ELSEVIER

Ammonium and potassium removal for anaerobically digested wastewater using natural clinoptilolite followed by membrane pretreatment

Xuejun Guo [a,b,*], Le(Larry) Zeng [a], Xiaomei Li [a], Hung-Suck Park [c]

[a] *Environmental Technologies, Alberta Research Council Inc. Vegreville, Alberta T9C 1T4, Canada*
[b] *College of Environmental Science and Engineering, Nankai University, Tianjin, 300071, China*
[c] *Department of Civil and Environmental Engineering. University of Ulsan, Ulsan 680 749, Republic of Korea*

Abstract

On the basis of the wastewater characteristic of anaerobically digested wastewater, this work studied the individual and simultaneous adsorption of ammonium and potassium ions by the natural clinoptilolite. *Langmuir*, *Freundlich*, *Langmuir–Freundlich*, and *Toth* model were employed to fit the experimental isotherm data and the fitting performances of different models were compared. Both the individual and simultaneous adsorption kinetics of ammonium and potassium were studied at various pHs and temperatures. The individual adsorption of ammonium was very fast and potassium uptake was even faster than that of ammonium. The adsorption approached equilibrium within 1 h in most cases. Five models, including pseudo-first-order, pseudo-second-order, *Vermeulen*'s model, squared driving force model and *Elovich* equation were used to fit the individual and simultaneous adsorption kinetics of ammonium and potassium. The validities of the fittings for the ammonium and potassium adsorption kinetics were also evaluated.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Clinoptilolite; Anaerobically digested wastewater; Ammonium; Potassium

1. Introduction

Anaerobic digestion of agricultural and municipal wastes has been increasingly applied for biogas production with the demand for renewal energy. After anaerobic digestion, significant amounts of nitrogen, phosphorus and other plant nutrients always remain in the digested effluents, which are valuable resources for plant growth but also pose potential risk of contamination to water bodies if improperly managed. Therefore, effective removal and recovery of nutrients from the digested effluents become necessary for pollution control and environmental sustainability [1,2]. One promising technology for treating anaerobically-digested effluents is membrane separation. However, after the membrane treatment of digested animal manure, a higher level of ammonium along with several other ions still remained in the effluent. The level of this residual ammonium may reach 250 mg l^{-1} of NH$_4^+$−N and coexist with about

200 mg l^{-1} of potassium, and other relatively lower concentration of cations such as sodium and calcium. The residual ammonia may lead to eutrophication, dissolved oxygen depletion and fish toxicity in receiving water if it is directly discharged. The removal and recovery of the residual ammonia will have both significant environmental and economic benefits. It is necessary to employ an ion exchange system to clean the residual ammonia and then the concentrated ammonia from the regeneration solution can be successfully recovered by the steam stripping [3,4].

Natural zeolite clinoptilolite has been broadly investigated as ion exchanger for this purpose due to its high ammonium-ion selectivity [5–9]. The utilization of this unique property for the removal of ammonium from wastewater has been studied by using zeolite from various origins or different monocationic forms [10–14]. Many studies have been performed to determine the optimum operating conditions, as well as its potential for continuous wastewater treatment [5,11,13,14].

In most municipal or agricultural wastewaters, the presence of other ionic or non-ionic chemical compositions may exert significant influence upon the ion exchange uptake of ammonium. Jorgensen and Weatherley [15] described the

effect of organic acids and proteins on ammonium removal from the simulated municipal wastewater by a New Zealand clinoptilolite. Co-existed cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} are typically presented with NH_4^+, the presence of these competing cations could affect NH_4^+ adsorption on clinoptilolite [5,7,11,16–19]. Their selectivity of ion-exchange on clinoptilolite was determined by Ames [20] in an order of $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$. Although different ammonium exchange capacities under the influence of those competing cations have been measured by the above named researchers, so far little information is available for the investigations of uptake and elution behaviors of K^+ on natural zeolite in batch tests and column runs, particularly from anaerobically digested manure with high concentrations of NH_4^+ and K^+.

Numerous publications in the literatures on adsorption isotherms and kinetics for ammonium by natural zeolite are available [15,18,21–25]. Adsorption isotherm data were usually determined and modeled by *Langmuir* and *Freundlich* equations in previous papers. The results of adsorption kinetics of ammonium on zeolite were fitted to different adsorption process rate equations for the design purposes too. The relationship between ammonium adsorption and contact time was dependent on several factors, such as pH, temperature, initial concentration and composition of adsorbate, solid liquid ratio, especially the structure properties of the tested zeolites. The adsorption time required to achieve the equilibrium was reported differently by previous literatures because of various experimental condition and different zeolite sources. Wang et al. [25] reported that the time to adsorption equilibrium was 2.5 h in leachate solution, while another article by Liu and Lo [22] reported less than 75% of the equilibrium value was observed even after 6 h contact with the composting leachate. Numerous publications in literatures on adsorption kinetics of ammonium uptake on zeolite are available [21–25]. A few models were used to model the adsorption kinetics [12,22,24,26–28]. However, the comprehensive comparison and screening of those models for both ammonium and potassium adsorption on the zeolite were not documented yet.

On the basis of certain wastewater background (containing relatively high concentration of ammonium and potassium) of anaerobically digested cattle manure effluent, the aim of this study was to investigate the individual and simultaneous uptake isotherm and kinetics of ammonium and potassium by clinoptilolite. Moreover, the uptakes of ammonium and potassium on zeolite, including at different pH and temperatures, were fitted to four isotherm models and five kinetics equations. The uptake capacities and ion-exchange kinetics were estimated based on the optimum models. This work will provide a further understanding of ammonium removal by clinoptilolite from wastewater containing relatively high concentration of ammonium and potassium such as anaerobically digested wastewater.

