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CPB Modified Cornstalk Biochar for Enhanced Adsorptive Removal of Acid Orange II

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ABSTRACT

Cornstalk biomass was utilized to prepare biochar as an adsorbent substrate. In order to significantly improve adsorption capability of the cornstalk biochar, a cationic surfactant hexadecylpyridinium bromide (CPB) was immobilized onto the cornstalk biochar, generating CPB-modified cornstalk biochar. CPB-modified cornstalk biochar performed slightly better than CPB-modified wheat straw biochar during adsorptive removal of an azo dye Orange II (ORII). It was observed that the adsorption capability of the raw cornstalk biochar for ORII was improved by as much as 183.5% after modification by CPB. The adsorption kinetics of the raw cornstalk biochar and the CPB-modified cornstalk biochar were compared and investigated at neutral solution pH. The experimental points were simulated by both pseudo-first-order and pseudo-second-order models using linear and non-linear fitting methods. Both linear and non-linear simulation results indicated that the pseudo-second-order kinetic model was more suitable to describe the adsorption kinetics, which demonstrates that the adsorption process might be chemisorption. Additionally, the calculated q_e value from non-linear pseudo-second-order model for the CPB-modified cornstalk biochar is 44.29 mg/g, which is much close to the experimental value of 44.20 mg/g.

INTRODUCTION

Various biomasses and wastes can be utilized to produce biochar, which has been paid increasing attention because biochar offers the chance to turn bioenergy to carbon-negative industry (Lehmann 2007, Lee et al. 2010). Biochar has a strong affinity for contaminants and ability for carbon sequestration (Ghosh et al. 2011, Shen et al. 2012). As such, considering a huge amount generated annually, biomass-based biochar is expected to have a wide application in practical contaminant remediation. Among these biomasses, agricultural wastes usually contain a large amount of floristic fibre and functional groups such as carboxyl, hydroxyl and amidogen, which are expected to be responsible for the biosorption process (Han et al. 2006, Gupta 2009). Once these agricultural wastes are utilized to produce biochar, the application of these low-cost adsorbents could be enlarged to a great extent as the use of biochar avoids the significant organic leaching from the raw biomasses. Further, biochars with different functional group compositions show contrasting affinity for inorganic (Shen et al. 2012) and organic contaminants (Luo et al. 2015). As such, biochar is actually being widely used in environmental management, including soil improvement, waste management, climate change mitigation and energy production (Ahmad et al. 2014).

On the other hand, among technologies for water and wastewater treatment, adsorption process is regarded as one of the most powerful, efficient and cost-effective water treatment technologies due to ease of operation and high efficiency. Adsorption process can transfer pollutants from one phase to another efficiently, and no toxic intermediates are generated. A number of adsorbents could be selected for different pollutants such as organic pollutants and heavy metals. Meanwhile, various studies demonstrated that composite adsorbents exhibited excellent performance as they could combine the properties and advantages of each of their components (Qu 2008, Zhu et al. 2016). The application of composite adsorbent is expected to solve more water-related problems.

In this research cornstalk, an agricultural waste, was utilized to produce stable biochar under low-temperature pyrolysis at 600°C. The resulting cornstalk biochar was intentionally modified by CPB to enhance its positive charge property and adsorption capability for negatively charged pollutants. An anionic dye, Orange II (ORII), was selected as a target organic pollutant for the adsorption process. Concurrently, raw wheat straw biochar and CPB-modified wheat straw biochar were compared with those of cornstalk biochar considering their adsorption capability. The adsorption kinetics was emphatically investigated and adsorption mechanism was discussed.

MATERIALS AND METHODS

Chemicals: Orange II (ORII) and cationic surfactant hexadecylpyridinium bromide (CPB) were purchased from Beijing Chemical Reagents Company, and used without further purification. The other chemicals used were of analytical grade. Deionized (DI) water was used throughout the study.

Preparation of CPB-modified biochars: Raw biomasses including cornstalk and wheat straw were collected from a farmland located in Zhengzhou (Henan Province, China). The collected biomass was washed, dried, crushed and sieved using a 40 mesh sieve. Then the pretreated biomasses were pyrolyzed at 600°C for 3 h in a furnace under an oxygen-limited condition. The resultant biochars were demineralized in a 4 mol/L HCl solution for 12 h and separated by filtration. Then the residues were rinsed with DI water to neutral solution pH and dried in an oven at 80°C overnight. One gram of the demineralized biochar was added into 100 mL of CPB solution (0.005 g/L). The mixture was shaken by an orbital shaker at 120 rpm for 24 h. Then the modified biochar was separated by filtration and dried at 60°C for 4 h. Finally, the prepared CPB-modified biochar was stored in a desiccator for further use.

