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Adsorption Effect of Phosphate Modified Grape Branch Biochar on Cd^{2+}

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Abstract

Two major problems facing agriculture at present are soil pollution and the disposal of solid wastes generated during plant growth. The method of preparing biochar from solid wastes produced by plants is a means of maximizing the use of resources to combat the problem of soil pollution. In this study, we did not choose straw in the traditional sense but the waste branches from grape pruning, which has higher lignin cellulose, as the raw material. The biochar derived from grape branches pyrolyzed at 300˚C for two hours was utilized as a raw material to prepare modified biochar with varying concentrations of phosphoric acid. The adsorption performance and mechanism of Cd^{2+} were explored through experiments involving different concentrations, addition amounts, reaction times, kinetic analyses, and isothermal adsorption tests. The findings indicated that the optimal adsorption of Cd^{2+} occurred with a 20% phosphoric acid concentration, achieving the highest adsorption rate of 84.62%. At a dosage of 10 g/L, the maximum adsorption capacity reached 7.02 mg/g. The adsorption kinetics and isothermal adsorption of Cd^{2+} on biochar modified with 0.2% phosphoric acid (0.2 PB) closely followed the pseudo-first-order kinetics model ($R^2 > 0.98$) and the Freundlich model ($R^2 > 0.97$), respectively. This suggests that the adsorption process involves both physical and chemical mechanisms. SEM and FTIR analyses revealed that phosphoric acid modification primarily increased the biochar's specific surface area and enhanced certain original functional groups. The adsorption process predominantly involved rapid ion diffusion and chemical adsorption, as confirmed by kinetic analysis and isothermal adsorption model analysis. In summary, the adsorption efficiency of 0.2 PB significantly improved, showing potential and feasibility for heavy metal remediation in soil. This supports the environmentally friendly concept of "treating waste with waste".

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Keywords

Phosphate Modified, Grape Branch Biochar, Adsorbs, Cd

1. Introduction

Cadmium is among the most prevalent and dangerous heavy metals encountered. The rapid growth of China's industrial and agricultural sectors has led to an escalation in soil heavy metal contamination (Luo et al., 2019). Cadmium (Cd), known for its high reactivity and mobility in soil, poses significant health risks, making the remediation of Cd in soils a critical issue. Currently, techniques for addressing soil heavy metal contamination primarily comprise soil amendment, chemical leaching, bioremediation, and in-situ immobilization (Moradi et al., 2019). In-situ immobilization, in particular, is becoming increasingly popular due to its cost-effectiveness and minimal soil disruption. This method involves applying immobilizing agents to polluted soils to decrease the heavy metals' availability and mobility. Frequently used immobilizing agents include clay minerals, activated carbon, zeolites, phosphate rocks, sepiolite, nano zero-valent iron, solid wastes, and biomass materials (Fan et al., 2020; Kang et al., 2021).

Studies have revealed that biochar produced from the thermal decomposition of agricultural waste, characterized by its extensive specific surface area, abundant surface active functional groups, and superior complexation and adsorption capacities, is at the forefront of research into the in-situ immobilization for the remediation of heavy metal contamination in agricultural soils (Cheng et al., 2021; Sun et al., 2020). Biochar primarily immobilizes heavy metals in the soil through adsorption, altering the form in which heavy metals are present in contaminated soils, thereby reducing their activity and bioavailability. Nevertheless, the performance of some biochars produced using traditional pyrolysis techniques may not meet the required standards due to variations in the structural characteristics of the biochar substrates, limiting their effectiveness in adsorption and environmental applications. Enhancing their properties through modification has been suggested as a strategy to improve the remedial effects of biochar on pollutants (Zhang et al., 2019; Asadullh et al., 2019; Shang et al., 2018).

Grapes are among the highest yielding and most extensively cultivated fruits globally, with China being a leading grape producer, ranking first and second worldwide in terms of production and cultivation area, respectively (OIV Database, 2022). Pruning, an essential annual task in grape cultivation management, results in significant amounts of grape pruning waste (Achaby et al., 2018; Pachón et al., 2020). However, for a long time, the treatment methods and channels of grapevine branches have been relatively single, without considering the problem of resource allocation. In China, every year, tens of millions of tons of grapevine residues are casually discarded, left to rot or directly open burning,

resulting in serious environmental pollution and safety hazards, causing a huge waste of resources (Cebrián-Tarancón et al., 2019; Sánchez-Gómez et al., 2017). The development of bioactivated carbon from grape pruning residues has become one of the most popular research topics (Pizzi et al., 2018; Zhang et al., 2021; Wang et al., 2021). Previous studies aimed to evaluate the possibility of producing activated carbon from grape berry residues, mainly using chemical activation methods, such as phosphoric acid activation (Corcho-Corral et al., 2006) and carbon dioxide activation (Nabais et al., 2010), which combined with physicochemical analysis and structural characterization probed that grape twigs are a suitable raw material for the preparation of activated carbon. Among them, acid-base modification in acid modification is a more effective and widely recognized method, phosphoric acid can dissolve cellulose, accelerate the dehydration reaction in the carbonization process to produce porous carbon materials, increase the specific surface area of the material, produce more characteristic surface functional groups for chemical adsorption, and the introduction of acidic surface functional groups can provide more adsorption sites for the biochar, and adsorb more heavy metals through complexation, so that the performance of the virgin performance of biochar was improved (Peng et al., 2017; Zhang et al., 2020; Li et al., 2017; Wang et al., 2020). Moreover, the activation temperature of phosphoric acid is low, about 450˚C, and the preparation of biochar at low temperature can save time and cost, and is less corrosive and harmful to the environment. Zhang et al. (2022) introduced a method for creating phosphoric acid-impregnated modified biochar (PRBC), demonstrating that phosphoric acid modification not only significantly boosts the biochar's specific surface area and oxygen-containing functional group count but also enhances its affinity towards Cd and Cu heavy metal ions, by forming —O—P surface groups.

