

NATURAL ZEOLITE CHARACTERIZATION FOR ADSORPTIVE COAGULATION FLOCCULATION (ACF) REMOVAL OF AMMONIUM IN DRINKING WATER TREATMENT PROCESS

Siti Shilatul Najwa Sharuddin¹, Jimmy Lye Wei Ping¹, Nurul Sakinah Othman¹, Safia Syazana Mohtar¹, Norasikin Saman¹, Khairiraihanna Johari¹, Song Xiao Tian¹, Nik Ahmad Nizam Nik Malek², Hanapi Mat^{1,2*}

¹Advanced Materials and Process Engineering Laboratory, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

²Novel Materials Research Group, Nanotechnology Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

*Corresponding author: hbmam@cheme.utm.my

ABSTRACT

The naturally occurring zeolite (NZO1) was characterized and used as an adsorbent for the removal of ammonium (N-NH_4^+) from water. The characterization results show that the NZO1 is mainly composed of clinoptilolite, quartz and plagioclase and has the cation-exchange capacity (CEC) of 64 cmol/kg. Batch adsorption results show that the best ammonia removal was at pH close to that of the natural water (\approx pH 7). The increase in initial ammonium nitrogen concentration from 5 to 50 ppm resulted in an increase of the adsorption capacity from 0.64 to 15.1 mg NH_4^+ -N/g. The Jar test experiments indicate the introduction of the NZO1 enhanced the ammonium removal efficiency. All these results demonstrate that the NZO1 is potential to be used for the removal of ammonium in drinking water treatment process.

1. INTRODUCTION

Basically, the conventional drinking water treatment processes are very efficient at removing of suspended solid, phosphorus, oil and heavy metals in water sources but unable to eliminate the soluble ammonium effectively. As known worldwide the presence of high ammonium content in drinking water which is readily transform into nitrate is very toxic for human beings (Kurama *et al.*, 2002). This trend has raised concern because nitrates cause methemoglobinemia in infants and seriously contribute to health problems of people. Besides that, according to Khosravi *et al.* (2012) ammonia and ammonium are the most common polluting nitrogen compounds in wastewater and

groundwater. The high level of ammonium in water imparts unpleasant taste and odor problems which can interfere with the life of aquatics and human populations (Ramasamy *et al.*, 2012). Other than that, natural clean waters can be only 0 to 3 mg/L limit of ammonia. This is because; higher concentrations correspond to pollution and can be toxic to aquatic organisms as well as human beings. Various techniques are developed and being used for removal of ammonium such as biological nitrification, air stripping, adsorption, ion exchange and breakthrough chlorination process (Ji *et al.*, 2007).

Considering a few solid reasons which are the technical, economical and health-related points, adsorption process seems to be more suitable technique for the removal of ammonia from drinking water treatment process. Adsorption is one of recommended technology since it has many advantages compared to the other treatment processes. One of the most important is the natural, low-cost materials are highly available to act as a cost effective sorbents in adsorption process such as natural zeolites (Shavandi *et al.*, 2012).

Various adsorbents such as activated alumina (Saha and Deng, 2010), limestone, rice husk and composite of BaCl₂/vermiculite are being used for the adsorption of ammonium from industrial effluents. However, among these adsorbents, natural zeolites have tendency to remove ammonia effectively (Coruh, 2008). These natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment

(Sarioglu, 2005). Different varieties of zeolites from across the world have been studied and several reports on zeolites have been published in the literature in recent years (Wang and Peng, 2010).

Natural Zeolites are basically porous aluminosilicate minerals containing exchangeable alkali or alkaline-earth metal cations (normally Na, K, Ca, and Mg), molecular sieving and have strong sorption capabilities (Wang and Peng, 2010). Nevertheless, zeolites from different sources have different ability in adsorption capability and thus it is required to evaluate their adsorption capability in removing ammonium before they can be implemented in drinking water treatment process. This study was carried out to meet this objective using NZ01 as an example towards its application in drinking water treatment process.

2. EXPERIMENTAL

2.1 Materials

Chemicals used in this study were obtained from local suppliers under various product brands. Ammonium chloride, ethyl alcohol (95%), sodium nitroprusside, kaolin and sodium hypochlorite were Merck (Germany) products and phenol used in ammonia determination method was product of Sigma-Aldrich (USA). The alum used was the product of Hach Company (USA). The natural zeolite which is denoted as NZ01 was supplied by NK Plus Sdn. Bhd. The double distilled water was used for all solution preparations.

