



# Synthesis and Use of Zeolite Na-A from Waste Sludge of Water Treatment Plant for Ammonium Removal

Jeatana Wongwichien [a], Suwimol Asavapisit [a] and Kwannate Sombatsompop\* [b]

[a] School of Energy Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT) Thongkru, Bangmod, Bangkok, 10140, Thailand.

[b] Department of Civil and Environmental Engineering Technology, College of Industrial Technology, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangsue, Bangkok, 10800, Thailand.

\*Author for correspondence; e-mail: [kwn@kmutnb.ac.th](mailto:kwn@kmutnb.ac.th)

Received: 7 March 2013

Accepted: 8 September 2013

## ABSTRACT

Zeolite Na-A from waste sludge of water treatment plants was synthesized via a hydrothermal process for the purpose of ammonium removal. Sludge samples, with and without burning at 700 °C for 3 hours, were used and reacted with 3M NaOH solution. The effects of contact time, pH and initial ammonium concentration on ammonium uptake and adsorption isotherms were investigated. An optimal condition for ammonium ion adsorption was determined and then compared with Langmuir and Freundlich isotherms. Analysis of the synthesized zeolite Na-A by SEM revealed that the zeolite Na-A was cubic in shape for all experimental conditions. Zeolite was clearly observed from samples with sludge burning at the reaction time of 9 h. The cation exchange capacity of zeolite Na-A synthesized was found to be 1.07 meq/g. The adsorption capacity showed that the optimum pH and contact time were 8 and 5 min, respectively. The Langmuir model provided a better description of ammonium adsorption than the Freundlich model, and the maximum adsorption capacity by the Langmuir Isotherm was 8.88 mg/g. It was concluded that the zeolite Na-A synthesized from waste sludge has a potential to remove ammonium from wastewater.

**Keywords:** zeolite, sludge, hydrothermal, adsorption, ammonium

## 1. INTRODUCTION

The discharge of ammonia nitrogen in wastewater into rivers and streams has strong effects and contributes to eutrophication of water resources. A low concentration of ammonia nitrogen leads to disease and inhibition of growth. The ammonia concentration in the range 0.2-0.5 mg/L can be lethal to fish and other aquatic animals [1]. An effective process for ammonia removal from domes-

tic and industrial wastewaters is increasingly required as discharge limits and disposal options decrease. The traditional solutions for removing ammonia from polluted water are either biological technology (biological filter, biological contact oxidation, and so on.) or physicochemical (air stripping, break-point chlorination and ion exchange, and so on.); however, limitations exist in both methods.

The biological filter is effective for ammonia removal but sensitive to temperature and climate conditions and costly due to construction of the filter [2]. Ion exchange using resins has a high operation cost and is limited to specific application due to the varieties of ion species in wastewater which may reduce the exchanging sites of resins [2]. However, compared with the above-mentioned methods, ion exchange is provided more useful and economical with the development of low cost and high exchangers' materials such as zeolite for removing ammonia from polluted water [3-4]. The capacity of zeolite for ammonium removal from aqueous solutions has been investigated by several studies [3-7].

Zeolites are usually synthesized from aqueous-basis aluminosilicate precursor gels under a hydrothermal process. Zeolite consists of a three-dimensional, open-framework structure which has voids and open spaces. This framework is formed as  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra, which are connected by a shared oxygen atom. The substitution of  $\text{SiO}_4$  and  $\text{AlO}_4$  accounts for a negative charge of the structure which is neutralized by the exchangeable cations [8]. The preparation of zeolite from chemical sources of Si and Al is also expensive due to the need for high purity and suitability for some specific applications such as pharmacy, electrochemistry and nanotechnology. For industrial production of zeolite, high amounts of zeolite have been required, so some lower-cost materials such as rice husk ash [7], fly ash [9, 10], paper sludge ash [11], oil shale ash [12], kaolin [13] and halloysite mineral [14] are commonly used as Si and Al sources.

Waste sludge is generated from water treatment plants (WTP) and there have been a large amount of waste sludge approximately 340 tons being discharged daily from water treatment plants, and this has been expected to increase [15]. The Metropolitan Waterworks Authority (Thailand) has paid 15.8 million baht

annually for sludge disposal [15]. However, disposal waste sludge is not the best environmental practice. The daily output of waste sludge and the limited landfill capacity could cause social and environmental problems in Thailand.

The way to minimize waste sludge disposal is to use it as starting material for the synthesis of zeolite because it contains high amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  that could be utilized for zeolite production. Based on existing published works [7-14], issues on use of zeolite material as an adsorbent are still open for wider and more challenging discussion, especially by taking account the ability of zeolite hydrothermally synthesized from waste sludge of water treatment plants in removing ammonium ions from aqueous solutions. The chemical compositions, microstructure, morphology, cation exchange capacity (CEC) of waste sludge and synthesized zeolite are analyzed. The adsorption isotherm for ammonium removal by Freundlich and Langmuir models are also considered.