2. Materials and experimental methods

2.1. Zeolite and feed water

The natural zeolite used in experiments was sourced from Bear River Zeolite Company, Idaho, USA. It has an approx-
imately 85% clinoptilolite content, with a general formula of $(Na, K, Ca)_{2–3}Al_3(Al, Si)_2Si_{13}O \cdot 12H_2O$. The balance is primarily opaline or non-crystalline silica. Original zeolite contains approximately 3.5% potassium, 1.6% calcium, and less than 0.5% sodium. Its chemical composition is listed as follows: SiO_2, 67.4%; Al_2O_3, 10.6%; Fe_2O_3, 1.7%; MgO, 0.45%; CaO, 2.23%; Na_2O, 0.59%; K_2O, 4.19%; TiO_2, 0.27%; Loss of ignition, 11.4%. Its cation exchange capacity (CEC) is about 160 to 180 meq/100 grams. Before it was used in ion-exchange experiments, the raw zeolite in a grain size of 0.25–2.36 mm was preconditioned with a $20\,g\,l^{-1}$ NaCl solution, washed with deionized water, and subsequently dried at 105 °C. Hence the actual zeolite used in the experiments was the Na-form clinoptilolite.

The effluent was produced from membrane treatment of anaerobically digested cattle manure effluents. The original wastewater characteristics of the anaerobically digested cattle manure effluents are exemplified as follows: total solids, $26.3\,g\,l^{-1}$; suspended solids, $21.2\,g\,l^{-1}$; alkalinity (CaCO₃), $3950\,mg\,l^{-1}$; pH 8.0–8.3; Na^+, $570\,mg\,l^{-1}$; NH_4^+, $1024\,mg\,l^{-1}$; K^+, $1536\,mg\,l^{-1}$; Ca^{2+}, $85\,mg\,l^{-1}$; Mg^{2+}, $76\,mg\,l^{-1}$; Cl^-, $1004\,mg\,l^{-1}$; SO_4^{2}, $10\,mg\,l^{-1}$; PO_4^{3-}, $27\,mg\,l^{-1}$. After the integrated process of ultrafiltration and reverse osmosis, the effluent still contained approximately $250\,mg\,l^{-1}$ of NH_4^+–N, $200\,mg\,l^{-1}$ of K^+, $50\,mg\,l^{-1}$ of Na^+ and less than $1\,mg\,l^{-1}$ of Mg^{2+} and Ca^{2+} with pH 9.1 and a turbidity <1 ntu. For batch isothermal and kinetics experiments, NH_4^+ or K^+ solutions were separately prepared by dissolving NH_4Cl powder (BDH, analytical reagent, 99.5% min) or KCl (BDH, analytical reagent, 99.5% min) in deionized (DI) water. The NH_4^+ and K^+ concentrations of liquid samples were measured by an ion chromatograph (Dionex ICS-1000).

2.2. Adsorption isotherm studies

Adsorption isotherm tests for NH_4^+ and K^+ were made in batch isothermal experiments with NH_4^+ or K^+ solution separately. In a series of 250-ml Erlenmeyer flasks, 50 ml of ammonium (0–30 mmol l^{-1}) or potassium (0–40 mmol l^{-1}) solutions and 1.00 g zeolite were added. The flasks were capped and placed on an orbital shaker at 150 rpm and room temperature (19–21 °C) for 18 h. The solution pH was initially adjusted to determined pH and readjusted to the same value several times till the supernatant pH kept constant at desired pH during the experiment with diluted HCl or NaOH solutions. At the end of the adsorption process, the suspension in each flask was filtered through a 0.45-μm membrane filter and the filtrate was analyzed for NH_4^+ or K^+. The quantity of NH_4^+ or K^+ uptake by zeolite was calculated from the decrease of its concentration in solution. The duplicate experiments demonstrated the high repeatability of this batch procedure and the experimental error for most cases could be controlled within 5%.

2.3. Adsorption kinetics tests

In a 1000-ml two-neck distilling flask, 20 g of zeolite and 500 ml of solution were added. The initial solution contained

24 mmol l^{-1} of NH$_4^+$(Cl$^-$) and K$^+$(Cl$^-$), respectively, or co-existed with 12 mmol l^{-1} of NH$_4^+$(Cl$^-$) and K$^+$(Cl$^-$). The flask was placed in a water bath and mechanically stirred at 200 rpm. The pH of the solution was adjusted to a determined constant value with few drops of around 1 M HCl or NaOH solutions and the temperature was maintained at determined degree by thermo-controller. One mililitre of supernatant was withdrawn with a 1 ml pipette at various time intervals between 0 and 2 h. The solid particles of zeolite would not be withdrawn because the inlet diameter of the pipette is relatively smaller than the size of zeolite. The sampled solution was simultaneously acidified to pH 3 when it was diluted to 12 ml, and filtered through a 0.45-μm membrane filter before the filtrate was taken for NH$_4^+$ and K$^+$ analyses by ion chromatograph.

3. Results and discussion

3.1. Adsorption isotherms

Ammonium and potassium isotherms at pH 6 and 9 are presented in Figs. 1 and 2. From the results shown, NH$_4^+$ uptake increased rapidly to 0.66 meq g^{-1} zeolite with its equilibrium concentration increased up to about 8 mmol l^{-1}. With the further
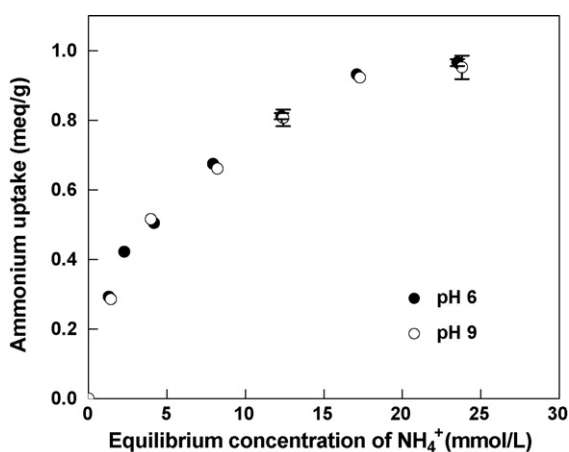

