Comparative sorption kinetic studies of ammonium onto zeolite

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Abstract

The sorption kinetics of ammonium onto three types of zeolite, natural zeolite, natural zeolite covered by biofilm and ammonium-bearing zeolite covered by biofilm, at two particle sizes were studied. The pseudo-first order and pseudo-second order models were fitted to the results by a non-linear method. The batch sorption model, based on a pseudo-second order mechanism, was applied to predict the rate constant of sorption, the equilibrium capacity and the initial sorption rate. Ion exchange between NH_4^+ and cations in the zeolite increased with decreasing particle size of the zeolite. Biofilm covered on the zeolite did not affect the ion exchange for the smaller particle size but decreased the ion exchange capacity by 22% for the larger particle size. In addition, bioregeneration should be considered for the recovery of ion exchange capacity of the bio-zeolite made from ammonium-bearing zeolite by the microorganisms in the biofilm, 78.0 and 63.9% regeneration for the smaller and larger particle size of zeolite, respectively.
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1. Introduction

Nitrogen pollution in hydrosphere is attracting increasing attention for eutrophication of lakes and rivers all over the world. Ammonium is the inorganic ion form of nitrogen pollution contained in municipal sewage, industrial wastewater and agricultural wastes or decomposed from organic nitrogen compounds in those wastewater and wastes. Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms [1]. Hence, removing ammonium from wastewater is of great importance to control nitrogen pollution. Considering from the technical efficiency and economic competition, zeolite, used as an ion exchanger, seems to be much more capable to remove ammonium from wastewater. Zeolite is natural porous mineral described as crystalline hydrated aluminosilicates. Inside the framework structure of zeolite, alkali or alkaline-earth cations are reversibly fixed in the cavities and can easily be exchanged by surrounding positive ions [2]. Early in 1970s, natural zeolite were tested for removing ammonium from wastewater [3]. In recent years, typical studies reported its use for removing ammonium from secondary efflu-

ent or sewage [4,5] as well as from industrial wastewaters, such as tannery wastewater [6], aquaculture wastewater [7] and piggery wastewater [8,9]. According to their composition, natural zeolite have different forms, of which clinoptilolite has the best performance for ammonium removal [10,11].

Sorption kinetics was available for describing the ammonium removing process by zeolite. The process was largely governed by intraparticle pore diffusion [12,13], and fitting first order kinetic model [14,15]. Other kinetic models including parabolic diffusion, Elovich and heterogeneous diffusion were also evaluated and all adequately described the ammonium sorption process [15].

Biological decomposition has been considered in the treatment system using zeolite, since microorganisms would probably grow on the surface of the zeolite immerged in aqueous solution or wastewater. Zeolite covered by biofilm was called bio-zeolite, acting as the ion-exchanger and growth media for microorganisms [16,17]. Compared to the virgin zeolite, the ion-exchange rate in the bio-zeolite was reduced about 25–30%, and the rate-controlling step for ion exchange shifted from pore diffusion in the virgin zeolite to film diffusion in the bio-zeolite [18].

In this study, the ammonium sorption by three zeolite, i.e. natural zeolite, natural zeolite covered by biofilm and ammonium-bearing zeolite covered by biofilm, at two zeolite particle sizes

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Table 1
Major chemical ingredients of the clinoptilolite produced in Jinyun, Zhejiang Province

Value	Zeolite concentration (%)	Chemical ingredient (%)											Ignition loss
		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O	
Minimum	65	66.21	0.13	10.99	0.08	–	0.04	0.13	2.59	2.22	0.92	–	–
Maximum	71	69.58	0.14	12.20	0.96	0.11	0.08	0.53	2.98	2.95	1.13	11.9	13.83
Average	69	68.43	0.14	11.41	0.63	0.07	0.06	0.26	2.72	2.59	1.06	6.11	8.28

Besides, the zeolite also contains microelements, such as Cu, Pb, As, Be, Zr, Ni, P, Mo, Sn, Ga, Cr, V, Yb, Y, Nb, La, etc.

were studied. A non-linear method of pseudo-second order kinetic model was examined the sorption of ammonium by zeolite. A trial-and-error procedure was used for the non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

2. Materials and methods

2.1. Zeolite materials

Zeolite produced in Jinyun, Zhejiang Province, China, was used as experiment material. The ore is mainly clinoptilolite accompanied with mordenite and heulandite. Its main chemical constitution was listed in Table 1. Internal structure of the natural zeolite was observed by electronic microscope as showed in Fig. 1. For the particle size of 1.0–3.2 mm, the zeolite has an specific surface area of 6.64 m^2/g and an average diameter of pores of 112.72 Å.

