



## Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powdered and granulated forms of mordenite

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### ABSTRACT

The removal of ammonium from aqueous solutions using zeolite NaY prepared from a local agricultural waste, rice husk ash waste was investigated and a naturally occurring zeolite mordenite in powdered and granulated forms was used as comparison. Zeolite NaY and mordenite were well characterized by powder X-ray diffraction (XRD), energy dispersive X-ray (EDX) analysis and the total cation exchange capacity (CEC). CEC of the zeolites were measured as 3.15, 1.46 and 1.34 meq g<sup>-1</sup> for zeolite Y, powdered mordenite and granular mordenite, respectively. Adsorption kinetics and equilibrium data for the removal of NH<sub>4</sub><sup>+</sup> ions were examined by fitting the experimental data to various models. Kinetic studies showed that the adsorption followed a pseudo-second-order reaction. The equilibrium pattern fits well with the Langmuir isotherm compared to the other isotherms. The monolayer adsorption capacity for zeolite Y (42.37 mg/g) was found to be higher than that powdered mordenite (15.13 mg/g) and granular mordenite (14.56 mg/g). Thus, it can be concluded that the low cost and economical rice husk ash-synthesized zeolite NaY could be a better sorbent for ammonium removal due to its rapid adsorption rate and higher adsorption capacity compared to natural mordenite.

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### 1. Introduction

Ammonium discharged together with municipal or industrial effluents is responsible for harmful effects such as eutrophication, toxicity to aquatic life and increased corrosion rate of soil materials. The toxicity of ammonium to aquatic life can cause convulsion, coma and death [1]. Traditionally, biological systems have provided an economical solution with the retrofitting of biological ammonium removal facilities to existing organic treatment systems [2]. While often effective, these systems require large land areas, due to the slowness of biological conversion of nutrients, thus imposing high capital costs. Physico-chemical wastewater treatment offers a high rate alternative to the conventional biological processes, requiring relatively small land areas for equivalent influent flows. Among the processes proposed to reduce ammonium ion concentrations in wastewater is ion exchange or adsorption using zeolite material which has been recognized as an efficient and cost competitive in both laboratory scale and commercial plants [3].

Increased awareness and understanding of the deleterious effects of ammonium, released from wastewater treatment facilities into natural water systems has resulted in stringent laws restricting ammonium discharge. The Interim National Water Quality Standard for Malaysia has set a guide level of 0.1 mg L<sup>-1</sup> for ammoniacal nitrogen for Class I water, 0.3 mg L<sup>-1</sup> of ammoniacal nitrogen for Class II water while 0.9 mg L<sup>-1</sup> of ammoniacal nitrogen for Class III water [4].

Natural zeolites such as clinoptilolite, mordenite, phillipsite from different deposits have been widely reported as an ion exchanger in wastewater ammonium removal installations owing to their ammonium ion selectivity and low cost [5,6]. Because of their low cost and economical, natural clays and zeolites especially from around Turkey such as bentonite (Resadiye) [7], sepiolite (Tacir) [8], natural zeolite (Yildizeli) [9] and natural clinoptilolite [10–12] were reported as suitable adsorbents for ammonium ion. However, the ammonium removal capacity of a zeolite varies with the source of the zeolite, the location within a particular deposit and the capacity measurement technique employed [13]. Although the use of zeolites as adsorbent for ammonium removal from water was investigated by many researchers over the last decades, still research on the removal of ammonium by zeolitic materials are ongoing. In a recent paper, Juan and his team [14] used powdered and granulated forms of zeolites NaP1, K-F and K-chabazite/phillipsite

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synthesized from coal fly ash to uptake ammonium in wastewater from a sewage treatment plant (STP). In other recent papers dealing with the removal of ammonium in water, Liang and Ni [15] found that the modification of natural zeolite clinoptilolite can improve and enhance the uptake of ammonium ion. The modification process includes pretreatment by grinding and sieving, modifying by sodium salt and finally, calcination. These modifications can improve the pore size and surface area of clinoptilolite which eventually increased the ammonium ion uptake by clinoptilolite. Therefore, it is important to improve the ammonium uptake in water using an economical approach such as utilizing synthetic zeolite synthesized from waste products and naturally occurring zeolite.