Fig. 1. Uptake isotherms for ammonium on zeolite at 20 ± 1 °C at pH 6 and 9.
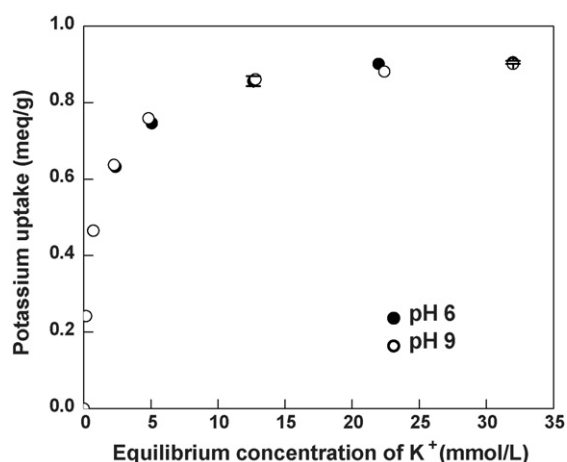

Fig. 2. Uptake isotherms for potassium on zeolite at 20 ± 1 °C at pH 6 and 9.

increase of NH$_4^+$ equilibrium concentration up to approximately 17 mmol l^{-1}, ammonium uptake progressively increased, but the speeds considerably decreased. With the equilibrium concentration >17 mmol l^{-1}, ammonium uptake closely approached the maximum uptake capacity. Comparison of ammonium uptake isotherms at pH 6 and pH 9 showed very similar results. The percentage of ammonia existing in ionized NH$_4^+$ form is governed by the solution pH and temperature. It is confirmed that at a pH below 7, ammonia exists essentially in NH$_4^+$ form at any temperature. Above pH 7, the amount of NH$_4^+$ decreases significantly. Correspondingly to this trend, the adsorption of ammonia should have significantly decreased at pH beyond 7, since NH$_4^+$ form is favored to ion exchange. However, the adsorption capacity of ammonia was not significantly hampered at pH 9. These results were probably ascribed to the shift of the NH$_4^+$–NH$_3$ species in the aqueous solution, in which NH$_4^+$ could be replenished by the hydrolysis of NH$_3$ while ammonium was adsorbed onto the solid phase. The second reason was likely related to the specifically adsorptive properties of the employed zeolite. However, corresponding well to the trend of ammonia species with pH, Lin et al. [26] reported equilibrium adsorption of ammonia almost decreased two times at initial pH 9 by a strong acid cationic ion exchange resin. This result indicated a pH adjustment should be conducted if the polymer exchanger is employed to treat the anaerobically-digested wastewater (pH 9.0). Insignificant hampered ammonium adsorption capacity at pH 9 on this zeolite had significantly practical importance because it indicated that the adjustment of pH is not required.

The uptake of potassium enhanced fast to 0.75 meq g^{-1} with the increase of equilibrium concentration up 5 mmol l^{-1}, which was higher than 0.55 meq g^{-1} for ammonium uptake at similar equilibrium concentration. With the equilibrium potassium more than 12.5 mmol l^{-1}, the uptake capacity of potassium by the zeolite approached the maximum value, while it was nearly at 17 mmol l^{-1} for the ammonium adsorption. This indicated that the natural zeolite had a higher affinity for potassium than for ammonium. At pH 6 and 9, potassium adsorption isotherms were almost overlapped. The identical potassium adsorption capability at pH 6 in comparison with pH 9 indicated a negligible competition of adsorptive sites between hydrogen ion and potassium at the slight acid pH. In fact, at pH 6, hydrogen ion is very difficult to express an evident effect on potassium adsorption due to much lower H$^+$ concentration in solution and extremely lower affinity with natural clinoptilolite compared with potassium.

3.2. Adsorption isotherms modeling

More than one model is required to correlate the experimental adsorption equilibrium data because there is no universal equilibrium model that provides an accurate fit for all adsorption isotherms. Thus, four typical isotherm models were applied in this study to fit ammonium and potassium adsorption isotherms by natural zeolite separately, attempting to obtain an optimum model by the comparison of the accuracy of different models. The simplest models are *Langmuir* and *Freundlich* equations, because they include only two parameters. *Langmuir* equation is widely used for adsorption equilibria because of its thermo-

dynamical basis. *Langmuir* isotherm model expressed as [29]:

$$q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}} \tag{1}$$

where, Q_{max} (mmol g^{-1}) is the maximum uptake capacity, C_{eq} (mmol l^{-1}) is the equilibrium solute concentration, and b is the equilibrium constant related to the energy of sorption (l mmol^{-1}).

Freundlich model is generally classified as an empirical equation. *Freundlich* model is represented by [29]:

$$q_{eq} = KC_{eq}^{1/n} \tag{2}$$

where, K is *Freundlich* constant and n is an empirical exponent. *Langmuir–Freundlich* model is written as [30]:

$$q_{eq} = \frac{bQ_{max}C_{eq}^{1/n}}{1 + bC_{eq}^{1/n}} \tag{3}$$

Toth model has been thought as a pure empirical model [30],

$$q_{eq} = \frac{Q_{max}C_{eq}}{(b + C_{eq}^{1/n})^n} \tag{4}$$

The computing software of Origin 7.0, which shows a strong capability of non-linear simulation, was employed as the computing program for all the model fittings. Estimated parameter values, confidence intervals, and coefficient of determination of four models fitting ammonium and potassium adsorption isotherm are presented in Table 1. As illustrated in Table 1, according to the value of $R^2 > 0.96$ for all the cases, it revealed that four equations well fitted the adsorption isotherm. Both *Langmuir* and *Freundlich* models predicted correctly the equilibrium adsorption isotherm of ammonium by natural zeolite, resulting in high coefficient of determinations ($R^2 > 0.988$) and small confidence intervals at two pHs. The coefficient of determination (R^2) below 0.97 indicated the modeling performance of *Freundlich* equation for potassium adsorption was slightly inferior to that of *Langmuir* model ($R^2 > 0.985$). The