2.2 Zeolite characterization

The natural zeolite (NZ01) used in this study has particle size of 200 mesh sieve. Before use the NZ01 was washed several times with double distilled water to remove any impurities, dried at 105 °C for 24 hours and then stored in desiccator for further use. The zeolite morphology was determined by scanning electron microscope (SEM) using S4 800/FEI-quanta-200F. The mineralogical analysis of the chemical composition of the NZ01 was carried out by X-ray diffraction (XRD) spectroscopy using Bruker-D8 Advance (USA), and X-ray fluorescence (XRF) spectroscopy using JEOL model JSX-3400R (JAPAN). The cation exchange capacity (CEC) of the NZ01 was determined according to British Standard (1995). The surface area, pore size and pore volume of the NZ01 was determined based on the nitrogen adsorption-desorption (NAD) analysis measured at 77.3K using Micromeritics model ASAP 2000

(USA). The surface functional groups of the NZ01 were determined using a Fourier transform infrared (FTIR) spectrophotometer (Model Nicolet IS5, Thermo Fisher Scientific, USA) equipped with Attenuated Total Reflectance (ATR) sampling technique with OMNIC operating system (Version 7.0, Thermo Nicolet). The FTIR spectra were obtained in the wavenumber range of 500-4000 cm^{-1} .

2.3 Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 0.05 g of zeolite mass with 50 ml of synthetic ammonium solution at desired concentrations and pHs. The conical flask was capped and agitated in a shaker at 200 rpm until the equilibrium was established which was found to be 24 hours (1 day). In this study, the effect of pH and ammonium concentration was investigated. The removal efficiency, RE (%) was calculated using the Eq.1 where C_o and C_e are the initial and final concentrations of ammonium in the solution (mg/L), respectively determined by using phenate method.

$$\text{Removal Efficiency (RE)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

According to Khosravi *et al.* (2012) the adsorption capacity, q_e (mg/g) of the NZ01 was calculated by Eq. 2 where M is the mass of NZ01 (g), C_o and C_e are the initial and equilibrium of the ammonium concentration in the solution (mg/L), respectively and V is the volume of solution (L).

$$q_e = \frac{C_o - C_e}{M} \times V \quad (2)$$

2.4 Jar test experiments

The Jar test experiment was carried out to evaluate the ammonium removal efficiency during the coagulation/flocculation process at selected experimental conditions using alum and kaolin as a flocculant and turbidity agent, respectively. In typical experiment, 500 ml beaker containing 300 ml solution having 50 ppm ammonium was used to study the effect of the NZ01, alum and kaolin dosages carried out at pH 7. In typical Jar test procedure, the coagulation/flocculation process was run at rapid mixing (200 rpm) for about 5 minutes, slow mixing (50 rpm) about 40 minutes carried out at different NZ01, kaolin and alum dosages. In selected experiments, this slow mixing was continued to extended time in order to

determine the effect of the NZ01 contact time measured for different dosages on the ammonium removal efficiency. The concentration of ammonia in solution before and after the coagulation/flocculation process was determined by using phenate method.

2.5 Analysis

The ammonium concentration was determined by phenate method according to the procedure described in the American Standard Method (APHA, 1998). The stock ammonium solution (1000mg/L) was prepared by dissolving accurately ammonium chloride (NH₄Cl) salt mass in freshly double distilled water. The ammonium solutions of different concentrations were prepared by diluting the stock solution with double distilled water.

3. RESULTS & DISCUSSION

3.1 Characterization of NZ01

Fig. 1 shows the SEM image of the NZ01 indicating the surface has some cavities which provide active sites for ammonium adsorption.

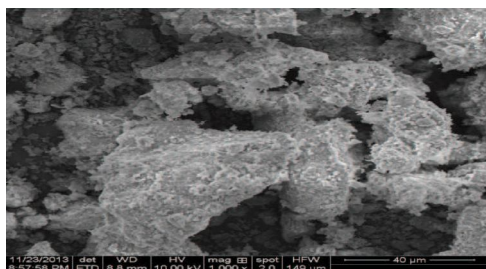


Fig. 1 SEM images of natural zeolite (NZ01).

The mineralogical analysis carried out by XRD spectroscopy shows that the zeolite mainly consisted of clinoptilolite, quartz and plagioclase as shown in Fig.2.