This paper aims to realize the value of low cost synthetic zeolite Y synthesized from rice husk ash, a local agricultural waste, as an efficient alternative sorbents for the removal of ammonium. A comparison was made with naturally occurring mordenite in powdered and granulated forms. An understanding of the kinetic and equilibrium behavior of these materials provides insights into its expected capacity as an adsorbent. Several adsorption isotherms such as Langmuir, Freundlich and Temkin models were employed to define the isotherm behavior. Comparison on the efficiencies of the sorbents investigated is also discussed in relation to ammonium removal.

## 2. Materials and method

### 2.1. Materials and chemicals

Zeolite Y in the sodium form was synthesized from rice husk ash as the source of silica via seeding and ageing techniques. The procedure for the synthesis of zeolite Y and the structure identification are described elsewhere [16]. Naturally occurring mordenite was obtained from a large deposit in Tasik Malaya, Indonesia. Stock solutions of the ammonium ions were prepared from analytical grade ammonium chloride,  $\text{NH}_4\text{Cl}$  (GCE).

### 2.2. Characterization techniques

The structure of the zeolite NaY and mordenite samples were examined by a powder X-ray diffraction using a Bruker AXS GmbH HR diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature provided the structural investigation of the sorbents with data collected in the range of  $5\text{--}50^\circ$  at a scan rate of  $0.05^\circ \text{ s}^{-1}$ . The elemental analysis of zeolites was performed by using energy dispersive X-ray (EDX) spectrum of the samples were recorded using a Zeiss Supra 35VP field-emission scanning electron microscope.

The total cation exchange capacity (CEC) of zeolite is the amount of all exchangeable cations and it is defined by the number of equivalents of fixed negative charges per amount of zeolite [17]. However, it should be noted that the total CEC does not correspond to the operating exchange capacity which is commonly lower in practice [17,18]. The total CEC measured by ammonium displacement from the sodium-saturated zeolite samples in this case was determined using a prescribed method [19]. Sodium-saturated zeolite was prepared by exhaustive exchange of the raw zeolite with pH-buffered sodium acetate (1.0N) solution. The resulting mixture was washed three times thoroughly with 2-propanol to remove excessive loosely bound sodium on the zeolite. The total CEC measurement was accomplished by mixing 1.0N ammonium acetate solution (3 folds) with the sodium-saturated zeolite. The two phases were separated by centrifugation and the washes mixed together prior to atomic absorption spectroscopy (AAS) analyses on a PerkinElmer, model AAnalyst 400. Total concentration of sodium in the solution constitutes the total CEC of the zeolite.

### 2.3. Ammonium removal study

#### 2.3.1. Kinetic studies

Kinetic studies were conducted at room temperature using 400 mL of ammonium solution (pH 7) and fixed amounts of adsorbents (1 g) in a 500 mL conical flask. The reaction mixture was stirred using a Teflon-coated magnetic bar driven by a magnetic stirrer. The two phases of samples taken at the designated times were separated by syringe filtration through a  $0.45 \mu\text{m}$  membrane filter or centrifugation. The initial and final ammonium concentrations in the supernatant were analyzed by the standard Nesslerization method using a Hach DR 4000 Spectrophotometer [20,21].

#### 2.3.2. Batch equilibrium studies

Equilibrium study on removal ammonium was carried out in batch system at room temperature with accurately known amount of 0.1 g of zeolite sample equilibrated with 40 mL of ammonium solution in a 50 mL polypropylene centrifuge tube. Shaking was applied by placing the sealed tubes in an orbital shaker with a constant shaking rate of 150 rpm. The shaking time for zeolite Y, powdered mordenite and granular mordenite were 2 h, 4 h, and 2 d, respectively which was proven through the kinetic studies, for the equilibrium of exchange to reach. At the end of the sorption experiments, centrifuge tubes were removed from the shaker and the solutions separated by centrifugation. The final ammonium concentrations remaining in the solutions were determined using a method described earlier. The adsorption equilibrium data were obtained by varying initial ammonium ion concentrations while other variables such as the mass of adsorbent, contact time, shaking rate and initial pH were kept constant.