This research focuses on grape branches as the raw material to examine the variation in surface physicochemical characteristics of grape branch biochar under different phosphoric acid modification scenarios. It aims to delve into the adsorption behaviors and mechanisms of such modified biochar against the heavy metal cadmium (Cd), offering insights for the efficient and resourceful application of grape branches and for the mitigation of soil heavy metal contamination.

2. Materials and Methods

2.1. Preparation of Phosphoric Acid-Modified Biochar

We prepared the biochar by pyrolyzing grape branches at 300˚C for two hours, then weighing 2.0 grams of this biochar into a 250 ml conical flask. To each flask, we added 100 ml of phosphoric acid at concentrations of 0.2 mol·L^{-1}, 0.3 mol·L^{-1}, and 0.4 mol·L^{-1}, respectively. After thorough stirring and sealing with film, the flasks were placed in a thermostatic shaker. The conditions were set to a speed of 200 revolutions per minute and a temperature of 25˚C, with shaking continuing for 6 hours followed by a rest period of 1 hour. Subsequent to filtering, the biochar was thoroughly washed with deionized water until the filtrate

was clear and then dried in an oven at 75˚C to a constant weight. This resulted in phosphoric acid-modified grape branch biochar at concentrations of 0.2 mol·L^{-1}, 0.3 mol·L^{-1}, and 0.4 mol·L^{-1}, denoted as 0.2-PB, 0.3-PB, and 0.4-PB, respectively. The biochar's structural and surface characteristics were analyzed using a FlexSEM scanning electron microscope to observe sample morphology, and an American PE company's Nicolet is 5 Fourier Transform Infrared Spectroscope (FTIR) to examine changes in the organic components within the biochar.

2.2. Experiments on Adsorption of Heavy Metal Cd by Phosphoric Acid-Modified Biochar

2.2.1. Experimental Procedure to Assess the Impact of Varying Modifier Concentrations on Adsorption Efficiency

Utilizing a 1% HNO_3 solution for dilution, precisely measure 0.1 g each of 0.2-PB, 0.3-PB, and 0.4-PB and place them into 100 ml plastic bottles. Then, introduce 60 ml of a 20 mg·L^{-1} Cd $(NO_3)_2$ solution into each bottle. The pH of these solutions is adjusted to 6.0 ± 0.2 using both 0.5 mol·L^{-1} NaOH and 0.5 mol·L^{-1} HNO_3 solutions, after which they are securely sealed with transparent plastic wrap. These preparations are then placed in a thermostatic shaker set at 25˚C and a shaking speed of 200 revolutions per minute for 12 hours. Following this, the samples are centrifuged at 4000 revolutions per minute for 5 minutes, and the supernatant is filtered using a 0.45 μm cellulose acetate membrane filter. The final step involves diluting the samples to a set volume and analyzing the concentration of Cd^{2+} ions in the filtrate using atomic absorption spectrophotometry, with each sample undergoing three replicate analyses. The quantity of Cd^{2+} adsorbed and the efficiency of its removal are determined using specific Formulas (1) and (2), which calculate the adsorption capacity and efficiency of the biochar for heavy metals at equilibrium.

$$Q_t = \frac{(C_i - C_t)\cdot V}{m} \tag{1}$$

$$E = \frac{C_i - C_t}{C_i} \times 100\% \tag{2}$$

The formula and its components are described as follows:

Q_t: The amount of Cd^{2+} adsorbed by the biochar at time t (mg/g);

C_i: The initial concentration of Cd^{2+} (mg/L);

C_t: The concentration of Cd^{2+} at time t (mg/L);

V: The volume of the Cd^{2+} solution added (L);

M: The mass of biochar added (g);

E: The removal rate of Cd^{2+}.

2.2.2. Experimental Procedure to Evaluate the Impact of the Amount of Biochar on Adsorption

A range of biochar quantities, including 0.02 g, 0.05 g, 0.1 g, 0.2 g, and 0.3 g of the phosphoric acid-modified biochars 0.2-PB, 0.3-PB, and 0.4-PB, are each

added to 100 ml plastic bottles. To these bottles, 60 ml of a 20 mg·L^{-1} cadmium nitrate (Cd $(NO_3)_2$) solution is also added. The pH of each solution is adjusted to 6.0 ± 0.2 using solutions of 0.5 mol·L^{-1} NaOH and 0.5 mol·L^{-1} HNO_3. The bottles are then sealed with clear cling film and placed into a thermostatic shaker at 25˚C with a rotation speed of 200 revolutions per minute for a duration of 12 hours. After shaking, the samples are centrifuged for 5 minutes at 4000 r·min^{-1}. The clear supernatant liquid is then filtered through a 0.45 μm cellulose acetate membrane filter. For analysis, the samples are diluted with a 1% HNO_3 solution and the concentration of Cd^{2+} in the filtrate is determined using atomic absorption spectrometry, with three replicates for each sample. The adsorbed quantity of Cd^{2+} and the rate of its removal are derived using the previously mentioned Formulas (1) and (2).

2.2.3. Experimental Procedure to Assess the Effect of Biochar Quantity on Adsorption Performance

For this set of experiments, 0.1 g of each biochar variant (0.2-PB, 0.3-PB, and 0.4-PB) is measured and placed into separate 100 ml plastic bottles. To each bottle, 60 ml of a 20 mg·L^{-1} cadmium nitrate ($Cd(NO_3)_2$) solution is introduced. The solution pH is then regulated to 6.0 ± 0.2 with 0.5 mol·L^{-1} solutions of NaOH and HNO_3. The bottles are sealed with transparent cling film and placed in a temperature-controlled shaker set at 25˚C, shaking at a rate of 200 revolutions per minute for varying time intervals: 5 minutes, 10 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 6 hours, and 12 hours. After shaking, the samples are centrifuged for 5 minutes at a speed of 4000 revolutions per minute, then the supernatant is filtered through a 0.45 μm cellulose acetate membrane. The filtrate is subsequently diluted to a known volume using a 1% HNO_3 solution, and the concentration of Cd^{2+} is measured with an atomic absorption spectrometer, with three repetitions for each sample. The amount of Cd^{2+} adsorbed by the biochar and the rate of its removal are computed using Formulas (1) and (2).