Batch adsorption studies: Stock solutions of ORII (1000 mg/L) were prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. The adsorption of ORII on the CPB-modified biochar was conducted in a series of 100-mL conical flasks. For the comparative study, 10 mg of the biochar and the CPB-modified biochar was added into 50 mL of ORII solution with an initial concentration of 15 mg/L. These flasks were shaken on a horizontal shaker for 24 h at a speed of 140 rpm to achieve adsorption equilibrium. For the kinetics study, 200 mg of CPB-modified cornstalk biochar was added into 1000 mL of ORII solution with an initial concentration of 15 mg/L. Constant stirring was maintained by a magnetic stirrer. Samples were collected at desired time intervals. The reaction temperature was controlled at a constant of 298 K unless otherwise stated. pH of all the solutions was maintained at neutral. Finally, samples were collected and filtered through a 0.45 μm pore-size membrane before measurement.

Analysis of ORII: The concentration of ORII was determined by measuring the maximum absorbance at a fixed wavelength of 484 nm, using an UVmini-1240 spectrophotometer (Shimadzu, Japan).

The quantity of ORII adsorbed on the CPB-modified cornstalk biochar was calculated by the following equations:

$$q_e = (C_0\text{-}C_e)\ V/W \qquad ...(1)$$

$$q_t = (C_0\text{-}C_t)\ V/W \qquad ...(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and t min; C_0 is the initial concentration of ORII in solution, C_e and C_t (mg/L) are the concentrations of ORII at equilibrium and t min, respectively; V (L) is the volume of solution; and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Selection of the CPB-modified biochar: As a comparison, both wheat straw and cornstalk biomasses, were utilized to produce biochar. The CPB modified biochars were prepared from both wheat straw and cornstalk biochars. These raw biochars and CPB-modified biochars are compared in terms of their adsorption performance for ORII, as illustrated in Fig. 1. The uptake of ORII on the raw wheat straw biochar, cornstalk biochar, CPB-modified wheat straw biochar and CPB-modified cornstalk biochar achieved 10.5, 13.9, 39.0 and 39.4 mg/g, respectively. Evidently, the raw cornstalk biochar performed better than wheat straw biochar. After modification by CPB, the adsorption capability of the raw cornstalk biochar for ORII was improved by 183.5%. The adsorption performance of, both CPB-modified wheat straw and cornstalk biochar are similar, although the CPB-modified cornstalk biochar performed slightly better. In the following experiments, the CPB-modified cornstalk biochar was used for the adsorption of ORII.

Effect of dose of the CPB-modified cornstalk biochar: Effect of the dose of the raw cornstalk biochar and the CPB-modified cornstalk biochar on ORII uptake was investigated concurrently. The dosage of the CPB-modified cornstalk biochar and the raw cornstalk biochar was 5, 10, 20, 40 and 80 mg. As presented in Fig. 2, the uptake of ORII decreased with the increasing dose of both the biochars. The adsorption capacity at the dose of 20 mg for the raw cornstalk biochar and the modified cornstalk biochar achieved 5.5 and 37.1 mg/g, respectively. This is because the increased dose of biochar provides more active sites for adsorption, yielding a decline of the adsorption capacity. In the following experiments, the dose of the CPB-modified cornstalk biochar was fixed at 10 mg.

Linear adsorption kinetics: The kinetics for the adsorption of ORII on the raw cornstalk biochar and the CPB-modified cornstalk biochar were compared and investigated at neutral solution pH. The experimental points were simulated by both pseudo-first-order and pseudo-second-order models using linear and non-linear fitting methods. The mathematical representations of the linear and non-linear models of pseudo-first-order and pseudo-second-order kinetics are given as (Lagergren 1898, Ho & McKay 1999):

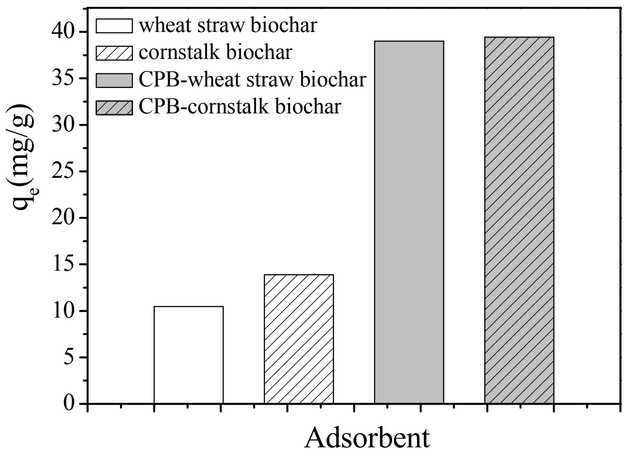

Fig. 1: Adsorption of ORII by the raw and CPB modified biochars.

