



## Adsorption behavior of ammonium by a bioadsorbent – Boston ivy leaf powder

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### Abstract

The adsorption behaviors of ammonium ions from aqueous solution by a novel bioadsorbent, the Boston ivy (*Parthenocissus tricuspidata*) leaf powder (BPTL) were investigated. The SEM images and FT-IR spectra were used to characterize BPTL. The mathematical models were used to analyze the adsorption kinetics and isotherms. The optimum pH range for ammonium adsorption by BPTL was found to be 5–10. The adsorption reached equilibrium at 14 hr, and the kinetic data were well fitted by the Logistic model. The intraparticle diffusion was the main rate-controlling step of the adsorption process. The high temperature was favorable to the ammonium adsorption by BPTL, indicating that the adsorption was endothermic. The adsorption equilibrium fitted well to both the Langmuir model and Freundlich model, and the maximum monolayer adsorption capacities calculated from Langmuir model were 3.37, 5.28 and 6.59 mg N/g at 15, 25 and 35°C, respectively, which were comparable to those by reported minerals. Both the separation factor ( $R_L$ ) from the Langmuir model and Freundlich exponent ( $n$ ) suggested that the ammonium adsorption by BPTL was favorable. Therefore, the Boston ivy leaf powder could be considered a novel bioadsorbent for ammonium removal from aqueous solution.

**Key words:** ammonium ion; bioadsorbent; isotherm; kinetics; plant material

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### Introduction

Industry factories and stock farms would discharge voluminous wastewater, which usually contain excess ammonia nitrogen ( $\text{NH}_3$  and  $\text{NH}_4^+$ ) before treatment. Excess ammonia nitrogen could enhance eutrophication of water bodies and toxicity to aquatic organisms. Comparing with traditional methods used to remove ammonia nitrogen from wastewater, e.g., biological nitrification-denitrification, air stripping and chemical precipitation, adsorption has received great attention of scientists in recent years, because it is more economically feasible and environmentally friendly.

The key issue of adsorption method is to find effective and low-cost adsorbents. Plant materials or agricultural residues had been used extensively as bioadsorbents in recent studies to remove a variety of pollutants from aqueous solution, e.g., heavy metal (Bulut and Tez, 2007), dyes (Han et al., 2008), nitrate (Orlando et al., 2002), phosphate (Eberhardt and Min, 2008) and phenol (Mohd Din et al., 2009). However, almost all efforts to adsorb ammonium ions from aqueous solution have been focused on mineral materials, such as zeolite (clinoptilolite or mordenite) (Nguyen and Tanner, 1998; Karadag et al., 2006; Zheng et al., 2008). Little information is available

on the adsorption behavior of ammonium onto plant materials or agricultural residues from aqueous solution. Our research group has screened several considerable ammonium adsorbent materials from 80 agricultural residues (Liu et al., 2010). For the present study, the purpose is to evaluate the adsorption potential of Boston ivy (*Parthenocissus tricuspidata* Planch) leaf powder.

### 1 Materials and methods

#### 1.1 Preparation of adsorbent and adsorbate

The Boston ivy leaves were collected in Nanjing, China. The leaves were washed repeatedly with tap water to remove dust and soluble impurities on surface and were dried for 5 hr at room temperature in the shade. The sample was then dried at 105°C for 15 min and at 70°C for 10 hr in an air oven. The dried sample was grinded to pass a 30 mesh sieve. The fine Boston ivy leaf powder was preserved in plastic bags for use as adsorbent.

The stock solution of  $\text{NH}_4^+\text{-N}$  (1000 mg/L) was prepared by dissolving 3.8190 g dried ammonium chloride ( $\text{NH}_4\text{Cl}$ ) in deionized water. The experimental solutions were prepared by diluting the stock solution with deionized water when necessary.

