Dedicated to my beloved
ACKNOWLEDGEMENTS

Alhamdulillah greatest thanks to the Almighty Allah (SWT) for His divine blessing and assists throughout the research. First and foremost, I would like to express my sincere appreciation to my supervisor Prof. Dr. Hanapi Bin Mat for his countless comments, expensive motivation words and limitless guidance throughout the completion of this research plus he was always there to provide everything needed in the research.

I would like to express my sincere gratitude and warmly thanks to all member of Advanced Materials and Process Engineering Research Group (AMPEN) laboratory and all my close friends (Junaidah, Nisa, Aishah, Aqilah and Akmal) for the big support and help in order for me to gain as much as useful information and data for this research. Thank you so much for all views, comments and the encourage critics. Special thanks to Mr. Yassin at Faculty Science, UTM for helping me in sample analysis.

Last but not least, I would like to express my very deep special appreciation to my lovely mother and father, Rugayah Ayob and Sharuddin Abdul Rahman and my dear siblings for their opinion, infinite love, encouragement, support and motivation throughout the process completing this research. Unfortunately, it is impossible to list all of them in this limited space. Hence, thanks to all those who directly or indirectly help in making this thesis succeed. Your support are really touched my deep heart. Thank you so much.
ABSTRACT

The nitrogen compounds such as ammonia (NH₃) and ammonium (NH₄⁺) are the most common pollutants in surface water, groundwater and wastewater. The increasing amount of NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ adsorption performance to reach equilibrium was detected in 12 hours contact time with adsorption capacity of 2.5mg/g observed at NH₄⁺ concentration of 20 mg/l and pH 7. The high NH₄⁺ removal was observed at pH 8 with 2.76 mg/g adsorption capacity. The NH₄⁺ adsorption capacity increased with increasing the initial NH₄⁺ 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 NH₄⁺ adsorption confirmed the process is exothermic in nature. The adsorptive coagulation-flocculation (ACF) results revealed that the NH₄⁺ removal increased with adsorbent dosage, ranging from 0.2 to 2.0 mg/ml at 5 hours contact time. The percentage removal of NH₄⁺ in ACF for the effect of initial NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ in drinking water treatment process.
ABSTRAK

Sebatian nitrogen seperti ammonia (NH₃) dan ammonium (NH₄⁺) merupakan bahan pencemar yang paling biasa dijumpai dalam air permukaan, air bawah tanah dan air sisa. Peningkatan jumlah NH₄⁺ 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 NH₄⁺ 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. Uji jeksi penyingkiran NH₄⁺ telah dilakukan menggunakan penjerapan berkelompok dan proses penjerapan pengentalan/pemberbukuan (ACF) pada pelbagai keadaan uji jeksi. Adalah didapati bahawa zeolit semulajadi yang digunakan ialah dari jenis Clinoptilolit dan 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 NH₄⁺ 20mg/l dan pH 7. Penyingkiran NH₄⁺ yang maksimum diperolehi di pH 8 pada 2.76 mg/g keupayaan penjerapan. Keupayaan penjerapan NH₄⁺ meningkat dengan peningkatan kepekatan kekatah awal NH₄⁺ 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 uji jeksi proses penjerapan pengentalan/pemberbukuan (ACF) menunjukkan penyingkiran NH₄⁺ meningkat dengan kenaikan dos penjerap dari 0.2 to 2.0 mg/ml dalam masa 5 jam. Peratus penyingkiran NH₄⁺ dalam ACF untuk kesan ke atas kepekatan awal NH₄⁺ (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 NH₄⁺ 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 NH₄⁺ dalam proses perawatan air minuman.
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qt - 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**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
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<tr>
<td>BET</td>
<td>Brunauer Emmet Teller</td>
</tr>
<tr>
<td>NAD</td>
<td>Nitrogen Adsorption/Desorption</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization’s</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
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<tr>
<td>NH₄⁺</td>
<td>Ammonium</td>
</tr>
<tr>
<td>ED</td>
<td>Electro dialysis</td>
</tr>
<tr>
<td>SBA</td>
<td>Strong Base Anion</td>
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<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
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<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>PBU</td>
<td>Primary Building Units</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrophotometer</td>
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<tr>
<td>NWQS</td>
<td>National Water Quality Standard</td>
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<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
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<tr>
<td>DBP</td>
<td>Disinfection Byproducts</td>
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<tr>
<td>CSTR</td>
<td>Continuous Stirred Tank Reactor</td>
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<tr>
<td>PAC</td>
<td>Powder Activated Carbon</td>
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<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
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<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>Anhydrous Ammonia Chloride</td>
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<tr>
<td>APHA</td>
<td>American Standard Method</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>SSE</td>
<td>Squared Error Analysis</td>
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<tr>
<td>ACF</td>
<td>Adsorptive Coagulation Flocculation</td>
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<tr>
<td>CF</td>
<td>Coagulation Flocculation</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Environmental</td>
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<tr>
<td>WQI</td>
<td>Water Quality Index</td>
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<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
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<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solid</td>
</tr>
<tr>
<td>WM</td>
<td>Weber Morris</td>
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<td>ACF</td>
<td>Adsorptive Coagulation-Flocculation</td>
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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 NOx (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 Peavvy 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 striping, 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 (\(\text{NH}_4^+\)) (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 \(\text{NH}_4^+\) 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 \(\text{NH}_4^+\) from other types of zeolites.

The performances of \(\text{NH}_4^+\) 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 \(\text{NH}_4^+\) 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 \(\text{NH}_4^+\) 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 \(\text{NH}_4^+\) 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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