### 2.4. Effect of pH on zeolite exchange performance

The effect of pH on adsorption of ammonium onto zeolite samples was investigated at room temperature by varying the initial pH of  $50 \text{ mg L}^{-1}$  of ammonium solution (40 mL) for a fixed zeolite dosage of 0.1 g. The pH of the solutions was adjusted to within 4–10 using HCl or NaOH. The clear supernatant solutions were extracted after centrifuge at the end of the equilibrium time. The initial and final ammonium concentrations remaining in solution were analyzed.

## 3. Result and discussion

### 3.1. Characteristics of zeolite samples

The identification of zeolite NaY from rice husk ash and mineralogical phase of natural mordenite in powdered and granulated forms was confirmed by matching the powder XRD patterns of the samples with the diffractograms of single-phase patterns from Powder Data File (PDF), compiled by the International Centre for Diffraction Data (ICDD) (Figs. 1 and 2).

The zeolite Y obtained is considered pure and highly crystalline as proven by the highly intense and narrow peaks without elevated baseline and extra peaks. The XRD peaks of the synthetic zeolite Y are well matched with the PDF 43-0168 (sodium aluminium silicate hydrate zeolite Y ( $\text{Na}$ )— $\text{Na}_2\text{Al}_2\text{Si}_4\cdot 5\text{O}_{13}\cdot x\text{H}_2\text{O}$ ) as shown in Fig. 1. Zeolites found in nature are rarely in their pure form but usually contain impurities such as other types of zeolite, other minerals or amorphous materials. In this case, quartz impurities found in mordenite are as indicated by the XRD pattern.

The elemental composition of zeolite samples calculated from EDX spectra was summarized in Table 1; each value represents an average of three spectra taken at different spots of the sample.

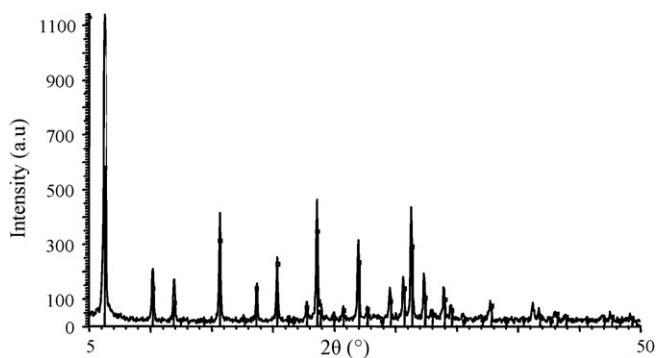


Fig. 1. X-ray diffraction pattern of synthesized zeolite NaY from rice husk ash. (Matched with sodium aluminum silicate hydrate zeolite Y pattern from PDF.)

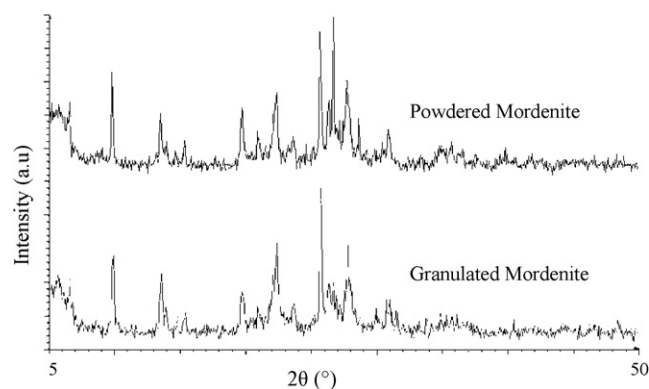


Fig. 2. X-ray diffractogram of powdered and granulated mordenite.

