Synthesis, Characterization, and Dye Removal of ZnCl₂-Modified Biochar Derived from Pulp and Paper Sludge

Fengxiao Zhao, Rui Shan, Wenjian Li, Yuyuan Zhang, Haoran Yuan, and Yong Chen

ABSTRACT: In this study, pulp sludge-derived biochar synthesized through modification with ZnCl₂ under multistep pyrolysis conditions was investigated for the effective removal of methylene blue (MB) from aqueous solution. Results showed that when the Zn2PT350-700 dosage was 10 mg, the largest adsorption amount of MB was 590.20 mg/g within 24 h under pH = 8. Kinetics and thermodynamics revealed that the adsorption process of MB can be described by the Freundlich isotherm model and the pseudo-second-order kinetic model, which means that multilayer sorption occurred on the heterogeneous surface of Zn2PT350-700. The analysis of the adsorption mechanism showed that electrostatic attraction between the deprotonated functional groups and MB⁺, cation exchange, and π-electron interaction played a major role in MB adsorption, followed by physical adsorption. After six cycles of desorption–adsorption, Zn2PT350-700 still maintained good adsorption performance. All results demonstrated that Zn2PT350-700 could perform as promising adsorbents for efficient MB removal from wastewater. Using biochar from paper and pulp sludge for wastewater remediation is an ingenious method, which can reduce the environmental and health risks related to industrial waste disposal, while providing remediation of water contaminated with industrial dye effluents.

1. INTRODUCTION

As the industrialization and urbanization of our country bloomed these years, the problem of water pollution has widely aroused public concern. Synthetic dye such as methylene blue (MB) has been widely applied in leather, paper, and textiles industries. Discharging a large amount of dyes into nature, along with bleach and salt, will affect the physical and chemical properties of fresh water, which may be toxic or even carcinogenic to aquatic organisms. At the same time, the wastewater entering the receiving water body will destroy the ecological balance and affect the photosynthetic activity due to the reduction of light penetration. There are a number of ways for removing synthetic dye nowadays, for instance, biodegradation methods, chemical processing, and adsorption. Adsorption plays an important role in wastewater treatment, featured as low-cost, efficient, and easy operation in comparison to other ways. There are several kinds of adsorbents for wastewater treatment, such as diatomite, alumina, calcite, zeolite, and so on. In recent years, biochar has been recognized as an effective adsorbent for dye removal due to its specific structural characteristics, economic feasibility, and environmental sustainability. Generally, biochar is normally obtained from the pyrolysis of all kinds of biomass, industrial and agricultural waste, as well as municipal sludge. The composition of biomass, heating rate, setting temperature, and residence time of the pyrolysis process and modified method all have a great influence on biochar properties. Pulp sludge (PS) from paper mill is the main organic residue produced in wastewater treatment of paper industry, including various organic compounds (fiber materials, such as cellulose, hemicellulose, lignin, etc.), as well as other inorganic wastes in the process, such as fillers, metal components, sand, etc. By 2020, China’s annual paper-making sludge production is about 12 million tons, mainly through landfill, land use, and incineration. To date, the methods for treating paper mill sludge are combustion landfill, recycling as a component of cement, etc. Some research has been done for using primary paper and pulp sludge (PS, a kind of residue produced in the primary treatment of wastewater from the pulp and paper industry) as a promising raw material of biochar for adsorbing pollutants in wastewater. For example, in Ferreira’s study, a simple and clean thermal treatment was proposed for preparing biochar from PS as fish anesthetics for removal of adsorbents,
the adsorption capacity of which reached 83.50 mg/g at 25 °C. In this study, biochar from PS showed a large specific surface area as well as rich surface functional groups, and the positively charged groups of the adsorbents could interact with the anesthetic solutions by electrostatic interactions, forming an electric double layer, which was conducive to the adsorption of organics. Calisto et al. reported the fabrication of a kind of biochar from PS by the pyrolysis at different temperatures and residence times for enhancing the antidepressant (citalopram) adsorption capacity. Physical and chemical characterization of these adsorbents revealed that pyrolysis effectively generated highly aromatic structures, and the best results were obtained by pyrolysis of PS at 800 °C for 150 min. In Coimbra’s research, the biochar obtained by the pyrolysis of primary pulp sludge was found to be capable of absorbing diclofenac, salicylic acid, ibuprofen, and acetaminophen, the adsorption mechanism of which is consistent with the above research. Besides, a kind of zero-valent iron magnetic biochar composites from the paper mill sludge was successfully synthesized for the treatment of real effluent containing pentachlorophenol, and the removal efficiency reached 79.7% after 240 min. Obviously, the above research provided references for using biochar prepared from paper mill sludge resources as adsorbents. However, most of the studies reported the removal of pharmaceuticals from wastewater, while a few of them reported the use of adsorbents derived from PS for the removal of dyes from wastewater. And the pyrolysis process adjustment and modified method have not been applied for the preparation of PS-derived biochar to improve the adsorption capacity for pollutants. Supposing that pulp sludge biochar served as an adsorbent through modification with ZnCl2, may meet the need of being a stable and highly efficient adsorbent for MB removal. Moreover, the utilization of pulp sludge biochar for adsorbent synthesis would not only help the commercialization of MB removal but also increase the environmental viability of the pyrolysis process. Consequently, this study aimed at investigating the adsorption performance of pulp sludge biochar modified by ZnCl2, and we chose MB to represent the typical synthetic dye contaminants of wastewaters to examine its adsorption capacity. To find the optimal preparation condition and explore the adsorption mechanism of contaminants, we discussed the impact of the impregnation ratio of modifiers and biomass as well as the temperature programming of pyrolysis. This study will comprehensively analyze the pyrolysis process of biomass and provide practical guidance for the preparation of biochar and the adsorption of pollutants.

