



## MODELING AND MECHANISM OF THE ADSORPTION OF LEAD ION ONTO NATURAL BAMBOO SAWDUST USING SURFACE COMPLEXATION MODEL

Xue-Tao ZHAO,<sup>a,b,c</sup> Cong-Yang ZOU,<sup>c</sup> Xue-Yan LI<sup>c</sup> and Hong-Wen GAO<sup>b,\*</sup>

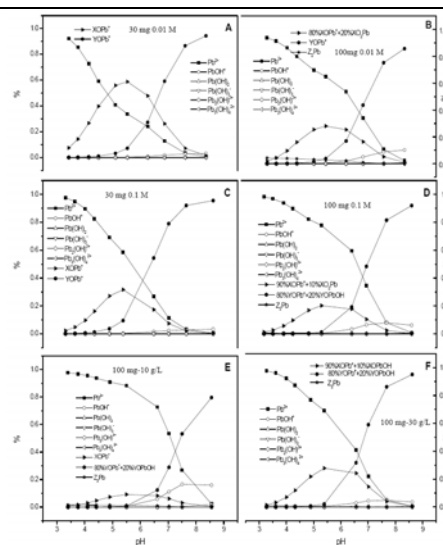
<sup>a</sup> Center for Separation and Purification Materials & Technologies, Suzhou University of Science and Technology, Suzhou, People's Republic of China

<sup>b</sup> State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China

<sup>c</sup> School of Environmental Science and Engineering, Suzhou University of Science and Technology, People's Republic of China

Received November 6, 2014

Adsorption technology is a kind of effective and practical purifying water and wastewater treatment technology. In the present study, natural bamboo sawdust as an adsorbent was used to adsorb lead ions from aqueous solutions with 0.01 or 0.1M potassium nitrate solution as background solution. pH edge curves showed that lead ions adsorption quantity increased with the rise of pH and initial lead ions concentration. The rise of ionic strength suppressed lead ions adsorption, but when the pH was above 7, the impact was negligible. NEM (the non-electrostatic mode) surface complexation model was used to fit pH edge curves. The fitting results showed that the proportion of potassium ion exchange reaction was relatively lower. Under high lead concentration and high ionic strength, the fitting result incorporating the hydroxospecies was better, indicating that nitrate ion participated in adsorption reaction. When pH was less than 6, low protons affinity sites played a leading role in the combination of lead ions. When pH was more than 6, the proportion of high protons affinity site increased gradually in the combination of lead ions.



## INTRODUCTION

With the rapid development of modern industry, the discharge of heavy metal from the production process has become a major environmental concern. Lead is one of the most toxic heavy metals which is released continuously from different industries, such as battery, mining, lead smelting, metal plating, paper and pulp, metallurgical finishing and metal processing into

the environment.<sup>1,2</sup> Unlike most organic pollutants, heavy metal can easily enter the food chains because of the toxic effects, non-biodegradability and accumulation in living tissues. Among the heavy metals, lead (Pb) is one of the non-essential trace elements and cause anemia, kidney malfunction, tissue damage of brain and even death in extreme poison.<sup>3-5</sup>

Various methods have been proposed for the treatment of lead-contaminated water such as

\* Corresponding author: [emsl@tongji.edu.cn](mailto:emsl@tongji.edu.cn)

chemical precipitation, electrochemical reduction, ion exchange and adsorption.<sup>6</sup> Among these treatment methods, the adsorption process is widely used for the removal of diverse contaminants.<sup>7</sup> Commercial activated carbon is a preferred adsorbent used to remove impurities from liquid solutions; however, its widespread use is restricted due to the high cost. As such, abundant research has been conducted to seek more cost-effective adsorbents for the removal of pollutant.<sup>8,9</sup>

Among these low-cost adsorbents, bamboo sawdust has received particular attention as an economical adsorbent for removing copper(II)<sup>10,11</sup> and zinc (II)<sup>12</sup> ions from aqueous solutions due to its abundance and low cost. In this paper, we use bamboo sawdust as a natural adsorbent to remove lead ion in water. Bamboo sawdust used in this study is not chemically modified to maintain its low cost.

Adsorption strongly depends on the charging status of adsorbent's surface. To explain the adsorption mechanism at the solid–aqueous interface, the non-electrostatic model (NEM) surface complexation model was utilized to interpret and predict the interfacial phenomena in previous paper of this series.<sup>10,13</sup> The intrinsic acidity constants and the density of different surface functional groups were obtained in the paper (Table 2 of reference 13). For these sites, the binding of proton and metal ions are closely related. Based on the series of articles published before,<sup>10,13</sup> the fitting data with alkali side pH 3.5 as starting point were chosen for lead ions adsorption fitting in the paper (Table 2 of reference 13). The proton binding constants and site density obtained from the paper,<sup>13</sup> were used as known parameters for lead ion pH edge adsorption curves fitting, and parameters such as lead ion binding constants and coordination numbers can be predicted by the software FITEQL 4.0.<sup>14</sup> This program solves the equilibrium model at each data point and optimizes adjustable parameters until the sum of the squares of the residuals (WSOS/DF) between the measured data and the calculated values is minimized.