2.2.4. Adsorption Kinetics Test

In order to delve into the adsorption dynamics of modified biochar towards Cd^{2+} ions, the sampling data obtained at varying time intervals during the aforementioned adsorption experiments are employed. Pseudo-first-order and pseudo-second-order kinetic models are utilized to simulate and fit the cadmium adsorption processes of the various modified biochars. The mathematical expressions for these models are as follows:

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

The formula and its components are described as follows:

Q_e represents the adsorption capacity at equilibrium, in mg·g^{-1};

Q_t is the capacity of adsorption at a given time t, in mg·g^{-1};

K_1 is the rate constant for the pseudo-first-order adsorption kinetics, in

$g \cdot mg^{-1} \cdot h^{-1}$;

K_2 denotes the rate constant for the pseudo-second-order adsorption kinetics, in $g \cdot mg^{-1} \cdot h^{-1}$.

2.2.5. Experiment on Isotherm Adsorption

A total of 0.1 g samples of biochar, which were modified using phosphoric acid solutions of varying concentrations, were each placed into 100 ml plastic bottles. Into each bottle, 60 ml of cadmium nitrate ($Cd(NO_3)_2$) solutions with concentrations of 2, 5, 10, 20, 40, 80 $mg \cdot L^{-1}$ were added. The pH of these solutions was adjusted to 6.0 ± 0.2 using both 0.5 $mol \cdot L^{-1}$ solutions of NaOH and HNO_3. The bottles were then sealed with transparent plastic film and the caps were securely tightened before being placed into a temperature-controlled orbital shaker. The samples were agitated at a speed of 200 revolutions per minute (rpm) at a constant temperature of 25˚C for 12 hours. Following agitation, the samples were centrifuged at 4000 rpm for 5 minutes, and the supernatant was collected and filtered through a 0.45 μm cellulose acetate membrane filter. The concentration of Cd^{2+} ions in the filtrate was then quantified using atomic absorption spectrophotometry, with three replicate experiments conducted for each sample.

For the analysis of the experimental data, the isothermal adsorption behavior of Cd^{2+} on the modified biochar was examined by fitting the data to both the Langmuir (5) and Freundlich (6) isotherm models. Isothermal adsorption curves were generated to identify the model that best fits the data, aiming to determine the maximum adsorption capacity of the biochar for Cd^{2+}. The calculations for the adsorption models are as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_1} \tag{5}$$

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_f \tag{6}$$

Within these formulas:

C_e: represents the equilibrium concentration in $mg \cdot L^{-1}$;

Q_e: the equilibrium adsorption amount, measured in $mg \cdot g^{-1}$;

Q_m: denotes the saturated adsorption capacity of the biochar, also in $mg \cdot g^{-1}$;

K_1, Q_m: the adsorption constants according to the Langmuir model;

K_f, $1/n$: the adsorption constants as per the Freundlich model.

2.2.6. Biochar Characterization

To analyze the surface morphology of biochar, samples are prepared and examined under a Scanning Electron Microscope (SEM). This technique scans the sample with a focused beam of electrons to reveal the microstructural characteristics and surface morphology of the biochar. The process includes mounting the biochar on a stage, applying a gold coat for conductivity, drying, and then observing under an SEM.

For the determination of functional groups, a Nicolet is 5 Fourier Transform Infrared Spectrometer (FTIR) is employed. This involves a pellet method where

1 - 2 mg of biochar is finely ground with dry potassium bromide (KBr), a chromatography-grade powder (around 100 mg, 200 mesh), in approximately a 1:100 ratio. This mixture is then compressed under 25 - 27 MPa into a pellet for analysis. The pellet is placed in the FTIR spectrometer, ensuring the light beam intersects the pellet at two points, and scanned with a resolution exceeding 0.4 cm^{-1}, covering a spectrum from 4000 cm^{-1} to 500 cm^{-1}.

3. Results and Discussion

3.1. The Effect of Different Modifier Concentrations on Adsorption Efficiency

The data presented in the charts (Figure 1) illustrate the influence of varying concentrations of phosphoric acid-modified biochar derived from grapevine branches (PBC) on the adsorption efficiency for Cd^{2+}, with an initial Cd^{2+} concentration set at 20 $mg{\cdot}L^{-1}$. The concentrations of phosphoric acid used for modification were 0.2 $mol{\cdot}L^{-1}$, 0.3 $mol{\cdot}L^{-1}$, and 0.4 $mol{\cdot}L^{-1}$. The results highlight a significant enhancement in Cd^{2+} adsorption by the biochar treated with phosphoric acid. It's noteworthy that the adsorption capacity and efficiency are influenced not only by the amount of biochar but also by the concentration of Cd^{2+}, showing a similar trend in their changes across different modification levels. The achieved adsorption capacity and efficiency at these concentrations were 7.19 mg/g at 63.99%, 6.37 mg/g at 63.02%, and 6.18 mg/g at 62.81%, respectively. However, an increase in phosphoric acid concentration led to a decrease in both adsorption capacity and efficiency for Cd^{2+}. This reduction could be attributed to the high levels of phosphoric acid, which might lead to the formation of an insulating layer of phosphates and polyphosphates around the