2. MATERIALS AND METHODS

2.1. Materials. The raw material of biochar was obtained from the residue produced during the primary treatment of pulp and paper wastewater from a paper mill in Guangzhou, Guangdong Province, China. The pulp sludge was washed several times with deionized water and then dried in an oven to a constant weight. After being dried, raw pulp sludge was crushed and passed through a 60-mesh sieve. The reagents used in this research, such as ZnCl2 and MB, were all analytical reagents bought from Aladdin.

2.2. Preparation of Biochar and Modified Biochar. The pulp sludge was pyrolyzed to 400 °C in a tube furnace under a nitrogen atmosphere and kept at a constant temperature for 2 h to obtain the raw biochar (PB400).

The biochar modified with ZnCl2 was named as Zn\textsubscript{x}PT\textsubscript{y}, where \(x\) denotes the impregnation rate and \(y\) denotes the pyrolysis temperature. Taking Zn2PT700 as an example, it was prepared by adding 3.0 g of pulp sludge and 6.0 g of ZnCl2 into 20 mL of deionized water, stirring on a magnetic stirrer for 24 h, and then drying in an oven at 80 °C to constant weight. The mixture was put into a tube furnace and pyrolyzed at 700 °C for 2 h in a N\textsubscript{2} atmosphere. After cooling to room temperature, the modified biochar Zn2PT700 was finally obtained by washing with deionized water to neutrality. In view of the fact that some researchers adopted the method of preparation first and then impregnation for the modification of biochar, we made a more comprehensive comparison of different modification processes by mixing 3.0 g of PB700, 6.0 g of ZnCl\textsubscript{2}, and 20 mL of deionized water, the other preparation processes of which were consistent with the preparation of Zn2PT700, and the biochar prepared was named PB700-Zn2. Some studies had mentioned that multistep pyrolysis could improve the adsorption efficiency of the biochar. To compare the effects of preheating, the mixture (ZnCl2/PS = 2:1 by mass ratio) was preheated at 350 °C for 30 min first, then heated at 700 °C for 90 min, and the remaining steps were the same as the Zn2PT700, which was named Zn2PT350-700.