## MATERIALS AND METHODS

### 1. Materials and reagents

Bamboo sawdust was obtained from a timber mill in South China. Bamboo sawdust was dried in

an oven at 70°C for 24 h, and then grounded and screened through a set of sieves to get particles with geometrical size from 100 to 200 μm. All solutions were prepared from de-ionized water, and chemicals were from Sinopharm Chemical Reagent Co. Ltd. Stock solution of Pb (II) ions with a concentration of 5000 mg/L was prepared by dissolving nitrate lead using high-purity (A.R.) reagents in de-ionized water, and adjusted to pH 2 before usage.

### 2. Sorption studies

All adsorption experiments were performed on a mechanical shaker equipped with a thermostatic air bath at 20 °C using 250 mL conical flasks. 50 ml of a certain concentration of KNO<sub>3</sub> solution (0.01M or 0.1M) and a certain amount of sawdust (20 g/L) were mixed together in 150 ml conical flask. The solution was first titrated into pH 3.5 with 0.1M HNO<sub>3</sub> solution, and then titrated into pH between 3.5~8 with 0.1M KOH solution. A certain amount of Pb<sup>2+</sup> (30mg/L or 100mg/L) were added into the solution. After 4h, adsorption equilibrium was reached. The initial and final pH was measured, and the supernatant was filtered through a 0.45-μm cellulose acetate membrane. The Pb concentration in the filtrate was determined by AAS (type AA-400, Perkin-Elmer Corporation). The above experiment was repeated with the sawdust concentration of 10 g/L and 30 g/L and with 0.1M KNO<sub>3</sub> concentration.

Mass of solute adsorbed per mass of adsorbent at equilibrium (mol/kg) was computed using the equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

The percentage of metal sorption by the adsorbent was computed using the equation (2):

$$\text{adsorption percentage}(\%) = \frac{C_0 - C_e}{C_i} \quad (2)$$

where, “W” is adsorbent dosage (kg), “V” is volume of aqueous solution (L), C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentration of lead ions (mol/L) in the solution.

### 3. Non-electrostatic surface complexation model

A non-electrostatic surface complexation model<sup>15,16</sup> was used to describe the lead ion

adsorption data. Proton dissociation from ligands on sawdust surfaces can be described by equilibrium reaction (3) in Table 1. The concentration of proton binding surface sites and the acidity constants can be quantified with the corresponding mass action equation which had been done in previous paper.<sup>10</sup> The ligands on sawdust surfaces are mainly composed of high proton affinity site (expressed as "YOH"), low proton affinity site (expressed as "XOH"), and permanently charged site (expressed as "ZK"). The possible complexation reaction of lead ion with sawdust can be described by the following equilibrium reactions (4)–(7) in Table 1. The nonlinear least-squares fitting program, FITEQL 4.0<sup>14, 17</sup> was used to fit adsorption data.

## RESULTS AND DISCUSSION

As shown in Fig. 1, adsorption for lead ion has similar changing rule with copper ion.<sup>10</sup> The adsorbed quantity of lead ion increased with the rise of pH, sawdust concentration and initial lead ion, and decreased with the rise of ion strength. When pH was more than 7, adsorption curves for different ion strength got together, suggesting that ion strength affected slightly. Even for individual data points, the adsorbed quantity for "0.1 M" system was higher than that of "0.01 M" system. When the initial concentration of lead ions increased from 30 mg/L to 100 mg/L, the adsorption

driving force increased, and the adsorption quantity per unit of sawdust increased, but adsorption percentage became lower (Fig. 2). When the concentration of sawdust increased, the adsorbed quantity per unit of sawdust decreased. But when pH was less than 7, such change trend is not obvious.

pH dependence of lead ion adsorption can also be reflected by pH edge curves shown in Fig. 1. Interestingly, a review of Dzombak and Morel<sup>17</sup> showed that out of 184 cation and anion adsorption data that can be described by surface complexation models, 83% were pH sorption edges and the rest 17% were equilibrium isotherms. This indicates that the adsorption equilibrium constants of the surface complexation models cannot be applied to wider ranges of metal concentrations. In this study, lead adsorption isotherms has also been attempted to be fitted using surface complexation models, but the fitting was poor (not shown in the paper).

