Research Article

Adsorptive Performance of Ni(II) from Aqueous Solutions Using Biochar Made of *Phragmites australis* by Adding Ammonium Polyphosphate as Flame Retardant

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The withered *Phragmites australis* (PA) surrounding the rivers can cause the secondary pollution of water. In this research, by changing the ratio (*R*) of ammonium polyphosphate (APP), used as flame retardant, to PA at different temperatures, a series of BC samples were prepared for further analysis in several perspectives, namely, surface morphologies, surface areas, surface functional groups, and yields. The analysis indicated that, after being charred, the produced BCs obtained enhanced yields and promoted surface acidity. As adsorbent to remove Ni(II) from aqueous solutions, the BCs with APP improved the sorption of Ni(II) dramatically, compared with those purely produced by pyrolysis of PA, and obtained the maximum of adsorption capacity with the *R* of 0.25 at 400°C.

1. Introduction

Biochar (BC), a kind of porous carbon material, is carbonization by biomass in anoxic or anaerobic conditions at low temperature. It has been widely used in carbon emission reduction, water purification, adsorption of heavy metals, and soil improvement [1, 2]. In winter, the withered *Phragmites australis* (PA) played a negative role in normal operation of the constructed wetland and the secondary pollution of water [3]. Therefore, the withered PA is used to produce biochar, which will be a “turning waste into wealth” method [4]. In order to enhance the yields and properties of BC, the common method is adding flame retardants. Ammonium polyphosphate (APP), a kind of excellent performance flame retardant, contains many advantages such as avirulent, insipidity, no corrosive gas produced, less hygroscopicity, and high thermal stability [5]. APP has been gradually used for the compound fertilizer and liquid fertilizer production and especially has been widely used in the developed countries. It is a good try to use APP as flame retardants for producing BC.

This research is designed (1) to evaluate the feasibility of APP as flame retardants for produced BC; (2) to study

the effect of additive amount of APP and charring temperature (300, 400, and 500°C) on the textural and chemical properties of produced BCs; and (3) to evaluate the sorption capacities of produced BCs toward Ni(II) by comparing with the BCs derived from pyrolysis of PA without adding APP.

2. Materials and Methods

2.1. Materials and Chemical Reagents. *Phragmites australis* (PA), with porous caudex system and large cell gap, can be used as a low-cost and efficient precursor for BC production. The PA grew in wetlands in Shandong, a province located in the eastern part of China. After being reaped in winter, the PA was washed in distilled water for a few times and aired in a 105°C environment for 24 hours and then smashed into pieces of approximately 0.45–1.0 mm [6]. Ammonium polyphosphate (APP) was used as flame retardant. By dissolving a weighted quantity of NiCl₂·5H₂O in distilled water, the Ni(II) solution was obtained. All chemical reagents used were of analytical grade.

2.2. Preparation of Activated Carbons. About 10 g PA were fully mixed with a weighted amount of APP and 10 mL distilled water, and the mixed samples were then aired in a 105°C environment for 12 hours to evaporate the moisture. The ratios (R , g APP/g PA) were 0, 0.25, 0.5, and 1.0, respectively. After being dried, the samples were placed in 150 mL ceramic crucibles, and each ceramic crucible was covered with a fitting lid. Then these samples were charred at 300, 400, and 500°C for 1 hour under N_2 flow of 500 mL/min in the muffle furnace (combustion chamber, 300 mm $\times$ 200 mm $\times$ 120 mm), respectively [7]. In order to assess the impacts of APP on the final BCs, another three BC samples without APP were prepared at the charring temperatures of 300, 400, and 500°C for 1 hour. After being cooled to room temperature, the charred residues were pulverized for subsequent demineralization with 0.1 mol/L HCl. The samples were thoroughly washed in distilled water until pH of the washing liquid attained and kept a constant degree and then aired for 9 hours at a 105°C environment. These BC samples were hereafter referred to as BC- X - Y s, in which X and Y represent the final charring temperature and the R , respectively.