Two different sizes of the zeolite were selected, 1.0–3.2 and 8.0–15 mm each. Two types of bio-zeolite were made from natural zeolite and ammonium-bearing zeolite. For obtaining the ammonium-bearing zeolite, the nature zeolite was immerged into high concentrated NH$_4$Cl solution prepared by de-ionized water and stirring for sufficient time so as to become ammonium-saturated zeolite, and then dried off in the air. Bio-zeolite were maded as the following cultivation: (1) prepare four beakers

of 2 dm^3, add 1000 g of natural fresh zeolite or ammonium-saturated zeolite with different particle sizes into every beaker, then add 1.2 dm^3 cultivation solution prepared by de-ionized water and 0.2 dm^3 activated sludge (MLSS = 1.45 g/dm^3) into the beaker. The cultivation solution were the mixture of glucose, NH$_4$Cl and K$_2$HPO$_4$ for the natural zeolite to provide COD 200 mg/dm^3, NH$_4$$^+$-N 100 mg/dm^3 and TP 2 mg/dm^3, and the mixture of glucose and K$_2$HPO$_4$ for the ammonium-saturated zeolite to provide COD 200 mg/dm^3 and TP 2 mg/dm^3; (2) aerate the zeolite-liquor systems from the bottom of the beakers, keeping DO in the range of 4.5–6.0 mg/dm^3. For compensating the loss from evaporation and sorption, dose the same cultivation solution into every beaker to maintain the liquor volume and nutrition everyday; (3) observe the occurrence of biofilm growing on the surface of the zeolite. In this study, the cultivation was stopped after 73 days while the zeolite became bio-zeolite wrapped by white biofilm and (4) dry off the four types of bio-zeolite in the air.

So, experiment materials included natural fresh zeolite (NZ), bio-zeolite made from natural fresh zeolite (BZ) and bio-zeolite made from ammonium-bearing zeolite (BAZ). Surface of the BZ was also scanned by electronic microscope and showed in Fig. 1. Biomass of the biofilm attached on the zeolite were measured as 62.5 and 55.9 g/kg for BZ with particle sizes of 1–3.2 and 8–15 mm, respectively, and 54.8 and 50.1 g/kg for BAZ with particle sizes of 1–3.2 and 8–15 mm, respectively.
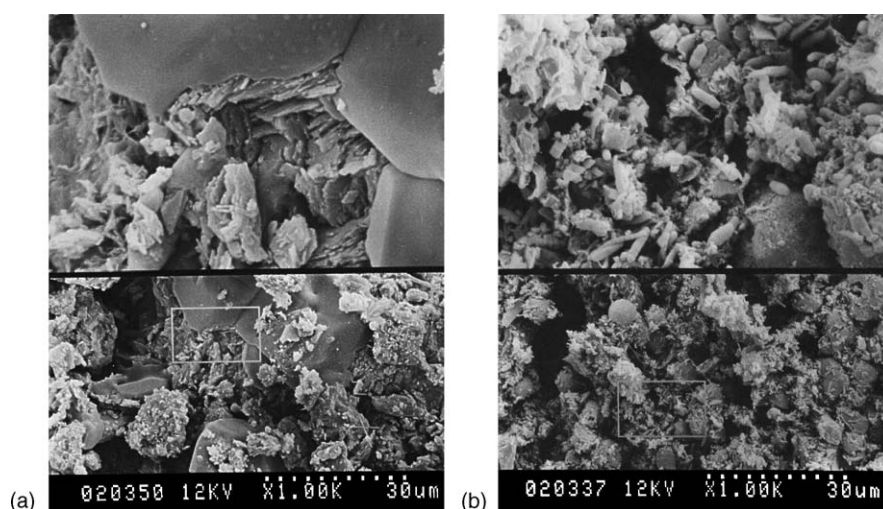

Fig. 1. Natural zeolite and bio-zeolite observed by SEM. (a) Internal structure of the natural zeolite produced in Zhejiang Province, China. (b) Surface of the bio-zeolite made from natural zeolite. *Note*: in each picture, the upper part is the amplified zone framed in the lower part.

