

Removal of Methylene Blue from Aqueous Solution by Phosphorus Tailings/Sludge-Derived Biochar

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Abstract

Municipal residual sludge and phosphorus tailings were used as raw materials to prepare biochar with pyrolysis temperatures of 300°C, 550°C and 800°C and phosphorus tailings addition ratios of 0.5%, 1% and 2%, respectively. The phosphorus tailings/sludge-based biochar with the best adsorption performance was determined by studying the adsorption of the phosphorus tailings/sludge-based biochar made under different conditions to a concentration of 100 mg/L methylene blue solution. The results of adsorption experiments, Boehm titration experiments and thermodynamic experiments showed that the phosphorus tailings/sludge biochar with a pyrolysis temperature of 800°C had the best removal rate of methylene blue at a concentration of 100 mg/L when the phosphorus tailings addition ratio was the same, and its biochar with a phosphorus tailings addition ratio of 1% could remove up to 90% of methylene blue. The phenolic hydroxyl group was beneficial to the adsorption of methylene blue by phosphorus tailings/sludge biochar. The adsorption process of methylene blue by phosphorus tailings/sludge biochar was consistent with the Freundlich equation, indicating that the adsorption process belonged to multilayer adsorption.

Keywords

physical biochar, adsorption mechanism, isothermal adsorption, Boehm titration

1. Introduction

The large volumes of excess sludge generated during urban wastewater treatment have become a major bottleneck hindering the sustainable development of the wastewater treatment industry. At the same time, the phosphate chemical industry produces hundreds of millions of tons of phosphate tailings annually; their long-term stockpiling not only consumes land resources but also poses environmental risks such as acid wastewater leakage and the leaching of heavy metal ions [1]. How to achieve the synergistic resource recovery of these two types of solid waste has become a major research focus in the field of environmental science and engineering [2]. Textile dyeing and printing wastewater is currently a key focus of water environmental protection efforts [3]. As a typical cationic dye, methylene blue is difficult to degrade naturally due to its stable aromatic ring structure. It exhibits high color intensity, high toxicity, and potential mutagenicity in aquatic environments, posing a serious threat to aquatic ecosystems and human health [4]. The development of

efficient, cost-effective, and environmentally friendly technologies for treating textile dyeing and printing wastewater is of great practical significance. Due to its large specific surface area, highly developed pore structure, and abundance of surface functional groups, biochar shows great promise for applications in the field of pollutant adsorption [5]. Research on sludge-based biochar has attracted particular attention, as it not only achieves the environmental management goal of “treating waste with waste,” but the organic matter and mineral components it contains may also enhance its ability to adsorb pollutants. In recent years, researchers have begun exploring the modification of biochar through the addition of exogenous minerals to further enhance its adsorption performance for specific pollutants. Phosphate tailings are rich in mineral components such as calcium and magnesium; their introduction into the sludge-biochar system may improve the adsorption capacity for cationic dyes through mechanisms such as enhanced precipitation and ion exchange [6].

This study used municipal sewage sludge and phosphate tailings as raw materials to prepare composite biochar under different pyrolysis temperatures (300°C, 550°C, 800°C) and phosphate tailings addition ratios (0.5%, 1%, 2%). The adsorption performance of the biochar on a 100 mg/L methylene blue solution was systematically investigated to determine the optimal conditions for the preparation of phosphate tailings/sludge biochar. By combining adsorption experiments, Boehm titration, and thermodynamic experiments, the adsorption mechanism was investigated. The aim is to provide a new approach for the resource utilization of sludge and phosphate tailings and to offer an efficient and cost-effective adsorbent material for the treatment of textile dyeing wastewater.

2. Materials and Methods

2.1 Laboratory equipment

XPM-Φ120X3 Three-Head Agate Grinder (Nanchang Liyuan Mining and Metallurgical Equipment Co., Ltd.), FT103 Miniature Soil Sample Crusher (Beijing Yongguangming Medical Instrument Factory), SHA-C Water Bath Shaker (Jinan Youke Laboratory Equipment Co., Ltd.), UV-5500 UV Spectrophotometer (Shanghai Yuanxi Instrument Co., Ltd.), JF2104 Analytical Balance (Yuyao Jinnuo Balance Instrument Co., Ltd.), SK-G06123K Vacuum Tube Electric Furnace (Tianjin Zhonghuan Electric Furnace Co., Ltd.).

2.2 Preparation of experimental materials and biochar

2.2.1 Experimental materials

Municipal sewage sludge and phosphorus tailings were used as raw materials. The two materials were separately crushed using a crusher and then further ground in an agate mill. The resulting powder was sieved through a 100-mesh screen, dried, and placed in a desiccator to cool to room temperature. Finally, the prepared sample was sealed in self-sealing bags for subsequent use.