Lead generates a series of hydrates in aqueous solution, and their main forms are  $Pb^{2+}$ ,  $PbOH^+$ ,  $Pb(OH)_2$ ,  $Pb(OH)_3^-$ ,  $Pb_3(OH)_4^{2+}$ ,  $Pb_4(OH)_4^{4+}$ ,  $Pb_6(OH)_8^{4+}$ .<sup>18</sup> All these hydrate forms were included when pH edge curves were fitted with surface complexation model using FITEQL software. Among these hydrates, apart from  $Pb^{2+}$ ,  $PbOH^+$ , other hydrate ion had negligible impact on the fitting result. This reflected that their concentration was too low, or it was hard for them in combination with sawdust.

Table 1

Surface complexation reaction

Species	Mass action relation	Equilibrium constant
$SO$	$SOH \rightleftharpoons SO^- + H^+$	$K_{SO} = \frac{[SO^-][H^+]}{[SOH]}$ (3)
$SOPb$	$SOH + Pb^{2+} \rightleftharpoons SOPb + H^+$	$K_{SOPb^+} = \frac{[SOPb^+][H^+]}{[SOH][Pb^{2+}]}$ (4)
$(SO)_2Pb$	$2 SOH + Pb^{2+} \rightleftharpoons (SO)_2Pb + 2H^+$	$K_{(SO)_2Pb} = \frac{[(SO)_2Pb][H^+]^2}{[SOH]^2[Pb^{2+}]}$ (5)
$SOPbOH$	$SOH + Pb^{2+} + H_2O \rightleftharpoons SOPbOH + 2H^+$	$K_{SOPbOH} = \frac{[SOPbOH][H^+]^2}{[SOH][Pb^{2+}]}$ (6)
$Z_2Pb$	$2 ZK + Pb^{2+} \rightleftharpoons Z_2Pb + 2K^+$	$K_{Z_2Pb} = \frac{[Z_2Pb][K^+]^2}{[ZK]^2[Pb^{2+}]}$ (7)

where ">SOH" represents both high proton affinity sites and low proton affinity sites, ">ZK" represents permanently charged sites, "{}" represents activity and "[ ]" represents concentration.

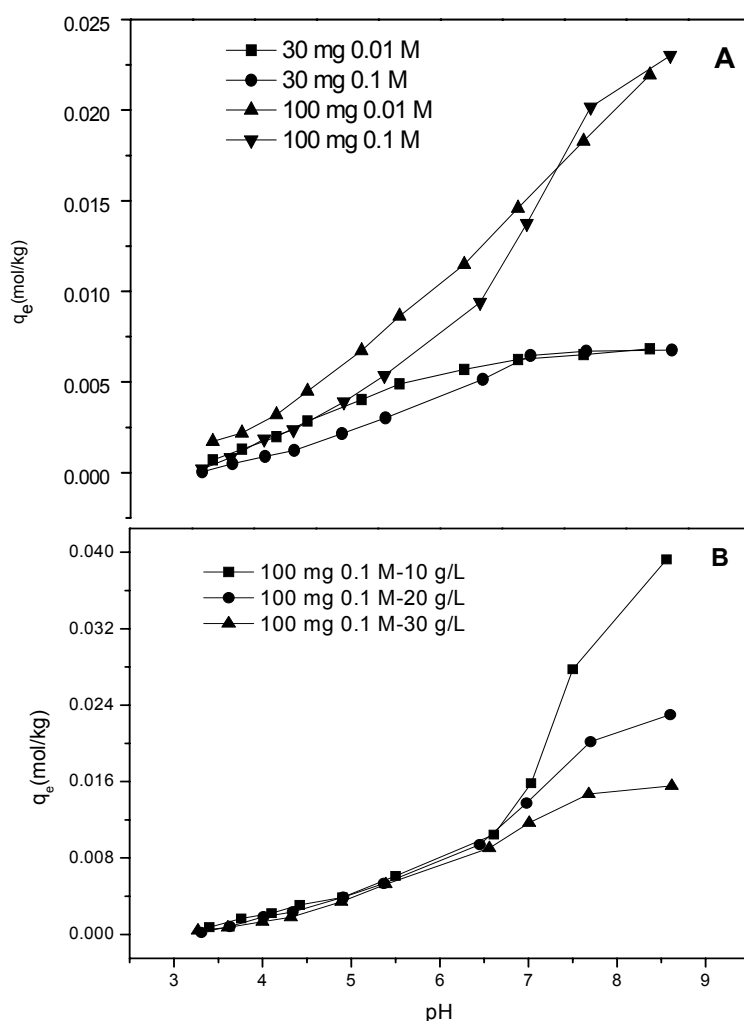


Fig. 1 –  $Pb^{2+}$  adsorption with the change of pH: A. with the initial lead ions concentration and ionic strength changed, B. with sawdust concentration changed

Annotation: for Sample “100 mg 0.1 M- 30 g/L”, “100 mg” represents the initial lead ion concentration, “0.1 M” represents potassium nitrate concentrations, “30 g/L” represents sawdust concentration. Other with, hereinafter the same.