2.2. Experimental methods

The contact time experiments were conducted under static conditions as the following procedure: prepare NH_4Cl solution by de-ionized water, its concentration is C_i (meq/dm^3); add zeolite or bio-zeolite with accurate weight m (g) and NH_4Cl solution of V (dm^3) into one 250 ml flask; seal the flask and put it on a orbital shaker; set the rotation rate and temperature of the shaker and let the zeolite-solution system interact sufficiently; exam the concentration of NH_4^+-N, C_e (meq/dm^3) in the solution against time.

The experiments were carried out with a constant initial ammonium concentration (C_i) of 5.5 meq/dm^3, and zeolite dose 400 g/dm^3 for ammonium sorption onto various types of zeolite under the temperature of 25 °C and the rotation rate of 110 rpm. The monitoring method of NH_4^+ is spectrophotometry with Shimadzu 2401 UV–vis spectrophotometer.

3. Results and discussion

In order to investigate the reaction order of sorption, the constants of sorption of ammonium were determined using equations of Lagergren [19] and a pseudo-second order mechanism [20,21] (Ho and McKay), respectively, which is as follows:

Pseudo-first order model: the sorption kinetics may be described by a pseudo-first order model as the following [19,22]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

$$q_t = q_e - \exp(\ln(q_e) - k_1 t) \tag{2}$$

where q_e is the amount of ammonium sorbed at equilibrium (meq/g); q_t the amount of ammonium sorbed at time t (meq/g) and k_1 is the equilibrium rate constant of pseudo-first order sorption (1/h).

Pseudo-second order model: the pseudo-second order rate expression has been applied to the sorption of metal ions, dyes and organic substances from aqueous solution [22,23]. The sorption kinetics may be described by a pseudo-second order model. The equation is as the following:

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{3}$$

where q_e is the amount of ammonium sorbed at equilibrium (meq/g) and k_2 is the equilibrium rate constant of pseudo-

second order sorption (g/(meq h)). If the initial sorption rate is defined as $h = q_t/t$, when t approaches 0, h (meq/(g h)) is

$$h = k_2 q_e^2 \tag{4}$$

Linear regression was frequently used to determine the best fitted model throughout the years and the method of least squares has been frequently used for finding the parameters of the models. However, transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares [24,25]. Thus, it is not appropriate to use the correlation coefficient of linear regression analysis for comparing the best fitting of models. Non-linear analysis could be a better method. The pseudo-first and pseudo-second order rate constants, correlation coefficients and equilibrium sorption capacities of ammonium under different conditions were calculated by a trial-and-error procedure for the non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. Table 2 lists the results.

3.1. Effect of particle size

The results calculated by the pseudo-second order model show that the sorption capacity of ammonium increases from 68.2 to 72.0 meq/100 g, from 53.2 to 73.2 meq/100 g and from 43.6 to 56.2 meq/100 g with the decrease of the zeolite particle size ranging from 8–15 to 1.0–3.2 mm for three types of zeolite, NZ, BZ and BAZ, respectively. It is clear that ion exchange increased with decreasing particle size of the zeolite. Due to the cations in the smaller zeolite are much easier to be exchanged into the aqueous solution.

Concerning the values of r^2, the kinetics of ammonium sorption onto zeolite follows the pseudo-second order rate expression. Furthermore, Fig. 2 shows the plots of q_t against t for the pseudo-first and pseudo-second order models for the sorption of ammonium onto zeolite, and confirms the agreement that the experimental data for the pseudo-second order model is better than that for the pseudo-first order model.