2.2.2 Preparation of biochar feedstock from phosphate tailings/sludge

Preparation of Phosphate Tailings/Sludge Biochar: Weigh a total of 20 g of phosphate tailings and sludge. Mix thoroughly with phosphate tailings at addition ratios of 0.5%, 1%, and 2%, then place the mixture in a tube furnace for pyrolysis at temperatures of 300°C, 550°C, and 800°C. SBC300-0.5% denotes sludge biochar produced at a pyrolysis temperature of 300°C with a 0.5% phosphorus tailings addition ratio; the remaining phosphorus tailings/ sludge biochar are denoted as SBC300-1%, SBC300-2%, SBC550-0.5%, SBC550-1%, SBC550-2%, SBC800-0.5%, SBC800-1%, and SBC800-2%, respectively.

2.3 Adsorption of methylene blue by phosphate tailings/sludge biochar

A 0.1 g sample of phosphorus tailings/sludge biochar was weighed and placed into a 100 mL conical flask, followed by the addition of 20 mL of methylene blue solution at a concentration of 100 mg/L. The flask was sealed and shaken in a constant-temperature air-bath shaker at 25 °C and 150 rpm for 2 hours. After shaking, the mixture was filtered through filter paper, and the absorbance of the filtrate was measured at 650 nm using a UV-Vis spectrophotometer. The concentration of methylene blue adsorbed by the biochar was calculated based on a standard curve using the following formula. All experiments were performed in duplicate.

$$q = (c_0 - c) \times \frac{v}{M} \quad (1)$$

$$E = \frac{(c_0 - c)}{c_0} \times 100\% \quad (2)$$

In the equations, q (mg/g) represents the adsorption capacity; C_0 and C (mg/L) are the initial and equilibrium concentrations of methylene blue, respectively; V (L) is the volume of the solution; m (g) is the mass of the biochar; and R (%) represents the removal efficiency of methylene blue.

2.4 Isothermal Adsorption

For the adsorption isotherm experiments, 0.1 g of phosphorus tailings/sludge biochar was added to 20 mL of methylene blue solutions at varying initial concentrations (25, 50, 75, 100, 125, 150, and 200 mg/L). The vials were placed in a constant-temperature air-bath shaker at 25 °C and shaken at 150 rpm for 2 h. All experiments were performed in duplicate. After filtration through filter paper, the absorbance of the filtrate was measured at 650 nm using a UV-Vis spectrophotometer. The concentration of methylene blue adsorbed was calculated based on a standard curve, and the adsorption capacity and removal efficiency were determined. The adsorption data were then fitted to the Langmuir and Freundlich isotherm models.

Langmuir model equation:

$$Q_e = \frac{K_L Q_{max} C_e}{1 + K_L C_e} \quad (3)$$

Freundlich model equation:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

In the equations, C_e (mg/L) is the equilibrium concentration of methylene blue in solution; q_e (mg/g) is the equilibrium adsorption capacity; q_m (mg/g) is the maximum adsorption capacity; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F ((mg/g)(L/mg)^{1/n}) is the Freundlich adsorption equilibrium constant; and n is the Freundlich intensity parameter, which indicates the favorability of adsorption.

2.5 Boehm titration

Samples of SBC300-1%, SBC550-1%, and SBC800-1% (0.5 g each) were accurately weighed using an electronic balance. Three aliquots of each biochar were transferred into separate 100 mL conical flasks. Subsequently, 25 mL of 0.05 mol/L standard solutions of NaOH, Na₂CO₃, and NaHCO₃ were added to the flasks containing the corresponding biochar samples. The mixtures were shaken for 24 h, then filtered and thoroughly rinsed with distilled water. The combined filtrate was collected and titrated with standard 0.05 mol/L HCl solution using methyl red as an indicator to determine the amount of unreacted alkali. Blank experiments without biochar were conducted under the same conditions to correct for any interference from atmospheric CO₂.

$$nNaOH = \frac{[C_{NaOH}V_{NaOH} - C_{HCl}(C_{HCl} - V_1 - V_b)]}{W} \quad (5)$$

$$nNa_2CO_3 = \frac{[C_{Na_2CO_3}V_{Na_2CO_3} - C_{HCl}(C_{HCl} - V_2 - V_b)]}{W} \quad (6)$$

$$nNaHCO_3 = \frac{[C_{NaHCO_3}V_{NaHCO_3} - C_{HCl}(C_{HCl} - V_3 - V_b)]}{W} \quad (7)$$

V_b (mL) is the volume of HCl consumed in the blank titration (without biochar); C_{HCl} (mol/L) is the concentration of the standard HCl solution; C_i (mol/L) is the concentration of the standard base solution (NaOH, Na₂CO₃, or NaHCO₃); W (g) is the mass of the biochar sample; n is the stoichiometric factor (e.g., for Na₂CO₃, $n = 2$; for NaOH and NaHCO₃, $n = 1$).

