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Modeling and mechanism of the adsorption of proton onto natural bamboo sawdust

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ABSTRACT

Natural bamboo sawdust with cellulose–lignin polymeric structure was used as a raw adsorbent to remove heavy metal and dyes in water. The analysis of surface properties showed that high proton affinity sites were mainly composed of phenolic and alcohol hydroxyl, while low proton affinity sites mainly consisted of carboxylic acid, silicon hydroxyl, aluminum hydroxyl and some low densities of sulfhydryl and phosphoryl groups. The results fitted by NEM surface complexation model showed: three-sites model fitted acid–base titration data better than two-sites and one-site model. Acid–base titration experiments showed the amount of acid and base consumed was not uniform between acid and alkali side. This was probably due to the swelling of cellulose in acid side, but the possibility that different reactions occurred in acid and alkali side cannot be completely excluded. Pznpc of sawdust was between pH 5.2 and 5.5.

1. Introduction

With the rapid development of modern industry, the discharge of heavy metal and dye wastewater from the production process has become a major environmental concern. The treatment of low-concentration wastewater is often difficult. As such, adsorption becomes an alternative and has grown into one of the most versatile processes. The most widely used adsorbent is activated carbon. However, its operation and maintenance cost is relatively high. Recently, abundant research has been conducted to seek more cost-effective adsorbents for the removal of pollutants. Sawdust is one of the promising materials which can be used to adsorb heavy metals (Ahmed, 2011; Lee, 2001; Naiya, Hattacharya, & Das, 2008; Sciban, Radetic, Kevresan, & Klašnja, 2007;Shukla, Zhang, Dubey, Margrave, & Shukla, 2002; Yasemin & Zek, 2007), dye (Batzias & Sidiras, 2005; Ferrero, 2007; Ofomaja, 2008; Özacar & Şengil, 2005) and some other organic contaminants (Ofomaja & Unuabonah, 2011; Ye et al., 2010) from water.

To better understand the adsorption of metal ions and dyes on natural sawdust, detailed information is required on the constitutive moieties of functional groups involved in the complexation reactions. The sorption characteristics of sawdust strongly depend on its charging status controlled by the types and numbers of functional groups on its surface. In this paper, surface complexation model was used to account for the surface property and reactivity of sawdust because it offered a specific mechanism by explaining surface chemical reactions with a set of thermodynamic constants. This model has been successfully applied to explain the sorption reaction of natural polysaccharide (Guo, Zhang, & Shan, 2008; Reddad, Cerente, Andres, & Clolrec, 2002), and wheat bran (Ravat, Dumonceau, & Monteil-Rivera, 2000).

It is well known that the binding of proton and metal ions and dyes are closely related (Ravat et al., 2000). But few research was conducted to study the proton binding property of sawdust. Natural bamboo sawdust is mainly composed of cellulose, hemicellulose and lignin. Among them, cellulose and hemicellulose, which account for about 50% of the dry matter, are complex carbohydrate polymers as the major constituents. The study not only lays the theoretical ground for the application of other sawdust adsorption materials, but also provides reference for that of agricultural waste with cellulose or lignin as the main components, such as waste tea leaves (Ahluwalia & Goyal, 2005), rice bran (Montanher, Oliveira, & Rollemberg, 2005; Singh, Rastogi, & Hasan, 2005; Sud, Mahajan, & Kaur, 2008;), bran shell, coconut fiber (Shukla & Pai, 2005) and cob (Khan & Wahab, 2006; Ngah & Hanafiah, 2008) in heavy metal removal and apple pomace, wheat straw (Robinson, Chandran, Naidu, & Nigam, 2002) and husk (Robinson, Chandran, & Nigam, 2002) in dyes removal.

In contrast to most other plants which need to grow for 10–100 years, bamboo is a fast-growing and renewable resource, which becomes mature in 4–6 years. Additionally, the wood processing in industrial and agricultural production often generates a massive amount of sawdust that needs to be reused. In view of this, we choose bamboo sawdust as a natural adsorbent for study. Bamboo sawdust used in this study is not chemically modified to maintain its low cost.

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Table 1
Acid–base titration surface complexation reaction.

Species	Mass action relation	Equilibrium constant	
$>XOH_2^+$	$>XOH + H^+ \Leftrightarrow >XOH_2^+$	K_1^+	(2)
$>XO^-$	$>XOH \Leftrightarrow >XO^- + H^+$	K_1^-	(3)
$>YO^-$	$>YOH \Leftrightarrow >YO^- + H^+$	K_2^-	(4)
>ZH	$>Z^- + H^+ \Leftrightarrow >ZH$	K_{ZH}	(5)
>ZK	$>ZH + K^+ \Leftrightarrow >ZK + H^+$	K_{ZK}	(6)
>ZH	$>ZK + H^+ \Leftrightarrow >ZH + K^+$	K_{ZH}	(7)

2. Materials and methods

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.

2.1. Acid–base titration

Experiments were fully automated by computer-controlled Metrohm 798 microprocessor pH meter. All potentiometric titration experiments were performed in a thermo-stated cell at 22 ± 1 °C under a nitrogen stream, using a glass electrode paired with an internal calomel electrode. One gram of sawdust was added into a 100 mL beaker and fully mixed with 50 mL 0.01, 0.1 or 1 M KNO_3 solution. The pH of solutions under different ionic strength was approximately 5.5 (acid side starting point). The sawdust suspension was first titrated to pH 3.5 (alkali side starting point) by HNO_3 solution and then to pH 10.5 by KOH solution. The titration rate was adjusted with a stability criterion of less than 0.01 pH unit. The total titration time was approximately 5 h. With the same titration method, the above experiments were repeated with no addition of sawdust.