2.3. Adsorbent Characterization. Scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and elemental analysis (energy-dispersive spectrometry, EDS) were used for surface morphology and elemental composition analysis of biochar. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS, ESCA Lab 250Xi, Thermo Fisher) characterized the types and contents of functional groups of biochar. X-ray diffraction (XRD, XPert Pro MPD, PANalytical, Netherlands) analysis indicated the crystal structure of biochar. The mass loss was detected in the range of 30–1000 °C by an SDT Q600 thermogravimetric analyzer (TGA). Specific surface area, pore size distribution, and total volume were calculated by adsorption of N\textsubscript{2} using an Autosorb1-MP Quantachrome. Raman spectra were obtained with a Raman spectrometer (LabRAM HR800-LSSS, France) with a 532 nm laser. The concentration of MB was measured at the wavelength of 664 nm by an ultraviolet spectrophotometer (Lambda750, PerkinElmer).

2.4. Experimental Design of MB Adsorption. MB was dissolved in deionized water and then diluted to the required concentration to prepare the MB stock solution with a concentration of 2000 mg/L. In the contrast experiment of MB adsorption by modified biochar, 10 mL of MB was put into a 15 mL test tube, 20 mg of adsorbent was added, 80 rpm was used to oscillate for 1440 min, and the final concentration was determined by filtration with a 0.22 μm syringe filter.

In the experiment of the influence of pH on adsorption, 10 mL of MB solution with an initial concentration of 1000 mg/L was added into the test tube and the pH was adjusted to 1.0–10.0. In the experiment of the effect of adsorbent dosage on the adsorption, 10–80 mg of adsorbent is added into 10 mL of MB solution with an initial concentration of 1000 mg/L.

In the adsorption kinetics experiment, the solution was adjusted to the optimum pH, 20 mg of adsorbent was added, the initial concentration of MB was 1000 mg/L, and the reaction time interval was set from 5 to 1440 min. While in the adsorption isotherms experiment, the initial concentration of MB was 50–1000 mg/L, the reaction time was 24 h, and other experimental conditions are consistent with the above.
The adsorption efficiency of MB by biochar is expressed by adsorption capacity $q_e$, and removal rate $E$, and the calculation formulas are shown in eqs 1 and 2, respectively.

$$q_e = \frac{(c_0 - c_e)V}{m}$$  

$$E = \frac{(c_0 - c_e)100\%}{c_0}$$  

where $q_e$ is the adsorption capacity of biochar on MB at equilibrium, mg/g; $c_0$ is the concentration of the initial MB solution, mg/L; $c_e$ is the concentration of MB solution at adsorption equilibrium, mg/L; $V$ is the MB solution’s concentration volume, mL; $m$ is the mass of biochar added, g; and $E$ is the removal efficiency, %.

2.5. Desorption and Reuse Experiment. Anhydrous ethanol was used in the desorption experiment for MB desorption, using an MB solution of 1000 mg/L and the rest of the experimental setup was consistent with the initial adsorption experiment.

3. RESULTS AND DISCUSSION

3.1. Characterization. Table 1 and Figure 1 show the specific surface area and nitrogen adsorption curves of different biochars.

![Nitrogen adsorption curves of biochar.](image_url)

Table 1. Specific Surface Area and Pore Size of Different Biochars

| Sorbent       | PB700 | Zn2PT400 | Zn2PT500 | Zn2PT700 | Zn2PT900 | Zn2PT350-700 | PB700-Zn2 |
|---------------|-------|----------|----------|----------|----------|--------------|-----------|
| BET surface area (m$^2$/g) | 78.553 | 19.287 | 43.364 | 592.783 | 429.175 | 877.251 | 100.429 |

With increasing pyrolysis temperature, the Brunauer–Emmett–Teller (BET) surface area ($S_{BET}$) increased significantly, which may be due to the reaction of ZnCl$_2$ with pulp sludge at a high temperature, increasing the formation of microporous and mesoporous structures. When the carbonization temperature exceeded 700 °C, the specific surface area decreased while the temperature increased. This may be due to the collapse of the pore structure at a high temperature. The biochar had a larger specific surface area when the mass ratio of ZnCl$_2$ to pulp sludge was 2:1. Furthermore, in terms of different preparation methods, Zn2PT350-700, prepared by multistep pyrolysis, was of the largest $S_{BET}$, while PB700-Zn2 was of the minimum $S_{BET}$.

