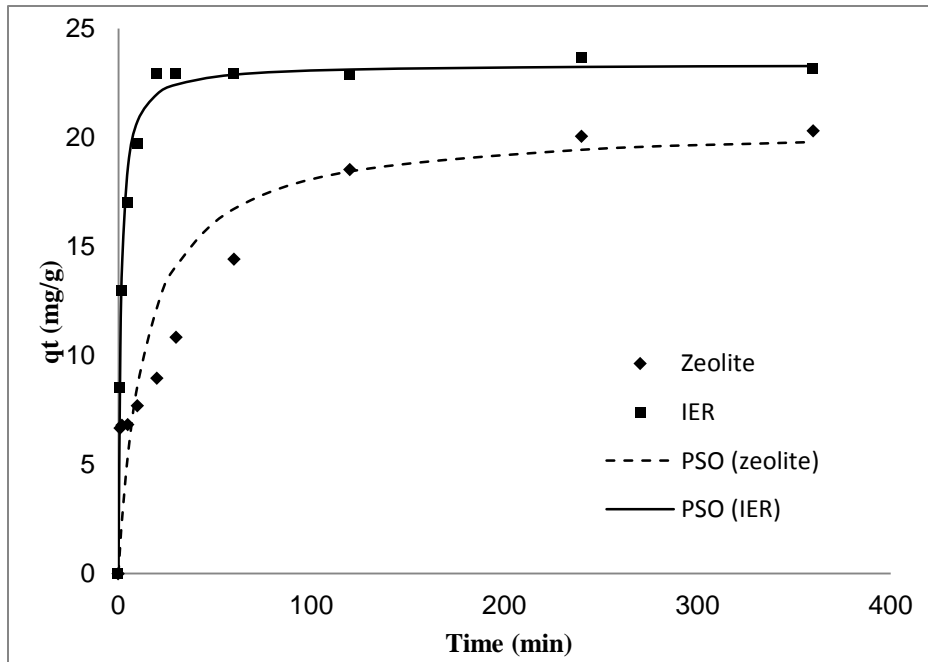


Fig. 6.2 Comparison between zeolite and ion-exchange resin (kinetics)

## 6.3 Isotherms

The ammonia loading ( $Q_e$ ) of ion-exchange resin was always higher than zeolite at any initial ammonia concentrations (see Fig. 6.3). Table 6.1 summarizes the isotherm models as well as model constants for zeolite and ion-exchange resin. Generally, the Langmuir constant  $a$  and Freundlich constant  $K_f$  are indicators of adsorption or exchange intensity. The values obtained for ion-exchange resin are higher than zeolite, which is

consistent with the experimental data.

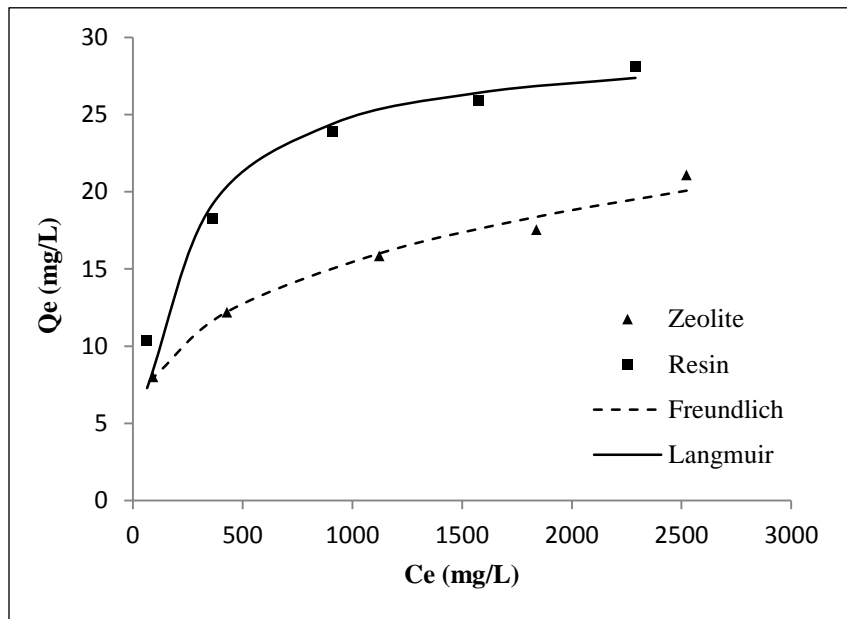


Fig. 6.3 Comparison between zeolite and ion-exchange resin (isotherms)

