

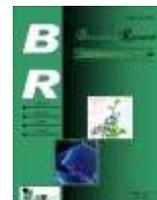


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## Elimination and Kinetics of Ammonium Ions from Waste Water Using by Zeolite (NaY) Preparing from Agriculture Waste

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Zeolite NaY prepared by ash from rice husk used for elimination of ammonium from aqueous solutions. Its performance investigation was compared with natural zeolite granulated formed and powdered mordenite. Natural zeolite mordenite and prepared Zeolite NaY were characterized by Energy Dispersive X-ray (EDX), X-ray Diffraction (XRD) and total cation exchange capacity (CEC) was measured. Measured cation exchange capacity (CEC) of zeolite NaY was 3.15 meq g<sup>-1</sup>, powdered mordenite was 1.46 meq g<sup>-1</sup> and granular mordenite 1.34 meq g<sup>-1</sup>. Kinetics of adsorption and for the deletion of NH<sub>4</sub><sup>+</sup> ions of equilibrium data from aqueous solutions were examined by fitting the investigational data to various models of reaction order. NH<sub>4</sub><sup>+</sup> adsorption on zeolite NaY and mordenite powder followed Pseudo-second-order reaction kinetically. Compared to all isotherms equations, the equilibrium pattern fits well to the Langmuir isotherm equation. The adsorption capacity of the monolayer for powdered mordenite 14.99 mg g<sup>-1</sup> and granular mordenite 13.56 mg g<sup>-1</sup> to be very lower than that zeolite Y was found 43.25 mg g<sup>-1</sup>. Compared to natural mordenite, it can be concluded that zeolite Y synthesized from ash husk is a better sorbent for ammonia removal from aqueous solutions predicted to its higher adsorption capacity and rapid adsorption rate.

**Keywords:** zeolite Y, ammonium ions, mordenite, waste water

### INTRODUCTION

Industrial effluents mainly the development and developing the country and effluents from the municipality is responsible for discharged ammonium ions to create different poisonous effects such as toxicity to aquatic life, eutrophication, the increased erosion rate of soil materials (Lei et al., 2009). Biological systems

have provided an important role in natural mixture with the retrofitting of biotic NH<sub>4</sub><sup>+</sup> (ammonium) ions removal facilities to existing environmental treatment systems (Adam et al., 2019b) and it is one kind of conventional method. It is an often effective and these methods require big open lands; more or less 1000 acres of land, oxidation from open air and the sun shining. It is a slow

process and the slowness of biotic conversion of nutrients, it imposing a big capital cost (Gil et al., 2019) at a time. So; this method can't be run for removing ammonium ions in the long run of investment. An alternative high effective wastewater treatment is Physico-chemical treatment and it offers a high effective compared to the typical biotic processes and it required relatively small land areas for equivalent influent flows (Nuernberg et al., 2016). Another process proposed to eliminate concentrations of ammonium ions in wastewater, through adsorption or ion exchange process using zeolite material has been recognized as highly efficient and budget competitive in both research and industrial plants (Adam et al., 2019a).

Mordenite, clinoptilolite, phillipsite are natural zeolites from the different sources of deposits in the worlds has been widely used as an ion exchanger in wastewater ammonium ions eliminated installations owing to ammonium ions selectivity and less investment (Xue et al., 2018). However, the ammonium removal capacity of a natural zeolite such as mordenite, clinoptilolite, phillipsite varies with the source of the zeolite, the location within a particular deposit and the capacity measurement technique employed (Wang et al., 2018).

Risen awareness and understanding of the vicious impressions of ammonium ions, discharged from wastewater treatment plants into natural surface water has resulted in stringent laws restricting free ammonium ions discharge into the environment (Li et al., 2010). Malaysian Interim National Water Quality Standard for Malaysia (INWQS) has set up guidelines of 0.9 mg/L of ammoniacal nitrogen for class III water and it is maximum, 0.3 mg/L of ammoniacal nitrogen for class II water while 0.1 mg/L of ammoniacal nitrogen for class I water and it be below than this value (INWQSM) (2000).

The naturally accumulated mordenite containing tuff could represent a significant source of zeolite to be used in processes for ammoniacal nitrogen neutralized or delaminated from various wastewaters in the environment (Ding and Sartaj, 2015). Synthetic zeolite (NaY) prepared from Malaysian paddy waste possess and it is low cost, highly efficient in ammonium removal is another interesting subject of study (Syukor et al., 2016). Since both commercial mining's of natural zeolite and industrial production of synthetic zeolite from husk ash in Malaysia are such a new undertaking, little was known of the ammonium adsorption characteristics of the materials (Krishnan et al.,

2017).

The studies reported in this paper purposes to understand the cost of this mordenite from natural sources and synthetic zeolite Y synthesized (low cost) from ash as an efficient alternative to the existing sorbent for ammonium ions removal from the surface water. The zeolites were well characterized before ammonium removal studies. An appreciative of the kinetic and equilibrium performance of these zeolites provided insight into its expected experience as an adsorbent. Many adsorption isotherms such as Freundlich, Langmuir and Temkin models were employed to standard the experimental isotherm data. Besides, the experimental results enable a simple relationship of the ammonium elimination from aqueous solution by both the mordenite and synthetic zeolite (NaY).

## MATERIALS AND METHODS

### Zeolite Y preparation

Some researcher has early attempts of direct synthesis of zeolite Y from rice hush ash without aging and seeding, the product produced as a mixture of zeolite Y and zeolite P as indicated by powder X-ray diffractogram. The phenomenon has occurred since zeolite Y is thermodynamically metastable, some of the crystallites will transform to zeolite P, or uniform zeolite P looks as the first and dominant crystalline phase in the products during hydrothermal reaction (Sun et al., 2018). Thus, aging and seeding methods were employed to avoid the co-crystallization of competing phases such as zeolite P (gismondine) to obtain the pure phase of zeolite Y (faujasite) (Krishnani et al., 2012).

Finally, zeolite Y synthesized with seed gel (10 % of Al) of the molar composition; 15 Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 15 SiO<sub>2</sub>: 220 H<sub>2</sub>O and feedstock gel aluminosilicate (90 % of Al) of the molar composition; 4 Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 10 SiO<sub>2</sub>: 180 H<sub>2</sub>O (Siddique et al., 2015). The reactants used sodium hydroxide, sodium aluminate, and rice husk ash with 96 % amorphous silica content. After preparation, the seed gel and feedstock gel were transferred to a Nalgene Teflon FEP (fluorinated ethylene propylene) bottle with a Tefzel ETFE (ethylene-tetrafluoroethylene) screw closure respectively and left to age at room temperature for one day. After an aging time, the seed gel was swelled slowly to the feed stocks gel under enthusiastic stirring for two hours. The overall mixture was aged again at room temperature for 24 h. Subsequently; a

hydrothermal reaction was carried out by heating the mixture at 100 °C in a drying oven. After 24 h reaction, the crystallization stopped by immersing the Teflon FEP bottle in water. Then the product was recovered by vacuum filtration and washed out of the entrained sodium salts with a copious quantity of warm deionised distilled water up to the pH of the filtrate is below 10. The filtrate was dry out in an oven at 100 °C overnight, ground to a fine powder. On the other hand, the natural zeolite, mordenite was supplied from a local wastewater treatment company in granular form and fine powdered form. That mined from the domestic deposits in Malaysia. The mordenite was used for analyses and ammonium removal studies as receive without any pre-treatment.

### Zeolite Characterizations

Structure of the sample tested by a powder X-ray diffractometer (GmbH HR Bruker AXS) with  $\text{CuK}\alpha$  radiation ( $\lambda=1.542 \text{ \AA}$ ) at room temperature 27 °C. Data collection the range was from 5° to 50° at a scan rate of 0.05°/s. Shimadzu 8300 spectrophotometer Fourier-transform infrared (FTIR) spectroscopy was implemented to gain information about the internal and external linkages. For the sample recorded, the Zeiss Supra 35VP Field-Emission Scanning Electron Microscope (FESEM) and energy Dispersive X-ray spectrum (EDX) has been used.