3.2. Effect of type of zeolite

Figs. 3 and 4 show the results of the process of ammonium sorption onto three types of zeolite with two particle sizes, respectively.

Table 2
Parameters for effect of particle size

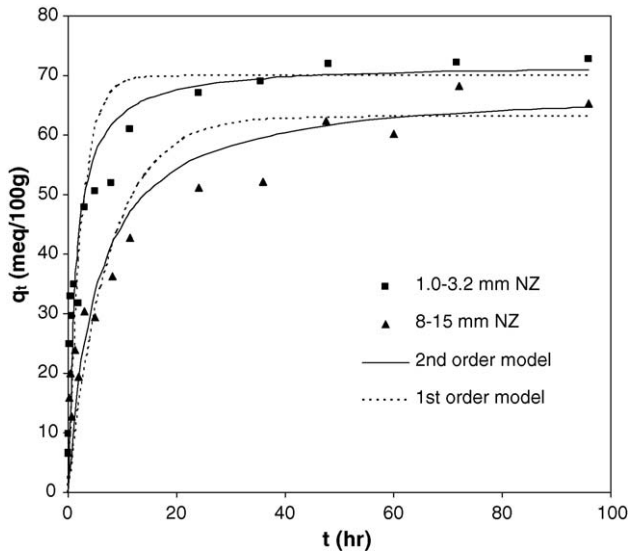| Zeolite	d_p (mm)	Second order				First order		
		q_e (meq/100 g)	k_2 (100 g/(meq h))	h (meq/100 g h)	r^2	q_e (meq/100 g)	k_1 (1/h)	r^2
NZ	1.0–3.2	72.0	0.0105	54.3	0.914	69.9	0.410	0.875
	8–15	68.2	0.00285	13.3	0.921	63.1	0.132	0.896
BZ	1.0–3.2	73.2	0.0121	65.0	0.886	70.5	0.499	0.851
	8–15	53.2	0.00173	4.90	0.929	46.5	0.0741	0.918
BAZ	1.0–3.2	56.2	0.0129	40.6	0.915	53.9	0.439	0.879
	8–15	43.6	0.00241	4.58	0.946	38.1	0.0861	0.931

Fig. 2. Pseudo-first and pseudo-second order kinetics for sorption of ammonium onto natural zeolite.

The capacity sequence is found to be NZ ≈ BZ ≫ BAZ while smaller particle size (1.0–3.2 mm) were used for ammonium sorption (Fig. 3). Compared with NZ, BZ has the similar equilibrium sorption, q_e, but higher initial sorption rate, h (Table 2). Therefore, the biofilm attached on the zeolite did not affect the rate of ion exchange between zeolite and aqueous solution, on the contrary, it made an additional contribution of bio-sorption to the total-sorption at the initial stage. In the case of BAZ, although it could not avoid to release NH_4^+ from the ammonium-saturated zeolite to the solution during the cultivation, large quantity of NH_4^+ were still remained in the zeolite. Bioregeneration of the ammonium-bearing zeolite by microorganism in the biofilm should be considered because the ammonium equilibrium capacity of BAZ
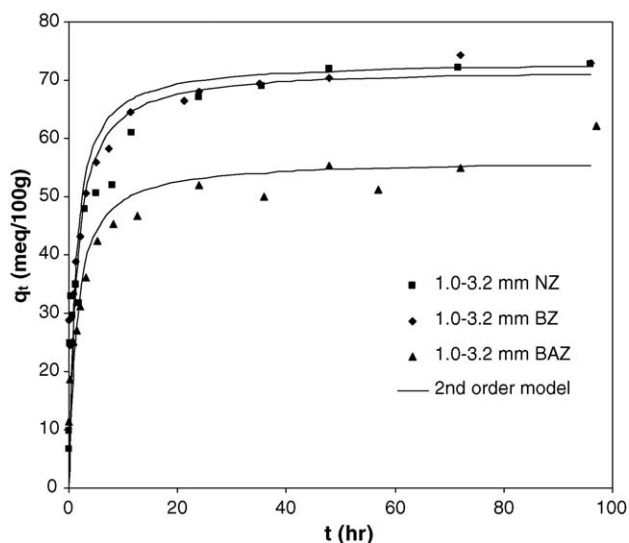