Table 6.1 Summary of isotherm models

Isotherm Model	Constants	Adsorbent	
		Zeolite	Ion-exchange Resin
Langmuir	$R^2$	0.974	0.997
	a	22.222	29.762
	b	0.003	0.005
Freundlich	$R^2$	0.992	0.987
	1/n	0.280	0.282
	$K_f$	2.241	3.300

## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1. Conclusions

The ability of zeolite and ion-exchange resin for ammonia removal from aqueous solution was studied. The results showed that both zeolite and ion-exchange resin were able to eliminate ammonia from aqueous solution with high efficiency (up to 87% of removal). Therefore, these two materials can be used in treating or pretreating wastewater containing high ammonia concentration such as landfill leachate.

Removal process strongly depended on the pH. Low pH conditions were preferred by both zeolite and ion-exchange resin due to the balance of two types of ammonia in liquid phase and ion-exchange being the dominant removal mechanism. The removal efficiency increased with the increasing dose, while  $Q_e$  decreased with the increasing zeolite dose.

Statistical analysis of experimental data based on a factorial design and RSM showed that temperature was not a significant parameter in the processes for zeolite and ion-exchange resin. The impact of initial TAN concentration was much more significant than that of pH. High  $R^2$  values were obtained for both zeolite ( $R^2=0.969$ ) and ion-exchange resin ( $R^2=0.957$ ), indicating that the observed results fitted well with the model predictions. For zeolite, surface plots and contour plots showed the optimum  $Q_e$  achieved within the range of experiment was 21.89 mg/g at a pH of 7 and initial TAN concentration of 3000 mg/L for zeolite. Maximum  $Q_e$  for ion-exchange resin was found to be 27.47 mg/g at a pH of 6 and initial TAN concentration of 3000 mg/L.

Pseudo-second order kinetic model provided good predications for ammonia removal process using zeolite and ion-exchange resin ( $R^2=0.998$  and  $R^2=0.999$ , respectively). The equilibrium data of zeolite was characterized by Freundlich isotherm with  $R^2=0.992$ , while Langmuir isotherm provided a slightly better prediction for ion-exchange resin ( $R^2=0.996$ ).

The ion-exchange resin used in this study was successfully regenerated with no noticeable lost in equilibrium exchange capacity by 2N  $H_2SO_4$ . Natural zeolite is still considered to a promising material in terms of ammonia removal from aqueous solution, although synthetic ion-exchange resin demonstrated higher exchange capacity and faster exchange speed.

## **7.2.Future work**

Based on the results from the current study, it was proved that zeolite and ion-exchange resin were effective for ammonia removal from aqueous solution. So far, only synthetic ammonia solution was used to simulate wastewater with high levels of ammonia. The presence of other compounds is likely to have impacts on the processes. In addition, other cations within the liquid phase may compete for the ion-exchange sites. Therefore, it is suggested to use real landfill leachate, which contains a variety of other constituents, to study the behavior of these two materials for ammonia removal under more realistic conditions

Furthermore, only batch experiments were conducted in this phase. Column studies could be conducted by packing zeolite and ion-exchange resin into small scale columns.

## APPENDIX

Table A1 ANOVA of reduced model (zeolite)

Source	DF	Sum of squares	F-value	Prob > F	Mean square
Model	4	1394.55	430.73	< 0.0001	348.64
pH	1	424.17	524.05	< 0.0001	424.17
TAN	1	930.56	1149.69	< 0.0001	930.56
pH*TAN	1	37.24	46.01	< 0.0001	37.24
TAN <sup>2</sup>	1	15.66	19.35	< 0.0001	15.66
Resid. error	55	44.52	-	-	0.81
Lack-of-fit	15	27.68	4.39	< 0.0001	1.85
Pure error	40	16.83	-	-	0.42
Total	59	1439.07	-	-	

Table A2 ANOVA of reduced model (ion-exchange resin)

Source	DF	Sum of squares	F-value	Prob > F	Mean square
Model	4	2370.72	308.82	< 0.0001	592.68
pH	1	287.59	149.85	< 0.0001	287.59
TAN	1	1743.86	908.64	< 0.0001	1743.86
pH*TAN	1	19.33	10.07	0.0025	19.33
TAN <sup>2</sup>	1	294.70	153.56	< 0.0001	294.70
Resid. error	55	105.56	-	-	1.92
Lack-of-fit	15	80.89	8.74	< 0.0001	5.39
Pure error	40	24.67	-	-	0.62
Total	59	2476.27	-	-	