### Total cation exchange capacity (CEC) determination

All interchangeable cations of zeolite total CEC is the quantity and is defined by the number of equals of fixed negative charges per amount of zeolite (Wlazło et al., 2016). Although, it must note that the total CEC of zeolite does not be steady to the operating substitute capacity, which is frequently lower in exercise (Liu et al., 2019). In this study, total CEC was calculated using the sodium-saturated zeolite samples (NaY) by ammonium displacement. The procedures were implemented from the classical "Ammonium Acetate Method at pH 7" with correct modification (Vitzthum von Eckstaedt et al., 2016). Zeolite (NaY) was prepared through the complete exchange of the raw zeolite in buffered pH with sodium acetate (1.0 N) solutions for four times. Then loosely bound sodium onto zeolite was removed thoroughly washed with 2-propanol for three times. Analysis of the cations (sodium) in buffered solution yields the total CEC of zeolite samples. Sodium content in solutions was analyzed in the air-acetylene flame using flame

atomic adsorption spectrometer of Perkin Elmer, model AAnalyst 400.

### Kinetic Study of $\text{NH}_4^+$ Adsorption

Kinetic study adsorption led at 27 °C warmth of adsorbate at pH level was 7 using 400 mL solution and immobile quantity adsorbents of 1 g in a 500 mL conical flask. The reaction mixture agitated by a magnetic bar (with Teflon-coated). The samples at different periods of times were taken from the reaction vessel. Using syringe filtration through a 0.45  $\mu\text{m}$  membrane filter, the two-phase at the time designed interval were separated within two hours or centrifugation. The preliminary and final ammonium ions concentrations residual in the supernatant were analyzed by the Hach DR 4000 Spectrophotometer using the method the standard Nesslerization (APHA, 1992).

### Batch equilibrium and pH Effect studies

At room temperature, 27 °C all equilibrium studies were brought out in a batch system. An exactly known amount of zeolite NaY sample (0.1 g) was equilibrated with 40 mL of  $\text{NH}_4^+$  solutions in a polypropylene centrifuge tube size was 50 mL. In the sealed tubes shaking was applied in an orbital shaker with a constant shaking velocity (rpm) at 140. Zeolite Y was agitating for two hours, powdered mordenite and for granular mordenite 4 and 48 hours respectively, it has confirmed through the kinetic studies that the equilibrium of exchange could reach earlier than fixed shaking time. At the ending of experiments on sorption, sealed centrifuge tubes were taken out from the shaker and the solutions were separated from the adsorbent by centrifugation. Finally, the remaining ammonium concentration in the solutions was fixed. The adsorption equilibrium data were documented by changing original ammonium ion concentrations while the mass of adsorbent, shaking rate, contact time but preliminary pH was kept uniform. pH effect of adsorption of  $\text{NH}_4^+$  ions in zeolite samples were studied at a fixed temperature (27 °C). The pH of the solutions was adjusted by using hydrochloric acid or sodium hydroxide and pH values maintaining from 4 to 10. After shaken for equilibrium time and the mixtures were centrifuged to gain clear supernatant. The beginning and last  $\text{NH}_4^+$  ions residual concentrations in solution were examined.

## RESULTS AND DISCUSSION

### Zeolite Characteristics

The International Centre for Diffraction Data (ICDD) PDF, assembled used for the mineralogical phase of synthesized zeolite and natural mordenite was approved by matching the powder X ray Diffraction (XRD) examples of the samples with the diffractograms of single-phase configurations from Powder Data File. The Xray Diffraction (XRD) patterns figures of the samples were presented in the Figs. 1 and 2. Photomicrographs of the zeolite samples obtained by the Field Emission Scanning Electron Microscope (FESEM) were shown in Figs. 3 to 5. As presented by the Xray Diffraction (XRD) and the Field Emission Scanning Electron Microscope (FESEM) images, the micro sized zeolite Y has been produced with homogenous cubic crystal size less than 1 $\mu$ m (Fig. 1). While the granular and powdered mordenite presented the similar results in the Xray Diffraction (XRD) and the Field Emission Scanning Electron Microscope (FESEM) analysis (Fig. 2, 4, 5), as compared to synthetic zeolite, the mordenite presented the irregular and inhomogeneous crystallites in terms of shape and size. The mordenite used was mined from local deposit; it is well known that zeolites are not merely found in a deposit in their pure form but containing it; dirtiness such as other types of silicate particles, minerals zeolite, amorphous materials or many others. This case, the quartz with silicates dirt's were found in mordenite as showed by XRD pattern (Fig. 2). The composition analysis of zeolite samples summarized in Table 1 from EDX spectra; each value was an average from three spectra taken on the different spots of the sample. It is noted that analysis results of EDX is a qualitative composition analysis and it was scanned from a tiny spot; this was not characteristic of an entire sample.

The CEC of the synthesized zeolite Y (NaY); obtained value is 3.15 meq/g, powdered mordenite (denoted as P-M) value is 1.46 meq/g and granular mordenite (indicated as G-M) value is 1.34 meq/g from the triplicate analysis.

### Adsorption Kinetic of Ammonium ions

It was an important criterion and to determine the equilibrium contact time required for the ammonium ions after the initial of batch adsorption equilibrium studies. From the point of process efficiency and required for choosing optimum running conditions for the full-scale batch process, the kinetics of adsorption is very important (Eskicioglu et al., 2018). Where the adsorption has taken place treated as a pseudo-

first-order, pseudo-second-order, intra-particle diffusion model, etc. various kinetic models were used (Miyaoaka et al., 2018). Different systems imitate to different models.

Ammonium ions uptake capacity against time displayed in Figure 6, the initial uptake of ammonium adsorbed very fast in zeolite Y and powdered mordenite, time to reached the equilibrium was less than 0.5 hour and 2 hours respectively. Granular mordenite adsorbed ammonium uptake very poorly and to reached equilibrium time was 48 hours. The rapid rate of NH<sub>4</sub><sup>+</sup> removal at the initial time might be the cause of initially all adsorbent sites were empty and the solute concentration gradient was robust (Feng et al., 2019). The NH<sub>4</sub><sup>+</sup> uptake rate on the zeolites slower significantly due to the reduced of adsorption sites.

One researcher (Zhou and Boyd, 2014) has carried out the kinetic experiments of NH<sub>4</sub><sup>+</sup> uptake for the four different particle sizes on natural zeolite. He obtained that the equilibrium time has increased with the increasing the particle size of sorbent and time ranged from 15 to 150 min. When the sorbent particle size is big, then it's surface area was very poor and then its equilibrium durations will be varied and adsorption taken time for the ammonium ions to distributed to sorption sites within the sorbent units will be varied. The reduced the sorbent units' size, the shorter the channels taken by the sorbate units to reach the effective sorption sites of zeolite and equilibrium time is shorter. To describe and explore the adsorption kinetics, pseudo first-order and pseudo second-order were applied.

The reaction pseudo first-order kinetic is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(1)

where  $q_t$  is the amount of adsorbate adsorbed at time  $t$  (mg g<sup>-1</sup>)  $q_e$  the adsorption capacity at equilibrium (mg g<sup>-1</sup>),  $k_1$  the pseudo first-order rate constant (min<sup>-1</sup>) and  $t$  is the contact time (min). The integration of Eq. (1) with the primary condition,  $q_t = 0$  at  $t = 0$  leads to:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

(2)

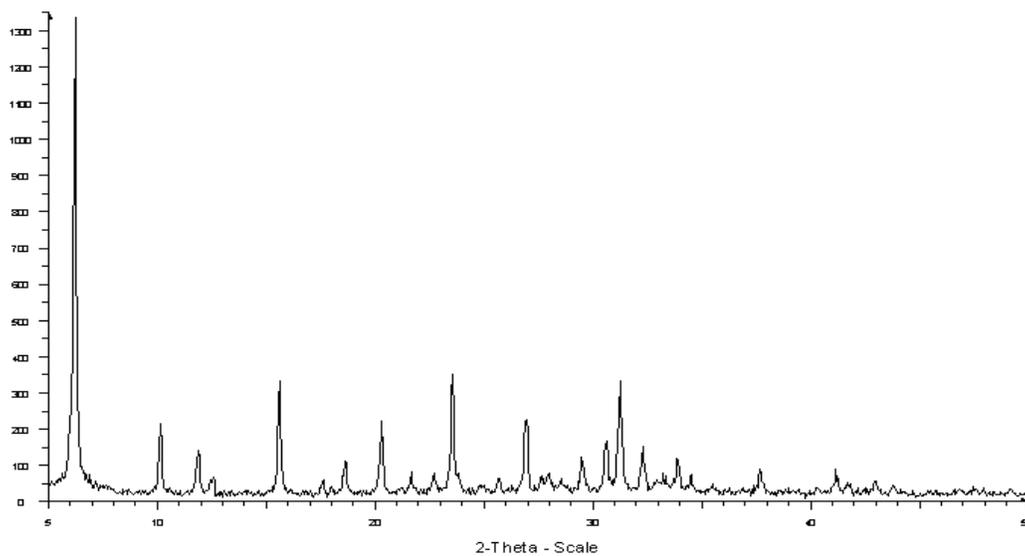
The pseudo second-order model can be corresponding to in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