Fig. 3. Pseudo-second order kinetic model for sorption of ammonium onto three types of zeolite with particle size 1.0–3.2 mm.
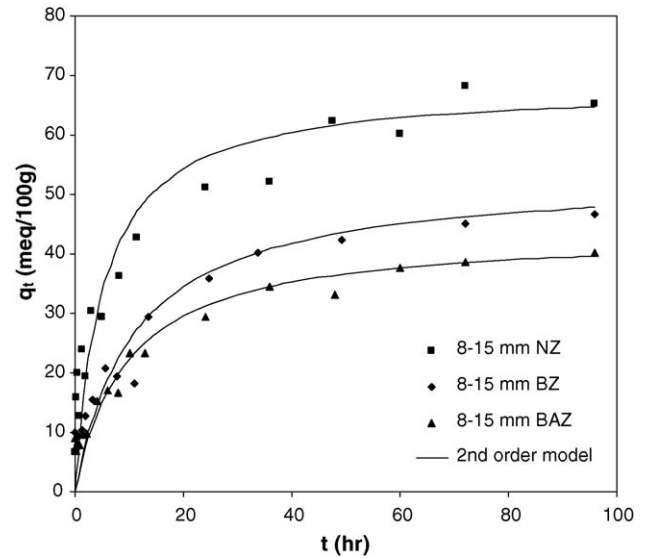

Fig. 4. Pseudo-second order kinetic model for sorption of ammonium onto three types of zeolite with particle size 8–15 mm.

(56.2 meq/100 g) reached as high as 78.0% of the capacity of NZ (72.0 meq/100 g).

The capacity sequence is found to be NZ > BZ > BAZ while larger particle size (8–15 mm) were used (Fig. 4). The sequence is also true for comparing the equilibrium sorption, q_e, and the initial sorption rate, h (Table 2). For larger particle size, the resistance to pore diffusion is much higher than that of smaller particle size, resulting in the lower values of q_e and h. Compared NZ with BZ, biofilm attached on the larger zeolite seemed to affect the rate of ion exchange, regarding the ammonium equilibrium capacities of NZ (68.2 meq/100 g) and BZ (53.2 meq/100 g), a drop of 22% was obtained. A similar study hypothesized that the biofilm adjacent to the zeolite (chabazite) was different from the rest of the biofilm and was characterized by a much higher density, which impedes the diffusion process [18]. However, the hypothesis cannot be applied to the smaller particle size of zeolite in this study. In the case of BAZ, with bioregeneration by microorganism in the biofilm, the ammonium equilibrium capacity of BAZ (43.6 meq/100 g) reached 63.9% of the capacity of NZ (68.2 meq/100 g).

4. Conclusions

The kinetics of pseudo-first order and pseudo-second order models of sorption of ammonium onto three types of zeolite, natural zeolite, bio-zeolite made from natural zeolite and bio-zeolite from ammonium-bearing zeolite, were compared in this study. Kinetics data were obtained by non-linear method that suggests the sorption system was found to follow pseudo-second order rate model. The sorption of ammonium is a function of zeolite particle size. Ion exchange increased with decreasing particle size of the zeolite. Biofilm covered on the zeolite with smaller particle size 1.0–3.2 mm did not affect the ion exchange, but improved the initial sorption rate due to bio-sorption. However, for the zeolite with particle size 8–15 mm, the attached biofilm reduced the ion exchange rate resulting in a drop of 22% of the

equilibrium capacity. Bioregeneration process should contribute for the recovery of ion exchange capacity of the bio-zeolite made from ammonium-bearing zeolite. After 73 days cultivation, microorganisms in the biofilm recovered 78.0 and 63.9% of the equilibrium capacities of the smaller and larger particle size of zeolite, respectively.