## 2. MATERIALS AND METHODS

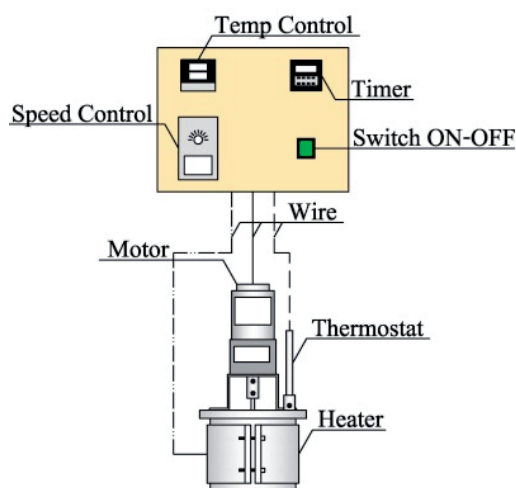
### 2.1 Raw Materials

The waste sludge was obtained from Bangkok water treatment plant in Bangkok, Thailand. Waste sludge was ground to reduce the particle size using a Los Angeles Abrasion Machine and then retrained on sieve No. 325 ( $45\mu\text{m}$ ) mesh less than 30%. The chemical compositions of the waste sludge, with and without calcining at  $700^\circ\text{C}$  for 3 hours, by X-ray fluorescence spectroscopy (XRF) (PHILLIPS, JEOL PW 2404, Japan) are given in Table 1. The main components of the sludge were  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of sludge with and without calcining were 1.68 and 1.75, respectively. Breck *et al.* [16] suggested that a ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio between 0.5 and 2.5 was suitable for synthesizing zeolite type A. The microstructure of waste

sludge with and without calcination was carried out by X-ray diffraction (XRD) equipment (Bruker AXS series D8). Scattering patterns were collected from  $10^\circ$  to  $80^\circ$  at incidence angle of  $2\theta$ . The morphological structure of waste sludge material was obtained by scanning electron microscope (SEM) (JEOL, JSM-6480 LV, Japan). Cation exchange capacity (CEC) was measured according to Zhang et al [6].

**Table 1.** Chemical compositions of the waste sludge material (wt%).

Composition of sludge	With calcination	Without calcination
SiO <sub>2</sub>	52.50	52.30
Al <sub>2</sub> O <sub>3</sub>	31.20	29.90
Fe <sub>2</sub> O <sub>3</sub>	9.49	10.60
K <sub>2</sub> O	2.51	2.60
CaO	1.00	1.11
MgO	1.04	0.95
TiO <sub>2</sub>	0.86	0.94
SO <sub>3</sub>	0.37	0.41
Na <sub>2</sub> O	0.23	0.18
Other	0.80	0.86
Loss of ignition (LOI)	0.15	1.70



**Figure 1.** Assembly of hydrothermal reactor.

## 2.2 Experimental Apparatus and Synthesis of Zeolite

A hydrothermal reactor used in this study consisted of a cylindrical stainless steel reactor with high alkali-resistant material stainless

steel grade AISI 304). The dimensions were 124.5 mm high, 4.5 mm thick and 125 mm in diameter with a working volume of 0.8 L. The reactor was equipped with a heater and a thermostat was located inside the cavity in order to monitor the reaction temperature. A motor was connected to a paddle, and stirring rate was controlled at 60 rpm for mixing the solution. The hydrothermal reactor assembly for the dissolution and crystallization process for synthesizing zeolite is shown in Figure 1.

Waste sludge sample as mentioned above (with and without calcination) was further synthesized to give zeolites via hydrothermal process with alkaline solution. 160 g of waste sludge sample and 800 mL of 3M NaOH solution as a mixed solution was finally crystallized with an agitator under hydrothermal treatment at  $90^\circ\text{C}$  for varying reaction times of 6, 9, 12 and 24 hours. After a period of crystallization, the precipitated sample was separated from the solution and then washed

with distilled water until its pH was 7. The sample was dried at  $100 \pm 5^\circ\text{C}$  for 24 hours in an air oven for further studies.

### 2.3 Analysis of Physicochemical Properties

The synthesized zeolite was characterized by X-ray diffraction spectroscopy (XRD) (Bruker AXS series D8) with a graphite monochromator and  $\text{CuK}_\alpha$  radiation. The sample was scanned from a 2-Theta range of  $10\text{--}80^\circ$ . The morphology of the sludge sample was studied by Scanning Electron Microscopy (SEM) (JEOL, JSM-6480 LV, Japan). The Cation Exchange Capacity (CEC) value was measured by titration with standard solution of concentrates  $1\text{ M H}_2\text{SO}_4$ . In addition, the surface area, total pore volume and mean pore diameter of synthesized zeolite using a surface analyzer (Autosorb-1 Chrantachrome, BET Model) were determined only from the optimum conditions of synthesized zeolite.

### 2.4 Adsorption Equilibrium Onto Synthesized Zeolite in Batch Experiments

Adsorption equilibrium was considered by certain constants that represent surface characteristics, affinity of the adsorbent, and adsorption capacity of the adsorbent. In batch experimental study, the ammonium ion stock solution ( $1000\text{ mg/L}$ ) was prepared by dissolving analytical grade  $(\text{NH}_4)_2\text{SO}_4$  in distilled water. Synthetic samples of aqueous solution were prepared by adding appropriate amounts of ammonium ion stock solution to distilled water to obtain ammonium ion concentrations of  $60, 80, 100, 120$  and  $140\text{ mg/L}$ . The effect of contact time on ammonium ion removal by the synthesized zeolite was determined under different contact times ranging from  $0$  to  $60$  min. The pH was adjusted by the addition of  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$  to achieve the pH values range from  $4$  to  $10$ .