With the rise of pH, there will be a lot of hydrated ion found in aqueous solution. The fitting results without incorporating hydrates were shown in Table 2, while the fitting results incorporating certain proportion of hydration ion  $PbOH^+$  (20~30%) participating in the reaction were shown in Table 3. With the complex “YOPbOH” participating in fitting, the absolute value of the fitting constant of “YOPb<sup>+</sup>” became bigger, indicating that the binding force between  $YO^-$  and  $PbOH^+$  was stronger. However, incorporating “YOPbOH” did not always improve fitting result according to Tables 2 and 3. In contrast, it was found that the fitting result which had lower

WSOS/DF in Table 2 was better than that in Table 3 for the sample “30 mg 0.01 M”, “100 mg 0.01 m”, “30 mg 0.1 m”, while the fitting result in Table 3 was better than that in Table 2 for the sample “100 mg 0.1 M”, “100 mg 0.1 M-10 g/L” and “100 mg 0.1 M-30 g/L”. Thus, it could be concluded that no complex “YOPbOH” form in the condition of low ionic strength and low lead concentrations. Under high  $Pb^{2+}$  concentration and ionic strength, high nitrate ion concentration could promote the combination of hydrated ion with high proton affinity sites, and thus an extra reaction may form. The reaction could be described as follows:



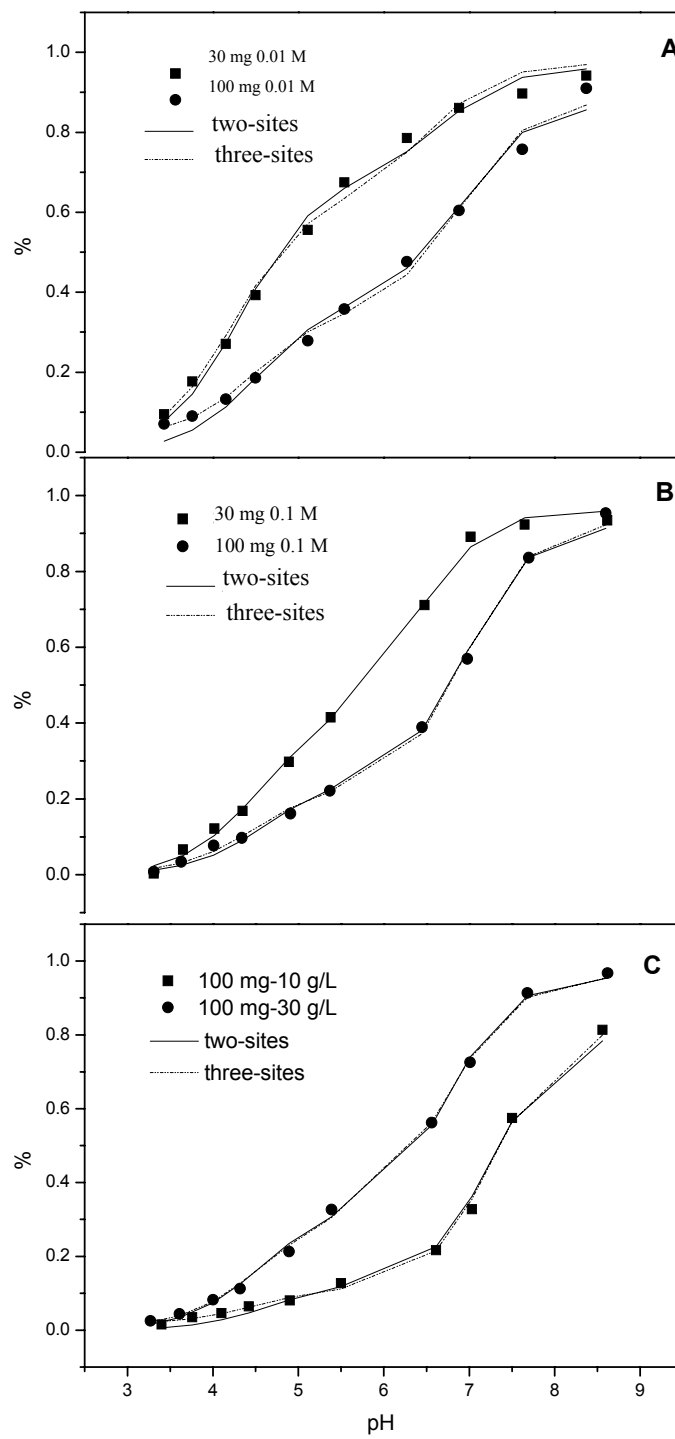


Fig. 2 – Fitting curve of  $Pb^{2+}$  adsorption pH edge curves by surface complexation model: A. 0.01 M  $KNO_3$ , B. 0.1 M  $KNO_3$ , C. with sawdust concentration changed.