It should be noted that EDX analysis is a qualitative or semi-quantitative composition analysis; it is scanned from a tiny spot thus is not representative of a sample. Hence values given in Table 1 serve as a general reference on the chemical composition of zeolite, rather than as an ultimate composition means.

The total CEC of the synthesized zeolite Y (denoted as Y), powdered mordenite (denoted as P-M) and granular mordenite (denoted as G-M) from triplicate analysis were measured as 3.15, 1.46 and 1.34 meq g<sup>-1</sup>, respectively. Zeolite Y has the highest CEC value because Si to Al (Si/Al) ratio of zeolite Y (2.82) is lower than Si/Al ratio of P-M (6.24) and G-M (5.62) according to EDX analysis. The lower Si/Al ratio indicates the higher exchange sites since one Al can provide one exchange site on zeolite framework.

### 3.2. Kinetic studies

Prior to the commencement of batch adsorption equilibrium studies, it was necessary to determine the equilibrium contact time required for the ammonium adsorption. The kinetics of adsorption is important from the viewpoint of process efficiency and is required for selecting optimum operating conditions for the full-scale batch process [22,23]. Several kinetic models are available to

Table 1  
Chemical composition (wt%) of the zeolites from EDX analysis.

Element	Zeolite Y	Powdered mordenite	Granular mordenite
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

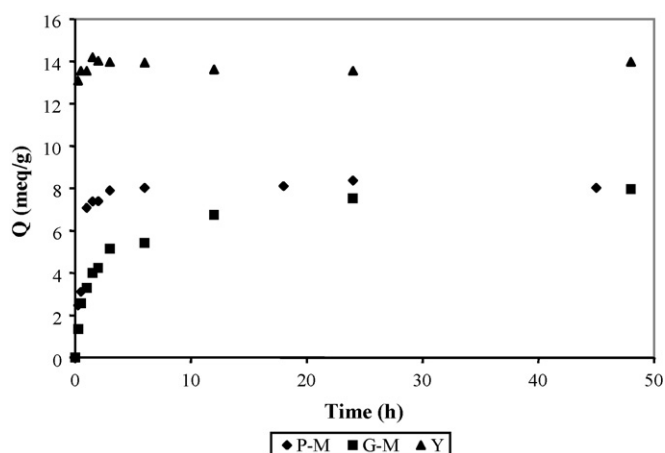


Fig. 3. Kinetic profile of ammonium uptake by powdered mordenite (P-M), granular mordenite (G-M) and zeolite Y (Y).

understand the behavior of the adsorbent with different system conforming to different models.

As illustrated in the plot of ammonium uptake capacity against time (Fig. 3), the initial uptake of ammonium occurred rather fast for zeolite Y and powdered mordenite and reached equilibrium in less than half and hour, and two hours respectively. Inversely, granular mordenite demonstrated slower ammonium uptake and reached equilibrium in about 24 h. The fast rate of ammonium removal at the initial stage of adsorption might be due to the fact that initially, all adsorbent sites were vacant and the solute concentration gradient was high [18]. Consequently the ammonium uptake rate by the zeolites decreased significantly due to a decrease in adsorption sites.

Njoroge and Mwamachi [24] carried out kinetic studies on ammonium uptake for the four particle size ranges of natural zeolite. They found that the equilibrium time increased with increasing sorbent particle size and ranged from 15 to 150 min. The variation in equilibrium time with the sorbent particle size can be explained in terms of the surface area and the time taken for the ammonium ions to diffuse to sorption sites within the sorbent particles [24]. The smaller the particle size, the shorter the routes taken by the sorbate particle to reach the effective targeted sorption sites of the zeolite.