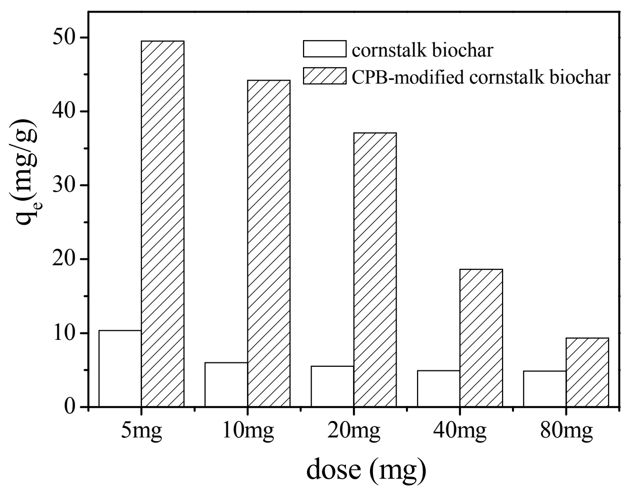

Fig. 2: Effect of the dose of the raw cornstalk biochar and CPB-modified cornstalk biochar on the uptake of ORII.

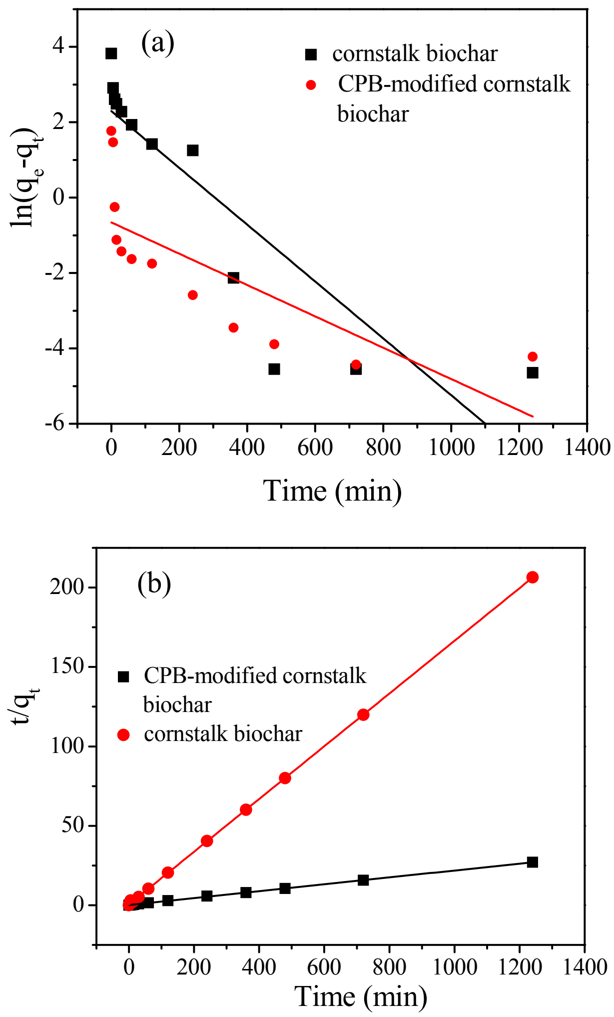

Fig. 3: Linear adsorption kinetic simulation for (a) pseudo-first-order and (b) pseudo-second-order models.

$$q_t = q_e(1-e^{-k_1 t}) \quad ...(3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad ...(4)$$

$$q_t = \frac{k_2 q_e^{\ 2} t}{(1+k_2 q_e t)} \quad ...(5)$$

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

Where, q_e and q_t are the adsorption capacities (mg/g) of ORII at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g /mg·min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

The experimental data were firstly fitted by linear kinetic models of pseudo-first-order and pseudo-second-order kinetics. The simulated curves are presented in Fig. 3 and kinetic parameters are also listed in Table 1. From Fig. 3, it can be observed that the linear pseudo-second-order kinetic model fitted the experimental data better as experimental points are much closer to the simulated pseudo-second-order kinetic curves than to the pseudo-first-order curves. Meanwhile, from Table 1, the values of correlation coefficient (R^2) of linear pseudo-second-order model are, 0.999 for both the raw and modified biochars, while those of linear pseudo-first-order model for the raw cornstalk biochar and CPB-modified cornstalk biochar are 0.55 and 0.76, respectively. The simulated q_e values by linear pseudo-second-order model are quite close to the experimental values for both the biochars as well. Apparently, linear pseudo-second-order model is more suitable to describe the experimental kinetics.

Table 1: The linear kinetic parameters for pseudo-first-order and pseudo-second-order models.

	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e(mg/g)	k_2(mg/g·min)	R^2
Raw biochar	0.52	4×10^3	0.55	6.03	0.03	0.999
CPB-modifiedbiochar	9.94	8×10^3	0.76	46.08	0.00	0.999

Table 2: The non-linear kinetic parameters for pseudo-first-order and pseudo-second-order models.