References

[1] X.C. Zheng, Y.X. Li, Technology of Phosphorus and Nitrogen Removal from Wastewater, China Architectural Industry Press, Beijing, 1998, pp. 4–11 (in Chinese).
[2] G.V. Tsitsishvili, T.G. Andronikashvili, Natural Zeolites, Redwood Press, Oxford, 1992, pp. 163–165.
[3] J.H. Koon, W.J. Kaufman, Ammonia removal from municipal wastewaters by ion-exchange, J. Water Pollut. Control Fed. 47 (1975) 448–465.
[4] N.A. Booker, E.L. Cooney, A.J. Priestly, Ammonia removal from sewage using natural Australian zeolite, Water Sci. Technol. 34 (1996) 17–24.
[5] A.H. Englert, J. Rubio, Characterization and environmental application of a Chilean natural zeolite, Int. J. Miner. Process. 75 (2005) 21–29.
[6] E. Chmielewska-Horvathova, J. Konecny, Z. Bosan, Ammonia removal from tannery wastewaters by selective ion-exchange on slovak clinoptilolite, Zeitschrift fur Wasser-und Abwasser-Forschung, J. Water Wastewater Res. Acta Hydrochim. Hydrobiol. 5 (1994) 269–272.
[7] D. Bergero, M. Boccignone, F. Di Natale, G. Forneris, G.B. Palmegiano, L. Roagna, B. Sicuro, Ammonia removal capacity of European natural zeolite tuffs: application to aquaculture waste water, Aquat. Fish. Manage. 25 (1994) 813–821.
[8] E. Sanchez, Z. Milan, R. Borja, P. Weiland, X. Rodriguez, Piggery waste treatment by anaerobic digestion and nutrient removal by ionic exchange, Resour. Conserv. Recycl. 15 (1995) 235–244.
[9] R. Cintoli, B. Di Sabatino, L. Galeotti, G. Bruno, Ammonium uptake by zeolite and treatment in UASB reactor of piggery wastewater, Water Sci. Technol. 32 (1995) 73–81.
[10] J.R. Klieve, M.J. Semmens, Evaluation of pretreated natural zeolites for ammonium removal, Water Res. 14 (1980) 161–168.
[11] K. Metropoulos, E. Maliou, M. Loizidou, N. Spyrellis, Comparative-studies between synthetic and natural zeolites for ammonium uptake, J. Environ. Sci. Health A 28 (1993) 1507–1518.
[12] S.M. Robinson, W.D. Arnold, C.H. Byers, Mass-transfer mechanisms for zeolite ion-exchange in waste-water treatment, AIChE J. 40 (1994) 2045–2054.
[13] B.N.K. Njoroge, S.G. Mwamachi, Ammonia removal from an aqueous solution by the use of a natural zeolite, J. Environ. Eng. Sci. 3 (2004) 147–154.
[14] M.P. Bernal, J.M. Lopez-Real, Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials, Bioresour. Technol. 43 (1993) 27–33.
[15] M. Kithome, J.W. Paul, L.M. Lavkulich, A.A. Bomke, Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite, Soil Sci. Soc. Am. J. 62 (1998) 622–629.
[16] H. Tsuno, F. Nishimura, I. Somiya, Removal of ammonium nitrogen in bio-zeolite reactor, Doboku Gakkai Bombun Hokokushu 503 (1994) 159–166.
[17] M. Oldenburg, I. Sekoulov, Multipurpose filters with ion-exchanger for the equalization of ammonia peeks, Water Sci. Technol. 32 (1995) 199–206.
[18] O. Lahav, M. Green, Bioregenerated ion-exchange process: the effect of the biofilm on ion-exchange capacity and kinetics, Water SA 26 (2000) 51–57.
[19] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.
[20] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[21] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[22] Y.S. Ho, Comment on removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: Kinetics and equilibrium, by S. Rengaraj, Y. Kim, C.K. Joo, and J. Yi, J. Colloid Interface Sci. 276 (2004) 255–258.
[23] Y.S. Ho, Comment on selective adsorption of tannins onto hide collagen fibres, Sci. China Ser. B: Chem. 48 (2005) 176.
[24] D.A. Ratkowsky, Handbook of Nonlinear Regression Models, Marcel Dekker Inc., New York, 1990.
[25] Y.S. Ho, Selection of optimum sorption isotherm, Carbon 42 (2004) 2115–2116.