

# **UNIVERSITI PUTRA MALAYSIA**

# KINETICS AND MECHANISM OF AMMONIUM ION ADSORPTION USING NATURAL ZEOLITE - MORDENITE

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## KINETICS AND MECHANISM OF AMMONIUM ION ADSORPTION USING NATURAL ZEOLITE – MORDENITE

By

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Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Food Science and Biotechnology University Putra Malaysia

February 2001

## DEDICATION

Bismillahirrahmannirahim,

Alhamdullillah.

Specially dedicated to:

– My Supervisor @ Prof. Dr. Mohamed Ismail Bin Abdul Karim

- My Committee Members @ Prof. Madya Dr. Arluskariya Bin Ariff
  - @ Prof. Madya Dr. Mohd Ali Bin Hassan
- My father @ Halimoon Bin Hamid
- My mother @ Rahamah Bt Mohd
- All my siblings
- All my friend
- And My special friend @ Khairul Husni Kamaruddin

Thanks for your loving support during the difficult time.

Amin.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Professor Dr. Mohamed Ismail Bin Abdul Karim

Faculty: Food Science and Biotechnology

Mordenite, one of the natural zeolites, has the capacity to remove ammonium ion from wastewaters through adsorption phenomenon. This study is a preliminary work of using mordenite to remove ammonium in effluent for tertiary treatment. The feasibility of using mordenite to remove ammonium ion in aqueous solution was carried out using shake flask, stirred tank batch reactor and packed-bed column experiments. The effect of mordenite particle size, ammonium concentration, mordenite concentration, pH, temperature and degree of agitation on the efficiency of adsorption were investigated. The kinetics of ammonium ion sorption was determined using Langmuir and Scatchard sorption isotherm models. The mechanism of ammonium adsorption was investigated using FTIR and electron microscope.

In shake flask experiment under equilibrium conditions, the efficiency of ammonium ion removal was optimum at resident time of 6 hours, for granules of 75  $\mu$ m size, in water containing less than 6 mg/L ammonium ion, in mordenite concentration of 3 g/L, at room temperature, with agitation of 200 rpm and near neutral initial pH (6.5-7.5). Ammonium ion removal of 94% (2.49 mg/g uptake) was achieved when 50 g/L mordenite was used to remove 100 mg/L ammonium concentration under optimum conditions. The sorption isotherm kinetic data of ammonium ion by mordenite fitted well to Langmuir model but did not fit well to Scatchard plot. SEM and FTIR data indicated that ammonium ion was adsorbed on the mordenite particle. When 2 L stirred tank reactor was used as a contactor, the ammonium uptake capacity ranging from 85-96% was obtained at agitation speed of 200 rpm, concentration of mordenite of 2.67 g/L and 6 mg/L ammonium concentration. Absolute removal of ammonium from solution was achieved when fixed packed-bed column was used as a contactor at low flowrate (2 mL/min) and increased weight of mordenite in the column (48 g), which show less than 5 mg/L ammonium in the effluent before breakthrough was achieved when 100 mg/L ammonium concentration was used. Desorption experiments showed that 37% ammonium recovery in the shake flask and 80-98% in the column contactor. From the study, the result indicated that mordenite has a potential to be promoted as adsorbent that could be used to removed ammonium from solution and can be apply for wastewater treatment.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan Ijazah Master Sains

## KINETIK DAN MEKANISMA PENJERAPAN ION AMMONIUM OLEH ZEOLITE SEMULAJADI- MORDENITE

Oleh

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Februari 2001

### Pengerusi : Profesor Dr. Mohamed Ismail Bin Abdul Karim

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Mordenite adalah satu daripada zeolite semulajadi yang mempunyai keupayaan untuk memindahkan ion ammonium dari air sisa secara penjerapan. Kajian ini adalah asas untuk memindahkan ammonium menggunakan mordenite dalam merawat air sisa peringkat ketiga. Kebolehan mordenite memindahkan ion ammonium dalam larutan akuas telah dijalankan dalam kelalang pengoncang, reaktor pengaduk dan turus 'packed-bed'. Kesan kecekapan penjerapan telah dijalankan ke atas saiz partikal, kepekatan ammonium, kepekatan mordenite, pH larutan, suhu dan darjah pengacauan pada keseimbangan. Kinetik jerapan ion ammonium ditentukan menggunakan model isotherma jerapan seperti Langmuir dan Scatchard. Manakala mekanisma penjerapan ditentukan menggunakan FTIR dan mikroskop elektron.