three-parameter *Langmuir–Freundlich* and *Toth* models provided greater coefficient of determination ($R^2 \geq 0.996$) than two-parameter *Langmuir* and *Freundlich* equations. However, the higher value of coefficient of determination did not guarantee the thermodynamical consistency of the isotherm models with experimental adsorption isotherms because the confidence intervals of the estimated model parameters must be considered. The estimated parameters are not statistically reliable if they are not thermodynamically consistent with the experimental data and the confidence intervals are unacceptably high. As shown in Table 1, the three-parameter *Langmuir–Freundlich* and *Toth* models for ammonium adsorption isotherm provided much higher confidence intervals of parameters than the two-parameter models. As an example, the standard errors of maximum adsorption capacity of ammonium (Q_{max}) obtained with *Langmuir–Freundlich* and *Toth* models were 28.6 and 62.5% at pH 6, and 19.9 and 34.1% at pH 9 respectively, averaging the overall error of 36.3% in comparison of that of 4.4% obtained with *Langmuir* model. Besides the greater confidence intervals, the adsorption capacities of ammonium (Q_{max}) obtained with the three-parameter models were 1.5–2 times higher than those of the experimental adsorption data. Therefore, it was demonstrated that *Langmuir–Freundlich* and *Toth* models for ammonium adsorption isotherm at the tested temperature showed poorer fittings than *Langmuir* model. Differently with ammonium, satisfactory correlations between potassium uptake and the equilibrium concentration were obtained while potassium adsorption isotherms were fitted to *Langmuir–Freundlich* and *Toth* models, both resulting in the coefficient of determination ($R^2 = 0.999$) and smaller confidence intervals (less than 5% for most cases). Comparison of *Langmuir–Freundlich* and *Toth* models for potassium uptake with the confidence intervals of parameters showed the former is slightly better than the latter.

According to *Langmuir* and *Langmuir–Freundlich* models, the maximum adsorption capacities of ammonium and potassium at pH 6 and 9 were 1.14–1.15 and 0.98–1.02 meq g^{-1}, respectively. The slightly lower value of maximum adsorp-

Table 1
Fitting results obtained with four models for ammonium and potassium uptake isotherms

Model type	Parameter	NH$_4^+$		K$^+$	
		pH 6	pH 9	pH 6	pH 9
Langmuir	R^2	0.988	0.993	0.985	0.989
	Q_{max}, (mmol g^{-1})	1.14 ± 0.05	1.15 ± 0.05	0.895 ± 0.027	0.893 ± 0.022
	b, (l mmol^{-1})	0.22 ± 0.03	0.197 ± 0.03	1.46 ± 0.25	1.50 ± 0.22
Freundlich	R^2	0.993	0.990	0.968	0.961
	K	0.297 ± 0.017	0.289 ± 0.025	0.494 ± 0.034	0.500 ± 0.037
	n	2.57 ± 0.15	2.55 ± 0.21	5.09 ± 0.67	5.24 ± 0.77
Langmuir–Freundlich	R^2	0.996	0.997	0.999	0.999
	Q_{max}, (mmol g^{-1})	1.78 ± 0.51	1.46 ± 0.29	1.02 ± 0.02	0.977 ± 0.015
	b	0.172 ± 0.047	0.188 ± 0.032	1.00 ± 0.07	1.13 ± 0.05
	n	1.59 ± 0.29	1.35 ± 0.24	1.57 ± 0.09	1.44 ± 0.06
Toth	R^2	0.996	0.996	0.999	0.999
	Q_{max}, (mmol g^{-1})	2.48 ± 1.55	1.67 ± 0.57	1.06 ± 0.03	1.00 ± 0.02
	b	1.33 ± 0.49	2.01 ± 0.93	0.452 ± 0.024	0.467 ± 0.023
	n	0.37 ± 0.18	0.55 ± 0.22	0.515 ± 0.042	0.586 ± 0.041

tion capacities of potassium than ammonium was rather likely attributed to the hamper influence of residual potassium on the clinoptilolite, which was initially conditioned by sodium chloride (see the material and experimental part). The reported maximum ammonium uptake capacities on a variety of clinoptilolite ranged from 5 to 15 mg NH_4–N g^{-1} (i.e. 0.36 to 1.1 meq g^{-1}) [13]. The current ammonium Q_{max} value was at the upper end of the reported range. The equilibrium constant b obtained with *Langmuir* equation was related to the energy of sorption and the affinity of sorbate with adsorbent. The value of equilibrium constant for potassium (1.51 mg^{-1}) was significantly greater than for ammonium of 0.21 mg^{-1}. The constant b from *Langmuir* model further confirmed a higher affinity for potassium than for ammonium on natural zeolite, which was consistent with previous publications [20].

3.3. Adsorption kinetics

Fig. 3 shows the individual adsorption of ammonium as a function of time at three temperatures. The adsorption of ammonium proceeded very fast at the beginning 10 min, within which ammonium uptake achieved 71, 75 and 81% of the equilibrium removal at 1.5, 20 and 35 °C, respectively. With the further increase of contact time, the rate of ammonium uptake gradually decreased till the equilibrium was approached. Ammonium uptake at 35 °C approached the equilibrium in approximately 40 min, while at low temperatures it required about 1 h. At a certain time before the equilibrium was approached, ammonium adsorption was greater at the higher temperature than at the lower temperature, which indicated the adsorption kinetics was facilitated as the temperature increased.

Fig. 4 presents the effect of contact time on the individual potassium adsorption onto zeolite at three temperatures. The trend of potassium uptake governed by contact time was similar with ammonium uptake, but the adsorption rate of potassium was even faster than ammonium. As an example, potassium uptakes within 10 min at three temperatures were 0.34, 0.40, 0.43 meq g^{-1}, respectively, higher than 0.32, 0.34, 0.37 meq g^{-1}