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## 1.2 Characterization of the adsorbent

The zeta potential of the Boston ivy (*P. tricuspidata*) leaf powder (BPTL) was determined by an electrokinetic analyzer JS94H (Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China). The specific surface area of BPTL was determined from the N<sub>2</sub> adsorption-desorption isotherms by Brunauer-Emmett-Teller (BET) method with ASAP 2020 accelerated surface area and porosimetry system (Micromeritics Instrument Corporation, USA). The relative pressures of N<sub>2</sub> were 0.05 to 0.35, and seven points were used to construct the monolayer adsorption capacity. A scanning electron microscope Quanta 600 (FEI Company, USA) was used for the microstructure analysis of the sample surface. The Fourier transform infrared spectrum (FT-IR) of BPTL before and after ammonium adsorption were obtained using a NEXUS 870 FT-IR spectrometer (Thermo Nicolet Company, USA) with KBr pellets method at a resolution of 2 cm<sup>-1</sup> in the range of 400–4000 cm<sup>-1</sup>.

## 1.3 Batch experiments

The adsorption experiments were performed using the batch equilibration method. In this method, 0.2 g BPTL was mixed with 25 mL ammonium solution of 25–1000 mg/L. The mixtures were sealed and shaken at 250 r/min and 25°C for 24 hr to reach equilibrium. The mixtures were then centrifuged at 4000 r/min for 5 min, and the supernatant was filtered using 0.45 μm microporous membrane filters. The concentration of ammonium ions in each filtrate was analyzed using the titrimetric method (APHA et al., 1998), and the determination limit of ammonia nitrogen was 0.2–1000 mg/L. Experiments were performed in triplicates and the averages were reported. Controls were obtained by mixing distilled water with each sample.

The effect of initial pH on ammonium adsorption was investigated within pH range 2–12, at initial ammonium concentration 50 mg/L. The initial pH of each solution was adjusted with 0.1 mol/L HCl or NaOH solution.

To assess the effects of initial ammonium concentration and temperature, a concentration range of 25–1000 mg/L was used, and the reaction temperatures were 15, 25 and 35°C. To assess the effects of contact time, kinetic studies were carried out where the samples were shaken from 1 to 24 hr, and the initial ammonium concentrations were 25 and 100 mg/L.

The ammonium adsorption capacity ( $q$ , mg/g) were calculated by Eq. (1).

$$q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where,  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium ammonium concentrations in the solution, respectively.  $V$  (L) is the solution volume, and  $M$  (g) is the mass of adsorbent.

## 2 Results and discussion

### 2.1 Characterization of the adsorbent

Some chemical and physical properties of BPTL were determined. The sample was composed of holocellulose (66.3%), protein (9.6%) and lignin (13.0%) as its major constituents, which may contain polar functional groups, such as alcohols, aldehydes, ketones, carboxyl, phenol and ether groups. These groups might have abilities to bind some pollutants (Pagnanelli et al., 2003). The considerable surface area data (32.0 m<sup>2</sup>/g) suggested that BPTL was porous, and this could be also proved by SEM images at 4000× magnifications, as shown in Fig. 1. This porous and irregular structure of BPTL results in a large surface interface, thus making adsorption of ammonium ions possible on different parts of the powder. The zeta potential was –27.4 mV at natural pH 5.5, thus the sample surface was negatively charged. The electrostatic attraction between the positively charged adsorbate species (NH<sub>4</sub><sup>+</sup>) and the negatively charged sample surface was favorable to adsorb NH<sub>4</sub><sup>+</sup> ions.

FT-IR analysis was carried out to identify the functional groups in BPTL that might relate to the adsorption process. As shown in Fig. 2, a number of absorption peaks in the spectrum indicate the complex nature of the adsorbent. The broad and strong band ranging from 3000 to 3700 cm<sup>-1</sup> might attribute to –OH stretching vibrations and peaks at 1319 and 1248 cm<sup>-1</sup> are resulted from bending vibration

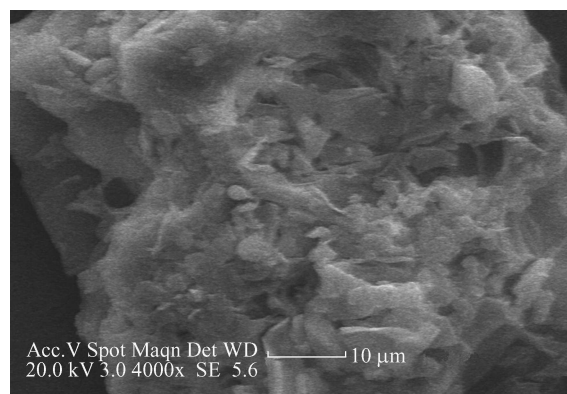


Fig. 1 SEM image of Boston ivy leaf powder (BPTL).