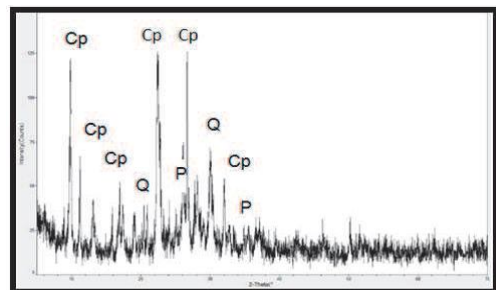


Fig.2 XRD pattern of the natural zeolite (NZ01). Cp=clinoptilolite, Q=quartz, P=plagioclase.2

The XRF analysis result indicated in Table 1 shows the percentage of chemical composition of the NZ01.

Table 1 Chemicals composition of NZ01.

Oxide	(Wt. %)
SiO ₂	47.99
Al ₂ O ₃	32.19
CaO	8.23
Fe ₂ O ₃	3.77
K ₂ O	3.64
P ₂ O ₅	3.61
TiO ₂	0.49
MnO	0.07
Total	99.99

The CEC of the NZ01 measured by respected technique is 64.42 cmol/kg. The BET surface area, total pore volume and mean pore diameter of the NZ01 were measured to be 28.19 m²/g, 0.07 cm³/g and 9.72 nm, respectively. The FTIR spectra of NZ01 over the 500-4000 cm⁻¹ region are shown in Fig.3.

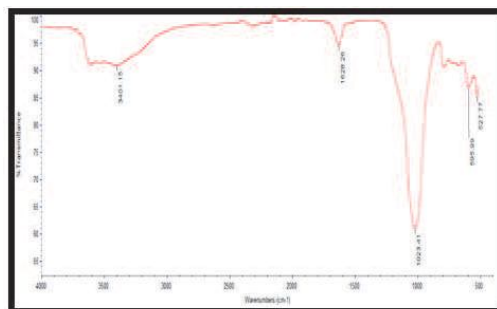


Fig.3 FTIR image of natural zeolite (NZ01).

Fig.3 shows the wide peak with strong intensity at 1023.41 cm⁻¹ and weak peak at 527.77 cm⁻¹ is referred to asymmetric and symmetric bonding of Si-O-Si bonds, respectively (Pouretedal and Kazemi, 2012). A strong broad bend is observed at 3401.15 cm⁻¹ due to the O-H stretching vibrations (Cross *et. al.*, 1989). On the other hand, a weaker peak at 1628.26 cm⁻¹ indicates the bending of the H-O-H bonds.

3.2 Batch ammonium adsorption

3.2.1 Influence of pH. The effect of pH on the removal of ammonium was studied by conducting the adsorption experiment at different pHs using 50 mg/L of ammonium solutions (Wahab *et al.*, 2010). The desired pH of the solution was adjusted by using either 0.1M NaOH or HNO₃ solution. Results of adsorption studies at different pH are presented in Fig. 4. The removal of ammonium by the NZ01 adsorption was highly dependent on the pH since it can influence both characters of exchanging ions and zeolite itself (Hedstrom, 2011).

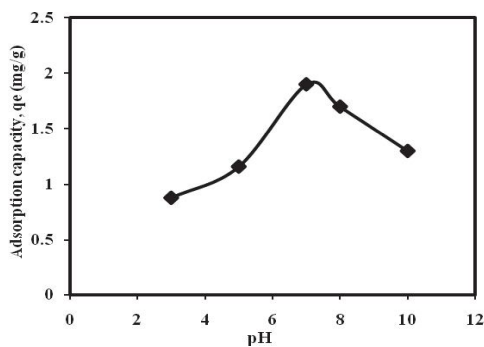
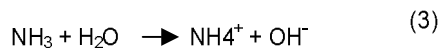


Fig. 4 Effect of pH on ammonium adsorption capacity of NZ01.

According to Sharifinia *et al.* (2013), the ammonium removal should be greater at lower pH values and becomes smaller at higher pH values which basically depend on the equilibrium reaction as given by the Bronsted-Lowry acid base reaction (Eq. 3).



However, the adsorption capacity (q_e) decreased at lower pH values which are due to the competition between H^+ and NH_4^+ to occupy the active sites of the NZ01 surface. On the other hand, at higher pH, the ammonium exists favourably in the form aqueous ammonia (Yusof *et al.*, 2010). The amount of ammonium adsorbed was minimum at pH 3 (0.88 mg/g), increased up to pH 5 (1.16 mg/g), and reached the maximum at pH 7 (1.86 mg/g) then decreased toward pH 10 which is in agreement with the underlined theory as given in Eq. 3.

3.2.2 Influence of initial ammonium concentration. The effect of initial ammonium

concentration was investigated at constant pH value of 7. Fig. 4 shows that the ammonium adsorption increases by increasing the initial ammonium concentrations. This trend can be explained that at higher concentration of ammonium in solution will enhance the driving force for the ammonium to occupy the anion sites on the effective pores of the NZ01 surfaces (Khosravi *et al.*, 2012).