Table 2

Fitting parameter of surface complexation models of Pb<sup>2+</sup> adsorption pH edge curves

Pb adsorption sample		logK <sub>XOPb+</sub>	logK <sub>YOPb+</sub>	logK <sub>Z2Pb</sub>	WSOS/DF	Note
<b>30mg</b>	Two-sites	-1.38	-3.39		1.61E-05	<b>Fig.2A</b>
<b>0.01M</b>	Three-sites	-1.23	-3.30	4.71	2.39E-05	<b>Fig.2A</b> <b>Fig.3A</b>
<b>100mg</b>	Two-sites	-1.83	-3.96		2.67E-04	<b>Fig.2A</b>
<b>0.01M</b>	Three-sites	-1.64	-3.97	5.13	2.26E-04	
<b>30mg</b>	Two-sites	-1.84	-3.49		7.39E-06	<b>Fig.2B</b>
<b>0.1M</b>	Three-sites				cannot be fitted	<b>Fig.3C</b>
<b>100mg</b>	Two-sites	-2.20	-4.08		4.21E-04	
<b>0.1M</b>	Three-sites	-2.00	-4.12	4.58	3.47E-04	
<b>100mg</b>	Two-sites	-2.33	-4.19		6.60E-04	
<b>0.1M</b>	Three-sites	-2.37	-4.23	5.74	5.05E-04	
<b>-10g/L</b>						
<b>100mg</b>	Two-sites	-2.18	-4.02		1.77E-04	
<b>0.1M</b>	Three-sites				cannot be fitted	
<b>-30g/L</b>						

Table 3

Fitting parameter of surface complexation model of Pb<sup>2+</sup> adsorption pH edge curve incorporating other complex forms

Pb adsorption sample		logK <sub>XOPb+</sub>	logK <sub>YOPb+</sub>	logK <sub>Z2Pb</sub>	WSOS/DF	Note
<b>30mg</b>	Two-sites	-1.62	-4.91		3.92E-05	
<b>0.01M</b>	Three-sites	(20%XO <sub>2</sub> Pb)	(20%YOPbOH)	5.48	3.25E-05	
<b>100mg</b>	Two-sites	-2.08	-5.49		3.58E-04	
<b>0.01M</b>	Three-sites	(20%XO <sub>2</sub> Pb)	(20%YOPbOH)	5.41	1.97E-04	<b>Fig.2A</b> <b>Fig.3B</b>
<b>30mg</b>	Two-sites	-1.79	-5.50(30%YOPbOH)		1.71E-05	
<b>0.1M</b>	Three-sites				cannot be fitted	
<b>100mg</b>	Two-sites	-2.13	-5.56(20%YOPbOH)		8.60E-05	<b>Fig.2B</b>
<b>0.1M</b>	Three-sites	-2.04	-5.59	4.27	7.33E-05	<b>Fig.2B</b> <b>Fig.3D</b>
<b>100mg</b>	Two-sites	-2.19	-5.72		1.00E-04	<b>Fig.2C</b>
<b>0.1M</b>	Three-sites	-2.02	-5.77	5.40	4.63E-05	<b>Fig.2C</b> <b>Fig.3E</b>
<b>100mg</b>	Two-sites	-2.13	-5.44		5.02E-05	<b>Fig.2C</b>
<b>0.1M</b>	Three-sites	-	-5.52	4.16	4.82E-05	<b>Fig.2C</b>
<b>30g/L</b>	Three-sites	2.43(10%XOPbOH)	(20%YOPbOH)			<b>Fig.3F</b>

In this reaction, nitrate ions form inner complex. Some other scholars put forward a similar reaction. Gunneriusson<sup>19</sup> performed a research about lead ions adsorption by ferric oxide and found that the complex "> FeOPbOHCl" formed, and the difference was just that the

chloride ion participated in reaction. Sarkar<sup>20</sup> applied TLM surface complex model to fit pH edge curves of mercury ion adsorbed by silica and alumina ore, and a better fitting result was found incorporating the complex "> SOHgOHCl" under high pH.