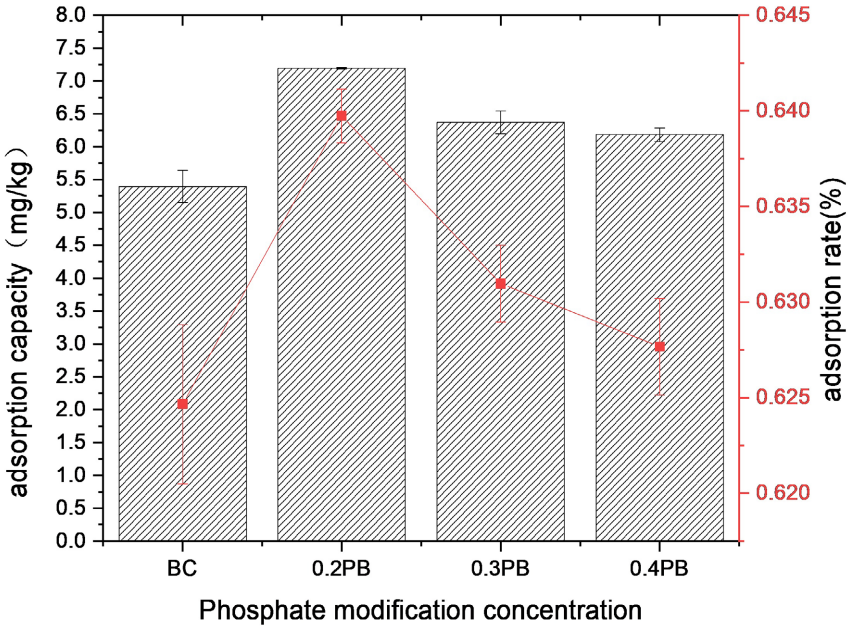


Figure 1. Effect of modified concentration on adsorption test.

biochar, thereby impeding the formation of pores conducive to metal ion adsorption (Wang et al., 2023). The variation in biochar's surface area due to acid modification, which depends on the type and concentration of the acid used, suggests that selecting the optimal acid concentration is crucial for maximizing adsorption efficiency (Wang & Liu, 2023). Accordingly, biochar modified with 0.2 mol·L^{-1} phosphoric acid demonstrated the most effective Cd^{2+} adsorption capability.

3.2. The Influence of Reaction Time on the Efficiency of Adsorption Processes

The study (**Figure 2**) illustrates the dynamic of Cd^{2+} adsorption by grapevine branch biochar treated with varying phosphoric acid concentrations (0.2-PB, 0.3-PB, and 0.4-PB), highlighting the relationship between unit adsorption capacity and different reaction times. The overall trend across the modifications shows a rapid acceleration of adsorption within the first 0 - 30 minutes, achieving adsorption saturation between 60 to 120 minutes. Beyond 120 minutes, the increase in adsorption levels off, indicating a state of equilibrium, a finding that aligns with the research conducted by Qin Siyuan (Qin, 2022). This rapid attainment of equilibrium is attributed to several factors: the biochar used in the adsorption tests has a relatively small diameter, a porous structure, a large specific surface area, and abundant surface functional groups. At the start of adsorption, the high porosity of the biochar facilitates extensive contact between Cd^{2+} and the biochar surface, providing numerous adsorption sites. The adsorption equilibrium is rapidly achieved through swift diffusion and chemical adsorption of ions present in the solution (Chen et al., 2023). At equilibrium, the adsorption capacities for Cd^{2+} by 0.2-PB, 0.3-PB, and 0.4-PB were 7.03, 6.94, and 6.70 mg/g, respectively, with the 0.2-PB modification showing the optimum performance.

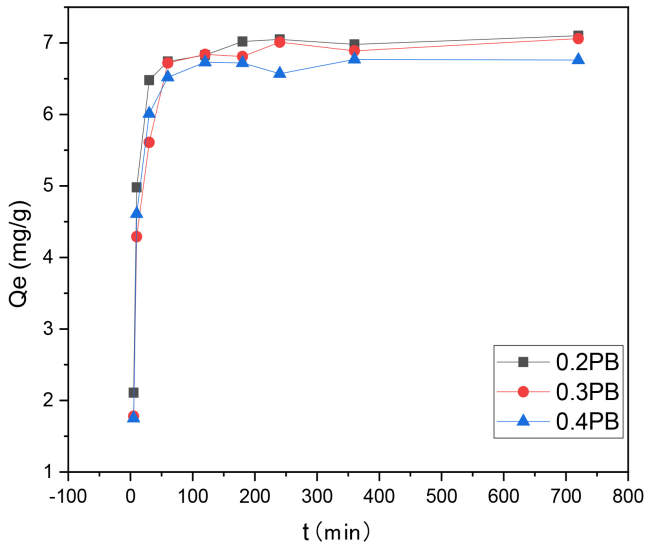


Figure 2. Effect of reaction time on adsorption capacity.

3.3. Impact of Biochar Application Rate on Adsorption Efficacy

The study (**Figure 3**) reveals how the amount of biochar added, varying by modification concentration, influences its capacity to adsorb Cd^{2+}. As the quantity of biochar is increased, the trend observed in adsorption efficiency for cadmium ions initially rises before falling. The peak adsorption occurs at a biochar addition rate of 0.1 g (10 g/L), with capacities recorded at 7.02 $mg \cdot g^{-1}$, 6.75 $mg \cdot g^{-1}$, and 6.54 $mg \cdot g^{-1}$, respectively. This pattern may stem from the lesser efficacy of modified biochar in physically or chemically binding Cd^{2+} at lower quantities. With an increase in biochar, the rate of adsorption improves, reaching saturation at 0.1 g. Upon saturation, the increment in added amounts leads to a slowed growth in adsorption rates, with phosphoric acid-modified biochar at 0.2 PB showcasing the most robust cadmium adsorption capacity, peaking at an 84.62% rate. Post-saturation, a negative correlation emerges between the amount of cadmium adsorbed and the adsorption rate, likely due to agglomeration that impedes Cd^{2+}'s diffusion to the biochar's surface (Ma et al., 2017). The findings underscore that variations in biochar quantities significantly impact cadmium adsorption efficiency. Taking into account the per-unit adsorption capacity, rate of adsorption, and associated costs, a concentration of 10 g/L 0.2-PB is recommended for optimal performance.