2.3. Characterization Methods. The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of PA and the different impregnations mixture of PA and APP were derived from a thermogravimetric analysis (TGA-50 analyzer). The PA samples were referred to as PA- X - Y s, in which X and Y represent the final charring temperature (300, 400, and 500°C) and the R (0, 0.25, 0.5, and 1.0), respectively. Each sample was heated up to a designed temperature and kept at this temperature for 1 hour at a heating rate of 10°C/min. The Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of BCs were measured by the adsorption of N_2 at 77 K in a surface area analyzer (Quantachrome Corporation, USA). The S_{BET} was also calculated from the isotherms in the BET equation. The surface textures of the BCs were observed by a scanning electron microscope (SEM Hitachi S4800, Japan). The surface functional groups of BCs were defined by using Boehm's titration method.

Adsorption experiments were conducted with the initial concentration of Ni(II) in the range of 10–60 mg/L. The adsorption dose was 600 mg/L using 100 mL flask. The initial pH was adjusted with addition of 0.01 M HCl or NaOH to the value of 6.00 ± 0.02 . The flasks were kept in an isothermal water bath and agitated at 180 rpm for 36 hours to ensure that equilibrium was reached. The amount of Ni(II) adsorbed at equilibrium (Q_e , mg/g) was calculated by

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

in which C_0 and C_e represent the initial and equilibrium concentration of Ni(II) (mg/L), respectively; V is the solution volume (L); and W is the mass of adsorbent (g).

3. Results and Discussion

Figure 1 shows the thermogravimetric analysis of PA- X - Y samples. It can be seen from TGA curves that PA- X - Y ($Y > 0$) samples displayed much lower weight loss than PA- X -0 samples, indicating that APP has good flame retardant

performance for PA. The yields of BCs, as listed in Table 1, were defined as the ratio of the weight of produced BC to the weight of PA used for charring. Yields of the BCs declined with increasing temperature and increased with increasing the amount of APP added. The yields of BC- X - Y ($Y > 0$) were dramatically much higher than BC- X -0, which also confirmed that APP used as fire retardant played a key role in BCs preparation.

The weight loss for the samples during thermogravimetric analysis could be divided into three stages. In the first stage, the small amount of weight loss was caused by loss of water and light volatile compounds in PA with the temperature rising from room temperature to 200°C. Then, a significant weight loss occurred with temperature from 200°C to the final temperature (300, 400, or 500°C), which was mainly caused by evolution of volatile compounds generated by decomposition of hemicellulose, cellulose, and lignin in PA. In the last stage, as temperature kept at a constant value of 300, 400, or 500°C, the samples displayed a continuous and slight weight loss. In the chemical reaction of PA with APP, PA is in the reducing atmosphere resulting from the formation of carbonization layer promoted by the presence of APP. Thereby, the char of PA is promoted at the high temperature in the muffle furnace. Besides, with the increase of temperature, APP can decompose into H_3PO_4 and phosphates. The fire retardation and dehydration condensation in reaction of H_3PO_4 with lignocellulose also contribute to the char of PA [8, 9].

SEM micrographs of the BCs are shown in Figure 2. After carbonization without APP, BCs showed a similar structure to PA, while the structure of BC-400-0.5 was obviously corroded. Some particles or flakes on the surfaces of BC-400-0.5 were observed, which could result from the chemical vapor deposition of pyrolysis products. As shown in Table 1, the BET surface area of BC- X -0 samples increased with increasing pyrolysis temperature. The production of volatile compounds inside PA particles gradually increased as the final temperature rises, which caused increase of porosity. Obviously, it could be drawn that the S_{BET} of BC- X - Y ($Y > 0$) were higher than that of BC- X -0, indicating that APP as a fire retardant was efficient to pore-forming in BCs preparation. And the results of Boehm's titrations were also showed in Table 1. The surface acidity of BC- X - Y ($Y > 0$), carboxyl, in particular, was much more than BC- X -0. This demonstrated that phosphoric acid was released by APP in BCs preparation. The previous researches indicated that the active surface acidic characteristic of carbons could contribute to adsorption of heavy metal [10]. Therefore, the Ni(II) adsorption of BCs would be improved.