2.2. Sawdust chemical and physical properties analysis

The elements and their contents in sawdust were analyzed by X-ray fluorescence (SRS3400 type, Bruker AXS corporation in Germany).

Infrared spectral analysis was done by using solid presser method. The data from 500 to 4000 cm^{-1} spectral range was collected by an infrared spectrometer (Nicolet 5700, Nicolet company in USA). Nine alkali side experimental data points of titration experiment were used for Zeta potential analysis. After titration, the pH of suspension was measured by pH meter and the supernatant was removed for zeta potential measurements after 10 min by zeta potential analyzer (Zetasizer Nano Z type, Malvern Instruments Ltd.).

3. Results and discussion

Since constant capacity model, diffusion layer model and three layer model were unable to fit the data well, this paper adopted the non-electrostatic model (NEM) (Kohler, Curtis, David, Meece, & Davis, 2004; Marmier & Fromage, 1999) to fit the data. Equilibrium constants and mass action relation were summarized in Table 1.

3.1. At alkali side with pH 3.5 as the starting point for the model fitting

When pH 3.5 was chosen as the starting point for data analysis and fitting, the charge variation of surface protons (mol/kg) resulting from the combination of H^+ or OH^- can be expressed as:

$$\Delta Q = \frac{-V_{OH}C_{OH} + V_{OHK}C_{OH}}{(V_0 + V_H + V_{OH})C_s} \quad (1)$$

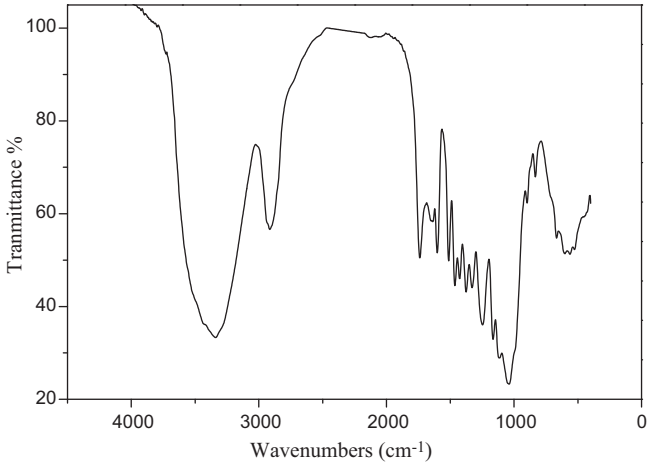

Fig. 1. Infrared spectra for natural bamboo sawdust.

where V_{OH} and V_H were acid and base volume (mL) added during titration, respectively. V_{OHK} was the base volume (mL) added during blank titration. C_{OH} was the base concentration (mol/L), V_0 was the initial volume of suspending liquid (mL), C_s was the sawdust concentration of suspending liquid (kg/L).

From infrared spectra (Fig. 1), the following conclusions were drawn: 3200–3600 cm^{-1} wide peak resulted from hydroxyl peak (including phenolic hydroxyl, alcohol hydroxyl of sawdust and water molecules) (Gode, Atalay, & Pehlivan, 2008), 2920 cm^{-1} peak can be attributed to methyl, methylene group and the extension vibration of C–H bond in the aromatic methoxyl group. 1641 and 1740 cm^{-1} corresponded to the vibration range of carbonyl groups. It had been shown that 1740 cm^{-1} was the free carbonyl stretching vibration of carboxylic acid group and 1641 cm^{-1} was the potentiometric anionic stretching vibration (Bouanda, Dupont, Dumonceau, & Aplincourt, 2002). 1602, 1425, 1511 cm^{-1} were characteristic of aromatic main structure vibration. Both 1517 and 1467 cm^{-1} were the deformation vibration of methoxy group on aromatic ring. 900, 1050 and 1384 cm^{-1} can be inferred as carbohydrate characteristic peaks. 835, 1045, 1160 and 1251 cm^{-1} should be guaiacyl characteristic peaks (Tejado, Pen, Labidi, Echeverria, & Mondragon, 2007), 1122 and 1330 cm^{-1} should be syringyl characteristic peaks and both of them were lignin endemic components. 1602, 1425 (Guo et al., 2008), 1511, 1467 and 1517 cm^{-1} all exhibited the main structure characteristics of aromatic ring, but only 1641 and 1740 cm^{-1} showed the unique structure of carboxylic acid groups. This suggests that phenolic groups and alcohol hydroxyl groups are more abundant than carboxylic acid groups in sawdust.

Sawdust surface contained a large number of hydroxyl groups. If the energy of these groups was equivalent, then only one type of surface functional group (in this case, XOH) participates in the reaction. Eq. (2) in Table 1 was a protonation reaction, while Eq. (3) was a deprotonation reaction. This was the so-called one-site model. In fact, the energy of different sawdust surface groups was significantly different and can be categorized into two types: low proton affinity sites (in this case, XOH) and high proton affinity sites (in this case, YOH). According to Fig. 1, low proton affinity sites generally referred to carboxylic acid group, while high proton affinity sites generally referred to alcohol hydroxyl and phenolic groups. This was the so-called two-sites model. Relatively, the proton at high proton affinity sites can be abstracted more hardly. Also, alcohol hydroxyl and phenolic hydroxyl groups were more difficult to be protonated, so their protonation reactions are negligible. Their deprotonation reaction was shown by Eq. (4).

Certainly, other types of affinity sites may also exist. The main components of sawdust were cellulose, hemi-cellulose and lignin