

REMOVAL OF AMMONIUM THROUGH ADSORPTIVE COAGULATION-
FLOCCULATION PROCESS IN DRINKING WATER TREATMENT

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Dedicated to my beloved

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ABSTRACT

The nitrogen compounds such as ammonia (NH_3) and ammonium (NH_4^+) are the most common pollutants in surface water, groundwater and wastewater. The increasing amount of NH_4^+ in the source of water supply emitted from agricultural activities, sewage and industries has caused problems to the existing drinking water treatment system to remove it to meet the required drinking water standards. The adsorption removal of NH_4^+ using natural zeolites and thus the adsorptive coagulation/flocculation process (ACF) was studied aiming for application in drinking water treatment process. The natural zeolites (i.e. NZ01, NZ02, and NZ03) were characterized using scanning electron microscope (SEM), X-ray diffractometer (XRD), nitrogen adsorption-desorption (NAD) analyzer, Fourier transform infrared spectrophotometer (FTIR), X-ray fluorescence (XRF) spectrophotometer. The cation exchange capacity (CEC) of natural zeolites was also determined. The NH_4^+ removal experiments were conducted in batch adsorption and adsorptive coagulation/flocculation (ACF) methods carried out at various experimental conditions. It was found that all natural zeolites used were of Clinoptilolite and Heundlite types. Natural zeolite (NZ01) had the highest (64.42 cmol/kg) cation exchange capacity (CEC) compared to NZ02 and NZ03 which both had 62.18 cmol/kg and 59.97 cmol/kg respectively. The time taken for NH_4^+ adsorption performance to reach equilibrium was detected in 12 hours contact time with adsorption capacity of 2.5mg/g observed at NH_4^+ concentration of 20 mg/l and pH 7. The high NH_4^+ removal was observed at pH 8 with 2.76 mg/g adsorption capacity. The NH_4^+ adsorption capacity increased with increasing the initial NH_4^+ concentration from 1 mg/l to 200 mg/l. Adsorption data followed the Langmuir isotherm at 34.48mg/g maximum adsorption capacity and it shows that the surface of NZ01 is homogeneous. The adsorption process obeys pseudo-second order kinetic models. The thermodynamic properties (ΔG , ΔS , and ΔH) were also studied at different temperatures (30, 40, 50, 70 °C). The negative value of ΔH for NH_4^+ adsorption confirmed the process is exothermic in nature. The adsorptive coagulation-flocculation (ACF) results revealed that the NH_4^+ removal increased with adsorbent dosage, ranging from 0.2 to 2.0 mg/ml at 5 hours contact time. The percentage removal of NH_4^+ in ACF for the effect of initial NH_4^+ concentrations (i.e. 1 mg/l, 20 mg/l, 50 mg/l and 100 mg/l) showed the increasing value up to 20% efficiency compared to adsorption. The NH_4^+ adsorption isotherm data for ACF followed the Temkin isotherm model and the kinetic adsorption data was observed to obey a pseudo-second order. All these results demonstrate that the natural zeolites can be potentially used for the removal of NH_4^+ in drinking water treatment process.