The adsorption isotherms of Ni(II) onto the BCs, as shown in Figure 3, were analyzed at different initial Ni(II) concentrations varying from 10 to 60 mg/L. In order to estimate the maximum adsorption capacity of Ni(II) onto the BCs, both of Langmuir (2) and Freundlich (3) isotherm models were conducted to simulate the sorption:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}, \quad (2)$$

$$Q_e = K_F C_e^{1/n}. \quad (3)$$

FIGURE 1: Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of PA-X-Y samples. (a) TGA curves of PA-300-Y samples; (b) DTG curves of PA-300-Y samples; (c) TGA curves of PA-400-Y samples; (d) DTG curves of PA-400-Y samples; (e) TGA curves of PA-500-Y samples; (f) DTG curves of PA-500-Y samples.

FIGURE 2: SEM micrographs of (a) PA sample, (b) BC-400-0 sample, and (c and d) BC-400-0.5 sample.

TABLE 1: Surface area, yields and surface functional groups of the BC samples.

Samples number	S_{BET} (m^2/g)	Yield (%)	Carboxyl (mmol/g)	Lactone (mmol/g)	Phenolic (mmol/g)	Total acidic functional groups (mmol/g)
BC-300-0	4.6	29.5	0.1964	0.3217	0.5741	1.0922
BC-300-0.25	167.9	56.0	0.3011	0.3719	1.1727	1.8457
BC-300-0.5	164.3	58.6	0.3036	0.2936	0.8999	1.4971
BC-300-1.0	151.7	66.8	0.2992	0.3300	0.8419	1.4711
BC-400-0	7.9	25.1	0.1841	0.2709	0.6449	1.0999
BC-400-0.25	177.7	48.0	0.3661	0.3284	1.0713	1.7657
BC-400-0.5	181.2	53.8	0.3663	0.3575	0.9701	1.7121
BC-400-1.0	171.4	57.8	0.3858	0.3359	0.9469	1.6686
BC-500-0	12.1	16.5	0.0790	0.4102	0.4923	0.9815
BC-500-0.25	165.8	43.4	0.6180	0.1099	1.1835	1.9744
BC-500-0.5	149.5	50.4	0.3567	0.3615	1.0829	1.8012
BC-500-1.0	157.2	54.8	0.5329	0.1220	0.9919	1.6469

FIGURE 3: Sorption isotherms of Ni(II) on the BCs. (a) BC-300-Y samples; (b) BC-400-Y samples; (c) BC-500-Y samples.

Here, Q_e represents the absorption amount (mg/g); C_e represents the equilibrium concentration (mg/L); Q_m represents the maximum sorption capacity (mg/g); K_L represents the Langmuir sorption constant; and K_F and $1/n$ are the Freundlich constants.

The constants of both models fitting into the adsorption data were presented in Table 2. The correlation coefficient (R^2) in Langmuir model were much higher than those obtained from Freundlich model, indicating that the adsorption of Ni(II) on the BCs was simulated better by Langmuir model than Freundlich model. This also is observed from Figure 3 that the Langmuir model fits the data better. The $1/n$ values of the BCs were between 0 and 1, representing a favorable sorption of Ni(II) onto the BCs. As shown in

Table 2 and Figure 3, the adsorption capacities of Ni(II) onto the BC-X-Y samples obtained its maximum at $Y = 0.25$ (BC-300-0.25, BC-400-0.25, and BC-500-0.25) for different charring temperatures and at $X = 400^\circ\text{C}$ for different R . The considerable Ni(II) sorption capacity of BC-400-Y sample ($Y > 0$) could be attributed to the roles of the higher surface area and more acid functional groups.

4. Conclusions

This study investigated the preparation of BCs by using APP as flame retardant. The results indicated that, by comparing with the BC-X-0 samples, (1) enhanced the porosity and surface acidity of BCs were developed by using APP as flame

TABLE 2: Langmuir and Freundlich constants related to the adsorption isotherms of Ni(II) for the BCs samples.