In order to find out the optimal contact time,  $1\text{ g}$  of zeolite dosage was added into

$100\text{ mL}$  of  $50\text{ mg/L}$  ammonium solutions in a  $250\text{ ml}$  beaker and stirred for  $0\text{--}60$  min at a fixed temperature ( $30^\circ\text{C}$ ) and rate ( $100\text{ rpm}$ ). Then, the effect of the initial ammonium concentrations ( $60\text{--}140\text{ mg/L}$ ) on the removal efficiency was investigated under the same working conditions ( $T=30^\circ\text{C}$ ;  $100\text{ rpm}$ ). The suspensions were adjusted to the desired pH by adding  $1\text{ M}$  of  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ . An ion sorption by a given synthesized zeolite sample was studied using the batch equilibrium method. The initial and final ammonium ion concentrations in the supernatant were determined by the standard Nesslerization method using a Hach DR 4000 spectrophotometer at  $410\text{ nm}$  after filtration of each sample [17]. The ammonium removal efficiency (%) was defined as:

$$\left[ \frac{(\text{influent value} - \text{effluent value})}{\text{influent value}} \right] \times 100.$$

The amount of ammonium exchanged by synthesized zeolite ( $q_e$  (mg/g)) was carried out by Equation (Eq.) 1.

$$q_e = V \frac{(C_0 - C_e)}{M} \quad \text{Eq. 1}$$

Where  $q_e$  is the equilibrium amount of ammonium uptake by zeolite Na-A (mg/g),  $C_0$  and  $C_e$  are the initial and equilibrium ammonium concentration in solution (mg/L) and  $M$  is the dry weight of zeolite Na-A (g).

*Langmuir model.* The Langmuir isotherm assumes that monolayer adsorption happens at specific homogeneous sites within the adsorbent, and that there is no interaction between the adsorbate molecules. The equation for the Langmuir isotherm is given in Equation 2.

$$\frac{1}{q_e} = \left( \frac{1}{q_m K_L} \right) \left( \frac{1}{C_e} \right) + \left( \frac{1}{q_m} \right) \quad \text{Eq. 2}$$

Where  $q_m$  is the maximum monolayer adsorption of ammonium capacity (mg/g) and  $K_L$  is the Langmuir adsorption constant (L./mg).

*Freundlich model.* The Freundlich isotherm is derived by assuming a heterogeneous surface (multilayer adsorption) with a nonuniform distribution of adsorption over the surface. The equation of the Freundlich isotherm is expressed by Eq. 3.

$$\text{Log } q_e = \text{Log}K_F + \frac{1}{n}\text{Log}C_e \quad \text{Eq.3}$$

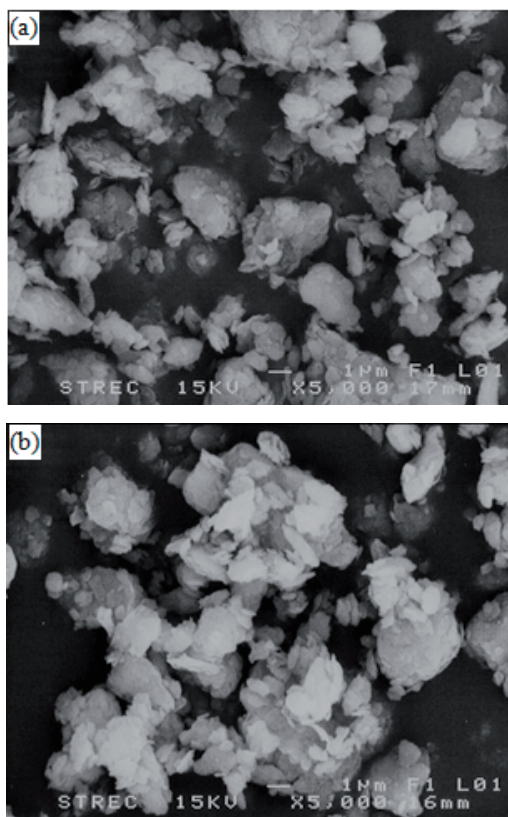
Where  $K_F$  is the Freundlich adsorption constant (mg/g), and  $1/n$  is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the material. The magnitude of the exponent  $1/n$  indicates the favorability of adsorption. A value of empirical parameter  $1/n$  between  $0.1 < 1/n < 1$  indicates favorable adsorption, whereas a value of the coefficient  $1/n$  of greater than 1 denotes that, in all the solutions, the adsorption equilibrium is not favorable [5].

### 3. RESULTS AND DISCUSSION

#### 3.1 Analysis of Physicochemical Properties of Raw Material and Zeolite

The physical properties of sludge waste with and without calcination pretreatment were characterized by scanning electron microscopy (SEM) and are illustrated in Figure 2. The morphologies of sludge surfaces with and without calcination pretreatment were very similar with a smooth surface because the surface was covered by an aluminosilicated glass phase. The sludge shape was not uniform. The observed micro-particles formed clusters and irregular shapes. After react with alkali (3 M NaOH) solution by hydrothermal treatment, the surface on the waste sludge generate fissure and became rough as shown in SEM images of the synthesized zeolite (Figure 3. a-h). In addition, the morphologies of the zeolite synthesized from the sludge with and without

calcining at 6, 9, 12 and 24 hours revealed the presence of octahedral habit crystals with the same cubic morphology and uniform sizes of 1–3  $\mu\text{m}$  for all experimental conditions. The cubic crystals of the zeolite were clearly observed in large amount in the calcinated sludge at the 9-hour reaction time as shown in Figure 3 (f). Type of zeolites obtained could be confirmed by XRD peak.