3.4. Analysis of Adsorption Kinetics

Kinetic models are commonly used to study the changes in rate during the adsorption process. The distinction between pseudo-first-order kinetics and pseudo-second-order kinetics lies in that the former can be better described by physical adsorption, mainly controlled by diffusion, while the latter is mainly characterized by chemical adsorption involving electron transfer. According to the graph, the measured values of different concentration phosphoric acid-modified grapevine biochar (**Figure 4** 0.2 PB, **Figure 4** 0.3 PB, and **Figure 4** 0.4 PB) basically conform to both models after convergence of the pseudo-first-order and pseudo-second-order kinetic model fittings. Under the pseudo-first-order kinetic model, the adsorption saturation amounts Qe (**Table 1**) of modified biochar for 0.2-PB, 0.3-PB, and 0.4-PB are shown as 0.2 PB (6.95 $mg \cdot g^{-1}$) > 0.3 PB (6.86 $mg \cdot g^{-1}$) > 0.4 PB (6.67 $mg \cdot g^{-1}$). Under the pseudo-second-order kinetic model, the adsorption saturation amounts Qe are 0.2 PB (7.32 $mg \cdot g^{-1}$) > 0.3 PB (7.28 $mg \cdot g^{-1}$) > 0.4 PB (7.05 $mg \cdot g^{-1}$).

The fitting coefficients of the pseudo-first-order kinetic equations (**Table 1**) for 0.2-PB, 0.3-PB, and 0.4-PB are 0.983, 0.982, and 0.9787, respectively; the fitting coefficients of the pseudo-second-order kinetic equations are 0.965, 0.978, and 0.961. After convergence, the kinetic equation fittings all show significant correlation ($R^2 > 0.9$), and the fitting coefficients of the pseudo-first-order kinetic equations are greater than those of the pseudo-second-order kinetic equations. In summary, the adsorption process of phosphoric acid-modified grapevine biochar on Cd is more in line with the pseudo-first-order kinetic model, mainly physical adsorption, and 0.2 PB has the best adsorption effect.

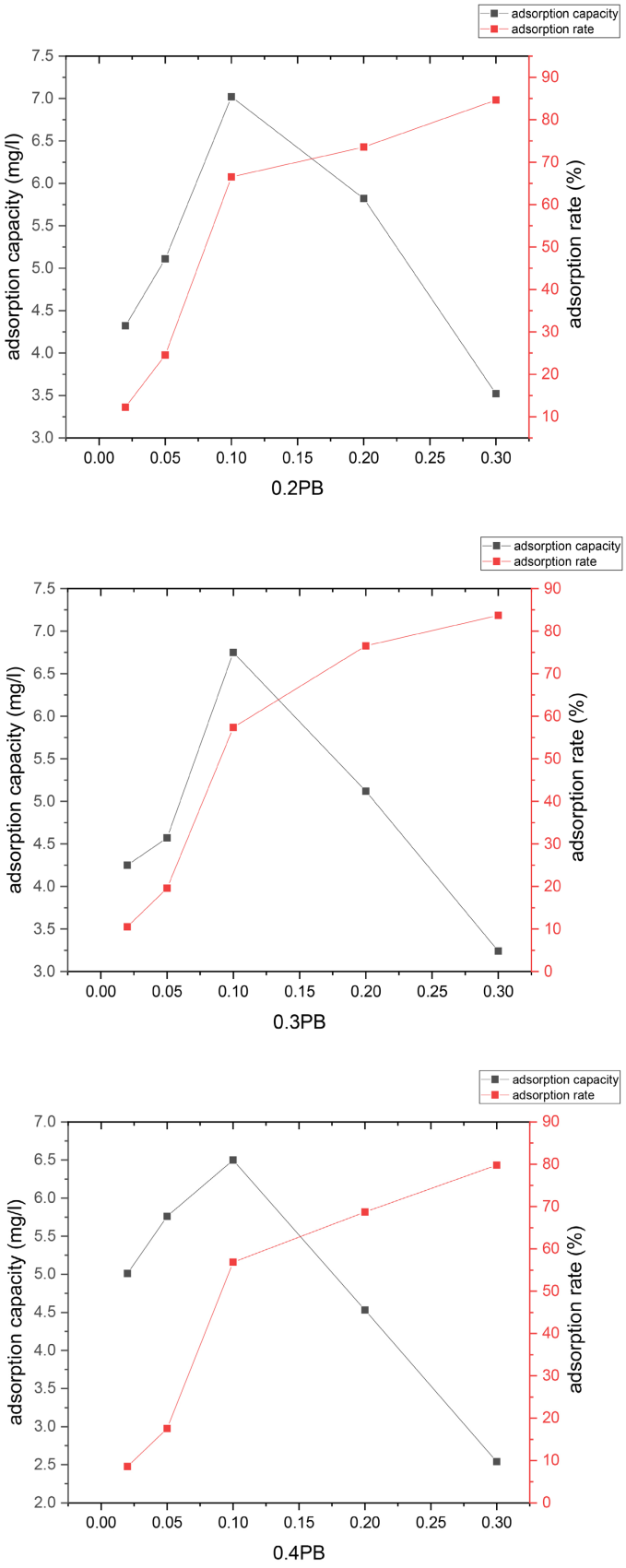


Figure 3. Effect of addition amount on adsorption test.

