Absorption of Cd（II） with Bamboo Charcoal Modified by Succinic Acid

Xi Wu[1, a *], Shaohua He[2,b], Xinjia Huang[3,c] and Jimin Tian

[1]School of Urban Construction, University of South China, Hengyang, Hunan, 421001, China

[a]wuxi9104@163.com, [b]hshwd2014@sina.com, [c]huangxinjia.cool@qq.com, [d]332097977@qq.com

Keywords: bamboo charcoal; modified; Cd（II）; succinic acid

Abstract. After the pretreatment, Bamboo Charcoal (BC) were chemically modified with succinic acid. Then explore the characters of Modified Bamboo Charcoal (EBC) and the adsorption of BC for Cd（II）. Fourier Transform Infrared Spectroscopy(FTIR) and Scanning Electron Microscope(SEM) were applied to analyze the material microstructure and its chemical bond of the adsorbent. The static test shows that effects of reaction time and pH value on the adsorption of BC for Cd（II）. The adsorption process are found to be well described by the pseudo-second order adsorption kinetics. Besides, the maximum adsorption mounts of BC after modification calculated from pseudo-second order adsorption kinetics raised from 6.05 to 10.94 mg • g^{-1}.

Introduction

Under the conditions of the anaerrobic or anoxia, biochar is a type of aromatization of solid product by pyrolysis biomass. Biochar exhibit high specific surface area and developed pore structures. In addition,it's physically and chemically stable.It's surface contains a large number of functional groups such as hydroxyl, carbonyl and phenolic hydroxyl[1].And its surface is possessed of negative charge[2,3]. Biochar is an effective and envirionment-friendly adsorbent.

The research mainly investigated the manufacturing technology of Modified Bamboo Charcoal (EBC) taking Bamboo Charcoal (BC) as main raw material using alkalization and esterification. Through static adsorption experiment, this paper compares the ability of adsorption of Cd (II) before and after the modification. This paper also exploring its dynamics and the mechanism of adsorption.

Materials and methods

Reagent and instrument. The main reagent as follows:Potassium hydroxide, sodium hydroxide, succinic acid, p-toluene sulfonic acid, hydrochloric acid, acetone, cadmium nitrate.All above reagents for the analysis is analytical reagents.

The main instrument as follows:Electronic analytical balance(AUY220,SHIMADZU), flame atomic absorption spectrophotometer(AA-6300,AA-6300), precise pH meters(PHS-3C,Rex Shanghai) incubator shakers(QYC-2112,Shanghai fuma laboratory instrument Co,Ltd) Energy Disperse Spectroscopy(Geneis,USA) Scanning electron microscopy(S4800,Japan) Fourier transform infrared spectroscopy (Scientific,USA).

Adsorbent preparation. After screening the BC, adding 22g of BC which the size is 0.2 ~ 0.3 mm to the 300mL 10% hydroxide solution. Then put 10g of alkaline BC into the 200mL15% Butanedioic acid.Take 19g of acidification BC, 30 g of succinici acid, 4 g of p-toluene sulfonic acid in 300 ml acetone. Using Heating circumfluence method to preparing EBC.

Static adsorption experiments. A certain quality of BC and EBC were added respectively into 100 mL 50mg/L Cd (II) solutions. Then according different test purpose, choose different test conditions. After sampling, Concentration of residual Cd（II） was determined by ultraviolet spectrophotometer. In order to investigate the effect of adsorption, removal efficiency (RE) and adsorption capacity were applied to anal yze the adsorption process, which are expressed as follows:

$$RE(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

where RE (%) is the removal efficiency percent of heavy metals; q_e ($mg \cdot g^{-1}$) is the adsorption capacity; C_o and C_e ($mg \cdot L^{-1}$) are the initial and residual concentration V (mL) is the volume of solutions; M (g) is the dosage of modified walnut shell.

Analysis of test method.