(3)

**Table 1; Chemical Composition of the zeolites from EDX analysis**

Element	Zeolite Y	Powdered Modernite	Granular Modernite
	Weight %	Weight %	Weight %
Na	7.99	0.82	2.58
Mg	—	1.06	0.73
Al	23.72	14.41	15.61
Si	66.84	89.98	87.74
K	0.25	1.43	0.32
Ca	1.21	1.73	2.94
Fe	—	1.93	2.00

**Figure 1; X-ray diffractogram of synthetic zeolite Y**

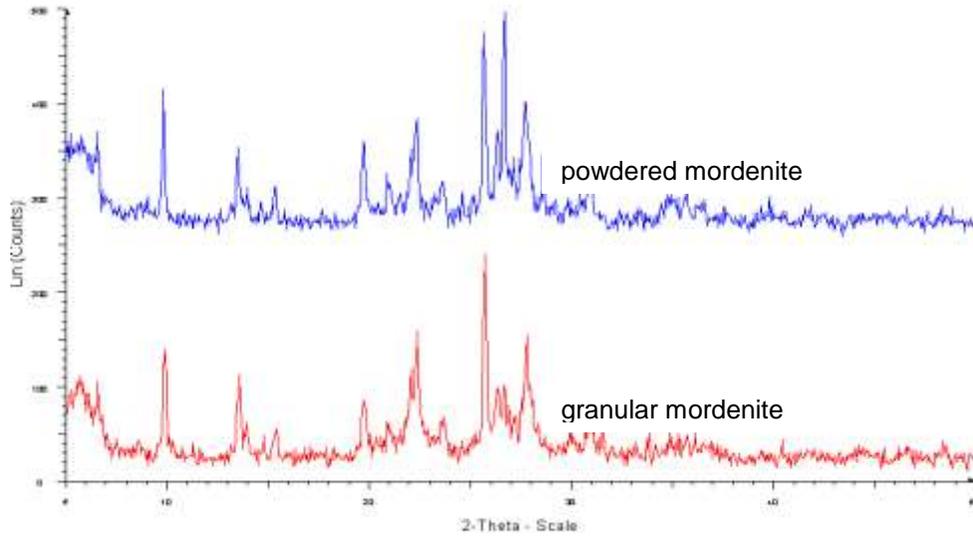
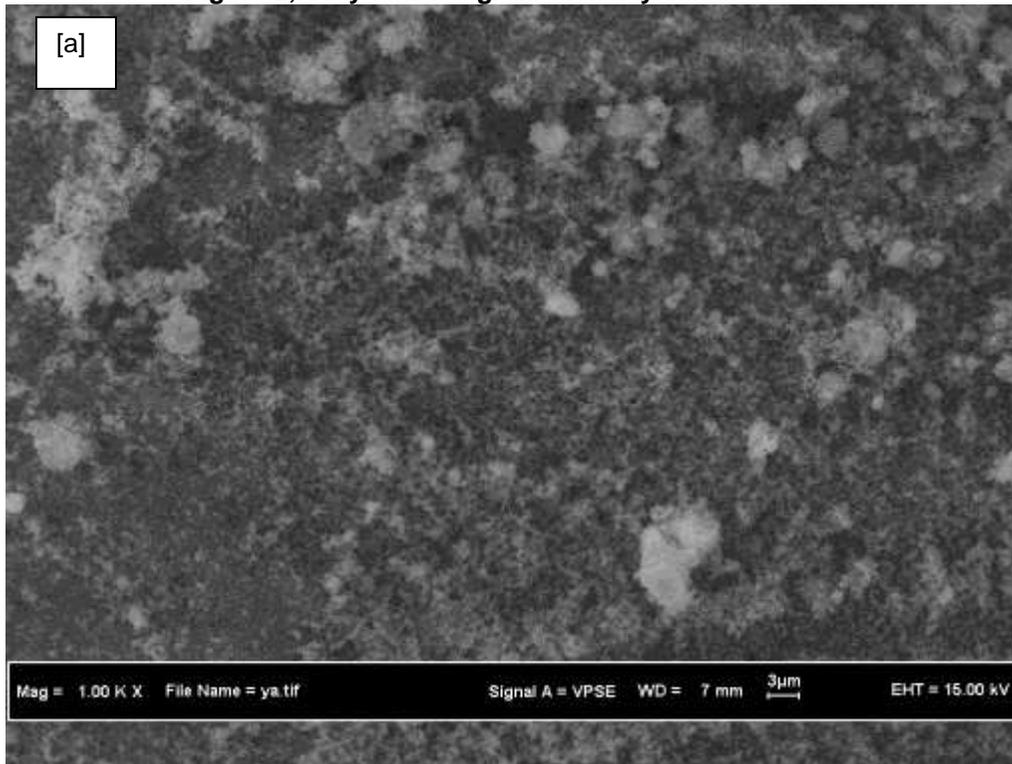


Figure 2; X-ray diffractogram of Malaysian Mordenite



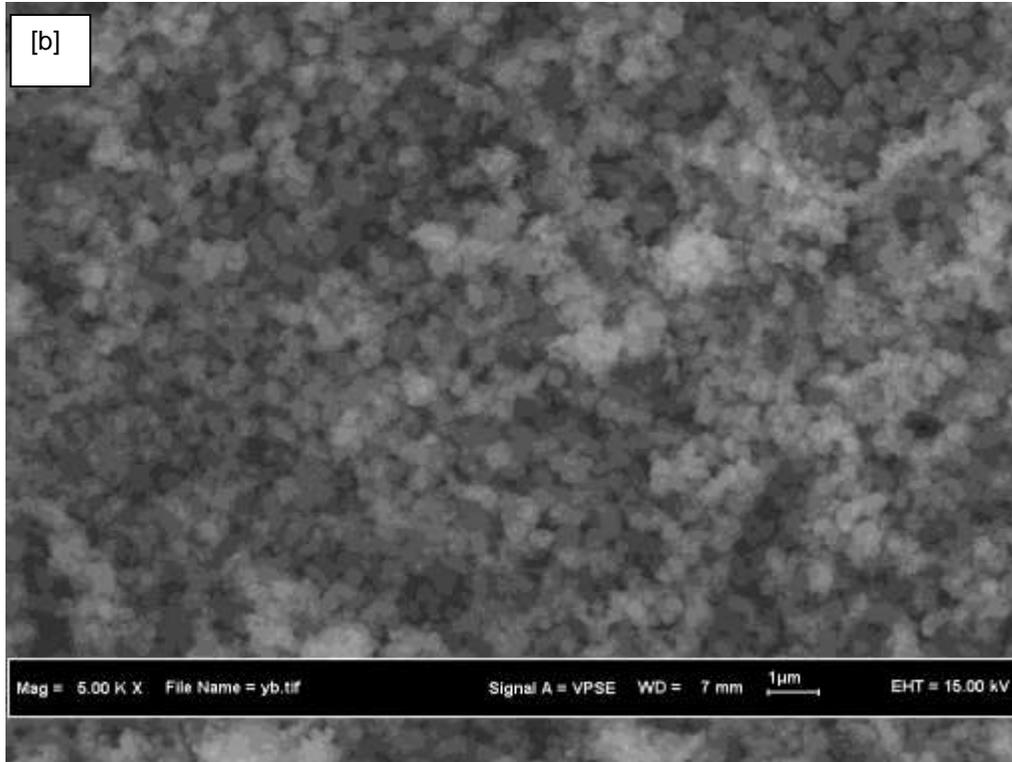
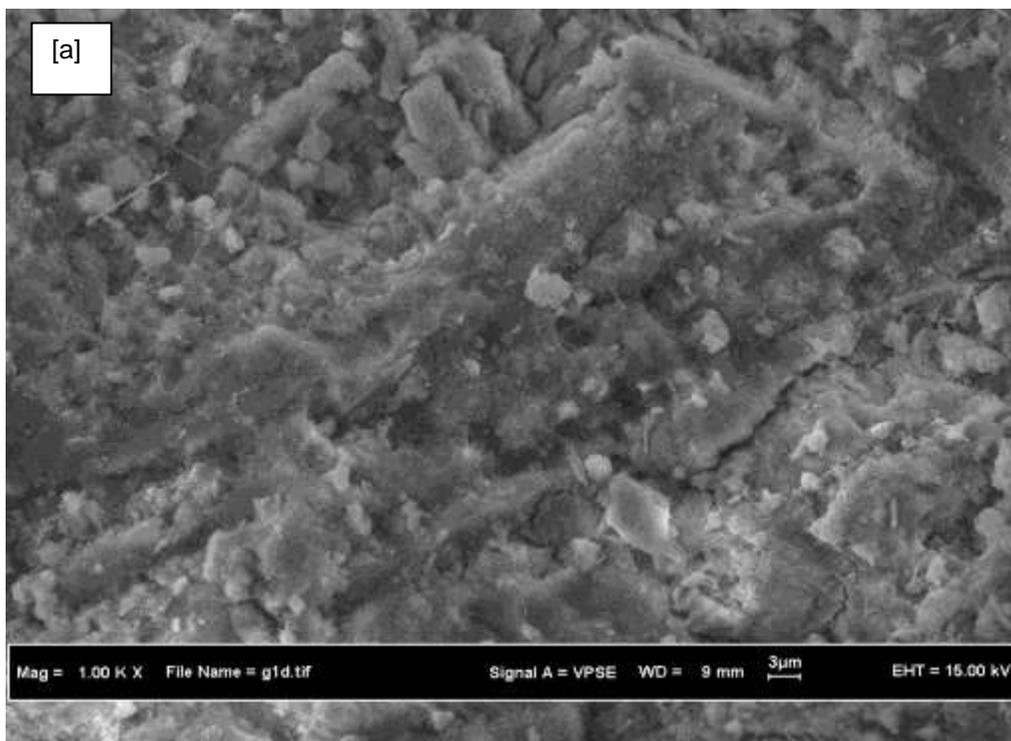