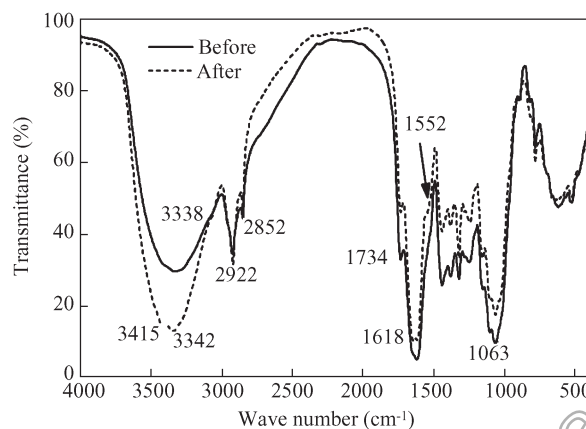


Fig. 2 FT-IR spectra of BPTL before and after ammonium adsorption.

of the surface –OH or O–H. The band around  $1618\text{ cm}^{-1}$  and peaks at  $1734\text{ cm}^{-1}$  correspond to the C=O stretching. The peaks ranging from  $1200$  to  $950\text{ cm}^{-1}$  are due to C–O stretching. The peaks at  $2922$ ,  $2852$ ,  $1441$ ,  $1381$  and  $896\text{ cm}^{-1}$  attribute to vibration of C–H or –CH (Sun et al., 2005).

Comparing with the FT-IR spectrum of adsorbent before adsorption, the spectrum of ammonium loaded adsorbent also presented integrated structure (Fig. 2). The wave numbers of BPTL shifted from  $3338$ ,  $1248$  and  $1103\text{ cm}^{-1}$  to  $3342$ ,  $1244$  and  $1101\text{ cm}^{-1}$ , respectively, after ammonium adsorption. These peaks represented –COOH and –OH groups. The mentioned total negative charge of the sample is mainly dependent on the amount of –COOH and –OH attached onto the sample surface (Feng et al., 2009). Therefore, the ammonium adsorption might relate to –COOH and –OH on the BPTL surface. In addition, there was a new peak at  $1552\text{ cm}^{-1}$  in the spectrum after adsorption. The peak at  $1552\text{ cm}^{-1}$  is an overlapped band of bending vibration of N–H and stretching vibration of C–N. It is confirmed that ammonium ions were adsorbed by BPTL.

## 2.2 Effect of pH

The effect of pH on ammonium adsorption was studied in pH range 2–12 (Fig. 3). The highest adsorption capacity was achieved at pH 7. The optimum pH range for ammonium adsorption was 5–10 in which adsorption capacities was  $3.02$ – $3.21\text{ mg/g}$ . For the pH above 10 and below 5, ammonium adsorption capacity was decreased rapidly. Low ammonium adsorption at pH below 5 might be due to the competition of  $\text{H}^+$  and  $\text{NH}_4^+$  ions for the active sites in the adsorbent surface (Karadag et al., 2007). At high pH values, ammonium ions ( $\text{NH}_4^+$ ) tend to be transformed aqueous ammonia ( $\text{NH}_3$ ). Previous studies

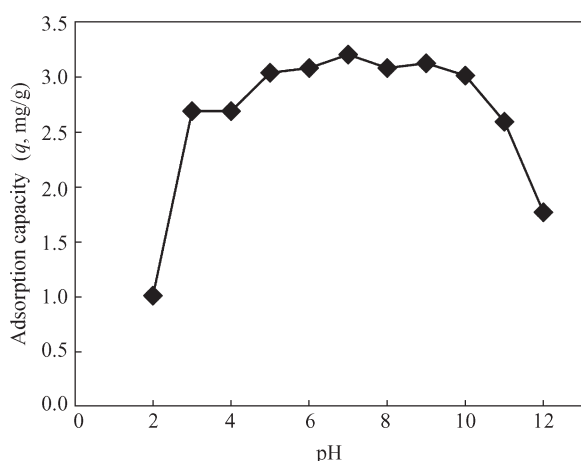


Fig. 3 Effect of pH on ammonium adsorption by BPTL.