Before the SEM scanning, BC and EBC were dealt with the gold jetting. Then material were observed under scanning electron microscope for their micro structures. Before the FTIR measurement, material and KBr were ground. The contents of Cd（II）in the solution were determined by spectrophotometric method.

Results and discussion

characterization results. Using FTIR and SEM to characterize the morphology and chemical group. The result as follow:

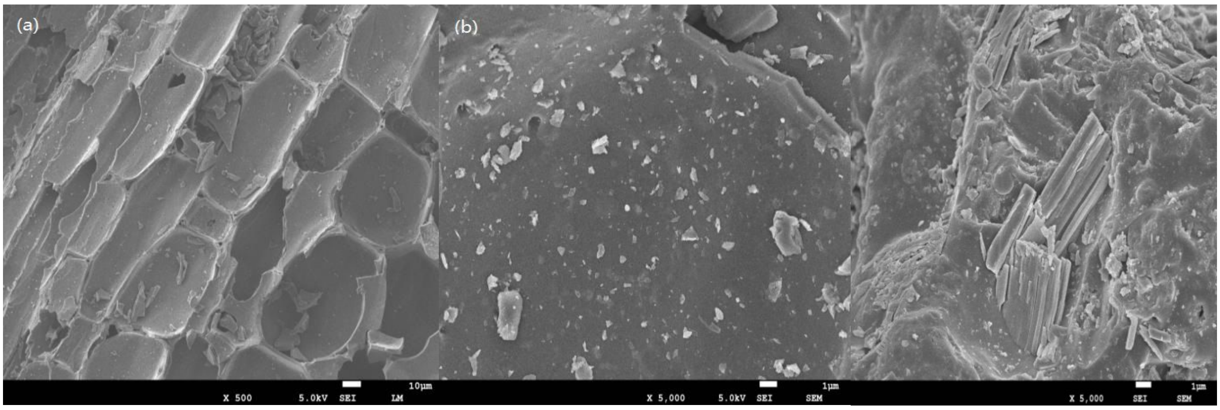
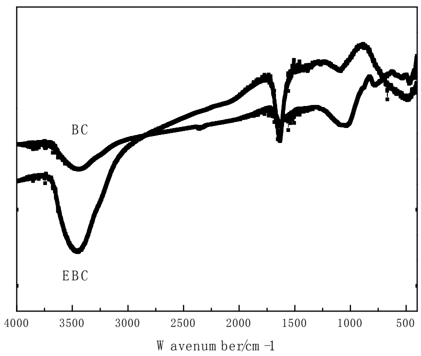


Fig.1 The SEM graph of BCF Fig.2 The SEM graph of EBC

Figure 1 a shows the structure of BC which processed at high temperature maintain the basic types of bamboo. Surface of BC shows poriferous structure. The pore structure is mainly consist of vascular bundle, the parenchyma cells and catheter formation[4]. The main reason of poriferous structure is the pore tubules in cell walls[5]. Because it dissolve cellulose, hemicellulose and lignin, figure 1 and figure 2 b shows EBC has high-- dispersion.



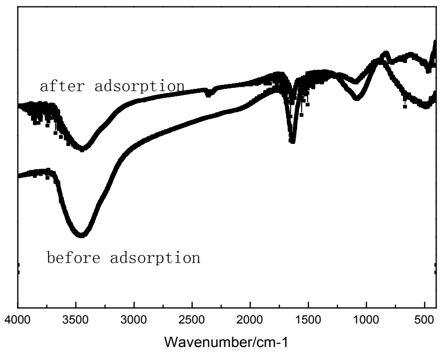


Fig.3a FTIR of BC before and after modification Fig.3b FTIR of EBC before and after Reaction

From figure 3a, there are a large number of hydroxyl at 3700 ~ 3100 cm^{-1} the broad peak[6]; After the modification, the absorption peak at 1740~1690cm^{-1} obvious enhancement. Which indicates that modification reaction add ester group which is beneficial to enhance the adsorption efficiency of

BC[4]. The peak at $779.7cm^{-1}$ were disppear. With compare, it finds the carboxyl group(-COOH) were increase, and hydroxyl group(-OH) were decrease.