Figure 3; Typical topographic images for the zeolite Y by FESEM at magnification of 1000 × (a) and 5000 × (b).



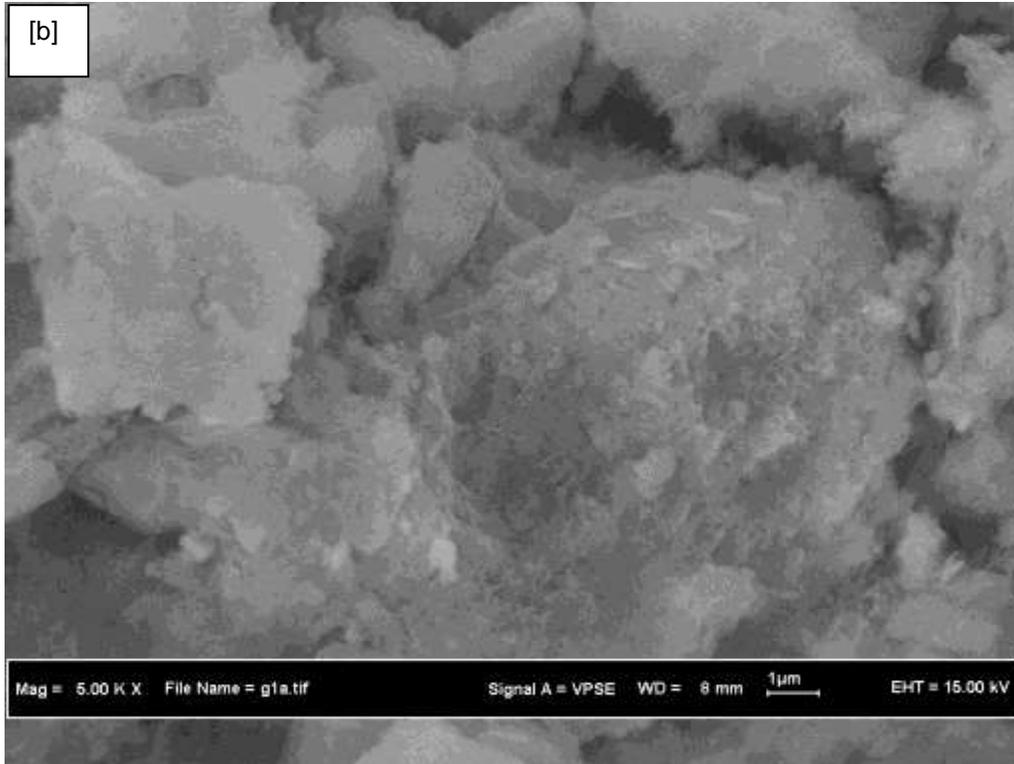
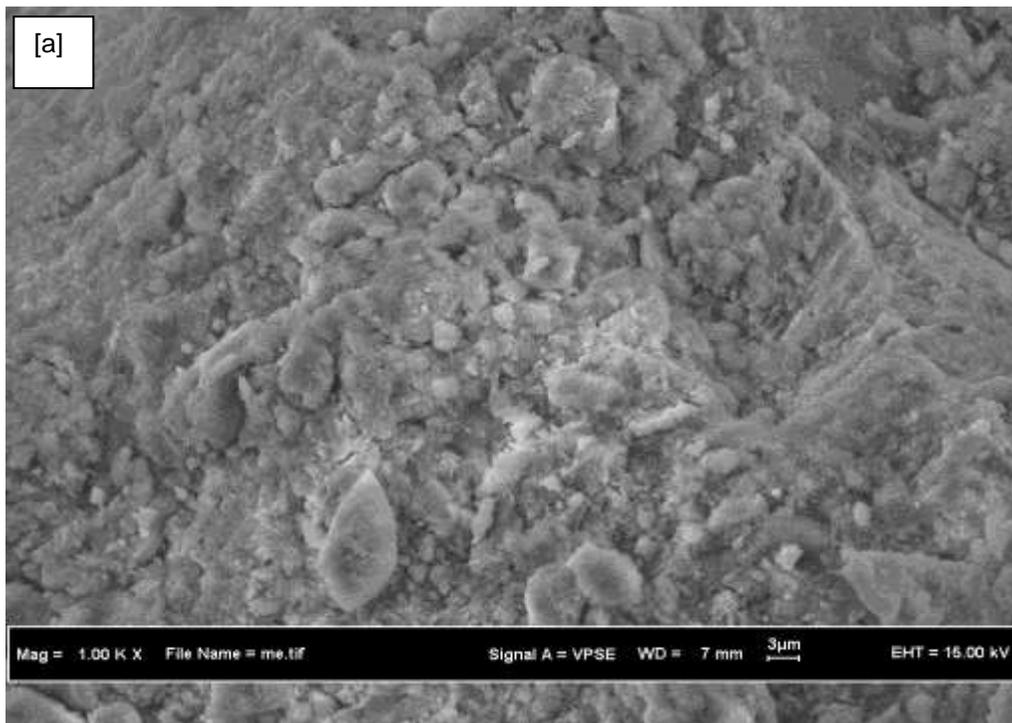
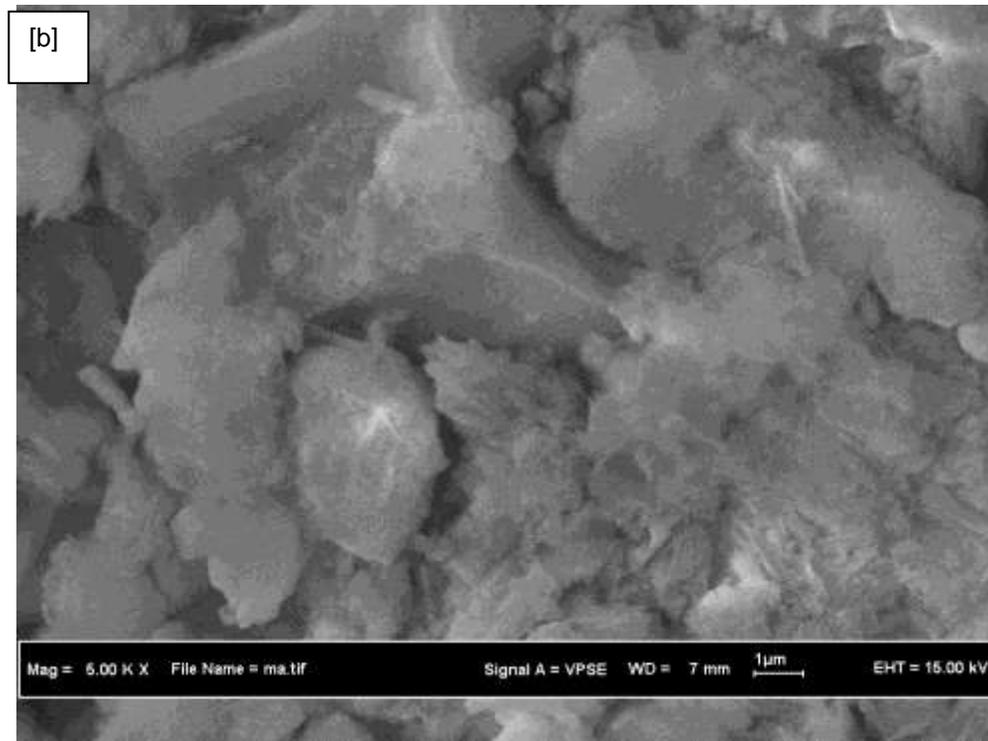


Figure 4; Typical topographic images for the granular modernite by FESEM at magnification of 1000 × (a) and 5000 × (b).