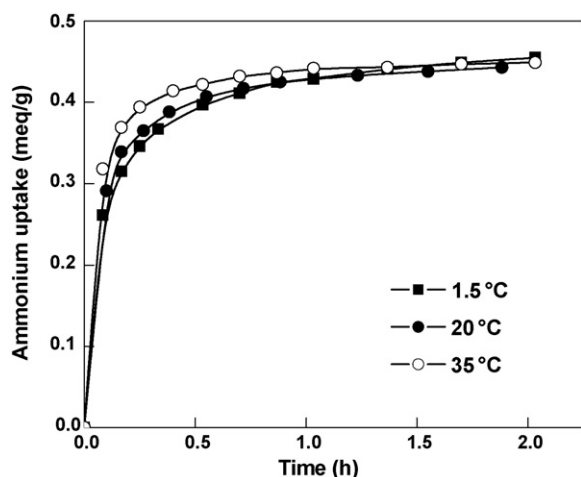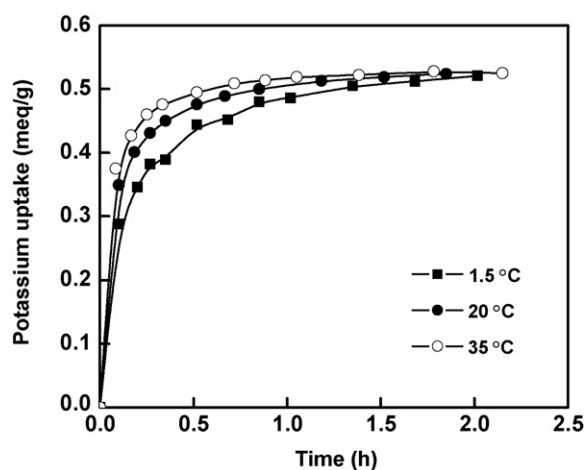Fig. 4. Kinetics of potassium uptake at different temperatures (pH 7.0 ± 0.1, initially 24 mmol K$^+$ l^{-1}).

with ammonium cases. Similar with the results from ammonium cases, the adsorption approached the equilibrium within a progressively less contact time as the temperature increased from 1.5 to 35 °C. Potassium uptake approached the equilibrium in 1 h at the tested three temperatures. The equilibrium uptake of potassium was about 0.54 meq g^{-1}, which was higher than 0.45 meq g^{-1} of ammonium. The results indicated a higher affinity for potassium than for ammonium by the zeolite, and were agreeable with the results obtained with the adsorption isotherm tests.

In the kinetic tests of simultaneous uptake of ammonium and potassium, both temperature and pH effects were studied. Overall, the trend of kinetic curves with multiple ion system was similar with individual ion system. Fig. 5 depicted the kinetics of simultaneous ammonium and potassium uptake at three temperatures. Similar with individual ion uptake tests, the increase of temperature accelerated adsorption rate of both ammonium and potassium on zeolite in the temperature range of 1.5–35 °C, whereas its effect on the amount of equilibrium uptake were insignificant. Simultaneous adsorption of ammonium and potassium approached the equilibrium in 1 h at higher temperature,

Fig. 3. Kinetics of ammonium uptake at different temperatures (pH 7.0 ± 0.1, initially 24 mmol NH$_4^+$ l^{-1}).

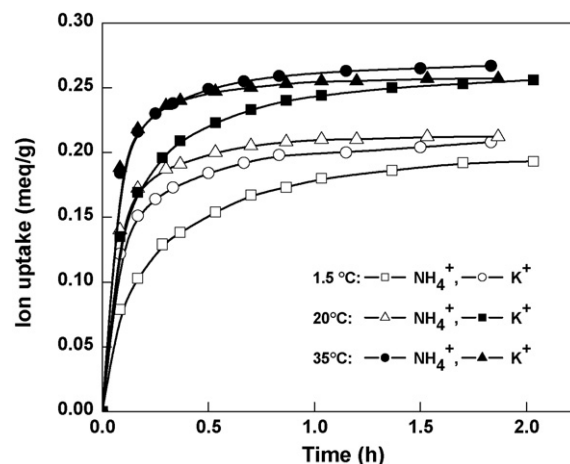
Fig. 5. Kinetics of simultaneous ammonium and potassium uptake at different temperatures (pH 7.0 ± 0.1, initially 12 mmol l^{-1} of NH$_4^+$ & K$^+$).
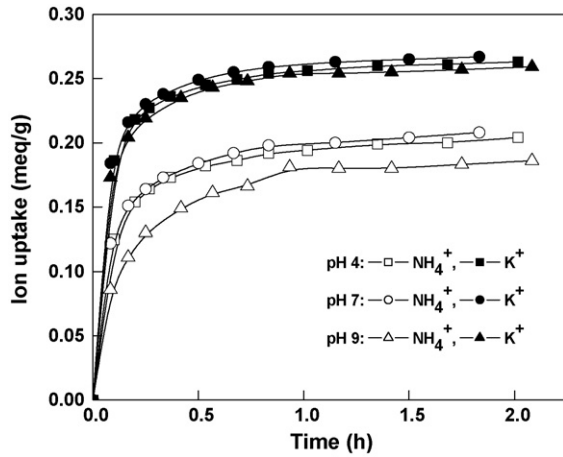
Fig. 6. Kinetics of simultaneous ammonium and potassium uptake at different pH (temperature = 20 ± 0.5, initially 12 mmol l^{-1} of NH$_4^+$ & K$^+$).

whereas at 1.5 °C, the equilibrium needed 2 h to be achieved. The uptake kinetics curves of potassium at three pHs, as shown from Fig. 6, were identical and almost overlapped.

For most cases of this study, the adsorption of both ammonium and potassium on the natural zeolite approached equilibrium within 1 h in the experimental condition. The fast adsorption kinetics for ammonium uptake in 1.5–35 °C is of significant importance with the continuous ammonium removal because it means that the ion-exchange operation will only be slightly affected by the low temperature, while the other ammonium removal technologies are usually limited in the low temperature, such as biological nitrification and denitrification, air and steam stripping.

3.4. Adsorption kinetics modeling

The following typical models were usually used in the adsorption kinetics: *Lagergren* pseudo-first-order [24], *Lagergren* pseudo-second-order [27,28], *Elovich* rate equation [28], squared driving force model [26], and *Vermeulen*'s model [12,22].