**Figure2.** SEM images of sludge characteristics (a) with and (b) without calcination.

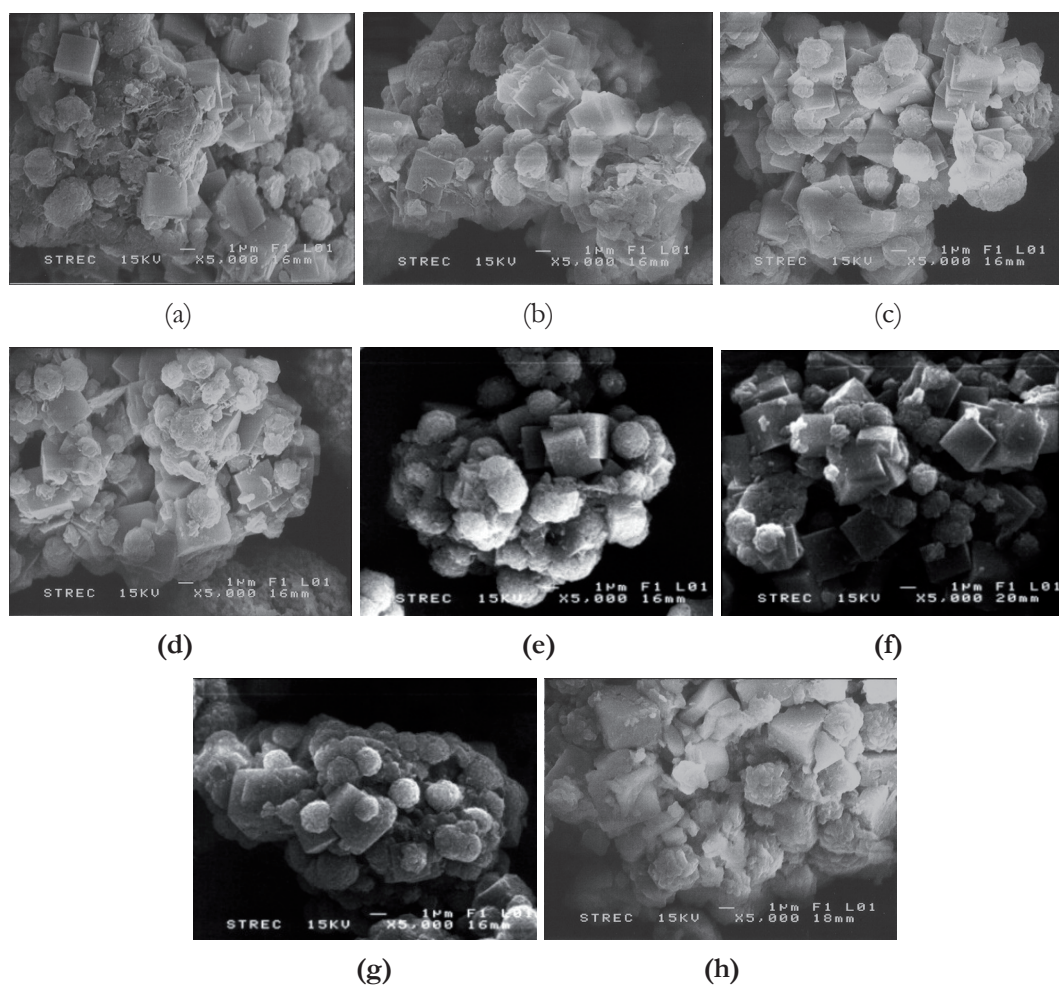
XRD is an important tool which can be used to evaluate the structure of crystalline material. It is especially useful for confirming the number of crystalline phases present in a sample. From the XRD results in Figure 4, it was found that the peak intensity of zeolite Na-A ( $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$ ) appeared at  $2\theta$  values of  $10.158^\circ$ ,  $12.449^\circ$ ,  $16.093^\circ$ ,  $21.649^\circ$ ,  $23.966^\circ$ ,  $27.092^\circ$ ,  $29.916^\circ$  and  $34.150^\circ$  for all