From figure 3b, the absorption peak at $1740\sim1690cm^{-1}$ obvious weaken. It show that the hydroxy were replaced. But no new peaks were found, and the peaks didn't move.This phenomenon mean the reaction has both physics and chemistry[7]。

Effects of reaction time on adsorption of Cd（II）. From figure 4. With the rising of time, the adsorption capacity increase. At the time of 5min, The adsorption capacity of BC reached the 89.53% of maximum adsorption capacity. But the adsorption capacity of EBC reached the 82.39% of maximum adsorption capacity. Hereafter, The adsorption capacity of BC leveled off gradually, but adsorption capacity of E BC still slow growth . Fist, the adsorption process is a fast previous phase, which main is surface adsorption. Then the adsorption process of BC is a slow previous phase, which is internal diffusion. But the adsorption process of EBC after the first stage is chemical absorption.

Effects of pH on adsorption of Cd（II）. When pH>6, Cd（II）may be hydrolyze. So we just study the effect of pH at 2~6; From figure 4, When pH is 2~3, The adsorption capacity of BC is less than $2.92mg.g^{-1}$ and EBC is less than $4.46mg.g^{-1}$. When pH is 3~4, The adsorption capacity have developed a lot. The adsorption capacity of BC reached to $4.8mg.g^{-1}$and EBC reached to $8.15mg.g^{-1}$. After that, its growth rate is slowing dowm. Because the biochar's equal charge is 2.0~3.7[8,9]. When pH is 2.0, the positive charge on the biochar's surface repel Cd（II）[10]. As pH decrease, the amount of hydrogen ions decrease; the amount of negative charge increase[11].It is benifit to adsorb heavy metals. As a result, high pH (5.0 ~ 6.0) is better for theadsorption of BC and EBC.

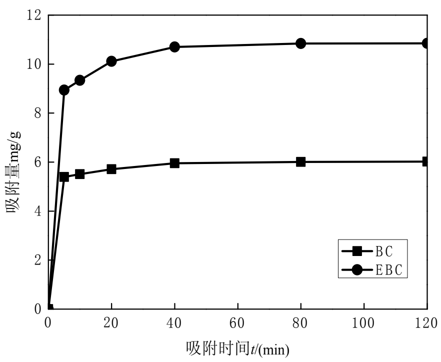


Fig.4 Effects of reaction time on adsorption of Cd（II）

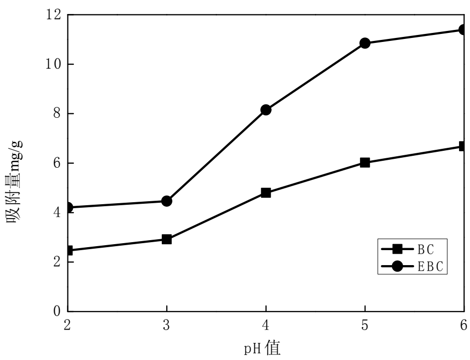


Fig.5 Effects of pH on adsorption of Cd（II）

research on adsorption kinetics

In order to investigate the mechanism of adsorption, the type(3)、type(4)and type(5) were applied to evaluate the equilibrium data[12], which were expressed as follows:

Pseudo-First order：

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} \qquad (3)$$

Pseudo-Second order：

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Intra-particle diffusion：

$$q_t = k_p \sqrt{t} + C \qquad (5)$$

Where q_e ($mg\cdot g^{-1}$) is the adsorption capacity; Ce ($mg\cdot L^{-1}$) is the equilibrium metal ion concentration in the solution; Q_0 K_L, K_F and n are respectively about the sorption constant .