A pseudo-first-order kinetic equation is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

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 initial condition,  $q_t = 0$  at  $t = 0$  leads to:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

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

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where  $k_2$  is the pseudo-second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>). Integrating Eq. (3) and noting that  $q_t = 0$  at  $t = 0$ , the following equation is obtained:

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

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

Adsorbent	$q_{e,exp}$ (mg g <sup>-1</sup> )	$q_{e,calc}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$
pseudo-first-order				
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 <sup>-1</sup> )	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
pseudo-second-order				
P-M	10.3413	0.21756	0.00331	0.9451
G-M	8.1833	0.07531	0.00119	0.9984
Y <sup>a</sup>	14.3472	7.33676	0.03642	0.9989

<sup>a</sup>  $q_{e,exp}$  of Y is 14.1940 mg/g.

The initial sorption rate,  $h$  (g mg<sup>-1</sup> min<sup>-1</sup>) at  $t \rightarrow 0$  is defined as

$$h = k_2 q_e^2 \tag{5}$$

The values of adsorption rate constant ( $k_1$ ) for ammonium uptake on zeolites were determined from the plots of  $\log(q_e - q_t)$  against  $t$ . The values ( $k_1 = 0.0194$  min<sup>-1</sup> for P-M and 1.6121 min<sup>-1</sup> for G-M) (Table 2) indicate that the rate of ammonium removal is faster on P-M compared to G-M.

The equilibrium adsorption capacity,  $q_e$  is obtained from the slope of the plot and the initial sorption rate  $h$  is obtained from the intercept. Since  $q_e$  is known from the slope, the pseudo-second-order constant  $k_2$  can be determined from the value of the initial sorption rate. The  $q_{e,exp}$  and the  $q_{e,calc}$  values along with linear correlation coefficient for the pseudo-first-order model and pseudo-second-order model are presented in Table 2.

The  $q_{e,exp}$  and the  $q_{e,calc}$  values 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. Consequently, the sorption process can be approximated more accurately by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model for all adsorbents. It is clearly seen that both  $k_2$  and  $h$  values for ammonium removal on zeolite Y are the highest followed by values from powdered mordenite and granular mordenite.

### 3.3. Batch equilibrium studies

The salient features of adsorption isotherms are necessary to optimize the design of an adsorption system for the adsorption of adsorbate. The dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Various models have been proposed and applied to explain the equilibrium characteristics of adsorption. However the most important factor is to have applicability over the entire range of process conditions. The most widely used isotherm models for solid-liquid adsorption are the Langmuir, Freundlich, Temkin, and Redlich-Peterson isotherms.

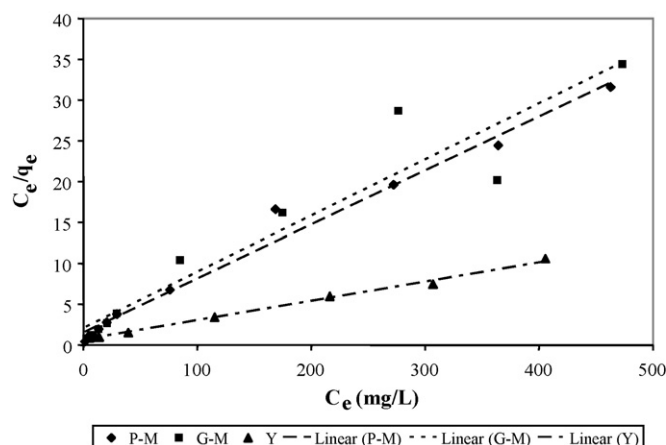
#### 3.3.1. Langmuir isotherm

The Langmuir isotherm is based on monolayer adsorption (constant heat of adsorption for all sites) on the active homogeneous sites within the adsorbent. It is given as

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

The linear form of the Langmuir is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{7}$$



**Fig. 4.** Langmuir isotherm plots for the removal of NH<sub>4</sub><sup>+</sup> by various sorbents.

where  $q_e$  = amount of adsorbate adsorbed at equilibrium per unit mass sorbent; (mg g<sup>-1</sup>);  $C_e$  = equilibrium concentration of adsorbate in solution (mg L<sup>-1</sup>);  $q_m$  = the maximum monolayer adsorption capacity (mg g<sup>-1</sup>);  $K_L$  = Langmuir adsorption constant (g<sup>-1</sup>).