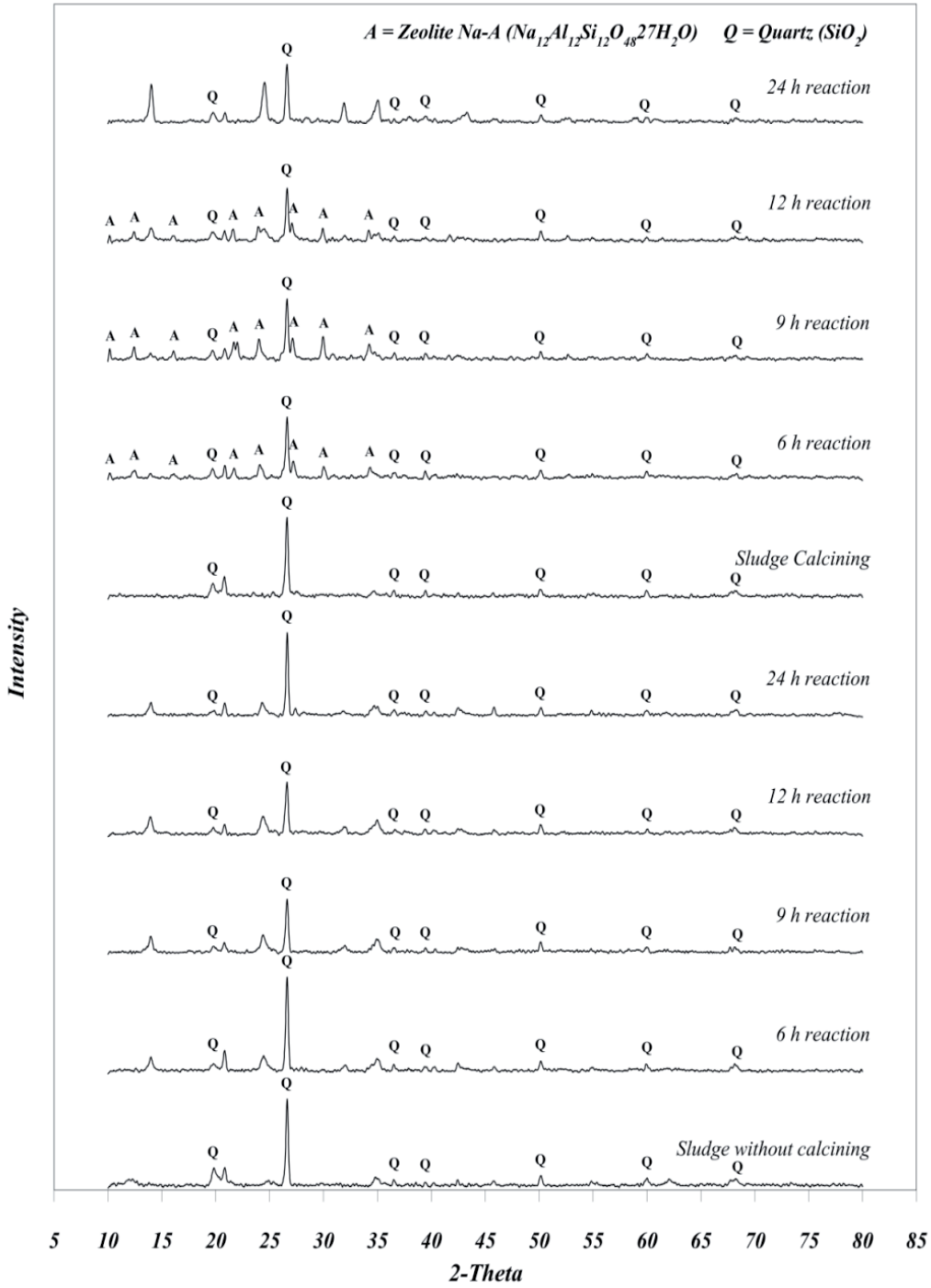
conditions of calcinated sludge, except those at 24 hours. This was because the prolonged period of 24 hours resulted in the amorphous material transforming into metastable phase. This statement was supported by Tounsi *et al.* [18].

The gelation of crystallization which formed corresponded to Figure 3(h). Moreover, there were no zeolites obtained in the conditions without calcination treatment. Meftah *et al.* [13] stated that calcining at 550-950°C would obtain more reactive metakaolin, which was then subjected to alkali hydro-

thermal treatment for zeolite crystallization. The structure of the calcinated sludge was changed by heat treatment, after which zeolite Na-crystallization formed. Quartz peak ( $\text{SiO}_2$ ) was also detected for all samples at 2 $\theta$  values of 20.860, 26.640, 36.544, 50.139, 59.960 and 68.144. Therefore, in order to obtain the zeolite, there action times of 6-12 hours should be used, but the most recommended reaction time is 9 hours. This observation is based on the peak intensities of zeolite Na-A at 2 $\theta$  values of 21.649°, 23.966°, 29.916° and 34.150°. In the recommended reaction time of 9 h, zeolite



**Figure 3.** SEM images of the zeolite synthesized from the sludge without calcination at (a) 6 h (b) 9 h (c) 12 h and (d) 24 h and the sludge with calcination at (e) 6 h (f) 9 h (g) 12 h and (h) 24 h.



**Figure 4.** XRD patterns of sludge and synthesized zeolite with and without calcination at different reaction times.

**Table 2.** CEC values of initial waste sludge, zeolite synthesized and other adsorbent materials.

Absorbent material	Original material	Treatment condition	CEC (meq/g)	References
Initial waste sludge	Sludge from WTP	Calcining at 700°C for 3 h	0.12	This study
Zeolite Na-A	Sludge from WTP	Hydrothermal Treatment (3M NaOH,6 h at 90°C )	0.99	This study
Zeolite Na-A	Sludge from WTP	Hydrothermal Treatment (3M NaOH,9 h at 90°C )	1.07	This study
Zeolite Na-A	Sludge from WTP	Hydrothermal Treatment (3M NaOH,12 h at 90°C )	0.78	This study
Zeolite Na-A	Sludge from WTP	Hydrothermal Treatment (3M NaOH,24 h at 90°C )	0.29	This study
Clinoptilolite	Natural Chinese	-	0.82	[4]
Zeolite 4A	Fly ash	2 h at 100°C in microwave	1.1	[9]
Zeolite 4A	Fly ash	1 h at 100°C in conventional treatment	1.6	[9]
Zeolite 4A	Fly ash	2 h at 100°C in conventional treatment	2.5	[9]
Zeolite 4A	Fly ash	1 h at 100°C in conventional treatment and 1 h at 100°C in microwave	5.5	[9]
Sodalite	Fly ash	Hydrothermal Treatment (0.5-3M NaOH, at 175-225°C )	0.30	[10]
Analcime	Fly ash	Hydrothermal Treatment (0.5-3M NaOH, at 175-225°C )	0.60	[10]
Zeolite Na-P	Paper sludge ash	Hydrothermal Treatment (3M NaOH, 24 h at 90°C )	0.50-1.3	[11]
Zeolite Na-P1	Oil shale ash	Heat treatment 24 h at 160°C	1.66	[12]

**Table 3.** Isotherm constant and regression data of Langmuir and Freundlich Isotherms of ammonium sulfate on the synthesized zeolite.