**Figure 5; Typical topographic images for the powdered modernite by FESEM at magnification of 1000 × (a) and 5000 × (b).**

where  $k_2$  is the pseudo second-order rate constant (g/mg/min). Integrating Eq. (3) and noting that  $q_t = 0$  at  $t = 0$ , the following equation is gained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The initial sorption rate,  $h$  [g/mg/min] at  $t \rightarrow 0$  is defined as

$$h = k^2 q_e^2 \quad (5)$$

Figure 7 and figure 8 demonstrate the kinetic model of plots of pseudo-first-order for  $\text{NH}_4^+$  sorption onto powdered modernite and granular modernite. Pseudo-first-order kinetic model was not valid due to the unfitness of the model for zeolite Y. The plots  $\log(q_e - q_t)$  against  $t$ , the values of adsorption rate constant ( $k_1$ ) for ammonium uptake on zeolites were determined. The values of adsorption rate constant  $k_1 = 0.0194/\text{min}$  for powdered modernite and

1.6121/min for granular modernite placed on Table 2 indicated that the rate of ammonium removal is faster on powdered modernite compared with granular modernite.

The plots of  $t/q_t$  (pseudo-second-order kinetic model) showed in figure 9 to 11. The  $q_e$ , equilibrium adsorption capacity achieved from the slope of the plot and the initial sorption rate  $h$  is derived from the intercept. From the incline  $q_e$  was known, the pseudo-second-order constant  $k_2$  can be determined from the value of the initial sorption rate. The  $q_{e,\text{exp}}$  and the  $q_{e,\text{calc}}$  values along with a linear correlation coefficient are shown in Table 2 for the pseudo-first-order model and pseudo-second-order model.

The values of  $q_{e,\text{exp}}$  and the  $q_{e,\text{calc}}$  from the pseudo-second-order kinetic model are very close to each other meanwhile the correlation coefficients,  $R^2$  are also closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetic model. Successively, for all adsorbents, the sorption process can be estimated more accurately by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model. The  $k_2$  and  $h$  values are listed in Table 2 calculated from fig. 9 to 11. It is observed

that both the  $k_2$  and  $h$  values are for ammonium adsorption through zeolite Y is the maximum followed by powdered mordenite and granular mordenite.

### Langmuir isotherm

For monolayer adsorption, the Langmuir isotherm equation is based on (constant heat of adsorption for all sites) on the active homogeneous sites within the adsorbent. It is written as

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$

(6)

The Langmuir linear form is as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

(7)

where,  $q_e$  = amount of adsorbate adsorbed at equilibrium per unit mass sorbent ( $\text{mg g}^{-1}$ );

$C_e$  = in solution ( $\text{mg L}^{-1}$ ) equilibrium concentration of adsorbate;

$q_m$  = the maximum monolayer adsorption capacity ( $\text{mg/g}$ );

$K_L$  = Langmuir adsorption constant ( $l/g$ ).

The plots of  $C_e/q_e$  against  $C_e$  for construction of the Langmuir isotherm shown in fig. 12. Calculated summary from the plots of the Langmuir constants was placed in Table 3. Monolayer adsorption capacity obtained the maximum from the Langmuir plots for zeolite Y, powdered mordenite and granular mordenite were 42.37, 15.13, 14.56  $\text{mg/g}$ , respectively.

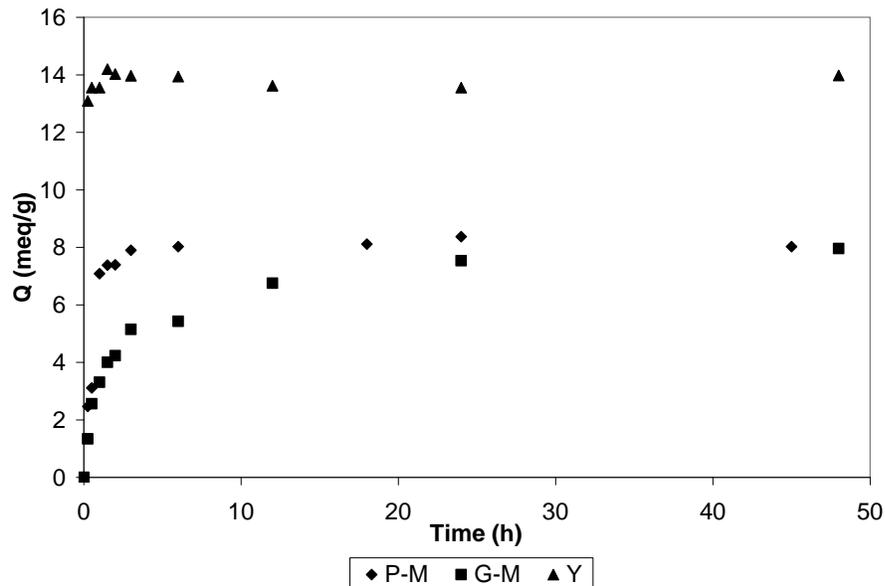


Figure 6. Kinetic profile of ammonium uptake by powdered modernite

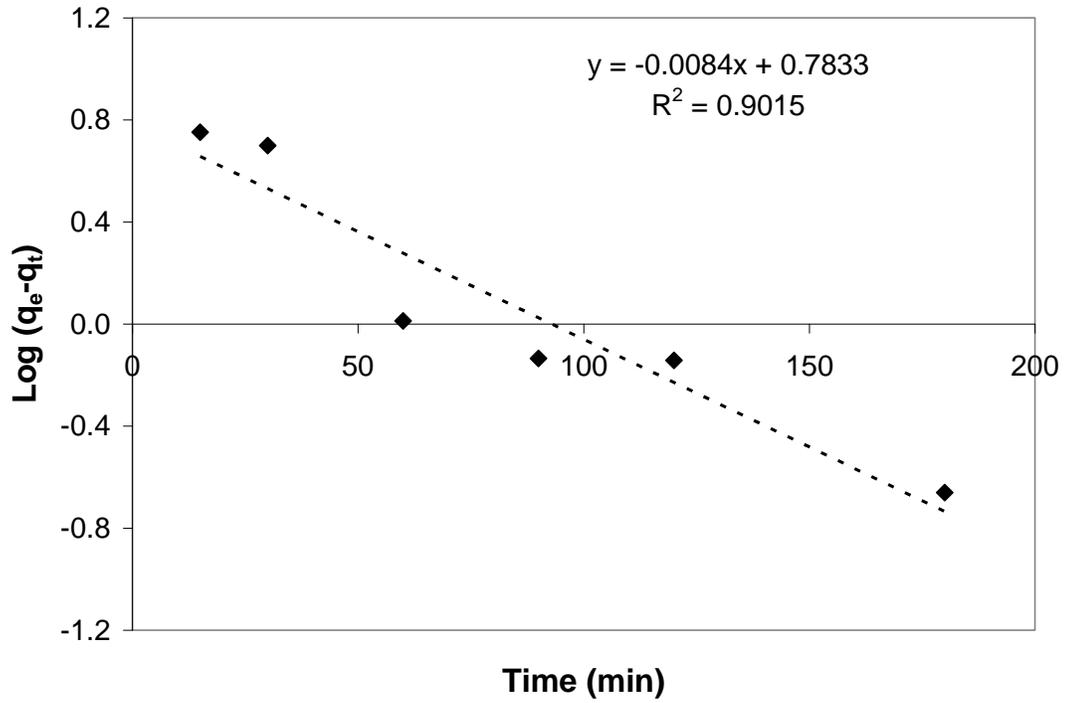


Figure 7. Plot of pseudo first-order kinetic model for NH<sub>4</sub><sup>+</sup> sorption into P-M