demonstrated that the optimum pH ranges for ammonium adsorption by zeolite, clinoptilolite and volcanic tuff were 5–8, 5–7 and 7–8, respectively (Karadag et al., 2007; Ji et al., 2007; Marañón et al., 2006). The broad optimum pH of ammonium adsorption was an advantage of BPTL as a new adsorbent.

## 2.3 Adsorption isotherms

The ammonium adsorption capacity of BPTL increased with the increase of initial ammonium concentration. This could be due to the high probability of collision between ammonium ions and adsorbent surface. Langmuir and Freundlich models were used to fit the experimental data. Langmuir model usually describes monolayer adsorption and adsorption occurring on a structurally homogeneous adsorbent (Ünlü and Ersoz, 2006). Its linearized form can be expressed as Eq. (2):

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{1}{q_m}C_e \quad (2)$$

where,  $q_m$  (mg/g) indicates the maximum monolayer adsorption capacity of the adsorbent, and  $b$  (L/mg) is Langmuir constant.

For the Langmuir model, the plot of  $C_e/q$  versus  $C_e$  showed that all the correlation coefficients ( $R^2$ ) of three straight lines at 15, 25 and  $35^\circ\text{C}$  were more than 0.98 (Fig. 4), suggesting the well fit of Langmuir model. The Langmuir parameters  $q_m$  and  $b$  were calculated by the slopes and intercepts of these straight lines in the plot, and shown in Table 1.

The essential features of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor  $R_L$ , as:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

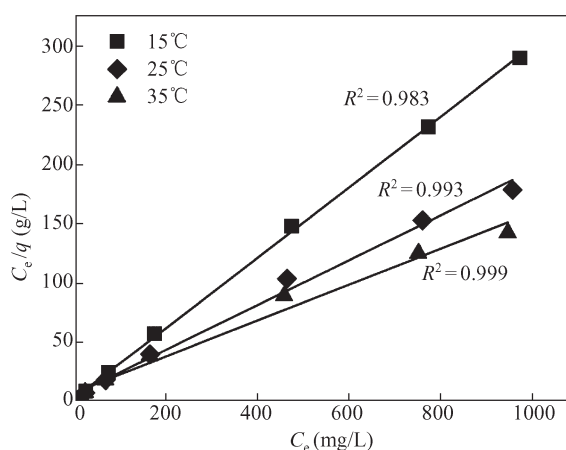


Fig. 4 Langmuir adsorption isotherms of ammonium by BPTL.

Table 1 Parameters of Langmuir and Freundlich isotherms

Temperature ( $^\circ\text{C}$ )	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$b$ (L/g)	$R^2$	$K$ (mg/g)(L/mg) $^{1/n}$	$n$	$R^2$
15	3.37	0.112	0.999	2.69	33.00	0.937
25	5.28	0.033	0.993	2.09	7.59	0.974
35	6.59	0.019	0.983	1.69	5.26	0.970

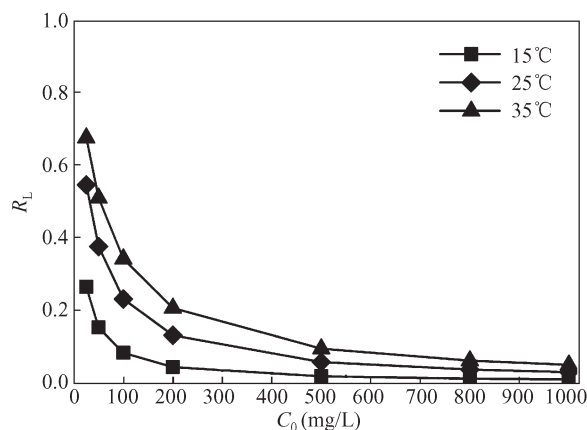
There are four probabilities for the  $R_L$  value: for favorable adsorption,  $0 < R_L < 1$ ; for unfavorable adsorption,  $R_L > 1$ ; for linear adsorption,  $R_L = 1$ ; for irreversible adsorption,  $R_L = 0$  (Ho et al., 2005). The variations in the separation factor ( $R_L$ ) with initial ammonium concentration are presented in Fig. 5.