For the pseudo-first-order process, the *Lagergren* equation is expressed as [24]:

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \tag{5}$$

Integrating Eq. (5) with the conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$), gives

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{6}$$

where, q_t is the solid-phase loading of ammonium or potassium at time t, and q_{eq} is the sorption capacity at equilibrium. K_1 represents the pseudo-first-order rate constant for the kinetic model. The pseudo-second-order process can be expressed as [27,28]:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \tag{7}$$

where, q_e and q_t have the same meaning as described above. K_2 represents the pseudo-second-order rate constant for the kinetic model. By integrating equation (7) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the following linear equation can be obtained:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e}t \tag{8}$$

$$V_0 = K_2 \cdot q_e^2 \tag{9}$$

where, V_0 (mmol g^{-1} h^{-1}) is the initial sorption rate. Therefore, the V_0 and q_{eq} values of kinetic tests can be determined experimentally by plotting t/q_t versus t. The *Elovich* equation is as follows [28]:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \tag{10}$$

By integrating Eq. (10) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the following linear equation can be obtained:

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t + t_0) \tag{11}$$

where, a and b are the parameters of the *Elovich* rate equation; t_0 is equal to $1/(ab)$. If $abt \gg 1$, Eq. (11) can further be simplified as

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \tag{12}$$

The squared driving force model employed can be represented as [26]

$$\frac{dq_t}{dt} = K_3 C_l(q_e - q_t) \tag{13}$$

where, q_e and q_t have the same meaning as described above. C_l is the ion concentration in the solution at time t. K_3 is the experimental rate coefficient. Because the mass balance between the solid and liquid phase give as

$$q_t V_s = (C_0 - C_l)V_l \tag{14}$$

in which V_l and V_s are respectively the volumes of liquid and solid phase and C_0 is the initial ion concentration in the aqueous solution. Eliminating C_l from Eq. (13) and (14) and integrating Eq. (13) yield [26]

$$\frac{1}{C_0 - mq_e} \ln\left[\frac{q_e(C_0 - mq_t)}{C_0(q_e - q_t)}\right] = Y = K_3 t \tag{15}$$

where, m is the volume ratio of the solid phase to the liquid phase (V_s/V_l). The *Vermeulen*'s model is written as [12,22]:

$$\frac{q_t}{q_e} = [1 - \exp(-K_4 t)]^{\wedge}\left(\frac{1}{2}\right) \tag{16}$$

where, q_e and q_t have the same meaning as described above. K_4 is the experimental coefficient related to the diffusion coefficient positively and the square of the particle radius inversely.

Table 2 presents the estimated parameter values, confidence intervals, and coefficient of determination of five models fitting ammonium and potassium adsorption kinetics. As illustrated

Table 2
Parameters of five kinetic models fitting the individual and simultaneous adsorption kinetics of ammonium and potassium at pH 7 and 20 °C

Model Type	Parameter	Single ion system		Composite ion system	
		NH_4^+	K^+	NH_4^+	K^+
Pseudo first order	R^2	0.982	0.976	0.973	0.981
	q_e, (mmol g^{-1})	0.421 ± 0.007	0.497 ± 0.01	0.195 ± 0.004	0.255 ± 0.004
	K_1, (h^{-1})	10.1 ± 0.97	9.88 ± 1.09	9.30 ± 1.06	13.2 ± 1.41
Pseudo second order	R^2	0.9996	0.9995	0.9999	0.9999
	q_e, (mmol g^{-1})	0.451 ± 0.004	0.535 ± 0.006	0.215 ± 0.001	0.273 ± 0.000
	K_2, (g mmol^{-1} h^{-1})	45.1	36.0	60.7	78.8
Elovich rate equation	R^2	0.976	0.982	0.981	0.967
	a	261	290	42.7	664
	b	20.2	16.9	37.2	39.1
Squared driving force	R^2	0.994	0.996	0.980	0.988
	q_e, (mmol g^{-1})	0.430 ± 0.005	0.515 ± 0.005	0.197 ± 0.004	0.257 ± 0.004
	K_3, (l mmol^{-1} h^{-1}	0.610 ± 0.040	0.666 ± 0.039	0.441 ± 0.045	0.665 ± 0.062
Vermeulen	R^2	0.994	0.992	0.993	0.993
	q_e, (mmol g^{-1})	0.429 ± 0.005	0.507 ± 0.006	0.201 ± 0.002	0.259 ± 0.003
	K_4, (h^{-1})	5.44 ± 0.41	5.27 ± 0.44	4.70 ± 0.35	7.15 ± 0.59

in Table 2, the coefficient determination (R^2) of five models was greater than 0.97 for almost all the cases. According to it with the five models, the validities of the fittings for the individual and simultaneous adsorption of ammonium and potassium were evaluated in the order of pseudo-second-order ($R^2 > 0.999$) > *Vermeulen*'s model ($R^2 > 0.992$) > squared driving force model ($R^2 > 0.98$) > *Elovich* and pseudo-first-order model ($R^2 > 0.96$). The pseudo-second-order equation was most agreeable with the experimental data among all the models. As an optimum model in this study for the adsorption kinetics of ammonium and potassium on the natural zeolite, *Lagergren* pseudo-second-order were widely used to model the other adsorption kinetics resulting with very accurate fitting results [27,28].

Aside from the diffusion model [29,30], *Vermulens*'s model can be used to identify the rate-controlling mechanism; an accurate fitting indicates a particle diffusion rate controlling mechanism [12,22]. *Vermeulen*'s model fitted the adsorption kinetics of ammonium and potassium very well ($R^2 > 0.992$) for all the cases and demonstrated that particle diffusion is the rate controlling mechanism for the adsorption of ammonium and potassium on the natural zeolite in both the individual and composite ion system. The same conclusion was drawn in the previous reports [12,22].

Concerning K_1–K_4, which presents the corresponding rate constant of pseudo-first-order, pseudo-second-order, squared force model and *Vermeulen*'s model respectively, the individual uptake of ammonium and potassium showed an equality (K_1, K_3, K_4) or a slightly higher value for ammonium than for potassium (K_2). Alternatively in the multiple component system, all the results from the four models implied a greater rate constant (K) for potassium than for ammonium. Anyway, although the rate constant (K) for ammonium and potassium expressed differently between two systems, one fact should be notified that a faster uptake rate (dq_t/dt) of potassium than ammonium occurred on the zeolite both in the individual ion system, but also in the two-ions system.