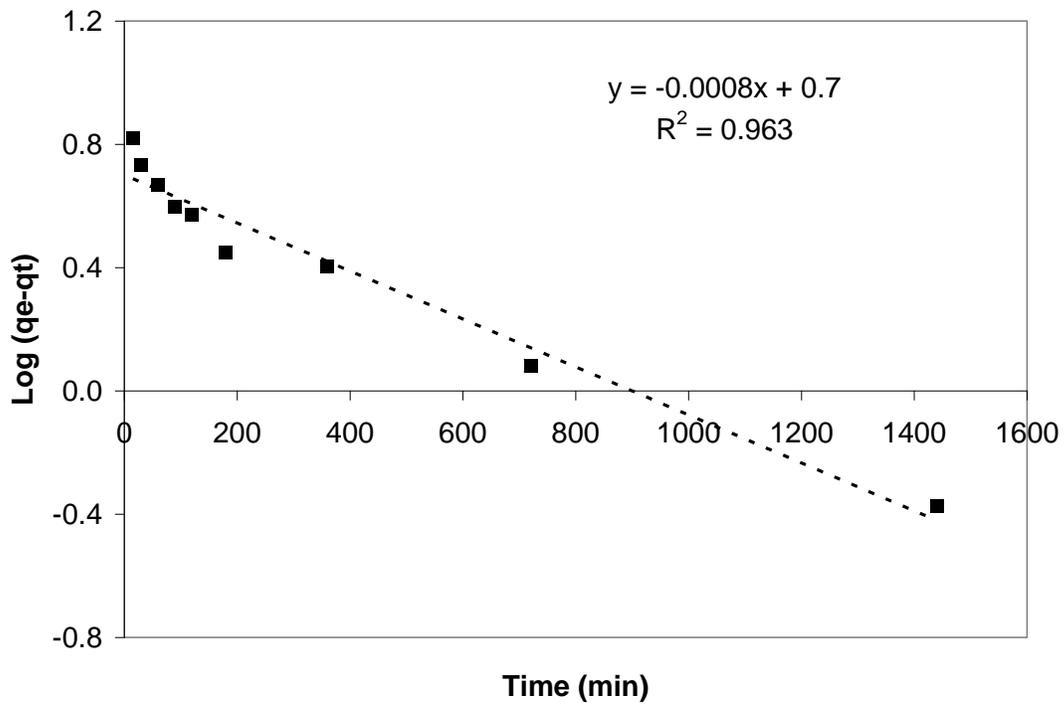


Figure 8; Plot of pseudo first-order kinetic model for NH<sub>4</sub><sup>+</sup> sorption into G-M