Absorbent	Initial concentration (mg/L)	CEC (meq/g)	Langmuir Isotherm				Freundlich Isotherm			References
			$K_L$	$q_m$	$R_L$	$R^2$	$K_F$	$1/n$	$R^2$	
Zeolite Na-A	60-140	1.07	0.06	8.88	0.11-0.22	0.989	1.70	0.35	0.954	This study
Turkish Clinoptilolite	25-150	0.95	0.03	8.12	0.17-0.60	0.927	0.61	0.52	0.952	[3]
Natural Chinese zeolite	50-300	0.82	0.06	6.47	-	0.985	0.64	0.53	0.995	[4]

Na-A ( $\text{Na}_{12}\text{Al}_2\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$ ) is a member of the sodalite group and the chemical compositions of synthesized zeolite was in %by weight were 43.2%  $\text{SiO}_2$ , 29.4%  $\text{Al}_2\text{O}_3$ , 8.51%  $\text{Fe}_2\text{O}_3$ , 1.67%  $\text{K}_2\text{O}$ , 5.88%  $\text{CaO}$ , 1.13%  $\text{MgO}$ , 0.74%  $\text{TiO}_2$ , 0.35%  $\text{SO}_3$ , 8.74%  $\text{Na}_2\text{O}$  and 0.34% other. The framework structure is composed of four and six membered rings of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. The pore properties of the synthesized zeolite have been examined using BET analysis. The values of the surface area, total pore volume and mean pore diameter were  $52.2\text{ m}^2/\text{g}$ ,  $0.16\text{ cm}^3/\text{g}$  and  $12.50\text{ nm}$  ( $125\text{ \AA}$ ), respectively. However, the pore size of the zeolite synthesized from waste sludge was large compared to that of zeolite 4A synthesized from fly ash ( $4.82\text{ \AA}$ ) and commercial zeolites ( $5.24\text{ \AA}$ ) [9]. The large pore size had more

benefit to migrating substance into the center of the construct, so that the pollutant may be more easily removed from solution. The cation capacity (CEC) of the synthesized zeolite and other adsorbent materials are compared and discussed in Table 2. The CEC value of the initial calcinated sludge was  $0.12\text{ meq/g}$  and the zeolite Na-A from calcinated sludge synthesized at reaction times of 6, 9, 12 and 24 h were 0.99, 1.07, 0.78 and  $0.29\text{ meq/g}$ , respectively. This was because the calcination resulted in more reactive metakaolin, which was then subjected to alkali hydrothermal treatment for zeolite crystallization. It should be noted that, based on the works carried out by Kim and Lee [9], the relationship between BET and CEC was relatively linear. Therefore, the zeolite that was synthesized at reaction



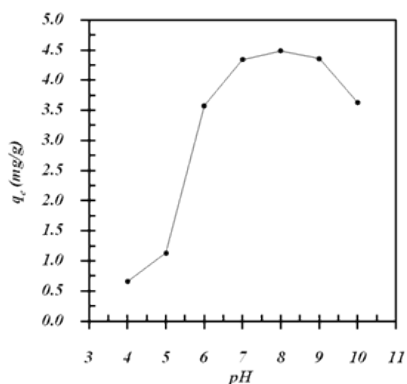
time of 9 hours and gave high CEC value was expected to yield high BET value.

Moreover, crystallization under the optimized condition of 9 h could considerably increase the CEC of zeolite product and then decrease. The decrease in CEC was because of the amorphous material transforming into metaphase as mentioned earlier. It should be noted that CEC values depend on the starting material and heating conditions [4, 9-12]. Kim and Lee [9] synthesized zeolite 4A from coal fly ash by different techniques (conventional and microwave heating), and found that the maximum CEC value of 5.5 meq/g was obtained by a combined treatment of conventional and microwave heating. Wajima *et al.* [11] suggested that the synthesized zeolite Na-P1 from paper sludge ash gave CEC values of 0.5-1.3.

### 3.2 Adsorption Equilibrium in Batch Experiments

#### *Effect of pH*

The effect of pH on ammonium uptake is given in Figure 5. The amount of ammonium exchanged by synthesized zeolite ( $q_e$  (mg/g)) was carried out. It was seen that the amount of ammonium ions adsorbed by the synthesized zeolite ( $q_e$ ) increased from 0.42 to 4.44 mg/g by increasing from pH 4 to pH 10 and reached a maximum value at pH 8. Afterwards,

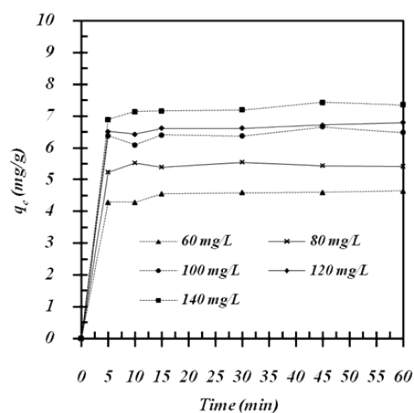


**Figure 5.** Effect of pH on amount of ammonium adsorbed by the synthesized zeolite.

the amount of ammonium ion adsorption decreased with a pH higher than 8 because the ammonium ions were converted to  $\text{NH}_3$ , which could not be removed by the synthesized zeolite. Since only the  $\text{NH}_4^+$  forms can be removed from the solution by ion exchange, at pH of less than 8, the  $\text{NH}_4^+$