Fourier transform infrared (FTIR) spectroscopy can test and characterize the chemical structure of compounds by detecting molecular vibration and rotation, including various surface functional groups, such as amino, carbonyl, carboxyl, and so on. As Figure 2 shows, the peaks around 3400 cm$^{-1}$ indicated the vibrations of $-\text{OH}$ and those of 1610 cm$^{-1}$ were attributed to $C=\text{C}$ and $C=\text{O}$. Compared to that of PB700, the raw biochar, the peak strength of ZnCl$_2$-modified biochar (Zn2PT400) increased obviously at this point, which indicated that ZnCl$_2$-modified biochar was beneficial to increase the surface functional group intensity. Figure 2 also revealed that the strength of the surface functional group on ZnCl$_2$-modified biochar decreased with increasing temperature. Figure 2b shows that the order of $-\text{OH}$ peak strength was: Zn2PT350-700 > Zn1PT700 > Zn3PT700 > Zn2PT700 > PB700-Zn2, indicating that different modification processes had a greater impact on the surface functional groups. Moreover, the peak around 1380 cm$^{-1}$ corresponded to the $-\text{CH}_2$ absorption.

The surface micromorphology of the adsorbent greatly affects its adsorption performance. Scanning electron microscopy can clearly and intuitively reflect the micromorphology of biochar. Through electron microscopy, the morphological changes of materials before and after modification and adsorption can be better observed. The SEM-EDS images of the biochar before and after modification are shown in Figure 3. It shows that there was a massive structure on the surface of PB700, while the pore structure was not obvious. EDS analysis indicated that the main elements on the surface were C, O, Na, Si, Mg, as well as a few Fe, Al, and P (Figure 3a,b). After ZnCl$_2$ modification (Zn2PT350-700), tubular and rodlike structures appeared, pore structures increased, and the content of Zn in EDS images significantly increased (Figure 3c,d).

3.2. Removal Performance by Different Modified Biochars. 3.2.1. Influence of Pyrolysis Temperature. Preparation temperature is the main factor affecting the adsorption performance of biochar, and the optimum preparation temperature of different biomass raw materials is different. Figure 4 shows MB removal by ZnCl$_2$-modified biochar at different pyrolysis temperatures. It can be seen from the figure that as the preparation temperature increased, the removal rate and adsorption capacity increased, reaching the maximum value when the pyrolysis temperature was 700 °C, then decreased as pyrolysis temperature further increased. This may be because proper heating promotes the increase of surface functional groups and pore structure, but very high temperatures will lead to the collapse of pore structure and the decrease of surface functional groups; furthermore, the process of transforming amorphous carbon structure into graphite microcrystalline structure may lead to the decrease of specific surface area, which agrees with the result of Table 1 and Figure 1. It can be seen from the results that the best preparation temperature of ZnCl$_2$-modified biochar is 700 °C.

3.2.2. Influence of Impregnation Ratio. The mass ratio of the modifier and biomass raw material, also known as the impregnation ratio, is one of the key factors that affect the physical and chemical properties of biochar. Figure 5 shows the removal of MB under 700 °C when the mass ratios of ZnCl$_2$ and pulp sludge were 1:1, 2:1, and 3:1. Figure 5 also shows that the adsorption capacity of biochar on MB increased as the mass ratio increased, of which Zn2PT700 showed remarkable
adsorption performance. Then, as the impregnation ratio increased continuously, the adsorption capacity decreased. The results may be due to the fact that the activation efficiency of organic components was improved with the increase of ZnCl$_2$, and there were more active sites on the biochar surface, which is conducive to the adsorption of MB.\textsuperscript{26} When the mass ratio is 2:1, almost all of the organic carbon is activated, and the activation rate reaches the maximum; further increasing the impregnation ratio may cause ZnCl$_2$ to block the original pore structure and affect the adsorption effect. Therefore, 2:1 was selected as the optimal impregnation ratio.