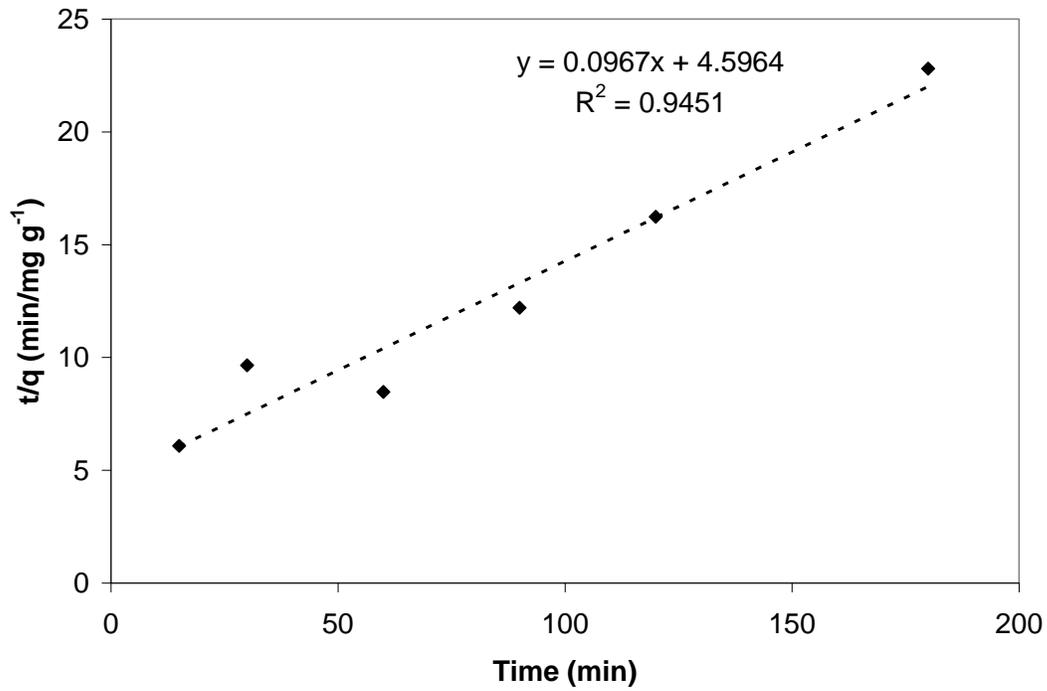


Figure 9. Pseudo second-order kinetic plot for the ammonium removal by P-M

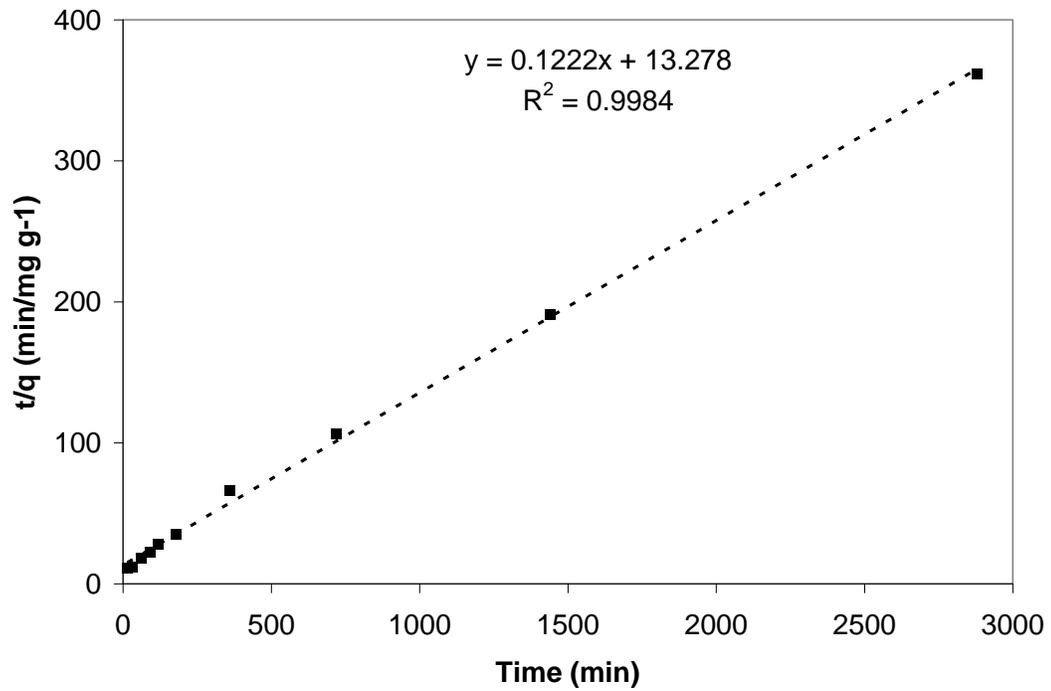


Figure 10. Pseudo second-order kinetic plot for the ammonium removal by G-M

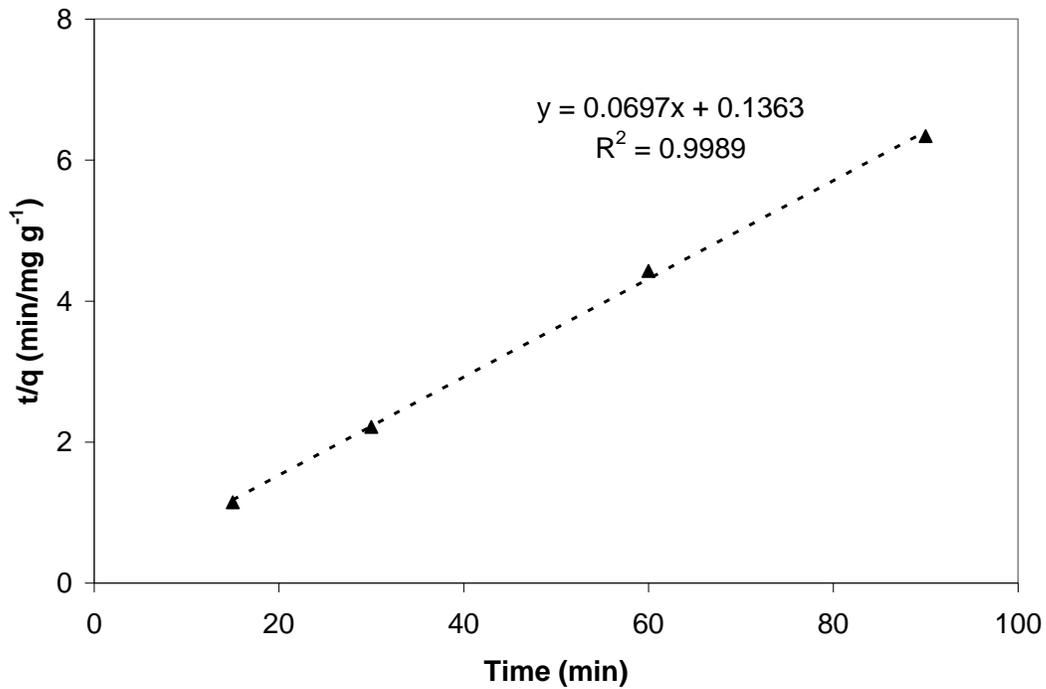


Figure 11. Pseudo second-order kinetic plot for the ammonium removal by Y

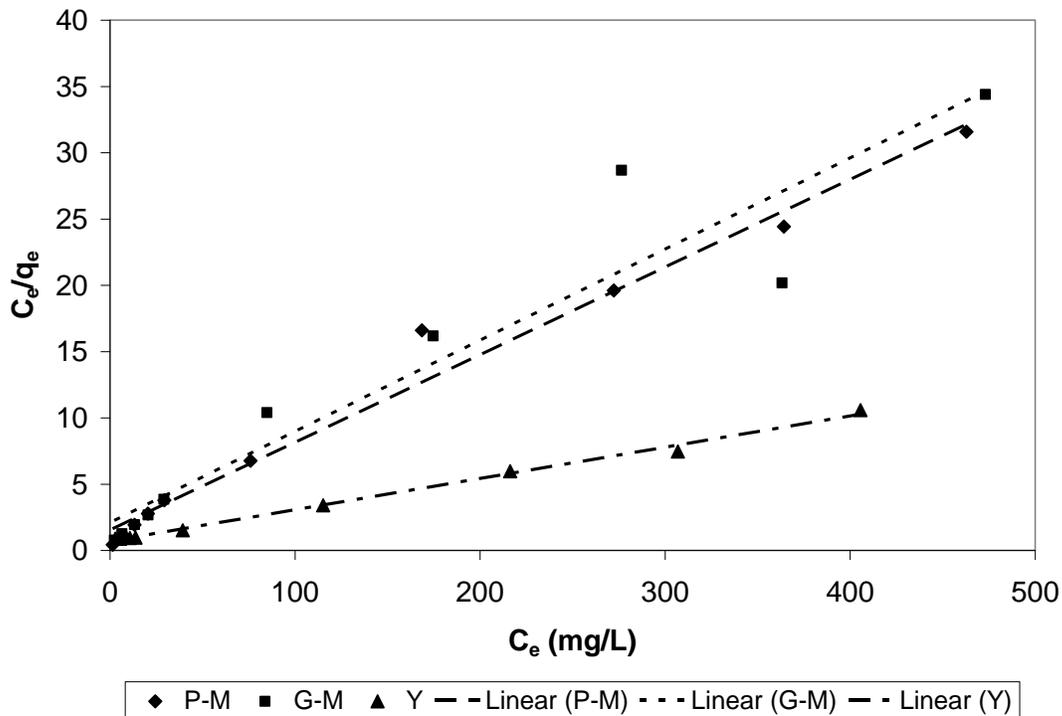


Figure 12; Langmuir isotherm plots for removal of NH<sub>4</sub><sup>+</sup> by various sorbents (pH = 7, temperature = room temperature, C<sub>o</sub> = 10 to 500 mg/L, zeolite dosage = 2.5 g/L)

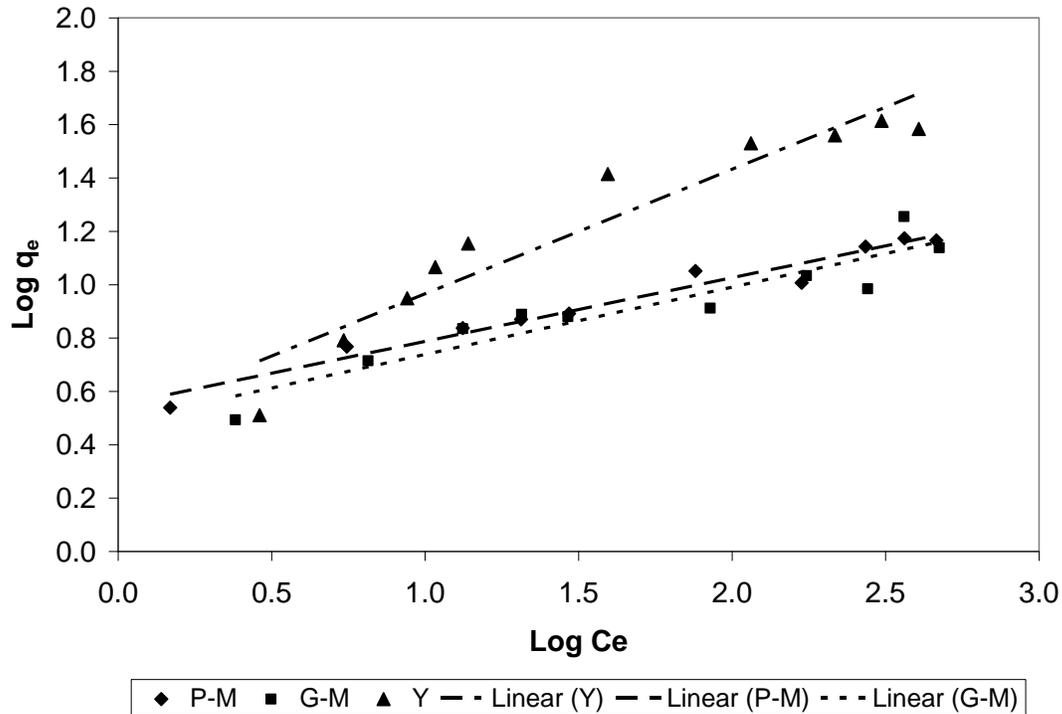


Figure 13. Freundlich isotherm plots for removal of  $\text{NH}_4^+$  by various sorbents (pH = 7, temperature = room temperature,  $C_o = 10$  to 500 mg/L, zeolite dosage = 2.5 g/L)

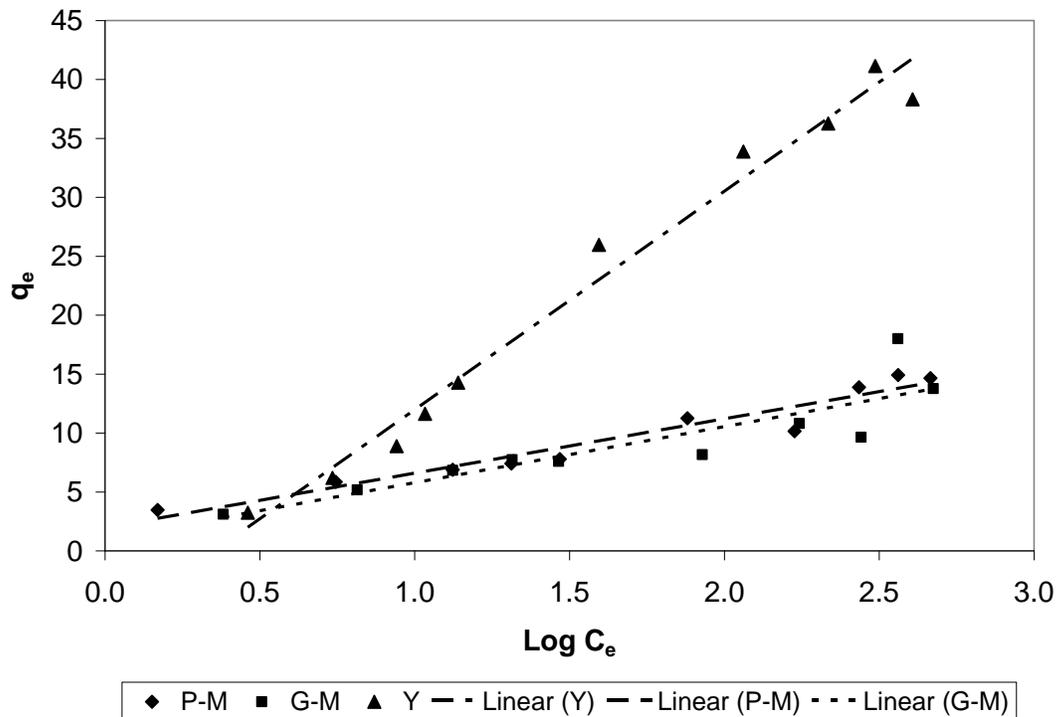


Figure 14; Temkin isotherm plots for removal of  $\text{NH}_4^+$  by various sorbents (pH = 7, temperature = room temperature,  $C_o = 10$  to 500 mg/L, zeolite dosage = 2.5 g/L)

These values are very close to the experimental values in Table 2.