	Pseudo-first-order model			Pseudo-second-order model		
	q_e(mg/g)	k_1 (min^{-1})	R^2	q_e(mg/g)	k_2(mg/g·min)	R^2
Raw biochar	5.60	0.13	0.932	6.21	0.04	0.879
CPB-modifiedbiochar	42.53	0.15	0.919	44.29	0.01	0.975

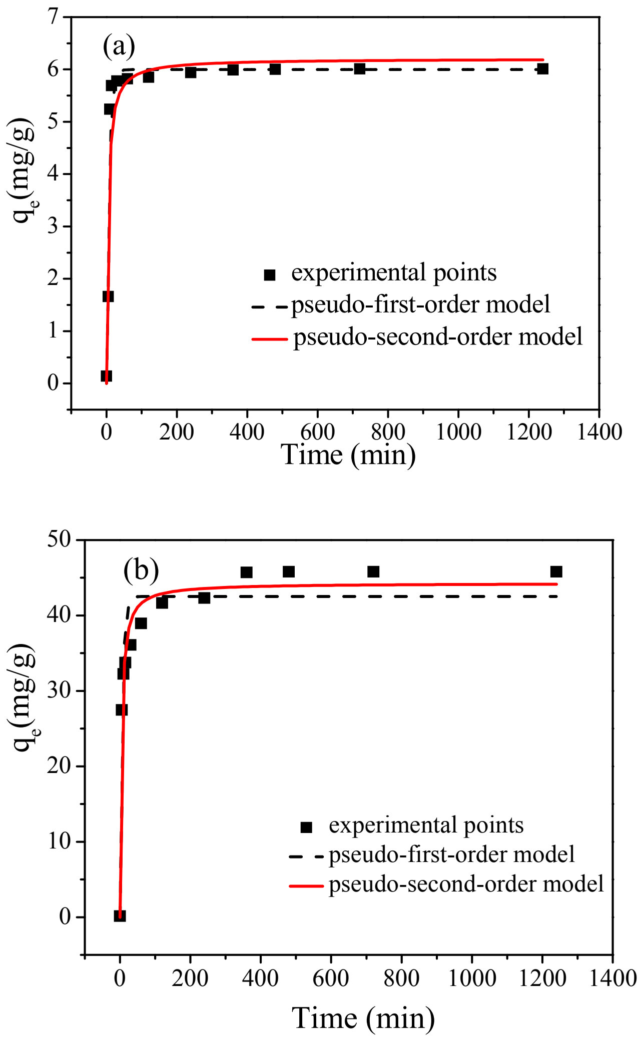

Fig. 4: Non-linear adsorption kinetic simulation for (a) pseudo-first-order and (b) pseudo-second-order models.

Non-linear adsorption kinetics: In addition to the linear simulation of the adsorption kinetics, the experimental data were also fitted by the non-linear pseudo-first-order and pseudo-second-order kinetic models, as shown in Fig. 4. Judged from the simulated curves in Fig. 4, it is evident that the non-linear kinetic models of both pseudo-first-order and pseudo-second-order models, well described the experimental points. Meanwhile, the values of correlation coefficient (R^2) of both pseudo-first-order and pseudo-second-order models are higher than 0.879. In contrast, for both the raw cornstalk biochar and the CPB-modified cornstalk biochar, the calculated q_e values from pseudo-second-order model are much closer to the experimental data than those of pseudo-first-order model as well. For example, the calculated q_e value from pseudo-second-order model for the CPB-modified cornstalk biochar is 44.29 mg/g, which is much closer to the experimental value of 44.20 mg/g. Totally, the pseudo-second-order kinetic model is more suitable to describe the adsorption kinetics, which demonstrates that the adsorption process might be chemisorption.

CONCLUSION

The composite adsorbent CPB-modified cornstalk biochar was successfully prepared from agricultural biomass cornstalk, which is generated in a huge amount annually. During adsorptive removal of negatively-charged anionic dye Orange II (ORII), CPB-modified cornstalk biochar performed slightly better than CPB-modified wheat straw biochar during adsorptive removal of ORII. The adsorption capability of the raw cornstalk biochar for ORII was improved by 183.5% after modification by CPB. The adsorption kinetics on the raw cornstalk biochar and the CPB-modified cornstalk biochar were compared and investigated at neutral solution pH. The experimental points were simulated by both, pseudo-first-order and pseudo-second-order models, using linear and non-linear fitting methods. Both linear and non-linear simulation indicated that the pseudo-second-order kinetic model is more suitable to describe the adsorption kinetics, which demonstrates that the adsorption process is chemisorption. Additionally, the calculated q_e value from non-linear pseudo-second-order model for the CPB-modified cornstalk biochar is 44.29 mg/g, which is much closer to the experimental value of 44.20 mg/g.

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