3.2.3. Influence of Preparation Method. The adsorption effect of biochar prepared by different methods on MB is shown in Figure 6. It can be seen from the figure that as the initial MB concentration increased, the adsorption effect of the four different modified biochar gradually improved. The MB
removal efficiency of these four biochars was in the order Zn2PT350-700 > Zn2PT700 > PB700-Zn2, and this can be attributed to their different specific surface area and surface functional groups. The adsorption performance of biochar prepared by preheating at 350 °C for 30 min was significantly improved, which may be due to the fact that ZnCl₂ can change the carbonization process of lignin. When the temperature increases from 200 to 350 °C, ZnCl₂ can be used as a dehydrating agent to accelerate the decomposition of volatile matter, which may promote the formation of micropores. Therefore, the two-step pyrolysis method is a good way for producing biochar.

3.3. Influence of Reaction Conditions on Adsorption Performance.

3.3.1. Influence of Zn2PT350-700 Dose. The amount of adsorbent is considered to be an important factor affecting the adsorption process. Too little dosage of adsorbent may lead to poor effect, while excessive adsorbent may also lead to low efficiency. Figure 7 shows MB adsorption effect with different doses of Zn2PT350-700. With intensification of adsorption effect, the quantity of adsorbed contaminants per unit adsorbent dropped. With the increase of adsorbent dosage, the amount of pollutants adsorbed by unit adsorbent decreased and the removal ratio increased. When the amount of the adsorbent increased from 10 to 20 mg, the adsorption capacity slightly reduced while the removal ratio increased sharply; then, with a continuous increase of adsorbent dosage, the adsorption capacity per unit decreased sharply and the removal ratio of adsorbent increased slowly. Therefore, 20 mg was the optimal adsorbent dosage for MB removal in this experiment.

3.3.2. Influence of Environment pH. The influence of solution pH on MB removal is exhibited in Figure 8. With the...
increase of pH value from 1 to 8, the removal ratio of MB increased and reached the maximum at pH 8; the removal efficiency decreased when continually increasing pH to 10. This might be explained as follows. MB is a cationic organic dye, which exists in water in the form of MB at a low pH, and H⁺ in the solution competing with the MB⁺ leads to the poor removal effect. With the increase of pH value, OH⁻ proportion improved and biochar had negative charges on its surface, which is beneficial to adsorbing MB through electrostatic interactions.²⁷,²⁸ However, in the intense alkaline (pH > 8), the electrostatic repulsion between deprotonated hydroxyl (−O⁻) and deprotonated carboxyl (−COO⁻) caused the decline of adsorption capacity. Under comprehensive consideration of the above results, the optimal pH value of MB is 8.

3.4. Adsorption Isotherm and Kinetic Study. Isotherm refers to the relationship curve between the equilibrium concentration of adsorbate and the adsorption capacity of adsorbate at a certain temperature, which can describe the interaction between adsorbate and adsorbent. The adsorption of MB by Zn2PT350-700 was simulated by Langmuir and Freundlich isotherm models, which are conducive to discussing the interaction between adsorbate and adsorbent. Figure 9 shows that compared with the Langmuir model, the Freundlich model is more suitable for describing the adsorption process of MB by Zn2PT350-700, whose correlation coefficients ($R^2$) in Table 2 were higher than 0.99. The Freundlich isotherm model indicated that the adsorption is multilayer adsorption on a heterogeneous surface, the adsorption curve of which is nonlinear. In addition, the $n_F$ value was less than 1, which indicates that it was chemical adsorption, and MB could be easily absorbed on the surface of Zn2PT350-700.