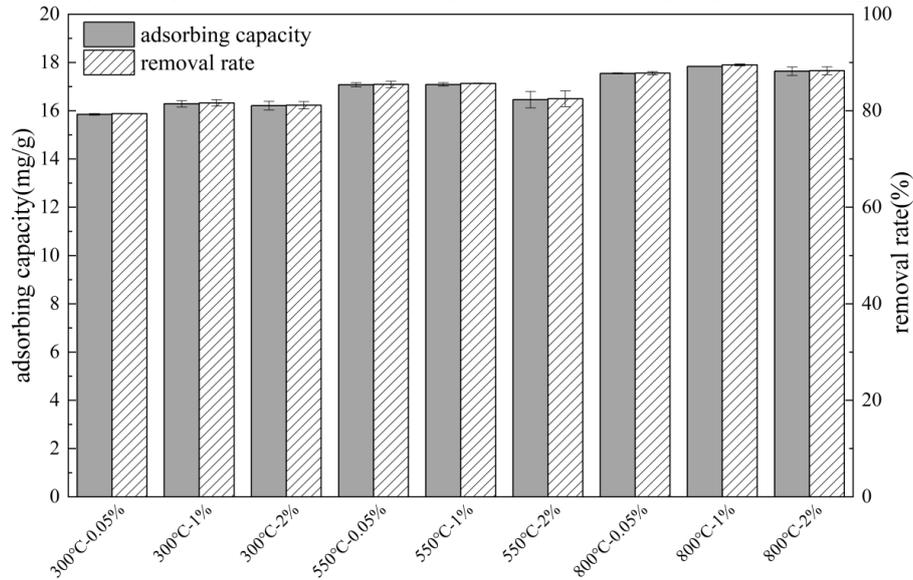
3. Results and Discussion

3.1 Adsorption Capacity and Removal Efficiency

The adsorption performance of phosphorus tailings/sludge-derived biochar toward methylene blue is presented in Figure 1. Under the pyrolysis temperature of 800°C, the biochar samples prepared with three phosphorus tailings addition ratios (0.5%, 1%, and 2%) achieved a maximum removal rate of 89% for methylene

blue, corresponding to an adsorption capacity of 17.84 mg/g. Experimental results indicate that, at a fixed phosphorus tailings addition ratio, the removal efficiency of methylene blue by the biochar increased with rising pyrolysis temperature. This trend can be attributed to the rapid release of volatile components such as tar at elevated temperatures, which modifies the internal pore structure and leads to the formation of a more developed pore network [7]. Moreover, at the same pyrolysis temperature, the biochar with a 1% phosphorus tailings addition ratio exhibited the best removal performance for methylene blue. The incorporation of an appropriate amount of phosphorus tailings may have enhanced the organic carbon content and surface activity of the biochar, thereby strengthening surface adsorption interactions and promoting the uptake of methylene blue [8].

Figure 1: Adsorption capacity and removal rate of methylene blue by phosphorus tailings/sludge biochar



3.2 Boehm Titration Results

While the Boehm titration method does not provide precise absolute quantification of surface functional groups on biochar, it yields semi-quantitative data that effectively reveal trends in oxygen-containing functional groups. Based on the adsorption performance, samples SBC300-1%, SBC550-1%, and SBC800-1% were selected for further characterization due to their superior adsorption capacities at different pyrolysis temperatures. These samples share the same phosphorus tailings addition ratio, ensuring good comparability and enabling meaningful correlation with subsequent isothermal adsorption experiments. Thus, the Boehm titration method was employed to analyze the surface functional groups of the three selected biochars, and the results are presented in Table 2. As the pyrolysis temperature increased from 300°C to 800°C, the phenolic hydroxyl content exhibited a continuous upward trend, with SBC800-1% showing the highest value. Notably, SBC800-1% demonstrated the best methylene blue removal efficiency and simultaneously possessed the highest phenolic hydroxyl content, suggesting that phenolic hydroxyl groups play a crucial role in the adsorption of methylene blue by phosphorus tailings/sludge biochar. This finding aligns with the results reported by Pereira et al. [9] in their investigation of the effect of activated carbon surface properties on benzene removal performance.