Fig. 4 shows the plots of  $C_e/q_e$  against  $C_e$  for construction of the Langmuir isotherm. The Langmuir constants were calculated from the plots and summarized in Table 3. The maximum monolayer adsorption capacity obtained from the Langmuir plots for Y, P-M, and G-M were 42.37, 15.13, 14.56 mg g<sup>-1</sup>, respectively. These values are close to those obtained from the experimental data.

The essential characteristics of Langmuir isotherm have been described by the dimensionless separation factor or equilibrium constant,  $R_L$  which is defined as

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

This indicates the nature of adsorption as

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

The values of  $R_L$  in the present investigation have been found to be below 1.0 for the whole concentration range of ammonium used confirming that the adsorption of ammonium is very favourable.

**Table 3**  
Isotherm parameters for ammonium removal by different zeolites.

Isotherm	Adsorbent	$q_{m,calc}$ ( $q_{m,exp}$ ) (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R^2$
Langmuir	Y	42.37 (41.14)	0.034	0.996
	P-M	15.13 (17.23)	0.043	0.983
	G-M	14.56 (13.76)	0.033	0.911
	Natural Zeolite [9]	9.64		
	Natural Turkish clinoptilolite [10]	8.121 (25 °C)		
	Clinoptilolite [15]	15.44 (treated)		
Freundlich	Sardinian natural zeolites [29]	8.15 (raw) 12.26 (Na-zeolite)		
	Chinese clinoptilolite [18]	1.364		
Isotherm	Adsorbent	$K_F$ (mg g <sup>-1</sup> )	1/n	$R^2$
Freundlich	Y	3.15	0.467	0.909
	P-M	3.54	0.239	0.963
	G-M	3.06	0.252	0.873
	Natural zeolite [9]	0.93		
	Natural Turkish clinoptilolite [10]	0.517 (25 °C)		
Isotherm	Adsorbent	$K_T$ (L mg <sup>-1</sup> )	$B_1$	$R^2$
Temkin	Y	0.4430	18.5260	0.9814
	P-M	2.6856	4.6100	0.9391
	G-M	3.9292	3.6799	0.9317



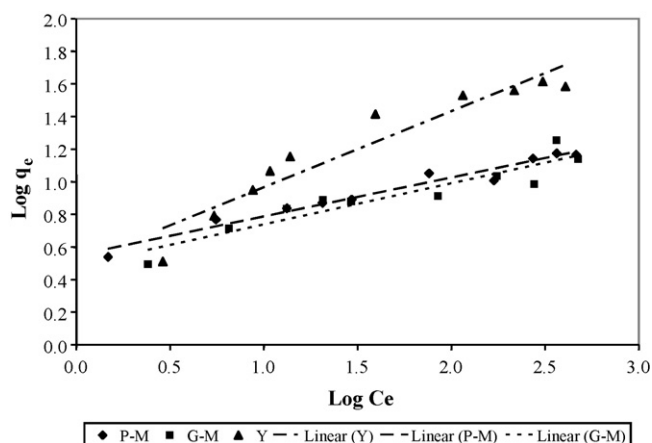


Fig. 5. Freundlich isotherm plots for removal of  $\text{NH}_4^+$  by various sorbents.

For instance, the values of  $R_L$  for Y, P-M and G-M are 0.2288, 0.1883, and 0.2342, respectively for  $C_0 = 100 \text{ mg L}^{-1}$ .

### 3.3.2. Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface (multilayer adsorption) with a non-uniform distribution of heat of adsorption over the surface. This isotherm assumes that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by

$$q_e = K_F C_e^{1/n} \quad (9)$$

and the linear form is given as:

$$\log q_e = \ln K_F + \frac{1}{n} \log C_e \quad (10)$$

where  $K_F$  ( $\text{mg g}^{-1}$ ) and  $1/n$  relates the multilayer adsorption capacity and intensity of adsorption,  $1/n$  also known as the heterogeneity factor. Freundlich isothermal plots are presented in Fig. 5 while the coefficients are shown in Table 3. The values of  $1/n$  were also found to be less than 1 for all the zeolites, signifying again that adsorption is favourable.