The study of adsorption kinetics of MB is helpful to explore the adsorption mechanism. Pseudo-first-order (PFO) adsorption kinetics and pseudo-second-order (PSO) adsorption kinetics model represent the single-core and double-core adsorption processes in the liquid—solid system, respectively. It can be seen from Figure 10 that MB has a better fitting effect on the PSO kinetic model, and its correlation coefficient ($R^2 = 0.98241$) is greater than that of the PFO kinetic model ($R^2 = 0.86810$). In the first few minutes of the reaction, the adsorption occurred fast because there were many adsorption sites. As time went by, the adsorption sites were gradually occupied by MB⁺, and then adsorption slowed down, eventually reaching equilibrium. The PSO model assumes that the chemical adsorption process controls the reaction rate, which involves shared electrons or electron transfer between adsorbents and adsorbates. These results are consistent with the results of adsorption isotherms, indicating that chemical adsorption plays a dominant role in the removal of MB by Zn2PT350-700.²⁹

Table 3 lists the comparison of the maximum adsorption capacity of different adsorbents for dyes in previous studies.

![Figure 9. Adsorption isotherm plots of MB by Zn2PT350-700 fitted with the Langmuir and Freundlich isotherm models.](image)

![Figure 10. Adsorption kinetic studies of MB by Zn2PT350-700.](image)

Table 2. Fitting Parameters of Adsorption Isotherm and Adsorption Kinetics

| adsorption isotherm parameters | adsorption kinetic parameters |
|-------------------------------|-------------------------------|
| Freundlich                  | Langmuir                      |
| $k_F = 250.056$ mg/g         | $q_m = 558.950$ mg/g          |
| $n_F = 0.18389$             | $k_L = 0.80447$               |
| $R^2 = 0.99361$             | $R^2 = 0.90655$               |
| $q_{eq}$ = 487.69 mg/g       | $q_i$ = 454.71 mg/g           |
| $k_1 = 0.04031$             | $k_1 = 0.00013$               |
| $R^2 = 0.86810$             | $R^2 = 0.98241$               |

Table 3. Comparison Adsorption Capacity of MB by Different Biochar Adsorbents

| adsorbents         | modification method | adsorption capacity (mg/g) | reference |
|--------------------|---------------------|---------------------------|-----------|
| rice straw         |                     | 90.91                     | 30        |
| banana pseudostem  | phosphomolybdic acid| 146.23                    | 31        |
| sorghum straw      | FeCl₃               | 166.67                    | 32        |
| peanut shell       | sodium dodecyl sulfite| 463.26                  | 33        |
| seaweed            |                     | 512.67                    | 34        |
| Zn2PT350-700       | ZnCl₂               | 590.20                    | this work |

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The compiled data suggested that Zn2PT350-700 showed comparable adsorption capacity to biomass-derived adsorbent materials reported in previous literature for MB removal.

3.5. Adsorption Mechanism of MB. Transmission electron microscopy (TEM) spectrum and mapping analysis of Zn2PT350-700 before and after MB adsorption are shown.
in Figures 11 and 12. It can be seen that the surface of Zn2PT350-700 mainly contains three elements: C, O, and Zn, and the dark color point may be metal oxide. Figure 11 shows that S and N elements appear in the mapping diagram of biochar after MB adsorption (S and N are important elements of MB), which indicates that a large amount of MB is adsorbed on the surface of biochar.

Raman spectrum is a nondestructive analysis technique, which is based on the interaction between light and chemical bonds in materials and can provide detailed information on the chemical structure, phase and morphology, crystallinity, and molecular interaction of samples. As shown in Figure 13, a D peak appeared at 1300 cm\(^{-1}\), which corresponded to sp\(^3\) vibration of disordered carbon and represented the defect of C atom lattice. The peak near 1580 cm\(^{-1}\) was the characteristic absorption G peak caused by in-plane sp\(^2\) hybrid C–C bond stretching vibration, which was derived from sp\(^2\) vibration of complete graphitized structure. The G′ peak around 2700 cm\(^{-1}\) is the characteristic peak of a few layers of graphene. I\(_D\) and I\(_G\) represent the peak intensities of D and G, respectively, and the ratio I\(_D\)/I\(_G\) can be used as an important basis for judging the graphitization degree of carbon materials. The lower the ratio, the higher the graphitization degree of biochar.