ABSTRAK

Sebatian nitrogen seperti ammonia (NH_3) dan ammonium (NH_4^+) merupakan bahan pencemar yang paling biasa dijumpai dalam air permukaan, air bawah tanah dan air sisa. Peningkatan jumlah NH_4^+ dalam sumber bekalan air yang berpunca daripada aktiviti pertanian, kumbahan dan industri telah menimbulkan banyak masalah kepada sistem perawatan air minuman yang sedia ada untuk menyingkirkan bagi mencapai tahap piawaian air minuman yang dibenarkan. Proses penyingkiran penjerapan NH_4^+ menggunakan zeolit semula jadi dan seterusnya proses penjerapan pengentalan/pemberbukuan (ACF) telah dikaji bertujuan untuk digunakan dalam proses perawatan air minuman. Zeolit semulajadi (NZ01, NZ02, dan NZ03) telah dicirikan menggunakan mikroskop imbasan elektron (SEM), pembalikan sinaran-X (XRD), penganalisa penjerapan dan penyahjerapan nitrogen (NAD), spektroskopi jelmaan Fourier inframerah (FTIR) dan spektrofotometer pendafluor sinar-X. Keupayaan penukaran kation (CEC) zeolit semulajadi juga ditentukan. Ujikaji penyingkiran NH_4^+ telah dilakukan menggunakan penjerapan berkelompok dan proses penjerapan pengentalan/pemberbukuan (ACF) pada pelbagai keadaan ujikaji. Adalah didapati bahawa zeolit semulajadi yang digunakan ialah daripada jenis Clinoptilolit and Heundlit. Zeolit semula jadi (NZ01) mempunyai nilai keupayaan penukaran kation (CEC) paling tinggi iaitu 64.42 smol/kg berbanding NZ02, 62.18 smol/kg dan NZ03, 59.97 smol/kg. Masa yang diambil bagi proses penjerapan untuk mencapai tahap keseimbangan adalah 12 jam dengan keupayaan penjerapan di catat ialah 2.5 mg/g pada nilai kepekatan awal NH_4^+ 20mg/l dan pH 7. Penyingkiran NH_4^+ yang maksimum diperolehi di pH 8 pada 2.76 mg/g keupayaan penjerapan. Keupayaan penjerapan NH_4^+ meningkat dengan peningkatan kepekatan awal NH_4^+ daripada 1 mg/l ke 200 mg/l. Data penjerapan mematuhi isoterma Langmuir pada 34.48 mg/g maksimum keupayaan penjerapan dan membuktikan bahawa permukaan zeolit semula jadi adalah homogen. Proses penjerapan mematuhi model kinetik pseudo-peringkat kedua. Sifat termodinamik (ΔG , ΔS , dan ΔH) juga telah dikaji pada empat suhu berlainan (30, 40, 50, 70 °C). Nilai negatif ΔH mengesahkan bahawa process penjerapan adalah bersifat luah haba. Keputusan ujikaji proses penjerapan pengentalan/pemberbukuan (ACF) menunjukkan penyingkiran NH_4^+ meningkat dengan kenaikan dos penjerap dari 0.2 to 2.0 mg/ml dalam masa 5 jam. Peratus penyingkiran NH_4^+ dalam ACF untuk kesan ke atas kepekatan awal NH_4^+ (1 mg/l, 20 mg/l, 50 mg/l and 100 mg/l) menunjukkan nilai keupayaan penjerapan meningkat sehingga 20 peratus kecekapan berbanding proses penjerapan biasa. Data penjerapan NH_4^+ bagi proses ACF mematuhi isoterma Temkin dan mematuhi model kinetik pseudo-peringkat kedua. Semua keputusan ini menunjukkan bahawa penjerap zeolit semulajadi adalah berpotensi untuk digunakan bagi penyingkiran NH_4^+ dalam proses perawatan air minuman.

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LIST OF SYMBOLS

Al	-	Aluminium
b_T	-	Variation of adsorption energy (J/mol)
Ca	-	Calcium
Ce	-	Equilibrium concentration (mg/l)
Co	-	Initial concentration (mg/l)
H	-	Hydrogen
k_1	-	Rate constant of Pseudo first order model (min^{-1})
k_2	-	Rate constant of Pseudo second order model (mg/g.min)
K_F	-	Equilibrium parameter of Freundlich model (1/g)
K_L	-	Equilibrium parameter of Langmuir model (1/mg)
K_{RP}	-	Equilibrium parameter of Redlich-Peterson model (1/g)
K_T	-	Equilibrium binding constant (1/g)
k_{id}	-	The intra-particle diffusion rate constant (mg/g min)
k_d	-	Equilibrium constant
Mg	-	Magnesium
NZ	-	Natural zeolite
N	-	Nitrogen
Na	-	Sodium
n	-	Heterogeneity factor in Freundlich isotherm
nm	-	Nanometer
q_e	-	Equilibrium adsorption capacity (mg/g)
$q_{e, \text{exp}}$	-	Experimental equilibrium adsorption capacity (mg/g)
$q_{e, \text{theory}}$	-	Theoretical equilibrium adsorption capacity (mg/g)
q_{max}	-	Maximum adsorption capacity (mg/g)

