Preparation of Sodium Humate-Modified Biochar Absorbents for Water Treatment

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ABSTRACT: Some chemical substances could improve the sorption capacity of biochars. In this paper, sodium humate was introduced to the pyrolysis of two biomass samples at 600 °C, and sodium humate–biochars have been successfully synthesized. The surface area and surface morphologies of all of the biochars were characterized, and the results indicated that sodium humate–biochars have higher surface areas, and sodium humate particles were grown on the surfaces of the biochars. Adsorption isotherm and kinetics of methylene blue (MB) onto the biochars were carried out by batch adsorption experiments. The results suggested that incorporation of sodium humate could increase the adsorption capacity of MB onto the biochars (from 10.79 to 16.21, 8.62 to 11.03 mg/g for peanut shells and white clover residues, respectively). The adsorption experimental results also suggest that the adsorption process of MB onto sodium humate–biochars is controlled by both intraparticle diffusion and film diffusion. As a whole, this work probes the possibility of sodium humate to modify the surface of biochar and improve its adsorption ability with contaminants.

1. INTRODUCTION

Nowadays, a variety of synthetic dyes have been developed and used in the textile industry.1−5 Given the complicated structure and high molecular weight, the synthetic dyes are toxic and nonbiodegradable.6 Every year, many dyes are discharged into wastewater, which are discharged directly into lakes and rivers, threatening the survival of aquatic life.7 Therefore, water pollution has become an increasingly serious concern. In recent years, adsorption approaches have been widely used to remove dyes from wastewater because of their capacity of adsorption, chelation, and ion-exchange.8−13 However, high price or low regeneration ability is the shortcoming, restricting the usage of these materials. Therefore, adsorbents with high adsorption capacity, high regeneration ability, and low cost should be developed.

Biochar, produced from the pyrolysis of inexpensive agricultural and forest residues, has been widely used as an alternative low-cost adsorbent to treat environmental pollution.14−19 Several research studies also indicated that some methods can be used to modify the biochars and enhance their sorption capacity for various chemical contaminants.20,21 For instance, the clay-implanted biochar has unique properties and functions inherited from both clay and biochar and has a much higher sorption ability to methylene blue (MB) than the original char.22,23 Some technologies incorporating engineered nanoparticles into biochar have been reported to improve the sorption ability to contaminants.24−26 Chitosan was reported as a dispersing and soldering reagent to attach fine ZVI particles onto bamboo biochar surfaces, and the composite biochar showed enhanced ability to sorb heavy metals and MB from aqueous solutions.27 Therefore, these reports do suggest that modification with some chemical substances could improve the sorption capacity of biochars.

Sodium humate (SH) is a water-soluble sodium salt of humic acid that is widespread in nature. It can be derived from extraction of lignite and peat.28 They have been reported to be widely used in biological farming and pollution treatment because of their capacity of adsorption, chelation, and ion-exchange.29−34 However, to the best of our knowledge, there have been no reports regarding the application of SH to modify the surface of biochars, thus improving the sorption capacity. Therefore, the main objective of this work was to probe the possibility of SH to modify the surface of biochar and improve its adsorption ability with contaminants.

2. RESULTS AND DISCUSSION

2.1. Characterization of Biochars. 2.1.1. SEM Analysis. The scanning electron microscopy (SEM) images of the surface morphologies of the raw and SH-modified biochars are shown in Figure 1. The images for all of the biochars suggested that the samples had rough surfaces because of the intrinsic nature of the biochar matrix. However, compared with the raw peanut shell and white clover biochar, the surfaces of SH-
modified biochars were covered with some prills. Although the prills on the surface of SH−PS were not homogeneous, some granules were still found on the biochar surface, which is different from that of raw PS biochar, indicating that SH was grown on the biochar surface.