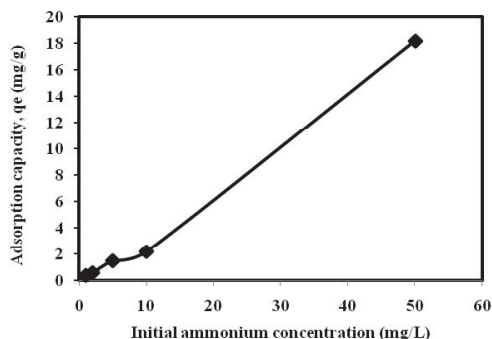


Fig. 4 Effect of initial ammonium concentrations on adsorption capacity of NZ01.

3.3 Jar test adsorption

The use of natural zeolite such as NZ01 into coagulation/flocculation process is one of the alternative methods that could be implemented in drinking water treatment process for the removal of ammonium. The Jar test experiment was conducted to evaluate the removal efficiency of the ammonium. The results of the introduction of the NZ01 into coagulation/flocculation process as well as other parameters are shown in Figs. 5 and 6.

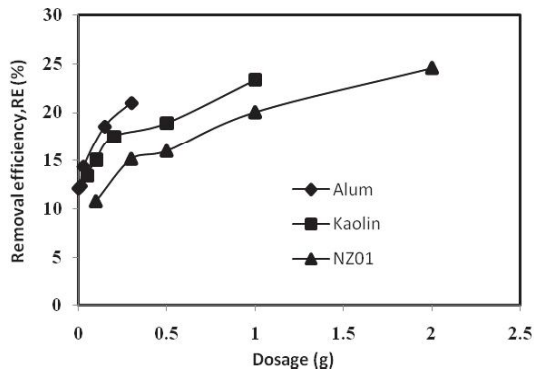


Fig. 5 Effect of alum, zeolite and kaolin dosages on removal efficiency of ammonium.

As shown in Fig. 5, there were slightly differences between the adsorption by alum, kaolin and zeolite on the removal efficiency of ammonium for 30 minutes of coagulation/flocculation process which was showed the performances of the NZ01 on ammonium removal is higher than the others. Meanwhile, Fig. 6 shows the removal efficiency of ammonium increased with the addition of The NZ01 into the solution during the coagulation/flocculation process.

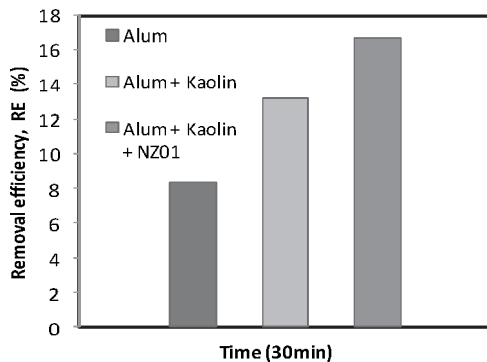


Fig. 6 Effect of alum, kaolin and NZ01 on the ammonium removal efficiency for 30 minutes of contact time.

Fig. 7 shows how the removal efficiency of the ammonium increased with the increase of contact time as well as the NZ01 dosage. This trend shows the ability of NZ01 as effective adsorbent to remove ammonium from aqueous solution.

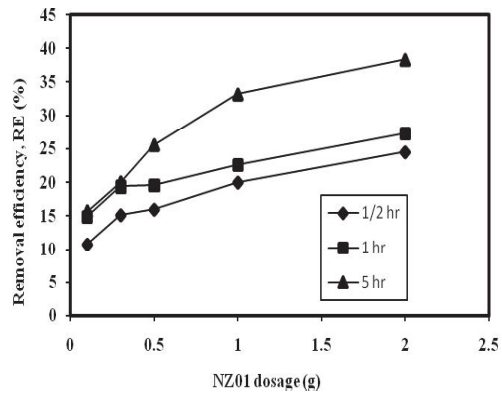


Fig. 7 Effect of NZ01 dosage and contact time on the removal efficiency of ammonium.

4. CONCLUSION

This study was carried out to investigate the effectiveness of the natural zeolite (NZ01) for the removal of ammonium in batch adsorption process as well as during coagulation/flocculation process. The characterization results show that the NZ01 comprises of clinoptilolite, quartz and plagioclase. Batch adsorption results show that the ammonium removal efficiency is dependent on the pH of the solution and initial ammonium concentration. The addition of the natural zeolite (NZ01) during the coagulation/flocculation process was clearly improved the removal efficiency of ammonium in which the pH, contact time and NZ01 dosage were significantly influenced the ammonium removal performance.