It can be seen that the  $R_L$  values were in the range of 0–1, indicating that the adsorption of ammonium ions onto BPTL was favorable. The  $R_L$  values approached zero with increased  $C_0$  which confirmed that the adsorption of ammonium ions on the adsorbent was more favorable at high initial ammonium concentrations than at low concentrations (Ho et al., 2005). The  $q_m$  values from the Langmuir model could infer the potential maximum monolayer adsorption capacities of the adsorbent, which were 3.37, 5.28 and 6.59 mg/g at 15, 25 and 35°C, respectively. The comparison of  $q_m$  values between BPTL and natural minerals (Table 2) suggested that the ammonium adsorption capability of BPTL were comparable to those of natural mineral materials.

The Freundlich model was derived to describe multilayer adsorption and the adsorption on heterogeneous surfaces (Ünlü and Ersoz, 2006). Its linearized form is as Eq. (4):

$$\ln q = \ln K + \frac{1}{n} \ln C_e \quad (4)$$

where,  $K$  (mg/g)(L/mg) $^{1/n}$  is the Freundlich constant and  $n$  is the Freundlich exponent related to adsorption intensity.



**Fig. 5** Variation in separation factors ( $R_L$ ) with different initial ammonium concentrations.

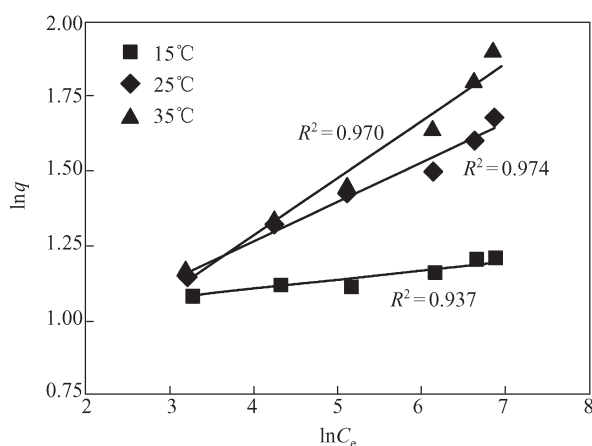
**Table 2** Maximum adsorption capabilities ( $q_m$ ) of natural low-cost ammonium adsorbents in references

Adsorbent	$q_m$ (mg N/g)	Temperature (°C)	Reference
Zeolite	8.91	25	Lebedynets et al., 2004
Zeolite	7.50	21	Saltah et al., 2007
Zeolite	4.49	30	Karadge et al., 2007
Zeolite	8.71	25	Wang et al., 2007
Zeolite	5.22	30	Liang and Ni, 2009
Clinoptilolite	5.74	21	Nguyen and Tanner, 1998
Clinoptilolite	6.32	25	Karadge et al., 2006
Clinoptilolite	4.79	40	Karadge et al., 2006
Clinoptilolite	4.02	55	Karadge et al., 2006
Mordenite	8.28	21	Nguyen and Tanner, 1998
Volcanic tuff	10.61	22	Marañón et al., 2006