#### *Effect of contact time and initial concentration*

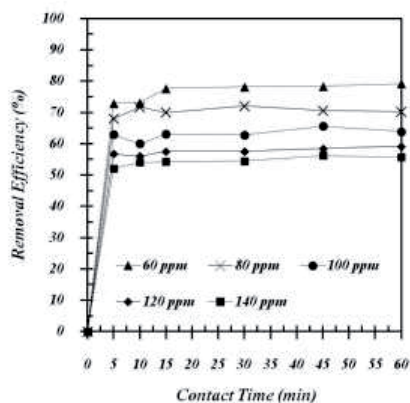
Figure 6 shows the amount of ammonium ions adsorbed by the synthesized zeolite ( $q_e$ ) at different contact times. It was found that the ammonium uptake by the synthesized zeolite was rapid in the initial stage and almost completed within 5 minutes of contact time. Synthesized zeolite (Zeolite Na-A) from waste



**Figure 6.** Ammonium uptake as a function of contact time for different initial ammonium concentrations.

sludge can be accepted as an efficient adsorbent for ammonium removal when its short contact time was considered. The accelerated uptake in  $q_e$  resulted from cations in the zeolite structures that exchanged easily with ammonium ions in the solution. This was supported by Zhang *et al.* [6] who found that ammonium uptake by the zeolite synthesized from fly ash was a fast process, and uptake equilibrium was achieved in a brief period of 10 minutes. The effect of initial ammonium concentrations (60, 80, 100, 120 and 140 mg/L) on ammo-

nium uptake was also discussed (Figure 6). As expected, the ammonium uptake behavior of the synthesized zeolite used in this work was quite similar to that of zeolite in other studies [3, 19]. The results indicated that the ammonium uptake capacity of the synthesized zeolite increased with higher initial ammonium concentration due to increased driving force. Karadag *et al.* [3] suggested that the rate of sorption to the surface was proportional to a driving force times an area where the initial concentration of the solution was regarded as the driving force and the amount of bare surface was the area. The equilibrium time of higher initial ammonium concentration was higher than that of lower initial ammonium concentration because of increased competition for the active sites. Figure 7 shows the result of removal efficiency of ammonium ions by zeolite, which depended on the initial ammonium concentration and contact time. The rate of ammonium ions removal by zeolite was initially very high, but thereafter leveled off. The decreasing ammonium uptake rate could be explained by the loss of vacant adsorbent sites and reduction of concentration gradient. [14]. As expected in this work, the average ammonium removal efficiencies in equilibrium were 78, 70, 63, 58 and 54% for

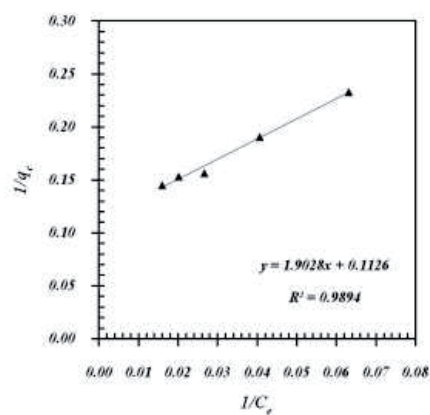


**Figure 7.** Ammonium removal efficiency vs. contact time for different initial ammonium concentrations.

initial ammonium concentrations of 60, 80, 100, 120 and 140 mg/L, respectively. The highest ammonium sulfate removal efficiency was achieved at the lowest initial ammonium concentration (60 mg/L).

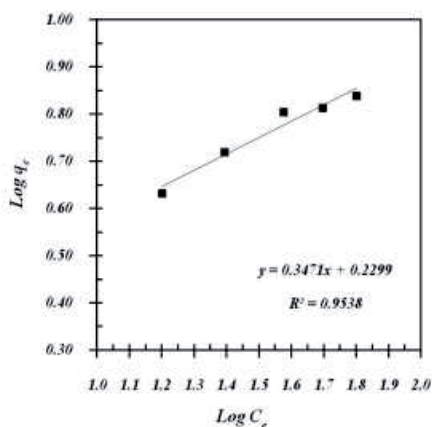
#### *Study of adsorption equilibrium isotherms*

In this work, the isotherm data were calculated at different initial ammonium concentrations using Equations 2 and 3. The linear plot of Langmuir isotherm is shown in Figure 8. The constant values of  $q_m$  and  $K_L$  were calculated from the slope and intercept of the



**Figure 8.** Linear plot of Langmuir isotherm for ammonium ion adsorption.

plot, respectively, and are presented in Table 3. The maximum capacity ( $q_m$ ) was found to be 8.88 mg/g by the Langmuir isotherm at the initial ammonium concentrations of 60–140 mg/L. The  $q_m$  value obtained in this work was found to be greater than some other work in literatures [3-4]. Karadag *et al.* [3] reported a  $q_m$  value of 8.12 mg/g ammonium adsorption on natural Turkish clinoptilolite at the initial ammonium concentrations of 25-150 mg/L, while a  $q_m$  of 6.47 mg/g with natural Chinese zeolite at the initial ammonium concentrations of 50-300 mg/L was reported by Huang *et al.* [4]. The  $q_m$  value of zeolite synthesized from waste sludge of water treatment plants was higher than those of Turkish clinoptilolite



**Figure 9.** Linear plot of Freundlich isotherm for ammonium ion adsorption.

and natural Chinese zeolite due to the highest cation exchange capacity (CEC) as mentioned in Table 3. The linear form of the Freundlich isotherm is given in Figure 9. The Freundlich constant can be calculated from the slope and intercept, and the results are presented in Table 3. It was found that based on the  $R^2$  value, the Langmuir model ( $R^2 = 0.989$ ) provided a more consistent fit to the experimental data compared with the Freundlich model ( $R^2 = 0.954$ ). The constants  $K_L$  and  $K_F$  were 0.06 and 1.70 L/mg, respectively. The Freundlich constant ( $1/n$ ) was a measure of exchange intensity or surface heterogeneity and ranged between 0 and 1. In this work, the Freundlich constant value of  $1/n$  was less than 1 which represents a favorable uptake condition. In addition, the  $R_L$  values in Table 3 were in the range of 0-1, indicating that the exchange of ammonium ion by the synthesized zeolite from waste sludge of water treatment was favorable.