2.1.2. Specific Surface Area and PSD. In order to study the influence of SH to the pyrolysis of biomass, the specific surface area and pore size distribution (PSD) of raw and SH-modified biochars were determined. Amongst, the specific surface area were investigated via the N2 Brunauer−Emmett−Teller (BET) adsorption method. The results are listed in Table 1.

Table 1. BET Surface Areas of Raw and SH-Modified Samples

| sample     | BET/m²/g |
|------------|-----------|
| PS         | 217.49    |
| SH−PS      | 280.47    |
| WC         | 12.02     |
| SH−WC      | 37.28     |

According to the BET results, raw PS and WC biochars showed low surface area (217.49 and 12.02 m²/g, respectively). In contrast, both biomass samples treated with SH yielded higher surface areas (280.47 m²/g for SH−PS, and 37.28 m²/g for SH−WC). Therefore, SH could increase the surface area of the biochars.

The PSD of raw and SH-modified PS and WC biochar samples was calculated by the Barrett−Joyner−Halenda (BJH) method and shown in Figure 2. The results indicated that PS, SH−PS, WC, and SH−WC have PSDs that extend in the mesopore region, and dV/dDs of SH-modified biochars were higher than those of raw biochars. This would imply that mesopore volumes of SH-modified biochars were significantly greater those that of raw biochars.

2.2. Adsorption Properties of Biochars. The capacity of the biochars to remove MB from aqueous solution was measured by the adsorption isotherm and kinetics.

2.2.1. Equilibrium Adsorption Isotherms. Equilibrium adsorption isotherm experiments were conducted at concentrations ranging from 1 to 200 mg/L of MB, with 10 mL of solution and 20 mg of biochars. Four isotherm models such as Langmuir, Freundlich, Langmuir−Freundlich, and Redlich−Peterson fitting to the experimental data were carried out, and their nonlinear equations were expressed as follows

\[
q_e = \frac{K_l Q C_e}{1 + K_l C_e} 
\]

(1)

\[
q_e = K_f C_e^n 
\]

(2)

\[
q_e = \frac{K_l Q C_e^n}{1 + K_f C_e^n} 
\]

(3)

\[
q_e = \frac{K_r C_e}{1 + K_r C_e} 
\]

(4)

where \( C_e \) (mg/L) and \( q_e \) (mg/g) are the equilibrium concentration and the amount of MB adsorbed by biochars, respectively. \( K_l \) (L/g), \( K_f \) (mg\( ^{(1-n)} \) L\(^n \) g\(^{-1} \)), \( K_l \) (L\(^n \) mg\(^{-n} \)) and \( K_r \) (L/g) are the isotherm constants of Langmuir, Freundlich, Langmuir−Freundlich, and Redlich−Peterson models, respectively. \( Q \) (mg/g) is the maximum adsorption capacity. All the plots are shown in Figure 3.

The isotherm parameters and the correlation coefficient values \( (R^2) \) are listed in Table 2.

Figure 1. SEM images of raw biochars and SH-modified biochars. (a) PS biochar; (b) SH−PS biochar; (c) WC biochar; (d) SH−WC biochar.

Figure 2. BJH PSD curves for raw and SH-modified PS and WC biochars.
The fitted data listed in Table 2 suggested that the Freundlich isotherm model best described the experimental data of MB on PS and WC biochars with $R^2$ values of 0.955 and 0.920, respectively, from which the adsorption of MB onto PS and WC biochars could be described by multilayer adsorption onto the heterogeneous surface. Different from raw PS and WC biochars, the equilibrium data of MB on SH−PS and SH−WC fitted the Redlich−Peterson isotherm model with $R^2$ values of 0.969 and 0.935, respectively. Because the Redlich−Peterson isotherm model is an empirical equation that combines elements from both Langmuir and Freundlich equations, so it does not follow ideal monolayer adsorption and is assumed to a hybrid adsorption on the heterogeneous surface. Therefore, the fitting results indicated that the adsorption of MB onto SH−PS and SH−WC was a hybrid chemical reaction−sorption process on the heterogeneous surface.