The dimensionless separation factor or equilibrium constant,  $R_L$  is the essential characteristics of Langmuir isotherm and it has been described and defined as

$$R_L = \frac{1}{(1 + K_L C_o)}$$

(8) The nature of adsorption indicates by this and can be explained as

- $R_L = 1$  linear;
- $0 < R_L < 1$  favourable;
- $R_L > 1$  unfavourable
- $R_L = 0$  irreversible;

$R_L$  values of the present investigation are below 1.0 for the whole concentration range of ammonium. So; it confirmed that the adsorption of ammonium is very favorable. The value of  $R_L$  for zeolite Y is 0.2288, powdered mordenite is 0.2883 and granular mordenite is 0.2342 for the solution

$C_o$  is 100 mg/L.

**Freundlich isotherm**

Multilayer adsorption by assuming a various surface the Freundlich isotherm is drawn with an un-event and uniform giving out of the heat of adsorption over the surface. This isotherm estimated that the adsorption links are distributed exponentially with respect to the heat of adsorption and written by

$$q_e = K_F C_e^{1/n}$$

(9) the linear form can be

$$\log q_e = \ln K_F + \frac{1}{n} \log C_e$$

(10) where  $K_F$  (mg g<sup>-1</sup>) and  $1/n$  links the multilayer concentration of adsorption and adsorption capacity. In Figure 13, Freundlich isothermal plots are presented and the values are shown in Table 3. The values of  $1/n$  were obtained less than 1 for all the zeolites. So; it can be assigned again that adsorption is favorable (Kuang et al., 2018).

**Table 2. Kinetic parameters for the removal of ammonium by different adsorbents**

Adsorbent	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	$k_1$ (min <sup>-1</sup> )	R <sup>2</sup>
<b>Pseudo first-order</b>				
P-M	8.1114	6.0716	0.0194	0.9015
G-M	7.9583	5.0119	1.6121	0.9630
Adsorbent	$q_{e,calc}$ (mg/g)	$h$ (mg/g/min)	$k_2$ (g/mg/min)	R <sup>2</sup>
<b>Pseudo second-order</b>				
P-M	10.3413	0.21756	0.00331	0.9451
G-M	8.1833	0.07531	0.00119	0.9984
Y*	14.3472	7.33676	0.03642	0.9989

\*  $q_{e,exp}$  of Y is 14.1940 mg/g

**Table 3; Isotherm parameters for ammonium removal by zeolites**

Adsorbent	$q_{m,calc}$ ( $q_{m,exp}$ ), mg/g	$K_L$ (L/mg)	R <sup>2</sup>
<b>Langmuir constants</b>			
Y	43.2461 (41.1429)	0.0337	0.9963
P-M	14.986 (17.2286)	0.0431	0.9826
G-M	13.456 (13.7571)	0.0327	0.9113
Adsorbent	$K_F$ (mg/g)	1/n	R <sup>2</sup>
<b>Freundlich constants</b>			

<b>Y</b>	3.1521	0.4667	0.9087
<b>P-M</b>	3.5383	0.2385	0.9631
<b>G-M</b>	3.0620	0.2522	0.8733
<b>Adsorbent</b>	$K_T$ (L/mg)	$B_1$	$R^2$
<b>Temkin constants</b>			
<b>Y</b>	0.4430	18.5260	0.9814
<b>P-M</b>	2.6856	4.6100	0.9391
<b>G-M</b>	3.9292	3.6799	0.9317

### Temkin isotherm

The effects of the heat of adsorption of all the molecules in the layer decline linearly with coverage due to adsorbent-adsorbate interfaces Temkin isotherm, which can be considered. A uniform distribution of the binding energies up to maximum binding energy the adsorption was characterized by Temkin isotherm. The Temkin isotherm equation is written as follows

$$q_e = \frac{RT}{b} \ln(K_T C_e)$$

(11)

Equation can linearize as

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

(12)

where  $K_T$  and  $B_1 = RT/b$  are the constants.  $K_T$  is the equilibrium binding constant (L/g) corresponding to the maximum binding energy and constant  $B_1$  is interrelated to the heat of adsorption. In Figure 14, the plot of  $q_e$  against  $\ln C_e$  allows to the determination of the isotherm constants  $B_1$  and  $K_T$ . In Table 3 the values of  $B_1$  and  $K_T$  as achieved were shown along with the correlation coefficient values.

A compares are shown in Table 3 for the predicted adsorption capacity and investigational adsorption capacity by the isotherms and the corresponding isotherm parameters, along with the deterioration coefficients, are listed on it. The better deterioration coefficients of the Langmuir model compared to the Freundlich model recommended that the adsorption process is in monolayer and adsorption has an equal activation energy of each molecule. The favourability of adsorption of  $\text{NH}_4^+$  onto zeolite Y and mordenite from Freundlich values of  $1/n$  between 0.2385 and 0.4667 ( $0 < 1/n < 1$ ) and Langmuir values of  $RL$  less than 1.0 were confirmed. The Temkin isotherm given high regression coefficient may occur due to the linear dependence of heat of

adsorption at low or medium coverage. Due to the repulsion between adsorbate species or to fundamental surface heterogeneity the linearity was observed.

The powdered mordenite adsorption capacity was nearly three times lower than the adsorption capacity of zeolite Y. The equilibrium findings revealed that powdered mordenite much lower uptake concentration compared with the zeolite Y and zeolite Y exhibited much higher uptake concentration at equilibrium. Particle size mordenite than powdered mordenite exhibited a much slower rate of ammonium uptake in the kinetic studies. The particle size mordenite used in the experiment did not have any significant effect on the amount of ammonium adsorbed in the zeolite at equilibrium as specified in values of total CEC and batch equilibrium studies (Wang et al., 2019). This is effective sense matching to the external surface of the particle accounts for only about 1 % of the total surface area of the zeolite according to Flanigan and Mumpton (Li et al., 2019).

### CONCLUSION

Synthesized zeolite Y, powdered mordenite and granular mordenite total cation exchange capacity (CEC) were calculated value as 3.1519 meq/g (equivalent to 56.85 mg  $\text{NH}_4^+$ /g), 1.4630 meq/g (equivalent to 26.39 mg  $\text{NH}_4^+$ /g) and 1.3423 meq/g (equivalent to 24.21 mg  $\text{NH}_4^+$ /g), respectively. The maximum monolayer adsorption capacity achieved from the Langmuir plots for zeolite Y, powdered mordenite and granular mordenite were 42.37, 15.13, 14.56 mg  $\text{NH}_4^+$ /g, respectively. Zeolite Y offerings the higher adsorption capacity which was three times larger than powdered mordenite. The values are closed to the investigational data and are lower than total CEC values. Kinetic findings wide-open that prompt ammonium removal process for zeolite in powdered form than granular form. A pseudo-second-order model can best represent adsorption kinetics with initial sorption rate being

highest for adsorption on zeolite Y. For equilibrium studies, the Langmuir model provided the best correlation proposed that the adsorption process is monolayer and adsorption of each molecule has equal activation energy. The overall study shows that zeolite Y and mordenite can be used to remove ammonium from water due to its prompt adsorption rate and extreme adsorption capacity.

### CONFLICT OF INTEREST

The authors declared that present study was performed in absence of any conflict of interest.

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### AUTHOR CONTRIBUTIONS

MMR, FM and F were performed the experiments, analysed the data, and prepared the manuscript, MAT, KY, MMR designed, supervised and edited the manuscript WBWN, AMY and MNIS critical data analysed and financial supported. AMY and MMR designed experiments and reviewed the manuscript. All authors read and approved the final version.

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