The pseudo-second-order process and *Vermeulen*'s model were screened to fit the adsorption kinetics of ammonium and potassium at different pHs and temperatures. Table 3 presents the fitting results for the individual adsorption of ammonium and potassium at three temperatures while Tables 4 and 5 were the results for the simultaneous adsorption of two ions in three temperatures and pHs respectively. As seen from Table 3, the difference in equilibrium uptake of individual ammonium and potassium at three temperatures was insignificant. This observation again indicated a slight effect of temperature on the adsorption of ammonium and potassium onto the natu-

Table 3
Results of Pseudo-second-order and *Vermeulen*'s model fitting the kinetics of individual adsorption of ammonium and potassium at three temperatures

Ion type	Temp.	Pseudo second order model			*Vermeulen* model		
		R^2	q_e, (mmol g^{-1})	K_2, (g mmol^{-1} h^{-1})	R^2	q_e, (mmol g^{-1})	K_4, (h^{-1})
NH_4^+	1.5 °C	0.9992	0.446 ± 0.006	29.9	0.990	0.437 ± 0.006	4.17 ± 0.36
	20 °C	0.9996	0.451 ± 0.004	45.1	0.994	0.429 ± 0.005	5.44 ± 0.41
	35 °C	0.9999	0.455 ± 0.002	68.1	0.994	0.437 ± 0.004	7.83 ± 0.27
K^+	1.5 °C	0.9985	0.539 ± 0.009	19.4	0.991	0.505 ± 0.008	3.05 ± 0.25
	20 °C	0.9995	0.535 ± 0.006	36.0	0.992	0.507 ± 0.006	5.27 ± 0.44
	35 °C	0.9999	0.534 ± 0.003	58.5	0.993	0.515 ± 0.005	7.49 ± 0.61

Table 4
Results of Pseudo-second-order and *Vermeulen*'s model fitting the kinetics of simultaneous adsorption of ammonium and potassium at three temperatures

Ion type	Temp.	Pseudo second order model			Vermeulen model		
		R^2	q_e, (mmol g^{-1})	K_2, (g mmol^{-1} h^{-1})	R^2	q_e, (mmol g^{-1})	K_4, (h^{-1})
NH$_4^+$	1.5 °C	0.9997	0.210 ± 0.002	27.0	0.999	0.193 ± 0.001	1.99 ± 0.06
	20 °C	0.9999	0.215 ± 0.001	60.7	0.993	0.201 ± 0.002	4.70 ± 0.35
	35 °C	0.9999	0.218 ± 0.001	102.5	0.995	0.208 ± 0.002	6.52 ± 0.43
K$^+$	1.5 °C	0.9999	0.268 ± 0.000	37.5	0.996	0.249 ± 0.002	3.71 ± 0.21
	20 °C	0.9999	0.273 ± 0.000	78.8	0.993	0.259 ± 0.003	7.15 ± 0.59
	35 °C	1.0	0.262 ± 0.000	115.3	0.996	0.252 ± 0.002	8.70 ± 0.58

Table 5
Results of Pseudo-second-order and *Vermeulen*'s model fitting the kinetics of simultaneous adsorption of ammonium and potassium at three pHs

Ion Type	pH	Pseudo second order model			Vermeulen model		
		R^2	q_e, (mmol g^{-1})	K_2, (g mmol^{-1} h^{-1})	R^2	q_e, (mmol g^{-1})	K_4, (h^{-1})
NH$_4^+$	4	0.9994	0.208 ± 0.002	78.2	0.994	0.197 ± 0.002	4.54 ± 0.31
	7	0.9999	0.215 ± 0.001	60.7	0.993	0.201 ± 0.002	4.70 ± 0.35
	9	0.9987	0.193 ± 0.003	54.3	0.998	0.184 ± 0.001	2.70 ± 0.11
K$^+$	4	0.9998	0.267 ± 0.000	95.5	0.994	0.256 ± 0.002	6.52 ± 0.48
	7	0.9999	0.273 ± 0.000	78.8	0.993	0.259 ± 0.003	7.15 ± 0.59
	9	0.9998	0.263 ± 0.000	99.2	0.994	0.252 ± 0.002	6.44 ± 0.47

ral clinoptilolite. According to the pseudo-second-order model, the individual uptake of ammonium at three temperatures was 0.446–0.455 meq g^{-1}, which was significantly lower than 0.534–0.539 meq g^{-1} of the individual potassium uptake. In contrast to the insignificance of the equilibrium uptake, the rate constant (K) obtained with pseudo-second-order process and *Vermeulen*'s model showed a significant increase with the increasing temperature.

Similar with the results obtained from the individual uptake of the ions, the rate constant (K) for the simultaneous uptake of ammonium and potassium on the zeolite increased significantly with the increase of the temperature. At the same temperature, both the two models confirmed that the rate constant for potassium cases were greater than for ammonium cases when the two ions were simultaneously presented in the supernatant. According to the pseudo-second-order model, the equilibrium uptake of ammonium and potassium were 0.210–0.218 and 0.262–0.273 meq g^{-1}, respectively. Consequently, the molar ratio of potassium uptake to ammonium uptake was about 1.25. This is another indication of higher selectivity of ion exchange for potassium than for ammonium on clinoptilolite. As apparently shown in Figs. 3, 4, 5, and 6, both NH$_4^+$ and K$^+$ adsorption significantly decreased for the case of simultaneous uptake, while their individual adsorptions are significantly higher. Thus, the presence of potassium would significantly affect ammonium removal from wastewater by the natural zeolite.

In the presence of potassium, the equilibrium uptake of ammonium at pH 4 and 9 based on the pseudo-second-order process were 0.208 and 0.193 meq g^{-1}, respectively, which were slightly lower than 0.215 at pH 7. In contrast, potassium uptakes on the zeolite at different pHs were at the same level, averaging the equilibrium value of 0.268 meq g^{-1}. The initial experiments (not shown) indicated that the individual uptake of potassium

was independent on the pH variation from 4 to 12. The slightly changed adsorption capacity of ammonium in the multiply ions system is consistent with the result of individual ammonium adsorption isotherm at pH 6 and 9. The insignificant effect of acidic pH 4 on both ammonium and potassium can be explained by a higher affinity of the clinoptilolite towards the two ions than the hydrogen ion.