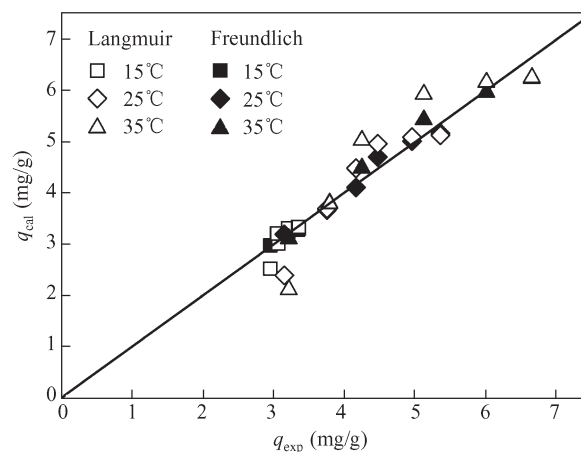
For the Freundlich model, the plot of  $\ln q$  versus  $\ln C_e$  in Fig. 6 also showed three straight lines which correlation coefficients ( $R^2$ ) were more than 0.93, suggesting that all equilibrium data could also fit to Freundlich model. It can also be seen from Table 1 that the  $n$  values were more than 1, which also showed favorable adsorption conditions (Zheng et al., 2008). This is a most common result and may be due to the distribution of surface sites or factors which could cause a decrease in the interaction between the adsorbent and the adsorbate with increasing surface density (Reed and Matsumoto, 1993). Graphical comparisons of the experimental and calculated ammonium adsorption capacities in the Langmuir model and Freundlich model are shown in Fig. 7. It appears that the Freundlich model provided a slightly more consistent fit to the data comparing with the Langmuir model. In addition, the ammonium adsorption capacity at each initial concentration increased with the temperature, indicating that the adsorption was endothermic.

## 2.4 Adsorption kinetics

The plots of ammonium adsorption capacities of BPTL with time are dramatic S-curves (Fig. 8). It seems as if the ammonium adsorption process occurred in three steps. The ammonium adsorption occurred slowly and steadily in



**Fig. 6** Freundlich adsorption isotherms of ammonium by BPTL.



**Fig. 7** Comparison of the experimental and calculated adsorption capacities in Langmuir and Freundlich model.

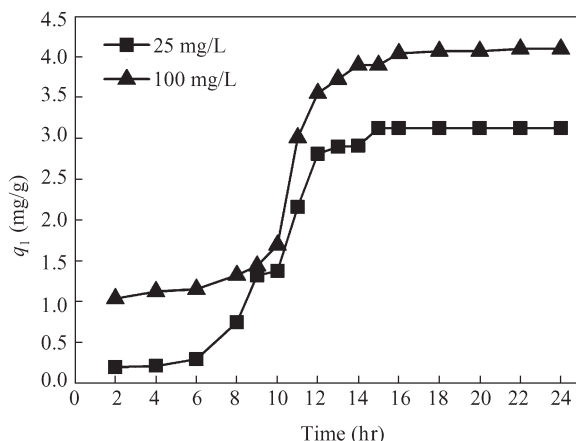


Fig. 8 Effect of contact time on ammonium adsorption by BPTL (25°C).

the first stage. The adsorption capacities increased sharply within the middle stage, and the adsorption processes reach equilibrium in 14 hr, which might be due to the saturation of the efficient active sites.

Three classic kinetic models, Lagergren pseudo first-order, pseudo second-order (Ho and McKay, 1999) and intraparticle diffusion equation (Karaca et al., 2004), are expressed as Eqs. (5), (6) and (7) respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

$$q_t = k_{id} t^{1/2} + C \quad (7)$$

where,  $k_1$  ( $\text{hr}^{-1}$ ),  $k_2$  ( $\text{g/mg}$ ) and  $k_{id}$  ( $\text{mg}/(\text{g}\cdot\text{hr}^{1/2})$ ) are pseudo first-order, pseudo second-order and intraparticle diffusion equation rate constant, respectively;  $q_e$  ( $\text{mg/g}$ ) and  $q_t$  ( $\text{mg/g}$ ) are the adsorption capacity at equilibrium and at time  $t$  (hr); and  $C$  ( $\text{mg/g}$ ) is the intercept of intraparticle diffusion equation.