REFERENCES

APHA, Standard methods for examination of water and wastewater, 20th ed., Washington, D.C., USA, 1998.

British Standard, 7755-3.3, Soil quality Part 3 chemical methods section 3.3: determination of effective cation exchange capacity and base saturation level using barium chloride solution, 1995.

Coruh, S., The removal of zinc ions by natural and conditioned clinoptilolites, *Desalination*, vol. 225, pp. 41-57, 2008.

Cross, J., Goswin, R., and Frickle, J., Mechanical Properties of SiO₂ – Aerogels: *J. de Physique*, vol. 50, pp. 4191-4196, 1989

Hedstrom, A., Ion exchange of ammonium in zeolites, *J. Environ. Eng.*, pp. 673-681, 2011.

- Ji, Z., Yuan, J., and Li, X., Removal of ammonium from wastewater using calcium form clinoptilolite, *J. Hazard. Mater.*, vol. 141, pp. 483-488, 2007.
- Khosravi, A., Esmhosseini, M., and Khezri, S., Optimization of ammonium removal from waste water by natural zeolite using central composite design approach, *J. Incl. Phenom. Macrocycl. Chem.*, vol. 74, pp. 383-390, 2012.
- Kurama, H., Poetzschke, J., and Haseneder, R., Application of membrane filtration for the removal of ammonium ions from potable water, *Water Res.*, vol. 36, pp. 2905-2909, 2002.
- Pouretedel, H.R., and Kazemi, M., Characterization of Modified Silica Aerogel Using Sodium Silicates Precursor and its Application of Cu^{2+} , Cd^{2+} and Pb^{2+} ions, *J. Chem. Eng.*, vol. 2, pp.1-8, 2012
- Ramasamy, B., Sekar, K., Asit, B.M., and Ganesan, S., Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: kinetic, isotherm and thermodynamic studies, *Environ. Sci. Pollut. Res.*, vol. 20, pp. 533-542, 2012.
- Shavandi, M.A., Haddadian Z., Ismail M.H.S., Abdullah N., and Abidin, Z.Z., Removal of Fe(III), Mn(II) and Zn(II) from palm oil mill effluent (POME) by natural zeolite., *J. Taiwan Chem. Inst.*, Vol. 43, pp. 750-759, 2012.
- Sarioglu, M., Removal of ammonium from municipal wastewater using natural Turkish zeolite, *Sep. Purif. Technol.*, vol. 41, pp. 1-11, 2005.
- Saha, D., and Deng, S., Characteristic of ammonia adsorption on activated alumina. *J. Chem. Eng. Data.*, vol. 55, pp. 5587-5593, 2012.
- Sharifnia, S., Khadivi, M.A., and Shavisi, Y., Characterization isotherm and kinetic studies for ammonium ion adsorption by light expanded clay aggregate (LECA), *J. Saudi Chem. Society*, pp. 1319-6103, 2013.
- Wang, S., and Peng, Y., Natural zeolites as effective adsorbents in water and wastewater treatment, *J. Chem. Eng.*, vol. 156, pp.11-24, 2010
- Yusof, A.M., Keat, L.K., Ibrahim Z., Majid, Z.A., and Nizam, N.A., Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solutions by rice husk ash synthesized zeolite Y and powdered and granulated forms of mordenite, *J. Hazard. Mater.*, vol. 174, pp. 380-385, 2010
- Wahab, M.A., Jellali, S., and Jedidi, N., Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling, *Bioresour. Technol.*, vol. 101, pp. 5070-5075, 2010.
- Wang, S., and Zhu, Z. H., Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *J. Hazard. Mater.*, vol. 136, pp. 946-952, 2006.



Siti Shilatul Najwa Sharuddin received the B.Eng (2013) degree in chemical engineering from Universiti Teknologi Malaysia, Malaysia. She is currently pursuing master degree in chemical engineering working on adsorptive coagulation flocculation (ACF) removal of ammonium in drinking water treatment process starting from 2013 at the Department of Chemical Engineering, Universiti Teknologi Malaysia under the supervision of Associate Professor Hanapi Mat.



Hanapi Mat received the Ph.D (1994) degree in chemical engineering from Imperial college of Science, Technology and Medicine, U.K. He is currently Associate Professor at the Department of Chemical Engineering, Universiti Teknologi Malaysia, Malaysia. His current research interests include immobilization enzymes and cells for pollutant degradation, waste utilization and treatment, and separation processes.