Dalam ujikaji kelalang penggoncang pada keseimbangan, kecekapan penjerapan adalah optima pada masa 6 jam, partikal size 75  $\mu$ m, kepekatan ion ammonium <6 mg/L, kepekatan mordenite 3 g/L, pada suhu bilik 30°C, pengacauan 200 rpm dan pH awal hampir natural (6.5-7.5). Pemindahan ion ammonium mencapai 94% (2.49 mg/g) menggunakan 50 g/L mordenite untuk memindahkan 100 mg/L ammonium pada keadaan optima. Data kinetik penjerapan isoterma ion ammonium oleh mordenite dari ujikaji menepati model Langmuir tetapi tidak menepati model Scatchard. Data SEM dan FtiR menunjukkan ammonium terjerap di atas partikal mordenite. Apabila tangki pengaduk 2 L digunakan sebagai kontaktor, pengambilan ammonium paling baik dalam julat 85-96% diperolehi pada kelajuan pengacauan 200 rpm, kepekatan mordenite 2.67 g/L dan kepekatan ammonium 6 mg/L. Pemindahan ammonium dalam larutan paling berkesan dicapai apabila turus 'packed bed' digunakan sebagai kontaktor pada kadar alir yang rendah (2 mL/min) dan pada berat mordenite yang paling tinggi dalam turus (48 g), yang menunjukkan kurang daripada 5 mg/L ammonium dalam larutan akhir sebelum 'breakthrough' dicapai pada kepekatan awal 100 mg/L. Ujikaji nyah-jerapan menunjukkan 37% ammonium diperolehi dalam kelalang penggoncang dan 80-98% dalam turus. Dari ujikaji ini, menunjukkan mordenite berpotensi sebagai bahan penjerap untuk memindahkan ammonium dalam larutan dan boleh diagihkan untuk merawat air sisa.

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# LIST OF ABBREVIATIONS

Ca	Calcium
$C_{eq}$	Adsorbate concentration at equilibrium (mg/L)
Cl	Chlorine
Co	Initial adsorbate concentration (mg/L)
COD	Chemical oxygen demand
Cs	Cesium
DOE	Development of Environment
EC	Environmental Center
Н	Hydrogen
H <sub>3</sub> O	Hydrosonium ion
$\Delta H^{\circ}$	Standard enthalpy
INWQS	The Interim National Water Quality Standard
K	Potassium
Mg	Magnesium
Na	Sodium
NH3	Ammonia gas
NH4 <sup>+</sup>	Ammonium ion
Nif	nitrogen fixation
O&G	oil and grease
OH-	Hydroxyl ion
pН	Hydrogen potential
Q	Experimental maximum ammonium ion adsorption (mg/g)
q	Amount of adsorbate adsorbed at time t (mg/g)
$q_{o}$	Amount of adsorbate adsorbed per unit weight of adsorbent
	at the beginning of adsorption process (mg/g)
<b>q</b> <sub>eq</sub>	Amount of adsorbate adsorbed per unit weight of adsorbent
	at equilibrium (mg/g)
Rb	Rubidium
SEM	Surface Electron Microscope
t	Time (minute)
TMA	Tetramethylammonium
TOC	Total organic carbon
TSS	Total Suspended solid
US	United State
Vo	Volume of solution in the contactor (L)
WHO	The World Health Organization
WQI	Water Quality Index
Wt	Weight
Xo	Amount or weight of adsorbent in the contactor (g)
Zeo	Zeolite

#### CHAPTER 1

### **INTRODUCTION**

Nowadays our environments are exposed to polluted water such as domestic sewage, industrial and animal wastewaters. The basic component of municipal wastewater is a mixture of domestic wastewater with small amounts of industrial, agro-zoo-technical and housing wastewater (Negulescu, 1986) and its composition varies from town to town. This type of wastewater is harmful to the environment if discharged at high concentrations because it contains solids, heavy metals and other organic compounds. One of the compounds in municipal wastewater is ammonium, which is present in wastewater streams including municipal, industrial and animal wastewaters. The concentration of ammoniacal nitrogen in raw domestic wastewater ranged from 12 to 50 mg/L (Long, 1990).