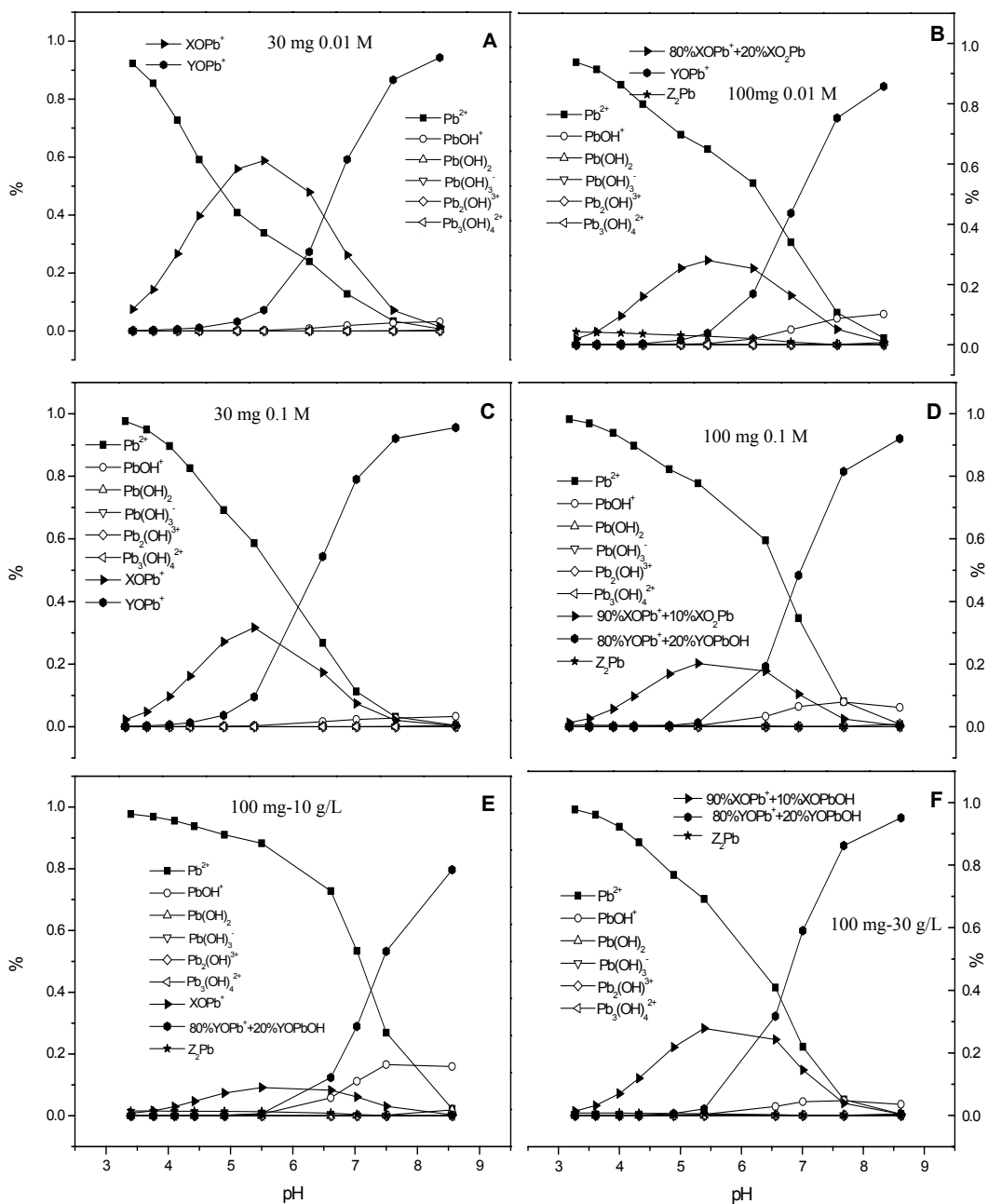


Fig. 3 – Speciation diagram of lead ion adsorption: A. 30 mg 0.01 M, B. 100 mg 0.01 M, C. 30 mg 0.1 M, D. 100 mg 0.1 M, E. 100 mg-10 g/L, F. 100 mg- 30 g/L.

In addition, the fitting result showed that  $PbOH^+$  tended to combine with high proton affinity sites, and the fitting result incorporating complex “XOPbOH” was far worse than that incorporating YOPbOH (not shown in the table). From Table 3, bi-dentate complexation was found in binding with a certain percentage of the low proton affinity sites. For the sample "100 mg 0.01 M", a good

fitting result was found, indicating the existence of bi-dentate complexation. Bi-dentate complex occurs mainly in 0.01 M  $KNO_3$  system.

As shown in Tables 2 and 3, three-sites model had a better fitting effect than two-sites model. This suggested that between lead ions and permanently charged sites, ion exchange reactions could occur, substituting for potassium ion. Ion

exchange reaction constant  $\log K_{Z_2Pb}$  ranged from 4 to 6, indicating this binding force was weaker than that of other lead ion complexing reaction. Unlike copper ion exchange reaction<sup>10</sup> with permanently charged site, lead ion concentration and ionic strength affected the reaction greatly. For the sample "30 mg 0.01 M", three-sites model incorporating ion exchange reaction of permanent charge did not fit data better than two-sites model.