The crystal structure of the modified biochar was analyzed by XRD. As shown in Figure 14, the diffraction peaks of the aluminum nitride structure (38.9, 65.6°) on the surface of biochar were observed, and the intensity of the peak changed little before and after adsorption. The peak around 25.2° corresponds to Zn\(_2\)SiO\(_4\) while the crystal structure of ZnO appears on 31.6, 34.2, 35.9, 47.3, 56.3, and 62.7°. The crystal structure of ZnCl\(_2\)-modified biochar changes with pyrolysis temperature. At a certain temperature, a large number of ZnO crystal structures appeared on the surface of the modified biochar, such as Zn2PT350-700. After MB adsorption, the peak strength of ZnO on Zn2PT350-700 decreased sharply, which shows that ZnO plays a major role in the adsorption process. In addition, a small amount of SiO\(_2\) was added to the pulp raw material for increasing toughness as well as defoaming and thickening. Zn\(_2\)SiO\(_4\) formed under the reaction of ZnO with SiO\(_2\) at a high temperature.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses of PS and ZnCl\(_2\)/PS mixture (mass ratio 2:1) are shown in Figure 15. There were two obvious mass losses in the curve of Figure 15a. The first weight loss corresponded to about 100 °C, which might be due to the free water removed without drying and the inherent bound water of biochar itself. The second weight loss occurred between 230 and 400 °C, which might be the decomposition of organic components in the raw materials, including cellulose and hemicellulose. The mass loss in this process was significant, about 50%. The second weight loss in Figure 15b occurred at 150–250 °C, which might be due to the reaction between modifier ZnCl\(_2\) and biochar, resulting in depolymerization and the formation of molten salt mixture; at the same time, ZnCl\(_2\) was transformed into Zn(OH)Cl. There was a large weight loss in the range of 500–700 °C, about 50%, and the maximum weight loss occurred at 580 °C, which corresponded to the transformation from Zn(OH)Cl to ZnO. When the pyrolysis temperature exceeded 800 °C, the last slight weight loss appeared. The reason is that the output of ZnO reacting with C was zinc vapor and CO or CO\(_2\) as well as SiO\(_2\) as mentioned above. The pyrolysis process of ZnCl\(_2\) and pulp mixture in nitrogen could be summarized as follows:

\[
\begin{align*}
\text{ZnCl}_2 + \text{H}_2\text{O} & \rightarrow \text{Zn(OH)}\text{Cl} + \text{HCl} \\
\text{Zn(OH)}\text{Cl} & \rightarrow \text{ZnO} + \text{HCl} \\
3\text{ZnO} + 2\text{C} & \rightarrow \text{CO}_2 + \text{CO} + 3\text{Zn} \\
2\text{ZnO} + \text{SiO}_2 & \rightarrow \text{Zn}_2\text{SiO}_4
\end{align*}
\]

For the purpose of further studying the adsorption mechanism of Zn2PT350-700 to MB, the composition and chemical states of biochar before and after adsorption were studied by XPS. XPS full spectrum analysis of Zn2PT350-700 manifested that the peaks of the surface of Zn2PT350-700 were mainly C, O, and Zn. As shown in Figure 16b, the C 1s signal could be divided into C=C/C–C (284.8 eV) and C–O–C (286.2 eV).
eV). Combined with infrared spectrum analysis, C≡C/C≡C, −OH, and −COOH are reductive, which can combine with electron–acceptor sites in MB via donor–acceptor π–electron interaction. The Zn 2p peak of Zn2PT350-700 is shown in Figure 16c, and the binding energies of 1045.2 and 1021.9 eV corresponded to the peaks of Zn 2p3/2 and Zn 2p1/2 of ZnO. The XRD and XPS results above showed that ZnO was the main form of Zn on the surface of biochar.

Figure 15. TG and DTG curves of PS (a) and ZnCl2/PS (b).