Generally, un-ionized ammonium enters water system as a pollutant and may become toxic to fish if nitrification does not convert the reduced form to nitrite and ultimately to nitrate (Thurston *et al.*, 1978). High amounts of ammonia in water supply also increases the chlorine dosage required achieving free residual chlorine in disinfection. When ammonia is present in the raw water at concentration higher than 0.3 mg/L, it can cause an unpleasant taste and odor when it is allowed to degrade anaerobically during treatment (Long, 1990). For this reason, ammonia in wastewater has to be reduced to concentration lower than

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0.2 mg/L before discharging to the river. The DOE Standard A show that the level of ammoniacal nitrogen in water supply and fishery uses is < 0.1 mg/L (Ministry of Agriculture, 1995). Out of 53 rivers monitored in Malaysia, as analyzed based on ammonical nitrogen index (Environmental Quality Report, 1990) (42%) was seriously polluted, 18 rivers (34%) were slightly polluted and 13 rivers (24%) were clean.

Activated carbon is known to effectively remove organic chemicals from water but ineffective for removing ammonia (Dawson *et al.*, 1976). Nitrification method, which has been used for treatment of wastewater is complicated and expensive. The usage of alum in the tap water treatment may end up as aluminium sulfate, which could endanger our health. Aluminium poisoning giving rise to tremors, loss of memory and jerking has first been reported in 1921 and there is evidence that aluminium can be a neurotoxin (Albery, 1996). Therefore, new alternative method to solve this problem of water treatment is urgently needed. There were some reports on the utilization of zeolite in wastewater treatment (Gottardi and Galli, 1985). Zeolite can be used as adsorbent to remove ammonium from solution. The first commercial application of zeolites, based on adsorption phenomenon was for the removal of ammonia from the effluent as the secondary step in the treatment of domestic wastewater (Gottardi and Galli, 1985).

Zeolites are inorganic aluminosilicate mineral containing exchangeable alkali and alkaline earth metal cations ( $Ca^{2+}$ ,  $Na^+$ ,  $K^+$  and  $Mg^{2+}$ ), that can be found

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in cavities in basaltic rocks. It is a sedimentary rock that was formed from hydrothermal alteration of volcanic rock, which is widely found in Indonesia. Having a high selectivity for ammonium, mordenite were considered to be the optimal zeolite for the removal of ammonium. It is also considered as a molecular sieve due to the pores roughly from 3-10 Å in the internal and external surface (Barrer, 1978). Zeolite is widely used in wastewater treatment because of its commercial factors such as 1) low cost, 2) good structural chemistry, 3) availability and 4) stability in a wide pH range 4-12. In 1970s, natural zeolites have became more significant to scientists who discover specifically their valuable chemical and physical properties, their large mineable deposits, and their potential application in industry and agricultural technology (Ouki *et al.*, 1994). Zeolites are used to adsorb a variety of materials such as inorganic compound, heavy metal (Pb, Ni, Zn), radioactive and others compound in the wastewater.

In this study, the effectiveness of ammonium removal by mordenite, one of the zeolite was determined. In this case, mordenite is used as the adsorbent and ammonium solution is the adsorbate. The kinetics of adsorption was studied using shake flask experiment. Experiments were undertaken to characterize the mordenite in terms of its rate of ammonium ion adsorption under various conditions. Equilibrium data from the uptake capacity of ammonium ions was analyzed using Langmuir and Scatchard adsorption isotherm model. The mechanism of NH<sub>4</sub><sup>+</sup> adsorption in the mordenite was also studied using electron microscope and FTIR technique. The adsorption of ammonium using reactor and

packed-bed column was investigated. Desorption of loaded mordenite using Na<sup>+</sup> pH 12 was also investigated. This parameter can be applied in wastewater treatment to remove ammonium in solution form.