Table 2: Number of functional groups on the surface of phosphorus tailings/sludge biochar

Biochars	Functional group content (mmol/g)		
	Carboxyl	Butylidene	Phenolic hydroxyl group
SBC300-1%	6.448×10^{-3}	4.136×10^{-3}	2.034×10^{-3}
SBC550-1%	5.449×10^{-4}	6.745×10^{-3}	7.836×10^{-3}
SBC800-1%	9.411×10^{-4}	2.786×10^{-3}	9.110×10^{-3}

3.3 Isothermal adsorption

The Langmuir adsorption isotherm model assumes that the adsorbent surface is homogeneous, with all adsorption sites possessing equivalent energy, and that adsorption occurs as a monolayer. Upon saturation of

the adsorbate, the adsorption capacity reaches a maximum value, and no intermolecular forces exist between the adsorbed molecules. In contrast, the Freundlich model is based on the assumption of a heterogeneous adsorbent surface with a non-uniform energy distribution, describing multilayer adsorption behavior on such surfaces. This model not only applies to monolayer adsorption on biochar but also provides a robust explanation for adsorption mechanisms on heterogeneous surfaces; however, its applicability is primarily confined to low-concentration adsorption systems. The thermodynamic fitting results for the adsorption of methylene blue onto phosphorus tailings/sludge biochar are presented in Table 3 and Figure 2. As shown by the correlation coefficients of the adsorption isotherms in Table 3, the R^2 values for the Langmuir model ranged from 0.930 to 0.988, while those for the Freundlich model ranged from 0.979 to 0.999. All R^2 values exceeded 0.80, indicating that both models are applicable for describing this adsorption process. However, the Freundlich model exhibited consistently higher R^2 values than the Langmuir model, suggesting a superior fit. This implies that the adsorption of methylene blue by phosphorus tailings/sludge biochar is not a simple monolayer process but rather a multilayer adsorption involving both physical and chemical interactions on a heterogeneous surface [10]. Further analysis of the Freundlich model parameters revealed that the $1/n$ values ranged from 0.3279 to 0.5733, all falling within the 0–1 interval. According to adsorption theory, $1/n$ values between 0 and 1 indicate favorable adsorption and high adsorption intensity, further confirming that phosphorus tailings/sludge biochar exhibits strong adsorption affinity toward methylene blue [11]. This finding is consistent with the results reported by Elkatory et al. [12] on methylene blue adsorption.

Figure 2: Fitting diagrams of the Langmuir (a) and Freundlich (b) equations

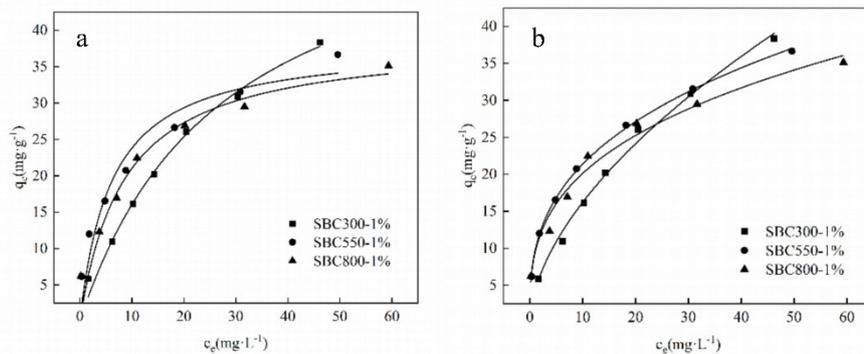


Table 2: Parameters of Langmuir Equation and Freundlich Equation

Biochars	Langmuir			Freundlich		
	K_L	$Q_m(\text{mg/g})$	R^2	K_F	$1/n$	R^2
SBC300-1%	0.036	60.52	0.988	4.318	0.574	0.993
SBC550-1%	0.164	38.30	0.930	9.692	0.343	0.999
SBC800-1%	0.117	38.89	0.937	9.453	0.328	0.979

4. Conclusion

(1) Under the same phosphorus tailings addition ratio, the biochar produced at a pyrolysis temperature of 800 °C exhibited superior adsorption performance, achieving the highest removal rate for methylene blue at an initial concentration of 100 mg/L. In contrast, at pyrolysis temperatures of 300°C and 550 °C, no significant differences were observed in either the adsorption capacity or removal rate among biochar samples prepared with varying phosphorus tailings addition ratios.

(2) The surface functional group content of the biochar was influenced by the pyrolysis temperature. The phenolic hydroxyl content reached its maximum at 800°C, suggesting that phenolic hydroxyl groups in phosphorus tailings/sludge biochar play a key role in facilitating the adsorption of methylene blue.

(3) The adsorption of methylene blue onto the biochar was better described by the Freundlich isotherm model, indicating a multilayer adsorption process. The $1/n$ values for all samples ranged between 0 and 1, suggesting that the adsorption occurred readily and with favorable affinity.

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Conflicts of Interest

The authors declare no conflict of interest.

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