The Logistic model is usually used to describe growth or diffusion with a limiting factor:

$$q_t = q_1 + \frac{q_0 - q_1}{1 + (t/t_1)^p} \quad (8)$$

where,  $q_0$  ( $\text{mg/g}$ ) and  $q_1$  ( $\text{mg/g}$ ) are the initial adsorption capacity and theoretical ammonium carrying capacity, respectively.  $t_1$  (hr) is the time when the adsorption capacity was half the value of  $q_0 + q_1$ .  $p$  is the temperature constant.

As shown in Table 3, three classic kinetic models, pseudo first-order, pseudo second-order and intraparticle diffusion equation, could not describe the kinetic data compatibly with  $R^2 < 0.86$ ,  $R^2 < 0.32$  and  $R^2 < 0.84$ , respectively. But the Logistic model could fit the kinetic data well ( $R^2 > 0.98$ ), probably because of the S-type of the kinetic plot. Considering the three stages of adsorption process, each stage was modeled with three classic models, and the correlation coefficients ( $R^2$ ) are given in Table 4. As noted above, the ammonium adsorption mostly occurred within middle stage, thus the middle stage was the key step of the process. The data of this key step could fit to intraparticle diffusion equation ( $R^2 > 0.91$ ).

There are four main stages in the process of adsorptions by porous adsorbents (Ho et al., 1996): bulk diffusion,

Table 3 Correlation coefficient ( $R^2$ ) values of kinetic models for ammonium adsorption

$C_0$ (mg/L)	Logistic	Pseudo first-order	Pseudo second-order	Intraparticle diffusion
25	0.987	0.756	0.313	0.838
100	0.992	0.857	0.101	0.802

Table 4 Correlation coefficient ( $R^2$ ) values of kinetic models for ammonium adsorption

$C_0$ (mg/L)	Period (hr)	Pseudo first-order	Pseudo second-order	Intraparticle diffusion
25	2–6	0.836	0.838	0.777
	6–12	0.759	0.862	0.914
	12–24	0.852	0.990	0.596
100	2–9	0.907	0.967	0.865
	9–12	0.929	0.889	0.936
	12–24	0.915	0.991	0.735

boundary film diffusion, intraparticle diffusion and adsorption. One or more of these four steps may control the rate and the amount of solute adsorbed onto the solid particles. Generally bulk diffusion and adsorption step are assumed to be rapid and therefore not rate determining, thus the film diffusion, intraparticle diffusion or both usually are rate controlling steps. Therefore, the modeling results of three stages indicated that the film diffusion might be the controlling-rate step of the first stage, and the intraparticle diffusion might control the rate of the middle stage in ammonium adsorption by BPTL. This is consistent with our primary results of ammonium adsorption onto other plant materials (Liu et al., 2010).

Previous study suggested the ammonium adsorption by minerals also involved three steps (Lei et al., 2008). The minerals were constructed by crystal unit of mineral compounds, such as aluminosilicate, thus the surface structure of minerals was much more regular than that of plant material, BPTL (Fig. 1). Therefore, ammonium adsorption by minerals was faster than that by BPTL in the beginning of adsorption. Because of the fast rate of the first step, the first and second steps usually were combined to one step. Therefore, most of the kinetic plots of ammonium adsorption by minerals were L-type rather than S-type. The kinetics data of ammonium adsorption by zeolite and limestone were reported well fitted the pseudo second-order equation and the intraparticle diffusion was also one of rate-controlling steps in the adsorption (Karadag et al., 2006; Lei et al., 2008).

### 3 Conclusions

The investigation of ammonium removal from aqueous solution by Boston ivy leaf powder (BPTL) as a novel adsorbent was performed. The results showed that the ammonium adsorption efficiency of BPTL was comparable with the mineral materials reported previously, and BPTL was a considerable adsorbent for ammonium removal from aqueous solution. BPTL had a porous structure mostly formed by holocellulose, lignin and protein, and was

negatively charged in solution. The optimum pH range for ammonium adsorption was 5–10. The higher temperature was favorable to the ammonium adsorption by BPTL. The equilibrium data fitted well to both the Langmuir and Freundlich model, of which the Langmuir model was best. The kinetic data were well described by Logistic model. The ammonium adsorption might relate to  $-\text{COOH}$  and  $-\text{OH}$  on the BPTL surface.

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