The objectives of this study are:

- To study the kinetics and mechanism of ammonium adsorption by mordenite using shake flask experiment.
- 2) To study the effect of different adsorption conditions especially particle size of mordenite, ammonium concentration, mordenite concentration, pH, temperature and agitation speed on the efficiency of ammonium adsorption by mordenite.
- To compare the performance of ammonium adsorption by mordenite in different contactors (shake flask, batch stirred tank reactor, sequential feeding reactor and fixed packed-bed column).

## **CHAPTER 2**

### LITERATURE REVIEW

### 2.1 Water Pollution and Wastewater

A supply of clean water is an essential requirement for the establishment and maintenance of a healthy community. Its acts not only as a source of potable water, but also provides valuable food supplements through supporting the growth of aquatic life, and also by its usage for irrigation in agriculture. Water, which has been utilized and discharged from domestic dwellings, institutions and commercial establishments, leachates from solid waste disposal sites, together with water discharged from manufacturing industries, contains a large number of potentially harmful compounds. Consequently, if it is discharged directly into a watercourse, serious damage might result to the many forms of life which inhabit this water. To ensure that such problems are avoided or minimized, attention should be paid to the management of our aquatic resources and also of the pollutants which enter them (Horan, 1990).

The organic and inorganic components of wastewater are present in both soluble and insoluble form. Watercourses receive pollution from many different sources, which vary both in strength and volume. Identification of the major sources of these pollutants is important, as they can be controlled most easily at the source (Long, 1990). The main source of both chemical and biological

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pollution in domestic sewage resulted from human excreta with a smaller contribution from wastewater resulting from laundry, food preparation and bath (Horan, 1990). The characteristic of typical domestic sewage at five countries is illustrated in Table 1 below:

Determinant	Manchester	Mafraq	Campina	Amman	Nairobi
	(UK)	(Abu Dhabi	Grande	(Jordan)	(Kenya)
		town)	(NE		
			Brazil)		
BOD (mg $O_2/L$ )	240	228	240	770	520
COD (mgO <sub>2</sub> /L)	520	600	570	1830	520
PV (mgO <sub>2</sub> /L)	-	75	-	-	-
Suspended	210	198	392	900	520
solids (mg/L)					
Ammonia (as	22	35.2	38	100	33
N (mg/L)					
PH	7.4	7.6	7.8	-	7.0
Temperature	14	-	2.6	22	24
(°C)					

Table 1: The Characteristic of Typical Domestic Sewage at Five Countries (Horan, 1990).

## 2.1.1 Characteristics of the Wastewater

In general, wastewater can be characterized based on its bulk organic parameters, physical characteristics and specific contaminants. The bulk organic wastewater quality parameters measure the amount of organic matter present in a waste stream (Belhateche, 1995). Typical parameters are total organic carbon (TOC), chemical oxygen demand (COD) and oil and grease (O&G). All these parameters measurements indicate the amount of organic matter present in a waste stream that require stabilization or oxidation stream (Belhateche, 1995). These parameters are useful for measuring the organic quality of wastewater only when such compounds are expected to be present in large qualities, such as in refinery wastewater as shown below:

- Physical characteristics The physical characteristics of wastewater include total suspended solids (TSS), temperature, pH, color, odour, turbidity, flow variability, conductivity, settleability and sometimes oxidation/reduction (redox) potential (Long, 1990).
- Biological characteristics Bacteriological testing determines the presence of pathogenic (disease causing) organisms or indicator bacteria for such organisms in the raw wastewater, processed streams, and treated effluent (Long, 1990).
- 3) Chemical composition chemical testing provides information on the concentrations of the specific substances for which the tests are designed. The determination composition of wastewater include pH, alkalinity, solids, BOD (Biological oxygen demand), COD (Chemical Oxygen Demand), Nitrogenorganic nitrogen, ammonia, nitrite and nitrate, phosphorus, chlorine, sulfide, fatoils-greases and priority pollutants (Long, 1990).