q_t	-	Adsorption capacity at times t (mg/g)
R_L	-	Equilibrium constant in Langmuir isotherm
R_m	-	Average pore diameter (nm)
R^2	-	Coefficients determination
Si	-	Silicon
S_{BET}	-	BET surface area (m^2/g)
μm	-	Micro meter
V_P	-	Pore Volume (cm^3/g)
a	-	Initial adsorption rate (mmol/g.min)
β	-	Elovich constant (g/mg)
χ	-	Non-linear coefficient
ΔH°	-	Different enthalpy of adsorption
ΔS°	-	Different entropy of adsorption
ΔG°	-	Gibbs free energy of adsorption

LIST OF ABBREVIATIONS

SEM	-	Scanning Electron Microscopy
XRD	-	X-ray diffraction
XRF	-	X-Ray Fluorescence
BET	-	Brunauer Emmet Teller
NAD	-	Nitrogen Adsorption/Desorption
FTIR	-	Fourier Transform Infrared
WHO	-	World Health Organization's
NH ₃	-	Ammonia
NH ₄ ⁺	-	Ammonium
ED	-	Electro dialysis
SBA	-	Strong Base Anion
RO	-	Reverse Osmosis
DC	-	Direct Current
PBU	-	Primary Building Units
AAS	-	Atomic Absorption Spectrophotometer
NWQS	-	National Water Quality Standard
NOM	-	Natural Organic Matter
DBP	-	Disinfection Byproducts
CSTR	-	Continuous Stirred Tank Reactor
PAC	-	Powder Activated Carbon
CEC	-	Cation Exchange Capacity
ATR	-	Attenuated Total Reflectance
NH ₄ Cl	-	Anhydrous Ammonia Chloride
APHA	-	American Standard Method

SSE	-	Squared Error Analysis
ACF	-	Adsorptive Coagulation Flocculation
CF	-	Coagulation Flocculation
DOE	-	Department of Environmental
WQI	-	Water Quality Index
DO	-	Dissolved Oxygen
BOD	-	Biochemical Oxygen Demand
COD	-	Chemical Oxygen Demand
TSS	-	Total Suspended Solid
WM	-	Weber Morris
ACF	-	Adsorptive Coagulation-Flocculation

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Ammonia (NH_3) and ammonium (NH_4^+) are considered as one of the important atmospheric species (Katalin and Lajos, 1993). In aqueous environments, ammonia usually occurs in the form of ammonium (NH_4^+) (Ying and Kong, 2014). This ammonium also can be the most abundant alkaline component which is basically neutralizing a certain amount of the acid generated in the atmosphere by undergoes oxidation of SO_2 and NO_x (Katalin and Lajos, 1993). However, very high concentration of NH_4^+ in aqueous environments as well as in raw surface water can cause direct damage to both human and ecosystem (Zhang *et al.*, 2013). This is because the high amount of NH_4^+ content in surface water used for drinking water will affect the taste and odor problems including the decreasing disinfection efficiency (Zhang *et al.*, 2013). Other than that, the high concentration of NH_4^+ can also be one of the potential reasons for the increasing concentration of nitrite (NO^{3-}) via nitrification process (Umezawa *et al.*, 2008). This problem can cause a serious effect to the human health since the high amount of nitrate in the digestive tract can lead to methemoglobinemia problems in human system (Umezawa *et al.*, 2008).

On the other hand, as discussed by Liu *et al.* (2010) and Zhao *et al.* (2013), the excessive amount of NH_4^+ in surrounding may contribute to many problems such as decrease the dissolved oxygen, eutrophication effect and lakes or rivers becomes more toxic. Ammonium compounds are emitted into the environment or surface water system by various ways which include the discharge from agricultural activities and mineral industries (Yang *et al.*, 2013). In addition, the nitrogen pollution which is mostly from agricultural over-application of synthetic fertilizers, aquaculture, municipal wastewater, and mineral processing industries are basically the main raw sources for NH_4^+ pollution in aqueous environment. It is reported that the other sources of NH_4^+ contamination also include fertilizer runoff, sewage releases into natural waters, and industrial releases (Buss *et al.*, 2004). The presence of NH_4^+ in surface water used for drinking water production is undesirable and has increased the awareness of the government to reduce the acceptable limit of NH_4^+ content in drinking water.