Figure 16. XPS spectrum of Zn2PT350-700: (a) XPS wide scan spectra of Zn2PT350-700, (b) C 1s binding state levels of Zn2PT350-700, and (c) Zn 2p binding state levels of Zn2PT350-700.
\( \zeta \)-Potential is the potential of the hydrodynamic shear surface of particles, which represents the surface charge property of interaction (repulsion or attraction) between particles and other particles or ions in the surrounding suspension. The \( \zeta \)-potential diagram of Zn2PT300-700 at different pH values (2–11) is shown in Figure 17. First, the \( \zeta \) potential decreased rapidly with an increase of pH value of the solution, then started to decrease slowly, and subsequently decreased rapidly again. The pH-dependent curve of \( \zeta \) potential is horizontal S-shaped, with two obvious inflection points. These inflection points indicated that there were two different types of pH-dependent functional groups on biochar, which affected the dissociation of functional groups in two different pH ranges. Combined with the infrared spectra of –OH and –COOH on biochar, \( \text{pH}_{d1} \) and \( \text{pH}_{d2} \) may be related to the dissociation of carboxyl and hydroxyl groups. When the \( \zeta \)-potential is zero, its corresponding pH is the isoelectric point \( \text{pH}_{\text{pzc}} \) of the sample. When the pH value of the environmental solution is less than \( \text{pH}_{\text{pzc}} \) the surface of the sample is positively charged and has an adsorption effect on anions; when the pH value of the environmental solution is greater than \( \text{pH}_{\text{pzc}} \) the surface of the sample is negatively charged, which can adsorb cations. The \( \text{pH}_{\text{pzc}} \) of Zn2PT300-700 is 2.09. It can be seen that under strong acidic conditions, a high concentration of \( H^+ \) makes the functional groups on the surface of biochar fully protonated and positively charged, which leads to the enhancement of electrostatic repulsion between MB\(^+\) and active sites on the surface of biochar. With the increase of \( OH^- \), the negative charge on the surface of biochar increases, which is beneficial to the adsorption of cation MB\(^+\). These results indicate that ion exchange may play a leading role in the adsorption of methylene blue under strong acidic conditions, while electrostatic interaction plays a leading role with the increase of alkalinity. Most biochars have been reported to range from 1.4 to 7.1, indicating that they carry a negative charge below circum-neutral pH. The same conclusion can be found in refs 36–38.

Zn2PT350-700 showed excellent performance for MB adsorption, the adsorption mechanisms of which include electrostatic attraction between the deprotonated functional groups and MB\(^+\); cation exchange; \( \pi \)-electron interaction; and the physical adsorption.

3.6. Desorption and Reuse of MB from Zn2PT350-700. The MB removal capacity of Zn2PT350-700 undergoing six cycles is shown in Figure 18, and ethanol was used for MB desorption. The adsorption and desorption processes were carried out at room temperature of 25 °C, which is closer to the conditions of practical engineering application. The removal efficiency of MB remained above 90%, and the adsorption capacity was about 500 mg/g after six adsorption–desorption cycles. The result indicated that Zn2PT350-700 can be reused efficiently for the removal of MB adsorption.

4. CONCLUSIONS

Several methods of modified pulp biochar preparation were investigated; the modified biochar Zn2PT350-700 was proved as a brilliant adsorbent for MB removal. When the Zn2PT350-700 dosage was 10 mg, the largest adsorption amount of MB was 590.20 mg/g. When the dosage was 80 mg, the removal ratio of MB could reach more than 99.9%. The optimal pH value for MB removal is 8. MB adsorption data fitted well with the PSO kinetic model and the Freundlich isotherm model, which means multilayer sorption occurred on the heterogeneous surface of Zn2PT350-700. The analysis of adsorption mechanism showed that electrostatic attraction between the deprotonated functional groups and MB\(^+\), cation exchange, and \( \pi \)-electron interaction played a major role in MB adsorption, followed by physical adsorption. After six cycles of desorption–adsorption, the adsorption capacity of the adsorbent only decreased by 10% and still maintained good adsorption performance. Zn2PT350-700 is expected to be used as a safe, efficient, and recyclable adsorbent to remove organic dyes from wastewater.

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