When the concentration of lead ions increased up to 100 mg/L, the reaction driving force increased. At this time, the advantage of three-sites model showed up finally. From Fig. 3B, it was found that about 5 to 10% of lead ion participated in ion exchange reaction in ZK site under low pH. Under the condition of 0.1 M  $KNO_3$ , the driving force of reaction became lower. For the sample "30 mg 0.1 M", the data cannot even be fitted, and in Fig. 3 C, D, E and F,  $Z_2Pb$  mole fraction was much smaller. Overall, the ability of lead ion which substituted for potassium ion in permanent charge site was weaker than that of copper ion.<sup>10</sup>

From Fig. 3, it was found that species "XOPb<sup>++</sup>" usually played a leading role under low pH, and species "YOPb<sup>++</sup>" gradually owned higher percentage of lead ions adsorption when pH was above 6. By comparing the adsorption constant in Tables 2 and 3, the binding strength of lead ion with high proton affinity sites was higher than with low proton affinity sites. But lead ion adsorption was mainly affected by the protons in the surface sites of sawdust. Under low pH, high proton affinity sites were occupied by hydrogen ions and cannot adsorb lead ion.

By comparing sub-Figs. 3 A, B, C and D, it was found that the competitive ability of lead ion against hydrogen ion improved, binding percentage of high proton affinity site increased, and the proportion of species "XOPb<sup>++</sup>" was on the decline with the rise of initial lead ion. Same reason can be

applied to explain sub-Figs. 3 E, F. The increase of sawdust concentration mean the increase of adsorption sites.

For site density of per unit sawdust, lead ion competitive ability decreased instead, which gave rise to the decline of binding proportion of high proton affinity sites. The influence of ion strength indicated that among the binding between low proton affinity site and lead ion, a certain proportion of binding can be attributed to outer complexation which tended to be affected by  $KNO_3$  concentration. This can be used to explain why the influence of ion strength on adsorption became smaller under high pH in Fig. 1A. This was due to the fact that lead ion adsorption by high proton affinity site was mainly inner complexation. Or another possibility may exist that the presence of nitrate ions contributed to  $PbOH^+$  adsorption by high proton affinity site (equation 8).

Table 4 showed pH change before and after lead ions adsorption. Under high pH, due to low hydrogen ion concentration in aqueous solution, hydrogen ion replaced by lead ion affected the pH greatly in aqueous solution; under low pH, due to high hydrogen ion concentration in aqueous solution, hydrogen ion replaced by lead ion affected the pH slightly in aqueous solution. The last line in Table 4 showed the sum of pH difference of each series before and after adsorption. On the whole, with the increase of initial concentration of lead ion, the pH change before and after adsorption became a little bigger, since more lead ions were replaced by hydrogen ion. The higher the ionic strength was, the smaller the hydrogen ion activity was, the higher the stability of pH value in aqueous solution was, and the smaller effect on pH the hydrogen ion replaced had. The higher the concentration of sawdust was, the better buffer the solution owned, and thus the smaller the change of pH was.

Table 4

pH value of corresponding points of  $Pb^{2+}$  adsorption pH edge curve before and after adsorption

serial number of data points	30mg 0.01M		100mg 0.01M		30mg 0.1M		100mg 0.1M		100mg 0.1M 10g/L		100mg 0.1M 30g/L	
	before	after	before	after	before	after	before	after	before	after	before	after
1	8.37	7.25	8.37	6.52	8.62	7.61	8.6	7.36	8.56	7.02	8.62	7.51
2	7.62	6.77	7.62	6.03	7.65	7.21	7.7	6.72	7.5	6.5	7.68	6.88
3	6.88	6.16	6.88	5.54	7.02	6.56	6.98	5.98	7.03	6.01	7.01	6.09
4	6.27	5.7	6.27	5.21	6.48	5.98	6.45	5.57	6.61	5.64	6.56	5.71
5	5.54	5.23	5.54	4.91	5.38	5.2	5.37	5.05	5.5	5.09	5.39	5.08
6	5.11	4.81	5.11	4.66	4.89	4.81	4.91	4.73	4.9	4.7	4.89	4.73



Table 4 (continued)

7	4.5	4.32	4.5	4.2	4.37	4.35	4.34	4.28	4.42	4.32	4.32	4.25
8	4.15	4	4.15	3.94	4.09	4.08	4.01	4	4.1	4.04	4	3.98
9	3.76	3.69	3.76	3.65	3.73	3.72	3.67	3.67	3.76	3.74	3.65	3.64
10	3.43	3.4	3.43	3.38	3.39	3.39	3.36	3.36	3.42	3.42	3.33	3.33
the sum of difference	4.3		7.59		2.71		4.67		5.32		4.25	

## CONCLUSIONS

In the present study, batch adsorption experiments for the adsorption of lead ions from aqueous solutions have been performed with natural bamboo sawdust as adsorbent. The adsorption characteristics have been evaluated by pH edge curves which are fitted by NEM surface complexation model at different pH values, initial lead ion concentrations, and different adsorbent dosage levels. The conclusion can be shown as follows.