In general, the maximum adsorption capacities for SH−PS and SH−WC are 16.21 and 11.03 mg/g, respectively, which are higher than raw biochars. That is to say, SH can improve the adsorption capacity of the biochars, which is consistent with the surface area observed above.

Table 2. Isotherm Model Parameters for MB Adsorption onto Biochars

| models                  | parameters | PS       | SH−PS    | WC        | SH−WC     |
|-------------------------|------------|----------|----------|-----------|-----------|
| Langmuir                | $K$        | 0.152    | 1.687    | 0.128     | 0.046     |
|                         | $Q$        | 10.845   | 14.328   | 9.226     | 14.691    |
|                         | $R^2$      | 0.890    | 0.877    | 0.881     | 0.933     |
| Freundlich              | $K_f$      | 3.630    | 7.296    | 2.120     | 1.471     |
|                         | $n$        | 0.229    | 0.163    | 0.331     | 0.480     |
|                         | $R^2$      | 0.955    | 0.931    | 0.920     | 0.892     |
| Langmuir−Freundlich     | $K_{lf}$   | $1.107 \times 10^{-4}$ | 0.779 | 0.121 | 0.038 |
|                         | $Q$        | $3.277 \times 10^4$ | 18.489 | 17.322 | 13.649 |
|                         | $n$        | 0.229    | 0.366    | 0.494     | 1.125     |
|                         | $R^2$      | 0.940    | 0.929    | 0.902     | 0.913     |
| Redlich−Peterson        | $K_r$      | $3.61 \times 10^{13}$ | 208.574 | 5.457 | 0.392 |
|                         | $a$        | $9.93 \times 10^{12}$ | 23.348 | 1.956 | 1.032 $\times 10^{-4}$ |
|                         | $n$        | 0.772    | 0.886    | 0.730     | 2.234     |
|                         | $R^2$      | 0.941    | 0.969    | 0.895     | 0.935     |
2.2.2. Adsorption Kinetics. Adsorption kinetics tests were conducted to evaluate the removal rate and adsorption mechanism of MB by raw and SH-modified biochars. As shown in Figure 3, the adsorption amount of MB increased rapidly in the first 60 min, and then, the MB adsorption capacity increased slowly and reached equilibrium.

In order to study the adsorption mechanism of MB onto biochars, the adsorption kinetic data were analyzed by pseudo-first-order kinetics, pseudo-second-order kinetics model, and Elovich model, which are shown as follows

\[
\text{Pseudo first order: } \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \\
\text{Pseudo second order: } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \\
\text{Elovich: } q_t = \frac{1}{\beta} \ln(1 + \alpha q_t)
\]

In these three adsorption kinetic models, \(q_e\) and \(q_t\) describe the amounts of MB adsorbed by the biochars at equilibrium and at time \(t\), respectively. \(k_1\) and \(k_2\) are the kinetic rate constants, respectively. \(\alpha\) and \(\beta\) are the initial adsorption rate and the desorption constant, respectively. The values of the kinetics parameters of MB adsorption onto the biochars were calculated based on the kinetic plots (Figure 4) and are given in Table 3 with corresponding correlation coefficients.

As shown in Table 3, among the three adsorption kinetics models tested, the adsorption kinetics data of MB onto biochars satisfied the Elovich model with the highest \(R^2\) in the range of 0.942–0.989. Because the Elovich kinetic model was developed by Zeldowitsch\(^{35}\) and assumed that the solid adsorbent surface is energetically heterogeneous, combined with the results of adsorption isotherm for the biochars discussed above, the MB adsorption onto raw and SH-pretreated biochars might be a combination of various adsorption processes.