#### 4. CONCLUSION

It was found that the synthesized zeolite Na-A consisted of octahedral crystals with the same cubic morphology for reaction times of 6-12 hours. More obvious zeolite was obtained from the sample with calcining treatment at the recommended reaction time of 9 hours.

The XRD results showed that the peaks for zeolite Na-A did not appear when the sludge was not calcined. In addition, the conditions for producing the highest cation exchange capacity (CEC) of synthesized zeolite were 1.07 meq/g for calcinated sludge at the reaction time of 9 hours. The optimal pH and contact time for ammonium ion adsorption were 8 and 5 minutes, respectively. The highest ammonium removal efficiency obtained in this work was 78%. The Langmuir model provided a more consistent fit to the experimental data compared with the Freundlich model. The maximum capacity for synthesized zeolite was 8.88 mg/g. The  $R_L$  value from the Langmuir model and  $1/n$  from the Freundlich model indicated that the zeolite fabricated from water treatment plant waste sludge could be an alternative sorbent for ammonium removal.

#### ACKNOWLEDGEMENTS

The authors would like to thank the King Mongkut's University of Technology North Bangkok (KMUTNB) for financial support

#### REFERENCES

- [1] Wiesmann U., Biological nitrogen removal from wastewater, *Adv. Biochem. Eng./Biotechnol.*, 1994; **51**: 114–153.
- [2] Li M., Zhu X., Zhu F., Ren G., Cao G. and Song L., Application of modified zeolite for ammonium removal from drinking water, *Desalination*, 2011; **271**: 295-300.
- [3] Karadag D., Koc Y., Turan M. and Armagan B., Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite, *J. Hazard. Mater.*, 2006; **136**: 604-609.
- [4] Huang H., Xiao X., Yan B. and Yang L., Ammonium removal from aqueous solution by using natural Chinese (Chende) zeolite as adsorbent, *J. Hazard. Mater.*, 2010; **175**: 247-252.

- [5] Malekian R., Abedi-Koupai J., Eslamian S. S., Mousavi S. F., Abbaspour K. C. and Afyuni M., Ion-exchange process for ammonium removal and release using natural Iranian zeolite, *Appl. Clay Sci.*, 2011; **51**: 323-329.
- [6] Zhang M., Zhang H., Xu D., Han L., Niu D., Tian B., Zhang J., Zhang L. and Wu W., Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method, *Desalination*, 2011; **271**: 111-121.
- [7] Jaroonvechatam N., Sansuksom P., Worathanakul P. and Kongkachuichay P., SUZ-4 zeolite synthesis derived from rice husk ash, *Chiang Mai J. Sci.*, 2013; **40**: 109-116.
- [8] Buasri A., Yongbut P., Chaiyut N. and Phattarasirichot, K., Adsorption equilibrium of zinc ions from aqueous solution by using modified clinophilolite, *Chiang Mai J. Sci.*, 2008; **35**: 56-62.
- [9] Kim J. K. and Lee H. D., Effects of step change of heating source on synthesis of zeolite 4A from coal fly ash, *J. Ind. Eng. Chem.*, 2009; **15**: 736-742.
- [10] Querol X., Moreno N., Umaña J. C., Alastuey A., Hernández E., López-Soler A. and Plana F., Synthesis of zeolite from coal fly ash: An overview, *Int. J. Coal Geol.* 2002; **50**: 413-423.
- [11] Wajima T., Haga M., Kuzawa K., Ishimoto H., Tamada O., Ito K., Nishiyama T., Downs R. T. and Rakovan J. F., Zeolite synthesis from paper sludge ash at low temperature (90°C) with addition of diatomite, *J. Hazard. Mater.*, 2005; **132**: 244-252.
- [12] Machado N. R. C. F. and Miotto D. M. M., Synthesis of Na-A and-X zeolites from oil shale ash, *Fuel*, 2005; **84**: 2289-2294.
- [13] Meftah M., Oueslati W. and Ben Haj Amara A., Synthesis process of zeolite P using a poorly crystallized kaolinite, *Physics Procedia*, 2009; **2**: 1081-1086.
- [14] Zhao Y., Zhang B., Zhang X., Wang J., Liu J. and Chen R., Preparation of highly ordered cubic NaA zeolite from halloysite mineral for adsorption of ammonium ions, *J Hazard. Mater.*, 2010; **178**: 658-664.
- [15] Metropolitan Waterworks Authority, *Sludge Disposal Process Annual Report*, Bangkok, Thailand, 2007.
- [16] Breck D.W., *Zeolite Molecular Sieve: Structure Chemistry and Use*, Wiley, New York, 1974.
- [17] Hach, DR 4000 Spectrophotometer Procedure Manual, Method 8038 1997
- [18] Tounsi H., Mseddi S. and Djemel S., Preparation and characterization of Na-LTA zeolite from Tunisian sand and aluminum scrap, *Physics Procedia*, 2009; **2**: 1065-1074.