The increasing water pollution problems due to the increasing amount of NH_4^+ not only decline the quality of water but also threaten the human health plus give a huge effect on aquatic habitat as well (Milovanovic, 2007). Therefore, by considering the view that the serious health problems are directly depending to the excess NH_4^+ in drinking water, many types of environmental regulatory agencies have set a maximum contaminant level of NH_4^+ in drinking water (Bhatnagar and Sillanpaa, 2011). As reported in Malaysia rivers and in drinking water treatment plants, the a NH_4^+ level of over 1.5 mg/L in raw and drinking water had exceed the Malaysian regulation limits and this phenomenon caused serious impact to the water treatment operation (Hasan *et al.*, 2011). Ammonium is considered one of the most harmful compound found in the environment, thus it is very important to remove it from aqueous water before they are being supplied to the people. The increasing amount of NH_4^+ in wastewater will highly effect the environment if it is discharged without any treatment (Zhao *et al.*, 2013).

Works by Peavy *et al.* (1985) have shown that most of the existing water treatments are only good in removing suspended solid, phosphorus, oil, heavy metals

and other contaminant in water sources but have some difficulties in the process to remove NH_4^+ content. This problem becomes the big issue to the environmental agency since NH_4^+ is stated as one of highly toxic contaminant which it must be clearly reduced and eliminated from the source of water supply. In addition, as for now there is no suitable method for NH_4^+ removal from drinking water treatment in Malaysia (Abu Hasan *et al.*, 2013). According to literature, generally this contaminant may be removed physico-chemically (by chlorination, ion exchange, or air stripping) or biologically (via an activated sludge system, trickling filter or rotating biological reactor). These groups of treatments are conventionally applied for the NH_4^+ removal in drinking water treatment process as presented by Ji *et al.* (2007). In addition, the other traditional drinking water treatment method like flocculation process also is not being able to remove NH_4^+ effectively (Li *et al.*, 2011). Other than that, the treatment by using biological filter is believed to be one of effective method of NH_4^+ removal but the method is highly cost and need for more safety attention in handling the process.

As presented by Zhao *et al.* (2013), the biological method is not practically uses in industrial application due to high cost for physical and chemical treatments and also take long period in operation. As stated by Liu *et al.* (2010), comparing with all the oldest drinking water treatment process used to remove NH_4^+ , adsorption has received a huge attention of scientists in many years because of many reasons such as simplicity of operation, low cost of operation, economically feasible and also environmentally friendly (Moussavi *et al.*, 2011). One of the most important issues of adsorption method is to have the effective, natural, low-cost materials to act as a cost effective adsorbents in adsorption process (Shavandi *et al.*, 2012). As defined by Yin and Kong (2014), organic resins and natural or modified zeolites are considered to be effective adsorbents for removing NH_4^+ from wastewaters because of their high cation exchange capacity (CEC). However, according to literature, among various adsorbents such as carbon, nanotube, fly ash, iron, cementite and activated charcoal, the most attractive adsorbents reported in many studies are zeolites (Zhao *et al.*, 2013).

There are more than hundreds types of naturally occurring zeolites in this century (Coruh, 2008). Natural zeolites have been proven to be one of effective adsorbents as ammonium removal because they have high ion exchange capacity, selectivity and compatibility with the natural environment (Sarioglu, 2005). Natural zeolites have some advantages as compared to other adsorbents including their physical structure which are basically porous aluminosilicate minerals containing exchangeable alkali or alkaline-earth metal cations (normally Na, K, Ca, and Mg), molecular sieve properties, high surface area and have strong sorption capabilities (Wang and Peng, 2010). Because of these criteria, natural zeolites becomes as one of promising adsorbent media that have high potential application as a metal ion adsorbent as discussed by Shavandi *et al.* (2012). Different varieties of zeolites from across the world have been studied and the uses of natural zeolites for NH_4^+ removal have also been published and reviewed by many researchers in recent years (Watanabe *et al.*, 2004).