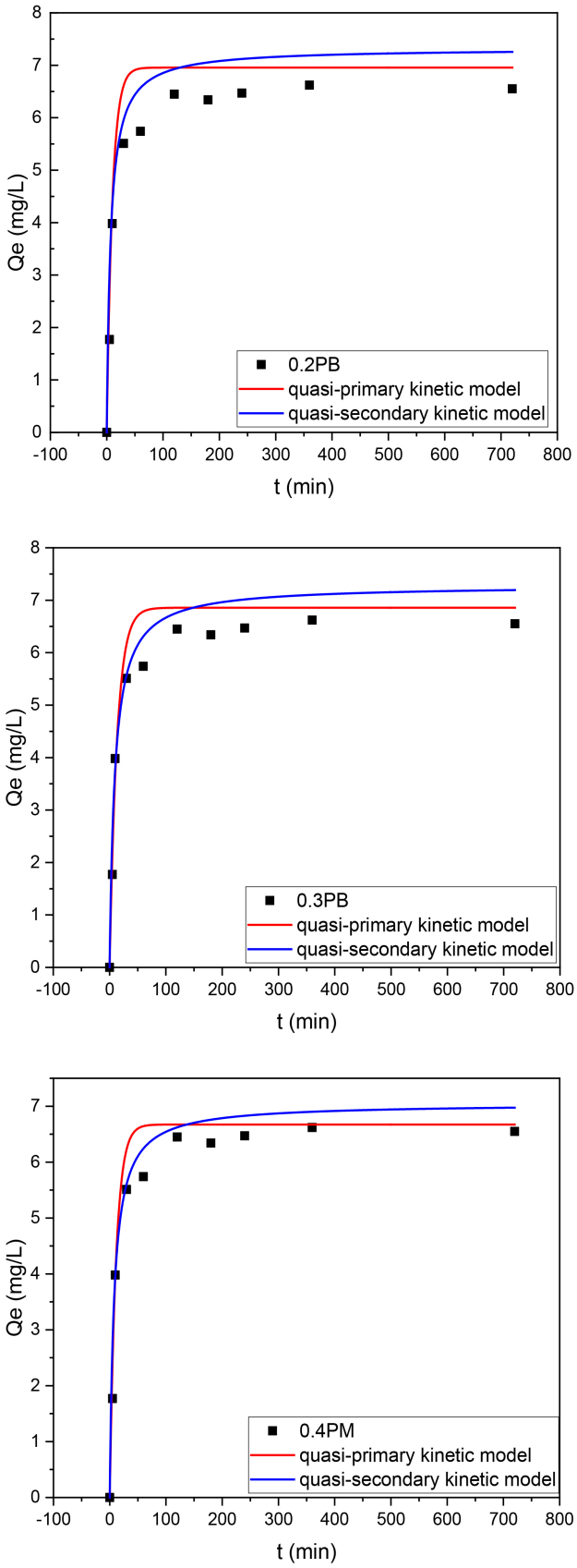


Figure 4. Kinetic model of modified biochar.

Table 1. Parameters of kinetic model.

Biochar	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	Q_e (mg/g)	K_1/h^{-1}	R^2	Q_e (mg/g)	K_2/h^{-1}	R^2
0.2 PB	6.95	0.10	0.983	7.32	0.01	0.965
0.3 PB	6.86	0.12	0.982	7.28	0.02	0.978
0.4 PB	6.67	0.09	0.9787	7.05	0.02	0.961

3.5. Isothermal Adsorption Curves

Isothermal adsorption curves reflect the relationship between the equilibrium concentration of the adsorbate and the maximum adsorption capacity of the adsorbent. These curves are derived from adsorption experiments under constant temperature conditions when adsorption equilibrium is reached. They not only explain the adsorption equilibrium relationship between the adsorbent and the adsorbate but also compare the adsorption capacity and remediation strength of adsorption materials for specific substances. The Langmuir model is primarily based on the assumption of monolayer adsorption on a uniform surface, where there is no interaction between adsorbate molecules. The Freundlich model describes physical adsorption and multilayer adsorption, and because its model parameters do not include a saturated adsorption amount, theoretically, the adsorption amount will increase at high concentrations.

As shown in the figure (**Figure 5**; **Table 2**), the charcoal of 0.2 PB in the isothermal adsorption curve model, after convergence fitting, all reach significant correlation ($R^2 > 0.9$), indicating that the measured values roughly conform to these two adsorption mathematical models. The Langmuir isothermal adsorption model fitting yields a maximum adsorption capacity qm of 14.023 mg/g for Cd^{2+}. The reason for the high adsorption capacity is mainly that Cd^{2+} in the solution can complex with oxygen-containing functional groups (—COOH, —OH) on the surface of phosphoric acid-modified grapevine biochar, and its aromatic structure acts as an electron donor to produce a relatively weak cation-π interaction with Cd^{2+} in solution, thereby adsorbing Cd^{2+} on the surface of biochar (Ma et al., 2017). For 0.2 PB, the correlation coefficient ($R^2 = 0.977$) of the Freundlich isotherm model is greater than that of the Langmuir isotherm model ($R^2 = 0.924$), indicating that the adsorption of Cd^{2+} by 0.2 PB modified biochar conforms more to the Freundlich isotherm model. This suggests that it mainly involves physical adsorption and multilayer adsorption, similar to the findings of Shen and Zhang (2016), proving that phosphoric acid can enhance the adsorption capacity of materials with high cellulose content by increasing their specific surface area.