According to the experimental results, Pseudo-Second order more suitable to test results. The process is more compatible with the mechanism of monolayer adsorption. At the same time, the reaction has both physics and chemistry. Adsorption mechanism is more complex[13].

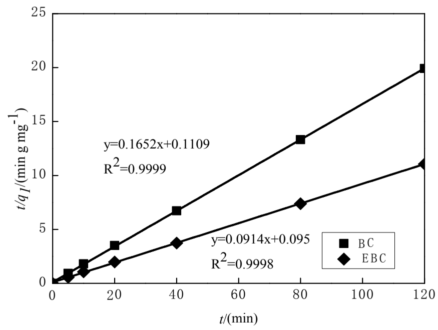


Fig.6 Pseudo-second-order kinetic profile for adsorptionof Cd（II）onto the BC

Table1 Kinetic perameters for adsorption of Cd（II）onto BC before and after modification

adsorbent	Pseudo-First order			Pseudo-Second order			Intra-particle diffusion		
	K_1/(min^{-1})	q_e/(mg/g)	R^2	k_2/(g/(mg·min))	q_e/(mg/g)	R^2	C	Kp	R^2
BC	0.041	1.396	0.959	0.246	6.05	0.999	5.321	0.074	0.856
EBC	0.075	3.033	0.995	0.088	10.94	0.999	8.823	0.217	0.808

Conclusions

(1) Infrared analysis showed that BC reacted with carboxyl of succinic acid. That add ester group which is beneficial to enhance the adsorption efficiency of BC. At the same time, the result of the scanning electron microscopy show that EBC is more dispersion than BC, and increased surface area.
(2) The results of the adsortion tese indicated that the adsorption capacityof BC and EBC increases over time. within 5 min, speed increases sharp. the adsorption rate then slowly increased to balance. adsorption capacity increases with the increase of pH, it has a lot to ascend between the pH of 3 ~ 4.
(3) Quasi secondary dynamics equation is more appropriate to describe the adsorption process. Indicates that the adsorption process has both physics and chemistry.

References

[1] Cheng C H, Lehmann J, Thies J E, et al. 2006,37(11):1477-1488.
[2] Liang B, Lehmann J, Solomon D, et al. Soil Science Society of America, 2006,70(5):1719-1730.
[3] Yu Wang, Baoyu Gao, Wenwen Yue, et al. Environmental science, 2008,29(3):703-708.In Chinese.
[4] Yunchao Li, Xianhua Wang, Haiping Yang, et al. Journal of Agricultural Engineering, 2012,28(12):257-263.In Chinese.
[5] Zengqiang Tan, Jianrong Qiu, Jun Xiang,et al. China Environmental Science, 2011,31(10):1625-1631.In Chinese.
[6] Shiqi Jie, Liyuan Qiao, Mingming Li, et al. The Chinese Journal of Nonferrous Metals, 2013,25(5):1362-1369.In Chinese.
[7] Mingen Mo, Hui Zhang, Huijin Wu, et al. Safety and Environmental Engineering, 2014,21(6):98-103.In Chinese.
[8] Yuan J H, Xu R K, Zhang H. Bioresource Technology, 2011,102:3488-3497.
[9] Zheng H, Wang Z Y, Zhao J, et al. Environmental Pollution,2013,181:60-67.
[10] Xu X Y, Cao X D, Zhao L, et al. Environmental Science Technology, 2003,36(17):3850-3854.
[11] Guangjie Xia, Ping Song, Yuping Qiu. Journal of Agro-environment Science.2014,33(3):569-575.In Chinese.
[12] Jigang Yuan, Xingyong Liu, Chengrui Wang, er al. Environmental Engineering, 2013,31(6):16-49.In Chinese.
[13] Jingru Bo, Qing Wang, Hong Qin, et al. Journal of Fuel Chemistry and Technology, 2011,39(5):378-384. In Chinese.