Many research studies have reported that the whole adsorption process of dye onto biochars can be divided into

Table 3. Constants for MB Adsorption onto Biochars

| biochars | \(k_1\) | \(q_e\) | \(R^2\) | \(k_2\) | \(q_e\) | \(R^2\) | \(\alpha\) | \(\beta\) | \(R^2\) |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| PS      | 0.040  | 1.851  | 0.661  | 0.034  | 1.946  | 0.916  | 13.289 | 6.013  | 0.942  |
| SH–PS   | 0.021  | 5.910  | 0.819  | 0.005  | 6.126  | 0.956  | 2.121  | 1.401  | 0.976  |
| WC      | 0.045  | 1.884  | 0.401  | 0.032  | 2.014  | 0.776  | 8.633  | 5.496  | 0.989  |
| SH–WC   | 0.031  | 1.795  | 0.538  | 0.026  | 1.890  | 0.778  | 2.032  | 5.096  | 0.944  |

Figure 4. Adsorption kinetics data and modeling for MB onto biochars: (a) PS; (b) SH–PS; (c) WC; (d) SH–WC.
surface adsorption, intraparticle diffusion, and equilibrium stages. Among all of the stages, the intraparticle diffusion stage is a dominant step. In order to understand the adsorption process better, the intraparticle diffusion model (eq 8) was used to describe the diffusion mechanisms.

\[ q_t = K_i t^{1/2} + C \]  

(8)

where \( q_t \) is the amount of MB adsorbed by the biochars at time \( t \), \( K_i \) and \( t \) are the slope and intercept of the linear plot of \( q \) versus \( t^{1/2} \), respectively. The linearized plots of \( q_t \) versus \( t^{1/2} \) for the adsorption of MB onto all the biochars were obtained and shown in Figure 5.

As shown in Figure 5, there are two lines in the linear relationship between \( q_t \) and the square root of time. The first line attributed to instantaneous adsorption or external surface adsorption, where MB adsorbed from aqueous solutions toward the external surface of the biochars, and the second attributed to the particle diffusion, where adsorbed MB travels within the pores of the biochars. As can be seen in Figure 5, the fitting lines of intraparticle diffusion were off the origin, that is to say, the fitting lines have intercepts, indicating that intraparticle diffusion was not the only rate-controlling step, and film diffusion was also the rate-limiting steps of the adsorption process.

2.2.3. Regeneration and Adsorption Mechanism. The evaluation of regeneration of the biochar adsorbent is vital for the selection in practical applications, therefore, a regeneration study was carried out to evaluate the cyclic performance of SH–PS as a model biochar adsorbent. The results are presented in Figure 6. It can be clearly seen that the regenerated biochar adsorbent can adsorb about 14.00 mg/g MB after each regeneration cycle, and the adsorption capacity remained 86.92% of the initial adsorption capacity after four cycles, reflecting that good regenerability was realized for SH–PS. Therefore, SH-modified biochars can be used as an effective absorbent to remove MB from water after repeated treatment.

In conclusion, SH could increase the sorption capacities of biochars. This can be explained from the characteristic of SH, which is composed of some functional groups, such as carboxyl and hydroxyl, and hydroxyl is reported to increase the active sites of biochars. Meanwhile, sodium is also reported to act as catalysts and enhance the overall pyrolysis process. Moreover, particle diffusion is the crucial step of the MB adsorption, and mesopores provide channels for the diffusion of adsorbents. As discussed above, the mesopore volumes of
SH-modified biochars were higher than that of the raw biochars, which make the great contribution to the adsorption capacities. Therefore, SH played a significant promoting effect in the sorption capacity of biochars.

3. CONCLUSIONS
The SH-modified biochars were synthesized by pyrolysis of peanut shell and white clover at 600 °C, and the comparison of adsorption capacities of raw and SH-modified biochars was studied. The results demonstrated that SH-modified biochars have much higher MB adsorption capacities, which is consistent with the result of the surface area. The adsorption kinetic study indicated that MB sorption to SH-modified biochars could be dominated by multiple mechanisms, and both intraparticle diffusion and film diffusion are the rate-limiting steps of the adsorption process. Therefore, SH—biochars can be used as an economically efficient adsorbent for removing MB from wastewater.