4. Conclusion

Langmuir and *Freundlich* model provided better fits than *Langmuir–Freundlich* and *Toth* equation for ammonium adsorption isotherm at 20 °C on natural zeolite, while for potassium adsorption isotherm at the tested temperature, the latter two equations offered more accurate prediction than the former two models. According to *Langmuir* and *Langmuir–Freundlich* model, the maximum adsorption capacities of ammonium and potassium at pH 6 and 9 were 1.14–1.15 and 0.98–1.02 meq g^{-1}, respectively. The validities of the fittings for the individual and simultaneous adsorption of ammonium and potassium were evaluated in the order of pseudo-second-order > *Vermeulen*'s model > squared driving force model > *Elovich* and pseudo-first-order model. Both adsorption isotherm and kinetic tests confirmed a higher selectivity for potassium than for ammonium on the clinoptilolite. Hence, ammonium removal will be significantly reduced under the condition of simultaneous potassium uptake.

References

[1] X. Lei, N. Sugiura, C. Feng, T. Maekawa, Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification, J. Hazard. Mater. 145 (2007) 391–397.

[2] K. Karim, R. Hoffmann, K.T. Klasson, M.H. Al-Dahhan, Anaerobic digestion of animal waste: effect of mode of mixing, Water Res. 39 (2005) 3597–3606.

[3] L. Zeng, C. Mangan, X. Li, Ammonia recovery from anaerobically cattle manure by steam stripping, Water Sci. Technol. 54 (2006) 137–145.

[4] EPA. Nitrogen control. Washington, DC: US EPA/625/R-93/010; 1993.

[5] J.H. Koon, W.J. Kaufman, Ammonia removal from municipal wastewaters by ion exchange, J. WPCF 47 (1975) 448–465.

[6] L. Liberti, G. Boari, D. Petruzzelli, R. Passino, Nutrient removal and recovery from wastewater by ion exchange, Water Res. 15 (1980) 337–342.

[7] S.E. Jorgensen, O. Libor, K.L. Grabir, K. Barkacs, Ammonia removal by use of clinoptilolite, Water Res. 10 (1976) 213–224.

[8] O. Lahav, M. Green, Ammonium removal using ion exchange and biological regeneration, Water Res. 32 (1998) 2019–2028.

[9] R.M. Burgess, M.M. Perron, M.G. Cantwell, K.T. Ho, J.R. Serbst, M.C. Pelletier, Use of zeolite for removing ammonia and ammonia-caused toxicity in marine toxicity identification evaluations, Arch. Environ. Contam. Toxicol. 47 (2004) 440–447.

[10] J.Y. Jung, Y.C. Chung, H.S. Shin, D.H. Son, Enhanced ammonia nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process, Water Res. 38 (2004) 347–354.

[11] E. Cooney, N.A. Booker, D.C. Shallcross, G.W. Stevens, Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process, Sep. Sci. Technol. 34 (1999) 2741–2760.

[12] N.A. Booker, E.L. Cooney, A.J. Priestley, Ammonia removal from sewage using natural Australian zeolite, Water Sci. Technol. 34 (1996) 17–24.

[13] M.L. Nguyen, C.C. Tanner, Ammonium removal from wastewaters using natural New Zealand zeolites, N.Z. J. Agric. Res. 41 (1998) 427–446.

[14] Q. Du, S. Liu, Z. Cao, Y. Wang, Ammonia removal from aqueous solution using natural chinese clinoptilolite, Sep. Purif. Technol. 44 (2005) 229–234.

[15] T.C. Jorgensen, L.R. Weatherley, Ammonia removal from wastewater by ion exchange in the presence of organic contaminants, Water Res. 37 (2003) 1723–1728.

[16] J.R. Klieve, M.J. Semmens, An evaluation of pretreated natural zeolites for ammonium removal, Water Res. 14 (1979) 161–168.

[17] H.T. Dryden, L.R. Weatherley, Aquaculture water treatment by ion exchange: continuous ammonium ion removal with clinoptilolite, Aqua. Eng. 8 (1989) 109–126.

[18] L.R. Weatherley, N.D. Miladinovic, Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite, Water Res. 38 (2004) 4305–4312.

[19] N.P. Hankins, S. Pliankarom, N. Hilal, Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: a dynamic study using a continuous packed-bed column in up-flow mode, Sep. Sci. Technol. 39 (2004) 1347–1364.

[20] L.L. Ames, The cation sieve properties of clinoptilolite, Amer. Mineral. 45 (1960) 689–700.

[21] A. Farkaš, M. Rožić, Ž.M. Barbarić, Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia, J. Hazard. Mater. B 117 (2005) 25–33.

[22] C.-H. Liu, K.V. Lo, Ammonia removal from composting leachate using zeolite. I. Characterization of the zeolite, J. Environ. Sci. Health A 39 (2001) 1671–1688.

[23] A. Demir, A. Günay, E. Debik, Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite, Water SA. 28 (2002) 329–336.

[24] M.P. Bernal, J.M. Lopez-Real, Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials, Bioresour. Technol. 43 (1993) 27–33.

[25] Y. Wang, S. Liu, T. Han, S. Chuan, T. Zhu, Ammonia removal from leachate solution using natural Chinese clinoptilolite, J. Hazard. Mater. 136 (2006) 735–740.

[26] S.H. Lin, C.L. Wu, Ammonia removal from aqueous solution by ion exchange, Ind. & Eng. Chem. Res. 35 (1996) 553–558.

[27] X. Guo, F. Chen, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, Environ. Sci. & Technol. 39 (2005) 6808–6818.

[28] C.F. Chang, C.Y. Chang, K.H. Chen, W.T. Tsai, J.L. Shie, Y.H. Chen, Adsorption of naphthalene on zeolite from aqueous solution, J. Colloid Interf. Sci. 277 (2004) 29–34.

[29] D.M. Ruthven, Principles of adsorption and Adsorption Processes, Wiley, New York, USA, 1984.

[30] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, UK, 1998.