Samples number	Langmuir				Freundlich	
	Q_m (mg/g)	K_L (L/mg)	R^2	$1/n$	K_F ($\text{mg}^{1-n}\text{L}^n\text{g}^{-1}$)	R^2
BC-300-0	9.7466	0.0451	0.8714	0.3942	1.4126	0.8888
BC-300-0.25	15.408	0.3169	0.9872	0.1071	9.4480	0.8983
BC-300-0.5	9.4787	0.3748	0.9975	0.0879	6.3414	0.8093
BC-300-1.0	7.1174	0.5569	0.9998	0.0957	4.7841	0.8950
BC-400-0	9.0090	0.2054	0.9917	0.1390	4.7119	0.9102
BC-400-0.25	19.231	0.4948	0.9979	0.1473	10.770	0.9567
BC-400-0.5	15.898	0.4565	0.9983	0.1216	9.6253	0.9766
BC-400-1.0	14.859	0.1760	0.9658	0.1438	7.4076	0.7877
BC-500-0	10.142	0.3728	0.9978	0.1427	5.6305	0.9224
BC-500-0.25	15.528	0.6002	0.9982	0.1328	9.3008	0.8772
BC-500-0.5	15.244	0.8200	0.9964	0.1098	10.046	0.7865
BC-500-1.0	14.025	0.2094	0.9932	0.1920	6.1398	0.9652

retardant; (2) using APP as flame retardant for BC production can dramatically enhance the Ni(II) adsorption capacities of the produced BCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] G. Shrestha, S. J. Traina, and C. W. Swanston, "Black carbon's properties and role in the environment: a comprehensive review," *Sustainability*, vol. 2, no. 1, pp. 294–320, 2010.
- [2] H. Asai, B. K. Samson, H. M. Stephan et al., "Biochar amendment techniques for upland rice production in Northern Laos: I. Soil physical properties, leaf SPAD and grain yield," *Field Crops Research*, vol. 111, no. 1-2, pp. 81–84, 2009.
- [3] Q. Wang, H. Xie, J. Zhang et al., "Effect of plant harvesting on the performance of constructed wetlands during winter: radial oxygen loss and microbial characteristics," *Environmental Science and Pollution Research*, vol. 22, pp. 7476–7484, 2015.
- [4] Z. Guo, X. Bian, J. Zhang et al., "Activated carbons with well-developed microporosity prepared from *Phragmites australis* by potassium silicate activation," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 5, pp. 2801–2804, 2014.
- [5] S. Nie, Y. Hu, L. Song, Q. He, D. Yang, and H. Chen, "Synergistic effect between a Char Forming Agent (CFA) and microencapsulated ammonium polyphosphate on the thermal and flame retardant properties of polypropylene," *Polymers for Advanced Technologies*, vol. 19, no. 8, pp. 1077–1083, 2008.
- [6] Z. Guo, J. Fan, J. Zhang et al., "Sorption heavy metal ions by activated carbons with well-developed microporosity and amino groups derived from *Phragmites australis* by ammonium phosphates activation," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 58, pp. 290–296, 2016.
- [7] Z. Guo, L. Xu, C. Liu, F. Sun, Y. Kang, and S. Liang, "Comparison of physicochemical properties of activated carbons derived from biomass wastes by $\text{H}_4\text{P}_2\text{O}_7$ activation: adsorption of trimethoprim," *Desalination and Water Treatment*, 2015.
- [8] M. Molina-Sabio, C. Almansa, and F. Rodríguez-Reinoso, "Phosphoric acid activated carbon discs for methane adsorption," *Carbon*, vol. 41, no. 11, pp. 2113–2119, 2003.
- [9] M. A. Nahil and P. T. Williams, "Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks," *Biomass and Bioenergy*, vol. 37, pp. 142–149, 2012.
- [10] H. Liu, S. Liang, J. Gao et al., "Development of biochars from pyrolysis of lotus stalks for Ni(II) sorption: using zinc borate as flame retardant," *Journal of Analytical and Applied Pyrolysis*, vol. 107, pp. 336–341, 2014.