4. MATERIALS AND METHODS
4.1. Materials. During our work, two agricultural residues are chosen as biomass materials: peanut shells and white clover residues.

Peanut is an important crop that is worldwide cultivated and brings large economic benefit, making the ability to convert amounts of peanut shells to a useable byproduct essential to improving the environmental burden of this crop. Peanuts were purchased from Xuzhou, Jiangsu Province, China. White clover is a perennial leguminous grass, which is widely planted in the world. White clover residues were obtained from the park nearby the school, Jiangsu, China. The obtained peanut shells and white clover residues were washed with deionized water and dried in the oven.

The two biomass samples were dried in an oven at 80 °C and grinded into 150–180 μm. SH at a purity of 99% was selected as an additive for the experiments, which was purchased from a local medical station.

The SH solution was prepared by dissolving 0.43 g of SH in 3 mL deionized water. Each 4.13 g of the ground peanut shells or white clover residues was immersed into the SH aqueous solution and stirred for 1 h. The mixture of biomass and SH was then dried in the oven at 85 °C to remove water. Finally, the samples were stored in desiccators until treated or for further analysis.

4.2. Biochar Production and Characterization. The raw and SH-treated biomass samples were placed in a porcelain boat in a 2” MTI tube furnace. The samples were heated in 100 mL/min flowing high purity N₂ to 600 °C at 5 °C/min and held for 1 h. After pyrolysis, the solid samples were cooled to room temperature under N₂ and removed from the furnace. The resulting raw and SH-modified biochars were labeled as PS, WC, SH—PS, and SH—WC.

The specific surface area and PSD of all the obtained biochars were performed with a Quantachrome Autosorb-iQ analyzer using the N₂ adsorption method over a partial pressure range of 0.05–0.3, and the samples were degassed at 180 °C for 18 h. The PSD was calculated by the BJH method. The surface morphologies of the biochars were recorded by a Quanta 250 field-emission scanning electron microscope.

4.3. Adsorption Experiments. Standard MB adsorption kinetics and isotherm experiments were used to investigate the capacity of the biochars to remove MB from water. The MB sorption capacity of the biochars was examined using a 1:500 (0.02 g biochar in 10 mL solution) at room temperature. The initial MB concentrations for isotherm analysis ranged from 1 to 200 mg/L. The vials were agitated at 200 rpm on an orbital shaker for 48 h, and then the samples were immediately separated to determine MB concentrations using a UV−vis spectrophotometer (MAPADA UV-1800PC) at 665 nm. The adsorption capacity of the biochars to MB at equilibrium was determined, according to the formula 1. Adsorption kinetics were examined using a 100 mg/L MB aqueous solution and time intervals of 5, 10, 20, 30 min and 1, 2, 5, 10, 20, 30, 48 h. All experimental treatments were performed in duplicate, and the average values are reported.

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

where \( q_e \) (mg/g) is the adsorption equilibrium capacity of the biochar, \( C_0 \) (mg/L) is the initial concentration of the MB aqueous solution, \( C_e \) (mg/L) is the equilibrium concentration of MB, \( m \) (g) is the weight of the biochar, and \( V \) (mL) is the volume of the MB aqueous solution.

4.4. Regeneration Experiments. SH-modified biochar absorbent regeneration experiments were carried out by using MB saturated SH-modified biochars obtained from adsorption isotherm experiments after separating the supernatant MB solution. The biochar absorbents were rinsed with DI water several times. The resulting absorbent was then desorbed in HCl solution (20 mL, 0.1 mol/L) for 60 min, which followed with neutralization by NaOH solution (20 mL, 0.1 mol/L) to pH = 7. Finally, the biochar absorbent was washed three times with DI water and then separated and dried at 80 °C for further MB sorption test with the same method described above. This sorption—regeneration experiment was repeated three times, and the average values are reported.

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The authors declare no competing financial interest.

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