### 3.3.3. Temkin isotherm

Temkin isotherm, which considers the effects of the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of the binding energies up to maximum binding energy. The Temkin isotherm equation is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (11)$$

and linearized as

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (12)$$

where  $B_1 = RT/b$  and  $K_T$  are the constants.  $K_T$  is the equilibrium binding constant ( $\text{L g}^{-1}$ ) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption. A plot of  $q_e$  against  $\ln C_e$  enables the determination of the isotherm constants  $K_T$  and  $B_1$  (Fig. 6). Values of  $K_T$  and  $B_1$  as obtained are shown in Table 3 along with the correlation coefficient value.

The experimental adsorption capacity and the predicted adsorption capacity by the isotherms and the corresponding isotherm parameters, along with the regression coefficients are listed and compared in Table 3. Superior regression coefficients for the Langmuir model compared to the Freundlich model suggested that the adsorption process is monolayer. Langmuir values of  $R_L$  below

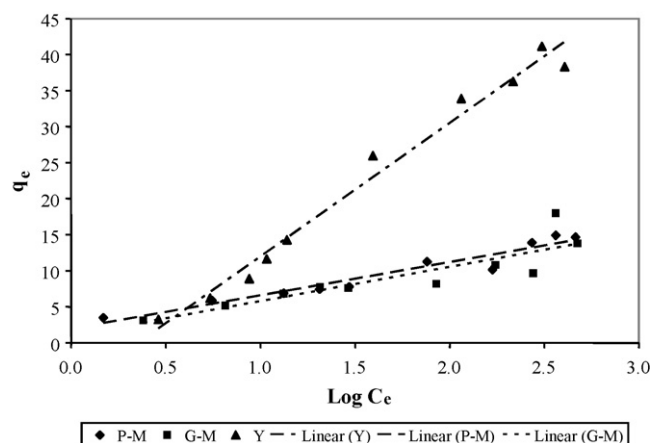


Fig. 6. Temkin isotherm plots for removal of  $\text{NH}_4^+$  by various sorbents.

1.0 and Freundlich values of  $1/n$  between 0.2385 and 0.4667 ( $0 < 1/n < 1$ ) revealed the favourability of adsorption of  $\text{NH}_4^+$  onto zeolite Y and mordenite. The high regression coefficient of the Temkin isotherm may be due to the linear dependence of heat of adsorption at low or medium coverage. The linearity may be due to the repulsion between adsorbate species or to intrinsic surface heterogeneity.

The equilibrium studies revealed that zeolite Y exhibited much higher overall uptake concentration of ammonium at equilibrium compared with mordenite. The adsorption capacity of zeolite Y is nearly three times higher than that of the mordenite. As far as mordenite particle size is concerned, although powdered mordenite exhibited much faster rate of ammonium uptake as indicated in the kinetic studies (Section 3.2), the particle size used did not have any effect on the amount of ammonium adsorbed in the zeolite at equilibrium as indicated by the total CEC values (Section 3.1) and batch equilibrium studies [25]. This is logical according to Flanigen and Mumpton [26] since the external surface of the particle accounts for only about 1% of the total surface area of the zeolite.

### 3.4. Effect of pH on zeolite exchange performance

pH has significant effect on ammonium removal by zeolite since it can influence both the characters of the exchanging ions and the zeolite itself. According to the equilibrium reaction of Bronsted–Lowry acid base reaction, given by Eq. (13) the ammonium removal should be greater at lower pH values and smaller at higher pH values, if the cation-exchange mechanism occurs only by means of the ammonium ions [27].