3.6. Characterization of Biochar

The electron microscopy (**Figure 6**) images provided for grapevine biochar

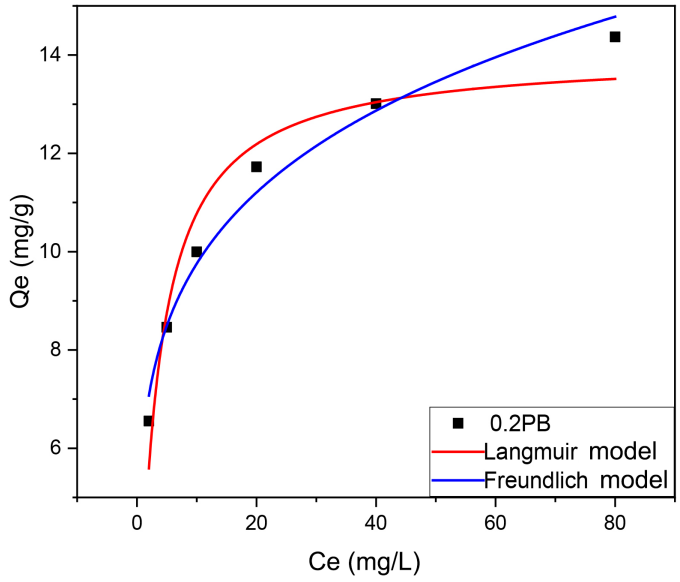


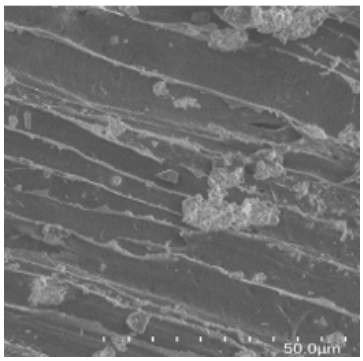
Figure 5. Isothermal adsorption model.

Table 2. Isothermal parameters.

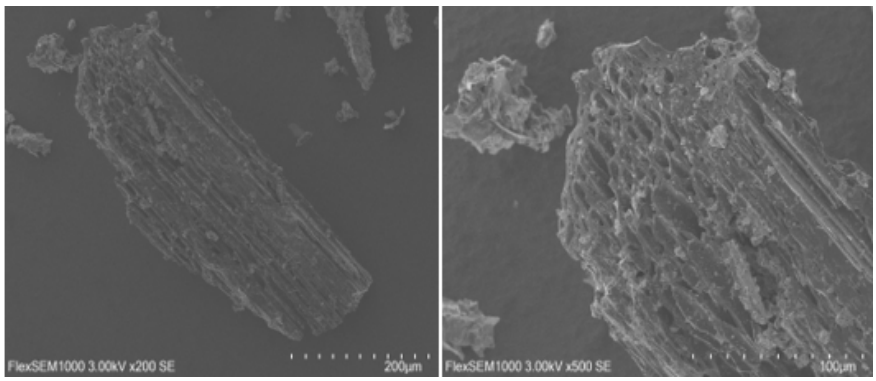
	Parameter 1	Parameter 2	Parameter 3	R^2
Langmuir	K_1 = 0.332	Q_m = 14.023		0.925
Freundlich	K_f = 6.156	n = −0.199		0.977

treated with varying concentrations of phosphoric acid reveal distinct surface and structural modifications. Initially, untreated biochar (**Figure 6(a)**) exhibits a relatively smooth and level surface, lacking pronounced porosity. The modification process with phosphoric acid, however, markedly alters the biochar's exterior. The treated biochar's surface not only becomes more textured and disorganized, with an evident increase in fragmented, wrinkled, and porous structures but also significantly enhances the material's interaction surface area with heavy metals like Cd. These observations suggest that phosphoric acid treatment effectively etches the biochar, modifying its surface morphology and pore architecture.

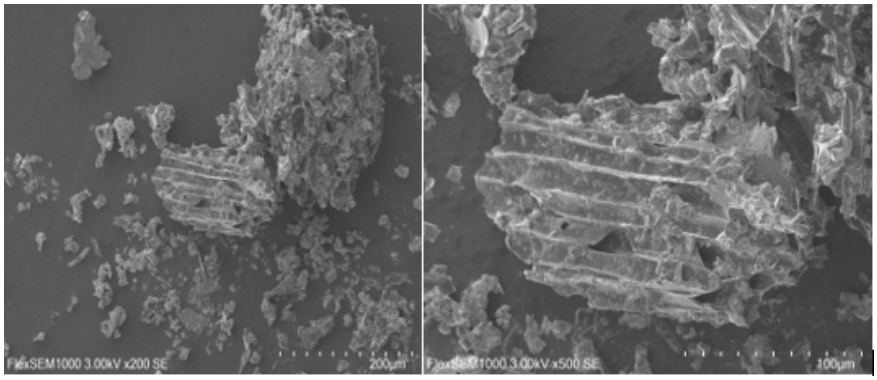
As the concentration of phosphoric acid increases, a noticeable trend is observed where the surfaces of biochar treated with (**Figure 6(c)**) and (**Figure 6(d)**) concentrations appear smoother, and their porosity decreases compared to the (**Figure 6(b)**) treated variant. This phenomenon could be attributed to higher phosphoric acid concentrations forming a barrier on the biochar's surface, hindering the development of adsorption pathways for metal ions. Consequently, this could result in a diminished adsorption capacity for heavy metals like Cd, aligning with the superior adsorption performance observed for biochar treated with 0.2 PB. This insight underscores the delicate balance between chemical modification concentration and the resulting adsorption efficacy of treated biochar materials.



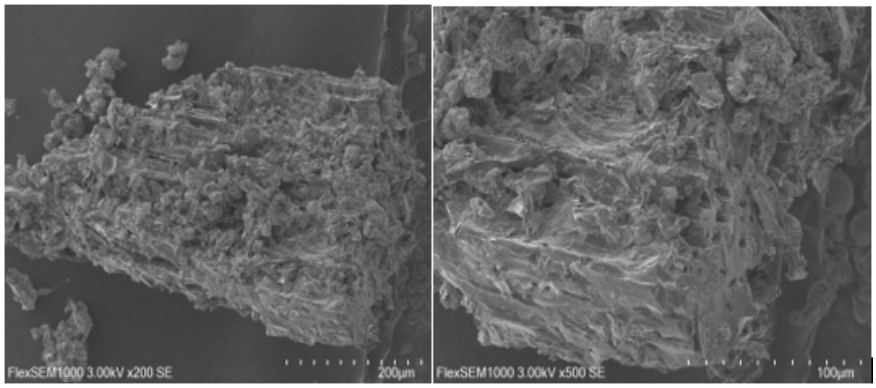
(a) BC



(b) 0.2 PB



(c) 0.3 PB



(d) 0.4 PB

Figure 6. SEM of biochar with different modified concentrations.