Lead ion adsorption by natural bamboo sawdust strongly depended on such variables as pH, initial lead ion, ion strength, sawdust concentration. Lead ions adsorption quantity increased when pH and initial lead ions concentration increase. The rise of ionic strength suppressed lead ions adsorption, but when the pH was above 7, the impact was negligible. This indicated that the complex with high proton affinity sites was mainly inner complex, and a certain proportion of outer complex form in low proton affinity sites.

The pH edge curve fitting results showed that the proportion of lead ions which participated in ion exchange reaction with potassium ion was lower than that of copper ion at low pH. Under high lead ion and high ionic strength, taking into account the lead (II) nitrate hydroxoquation complex formation, gave a better fitting result, suggesting that nitrate ion participated in reaction. When pH was less than 6, the combination of low proton affinity sites and lead ions played a leading role, while when pH was more than 6, the binding percentage of high proton affinity sites increased gradually. Under the condition of certain pH and ionic strength, a better fitting result can be obtained by incorporating certain percentage of hydrated ion  $PbOH^+$  or bi-dentate adsorption reaction, reflecting the complexity of the lead adsorption mechanism.

*Acknowledgements:* This research was supported by funding from the National Natural Science Foundation of China (grant no. 51108291) and the open topic for Key

Laboratory of Environmental Science and Engineering of Jiangsu Province of China (grant no. Zd131204).

## REFERENCES

- H. B. H. Ahmad, K. Mohammad, S. Masoud, A. Heydarbeigi, S.H. Hosseini, M. Nedaie and H. Shoghi, *Chem. Eng. Res. Des.*, **2014**, *92*, 581-591.
- C. K. Singh, J. N. Sahu, K. K. Mahalik, C. R. Mohanty, B. R. Mohan and B. C. Meikap, *J. Hazard. Mater.*, **2008**, *153*, 221-228.
- E. I. Ugwuja, U. A. Ibiom, B. N. Ejikeme, J. A. Obuna and K. N. Agbafor, Blood Pb Levels in pregnant Nigerian women in Abakaliki, South-Eastern Nigeria, *Environ. Monit. Assess.*, **2013**, *185*, 3795-3801.
- K.S. Rao, P.K. Dash, D. Sarangi, G.R. Chaudhury and V.N. Misra, *J. Chem. Technol. and Biot.*, **2005**, *80*, 892-898.
- S. Tunali, T. Akar, A.S. Ozcan, I. Kiran and A. Ozcan, *Sep. Purif. Technol.*, **2006**, *47*, 105-112.
- Y. Huang, S.X. Li, J.H. Chen, X.L. Zhang and Y.P. Chen, *Appl. Surf. Sci.*, **2014**, *293*, 160-168.
- D. Zhou, L.N. Zhang, J.P. Zhou and S.L. Guo, *Water. Res.*, **2004**, *38*, 2643-2650.
- A. Demirbas, *J. Hazard. Mater.*, **2008**, *157*, 220-229.
- D. Sud, G. Mahajan and M.P. Kaur, *Bioresour. Technol.*, **2008**, *99*, 6017-6027.
- X.T. Zhao, T. Zeng, X.Y. Li, Z. J. Hu, H.W. Gao and Z. Xie, *Carbohydr. Polym.*, **2012**, *89*, 185-192.
- X.T. Zhao, T. Zeng, X. Y. Li and H.W. Gao, *J. Dispersion Sci. Technol.*, **2015**, *36*, 703-713.
- O. Sulaiman, N. S. Ghani, M. Rafatullah, R. Hashim, and A. Ahmad, *J. Dispersion Sci. Technol.*, **2011**, *32*, 583-590.
- X.T. Zhao, T. Zeng, Z.J. Hu, H.W. Gao and C.Y. Zou *Carbohydr. Polym.*, **2012**, *87*, 1199-1205.
- A. Herbelin and J. Westall, FITEQL: A computer Program for determination of chemical equilibrium constants from experimental data. Version 4.0. Corvallis, OR: Department of Chemistry, Oregon State University, **1999**.
- M. Kohler, G. P. Curtis, D.E. Meece and J.A. Davis, *Environ. Sci. Technol.*, **2004**, *38*, 240-247.
- N. Marmier and F. Fromage, *J. Colloid. Interf. Sci.*, **1999**, *212*, 252-263.
- D.A. Dzombak and F.M.M. Morel, "Surface Complexation Modeling: Hydrous Ferric Oxide", New York: Wiley, 1990, p. 1-393.
- C. F. Baes and J. R. E. Mesmer, "The hydrolysis of cations", New York: John Wiley, 1976, p. 1-489.
- L. Gunneriusson, L. Lovgren and S. Sjoberg, *Geochim. Cosmochim. Acta*, **1994**, *58*, 4973-4983.
- D. Sarkar, M.E. Essington and K.C. Misra, *Soil Sci. Soc. Ant. J.*, **1999**, *63*, 1626-1636.