However, the lower capacities obtained at lower pH may be due to the ammonium ions having to compete with hydrogen ions among the exchange sites. On the other hand, at high pH, ammonium ions are transformed to aqueous ammonia. The effect of solution pH on the sorption process of ammonium is presented in Fig. 7.

Fig. 7 shows the removal efficiency of ammonium ions at equilibrium from a solution containing  $50 \text{ mg L}^{-1} \text{ NH}_4^+$  while varying the pH values of between 4 and 10. The higher removal efficiency is achieved when operating at pH between 4 and 6 for the zeolites which is in agreement with the theory mentioned in the above section and literature findings. Koon and Kaufman [3] and Du et al. [18] investigated the impact of pH on the ammonium exchange in clinoptilolite at a pH range of between 4 and 10 and observed that the optimum operating pH was 6; Sarioglu [28] considered that the optimum pH was 4 for ammonium removal from wastewater by Dogantepe zeolite (mainly composed of clinoptilolite and

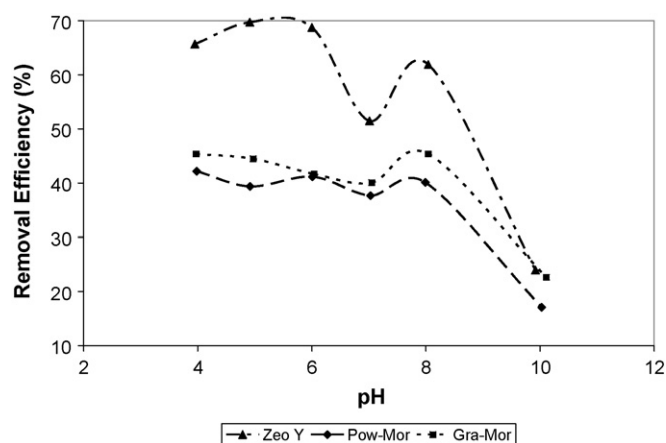


Fig. 7. Effect of pH on the ammonium sorption process.

mordenite) in column experiments (breakthrough analysis). However, other research groups reported different optimum pH values for ammonium removal by zeolite such as Njoroge and Mwamachi [24], who showed that the ammonium removal increased with increasing pH from 4 to 10. The variation in optimum pH reported in these studies may be due to the different species and zeolite deposits used with different experimental conditions and procedures which require further investigation.

#### 4. Conclusions

The total CEC of the synthesized zeolite Y, powdered mordenite (P-M) and granular mordenite (G-M) were measured as  $3.1519 \text{ meq g}^{-1}$  (equivalent to  $56.85 \text{ mg NH}_4^+ \text{ g}^{-1}$ ),  $1.4630 \text{ meq g}^{-1}$  (equivalent to  $26.39 \text{ mg NH}_4^+ \text{ g}^{-1}$ ) and  $1.3423 \text{ meq g}^{-1}$  (equivalent to  $24.21 \text{ mg NH}_4^+ \text{ g}^{-1}$ ), respectively. The maximum monolayer adsorption capacity obtained from the Langmuir plots for Y, P-M, and G-M were  $42.37$ ,  $15.13$ ,  $14.56 \text{ mg NH}_4^+ \text{ g}^{-1}$ , respectively. Zeolite Y presents the superior adsorption capacity which is 3 times greater than mordenite. The values are closed to the experimental data and are lower than total CEC values. Kinetic studies revealed that rapid ammonium removal process for zeolite in powdered form. Adsorption kinetics can be best represented by a pseudo-second-order model with initial sorption rate being highest for adsorption on zeolite Y. The Langmuir model provided the best correlation proposing that the adsorption process is monolayer and adsorption of each molecule has equal activation energy. To sum up, zeolite Y synthesized from rice husk ash can be utilized as an alternative sorbent to remove ammonium from water due to their rapid adsorption rate and high adsorption capacities compared to naturally occurring mordenite and with their production cost low and economical, it is considered as a suitable candidate to replace other more expensive adsorbents available in the market.

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