To further explore the surface functional groups of the materials, FTIR analysis was conducted on BC, 0.2 PB, 0.3 PB, and 0.4 PB in the infrared region of 500 - 4000 cm^{-1}, and the corresponding FTIR spectra are shown in the figure (**Figure 7**). The characteristic infrared absorption peaks of biochar modified with different concentrations of phosphoric acid are roughly the same. Compared to the original biochar, increasing or decreasing the quantity of some functional groups enhanced the adsorption effect of biochar on Cd^{2+}. A broader peak exists near the wavenumber of 3715 cm^{-1}, caused by O-H stretching vibrations. With the increase in modification concentration, the intensity of hydroxyl stretching vibrations increased, indicating that modification has caused certain changes in the O-H absorption peak in terms of peak strength and position, with phosphoric acid modification increasing the number of surface groups on biochar. Peaks around 1809 cm^{-1} and 1443 cm^{-1} increased in stretching vibration intensity with increasing modification concentration, attributed to C=O double bond and -CH2 stretching vibrations. Moreover, after phosphoric acid modification, a new stretching vibration peak appeared at 1046 cm^{-1} in BC, possibly due to the formation of a P-O-P bond after successful grafting of phosphoric acid groups onto the BC surface. The result of modification is that phosphoric acid modification did not increase the types of functional groups on grapevine biochar but increased the quantity of some original functional groups, such as -OH groups and C=O double bond peaks, and produced a new P-O-P bond (Liu, 2022; Liu et al., 2021).

4. Discussion

This experiment investigated the adsorption effect of heavy metal Cd under different modification concentrations, reaction times, and dosages. It was found that the adsorption capacity of grapevine biochar for cadmium was enhanced

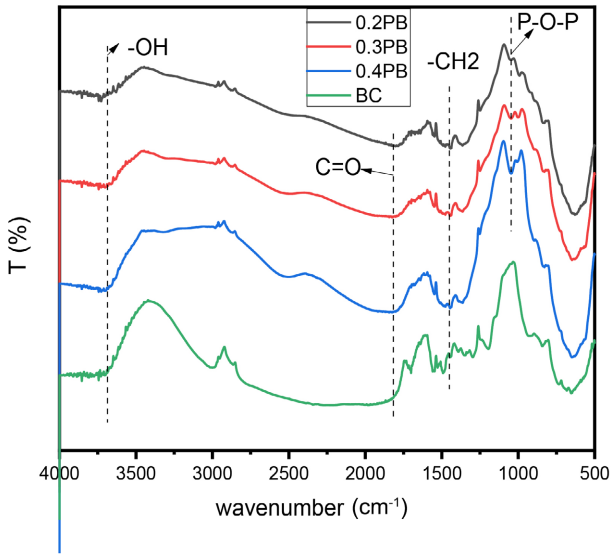


Figure 7. FTIR of biochar with different phosphoric acid modification concentrations.

after phosphoric acid modification. However, as the modification concentration increased, phosphates and polyphosphates produced by the phosphoric acid activation reaction formed an insulating layer around the biochar, making it difficult for metal ion adsorption channels to form. Therefore, the best adsorption effect for heavy metal Cd was observed at 0.2 PB. The kinetics and isotherm adsorption models show that the kinetics are more suitable for description by the pseudo-first-order kinetic model, and the isotherm adsorption conforms more to the Freundlich isotherm model, indicating that the adsorption of Cd by phosphoric acid-modified grapevine is mainly physical adsorption and multilayer adsorption. This may be because the main purpose of acid modification is to increase the specific surface area of biochar (Zhu, 2022), and a larger surface area allows for a wider contact area between Cd^{2+} and the biochar surface at the beginning of adsorption. This is consistent with the research results of Liu Yuning (Liu et al., 2022) and others, who found that the specific surface area of phosphoric acid-modified biochar increased 8.6 times compared to before modification after treatment with three modification methods. Moreover, during the modification process of biochar with phosphoric acid, a large amount of phosphates and polyphosphates formed by dehydration filled the pore structures inside the biochar, which, after washing, would increase the microporous structure inside the biochar (Yi et al., 2020), consistent with SEM study results. At the same time, FTIR showed that phosphoric acid modification did not increase the types of functional groups on grapevine biochar, but only increased the quantity of some original functional groups, providing more adsorption sites for heavy metal Cd, corroborating with the kinetic analysis and isotherm adsorption model analysis.

5. Conclusion

This study concludes that biochar derived from grapevine branches, modified with phosphoric acid, demonstrates an enhanced microporous structure and increased presence of oxygen-containing functional groups. Such modifications significantly improve its adsorption efficiency for cadmium ions (Cd^{2+}). Notably, biochar treated with 0.2 PB exhibits superior adsorption capabilities, achieving an optimal adsorption rate of 84.62%, and when applied at a concentration of 10 g/L, it reaches a maximum adsorption capacity of 7.02 mg/g. The adsorption behavior of 0.2 PB towards Cd aligns with kinetic models, fitting particularly well with the Freundlich isotherm model. The predominant mechanisms for Cd^{2+} removal are identified as rapid ionic diffusion adsorption and chemical adsorption, highlighting its potential as an effective adsorbent for cadmium, a hazardous heavy metal.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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