1.2 Problem Statement

An inorganic pollutant such as NH_4^+ is the main problem in drinking water treatment plants (DWTPs). The pollutant exists in water via naturally creation, domestic effluents and sludge discharge. Basically, NH_4^+ is formed at low concentration through nitrogen mineralization process from organic matters (Hasan *et al.*, 2011). Once, the drinking water is contaminated by high NH_4^+ source, the NH_4^+ levels increased to a high concentration exceeding the Malaysian regulated standard limit. However, current methods use for NH_4^+ removal including air stripping, reverse osmosis, chemical precipitation, break-point chlorination, ion exchange and biological nitrification are surrounding by many disadvantages such as they are not practically uses in industrial application due to high cost and also require for more safety attention in handling the process. Hence, adsorption method becomes the chosen treatment because of simple process and low operation cost.

Besides, the selection of natural zeolite as potential adsorbent become the best alternatives due to their physical structure that have alkali or alkaline earth cations reversibly fixed in the cavities which can easily be exchanged by surrounding positive ions (NH_4^+) (Zheng *et al.*, 2008). Natural zeolites also are very cheap material and also can be easily obtain in large quantities all around the world (Sprynsky *et al.*, 2005). The main features of zeolites as promising good adsorbent are having high ion exchange capacity, porous structure and high molecular sieve. According to the previous study, the discovery of natural zeolites deposits have lead to an increasing use of these minerals for the purpose of eliminating, or at least reducing the water pollution due to high NH_4^+ content in aqueous water (Wang *et al.*, 2007). However, zeolites from different sources have different ability in adsorption capability then further research is required to determine the adsorption potential of NH_4^+ from other types of zeolites.

The performances of NH_4^+ removal by using adsorption and natural zeolites as adsorbent are the most promising treatment use in industry. However, the combination processes of adsorption and coagulation-flocculation (ACF) have been suggested to improve the NH_4^+ removal by using natural zeolites as adsorbent. The conventional treatment of coagulation and flocculation in drinking water treatment plant involves the addition of chemicals or coagulants to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation (Duan and Gregory, 2003; Verma *et al.*, 2012; Matilainen *et al.*, 2010). Thus, this study has been conducted to investigate the combination of adsorption and coagulation or adsorptive coagulation/flocculation (ACF) treatment where natural zeolites were added into the solution together with the coagulants. As the new method, this process has not highly been reported even though it was believed to give good results of NH_4^+ removal and thus, provide valuable statistical data for further process development. Moreover, each zeolite material has its special characteristics and still requires to be researched individually (Huang *et al.*, 2010). Besides, the use of natural zeolites in the combination process may offer better alternative or enhancing the existing process for NH_4^+ removal.

1.3 Research Objectives and Scope

The detailed objectives and scopes for this research are:

- 1) To characterize natural zeolite samples as adsorbents for NH_4^+ removal process.

Three types of natural zeolites from different sources namely NZ01, NZ02, and NZ03 were used in the present study. The natural zeolite samples were characterized using various techniques. The surface morphology of the natural zeolite samples was characterized using scanning electron microscopy (SEM) technique. The mineralogical analysis was carried out by X-ray diffraction (XRD) and the chemical composition was determined by X-ray fluorescence (XRF). The zeolite surface area was determined by Brunauer-Emmet-Teller (BET) method by using N_2 Adsorption/Desorption (NAD) analysis. The functional group of the zeolite samples was determined by Fourier transform infrared (FTIR) spectrophotometer. In addition, the cation exchange capacity (CEC) was also determined for all three natural zeolite samples.

- 2) To determine the NH_4^+ adsorption performance by the natural zeolite samples.

The concentration of NH_4^+ removal by natural zeolite was measured by using Uv-Vis spectrophotometer at 640nm wavelength. The isotherm and kinetic studies of NH_4^+ adsorption were carried out using batch adsorption procedure. Several removal parameters such as pH, contact time, dosage, temperature and initial NH_4^+ concentration were studied, followed by adsorption data analysis using adsorption isotherm and kinetic models. The regeneration of the natural zeolites was also carried out by using sodium chloride (NaCl) as desorption agent.

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