Adsorption of Pb(II) by montmorillonite modified biochars and reduction Pb(II)-stress in plants of microcosms of constructed wetlands: mechanism and treatment performances

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Abstract

In the study, the peanut shell was selected as original biochar and modified by adding montmorillonite to obtain modified biochar (B@M). The adsorbent was characterized by scanning electron microscopy, Brunauer–Emmett–Teller, Fourier-transform infrared spectroscopy and X-ray diffraction. The adsorption kinetics study of Pb(II) on B@M showed that the adsorption process of Pb(II) was according to the pseudo-second-order model and Langmuir adsorption model. The maximum adsorption capacity of B@M (61.5 mg g\textsuperscript{-1}) was significantly higher than that of the biochar (35.5 mg g\textsuperscript{-1}) and montmorillonite (54.4 mg g\textsuperscript{-1}) and the reproducibility study indicated that B@M had good reproducibility. When the B@M was added to the microcosms of constructed wetlands (MCW), it showed that with the increase of the amount of B@M, the removal rate of lead in water increased significantly, which was 31.3%, 48.3% and 86.1%, respectively and can reduce the stress of Pb(II) in plants of MCW. Therefore, B@M can be used as a new substrate material and heavy metal Pb(II) adsorbent for constructed wetlands.

Keywords: Modified biochars; Constructed wetland; Pb(II); Plant; Stress

1. Introduction

Currently, untreated sewage containing heavy metals is a serious universal problem. In the industrial processes of mining, smelting, processing, electroplating, etc., the wastewater has not been treated effectively \cite{1}, resulting in serious levels of heavy metals in water. The main hazards of heavy metals are toxicity, durability and accumulation \cite{2}. So, metal ions should be removed from wastewater before reusing for agricultural purposes. Pb(II) is one of the main heavy metals and is harmful to biological health \cite{3,4}. At present, the main methods of heavy metal treatment of untreated sewage are chemical, membrane filtration, reverse osmosis and adsorption \cite{1,5}. Among them, adsorption is the most widely used method because of its simplicity, rapid and high-efficiency \cite{6}. The emerging adsorbents have been studied that hollow Fe\textsubscript{3}\textsuperscript{4}O\textsubscript{4}@PDA nanoparticles \cite{7}, Cu\textsuperscript{2+} Graphitic carbon \cite{8} and Go \cite{9}. Hence, the shortcomings of the prohibitive cost, complex preparations are limited their application and development. Therefore, it is highly desirable to develop much cheaper, and more efficient water-absorbing agents to be used in the treatment of sewage.

Biochar is produced from the pyrolysis of agriculture wastes at a high temperature with an oxygen-limited
atmosphere, which has the advantage of easy available and low-cost [10, 11]. Biochar have dense porous materials, abundant organic oxygen-containing functional groups and high ion-exchange capacity [2], which is beneficial to the adsorption of heavy metal from raw sewage. The adsorption capacities of biochars from different raw materials are naturally reformed. Many factors affect the adsorption efficiency of heavy metals, such as pyrolysis temperature, pH value, reaction temperature, and modification [12]. Hence, some original biochars has low adsorption rates for heavy metal, which limits the application of biochar [13]. The determinants of improving the adsorption capacity of biochar are raw materials and modification processes [12]. Thus through modification can significantly improve the adsorption capacity of biochar. Clay’s minerals are a part of the earliest developed adsorbents [14]. Yao et al. [15] developed material for adhering clay minerals to the surface of biochar. It was noted that clay minerals enlarged the adsorption capacity of biochar to methylene blue. The adsorption is mainly ion-exchange (clay minerals) and electrostatic interaction (biochar). These studies showed that clay minerals have definite potential for the modification of biochar [15, 16]. Therefore, clay mineral montmorillonite was selected to modify the original biochar in the work.

Peanut shell was a cheap and usable solid agricultural waste, which was chosen as the main raw material for biochar. The biochar was prepared at 523 K and modified with montmorillonite. The adsorption capacity of composite materials for heavy-metal Pb(II) in water was studied, and the adsorption mechanism was discussed. After all, modified biochar (B@M) with good adsorption capacity was applied to microcosms of constructed wetlands (MCW, Fig. 1). The potential applications of biochar as a growth medium in hydroponic systems [17–19] or as a safeguard against the harmful effects of pollutants [17, 19] have been investigated previously and the studies indicated that biochar with good adsorption capacity can reduce the toxic stress of heavy metal on hydroponic plants [19]. Other studies of constructed wetlands have demonstrated that the use of biochar from wood, bamboo and corn cobs can improve its ability to remove biochemical oxygen demand (BOD$_5$), total suspended solids [20, 21], total nitrogen, total phosphorus and NH$_4^+$–N [21–26]. However, few studies have investigated the performance of biochar (different dosages of B@M, and recycled B@M) for MCW treating Pb(II) in wastewater.

The principal contents of this study were divided into two parts. The first part included: (1) Composite materials of B@M from peanut shell were prepared at 523 K and were characterized by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). (2) The effects of different adsorption conditions (pH values, temperature and solution concentration) on the adsorption of Pb(II) in water by B@M from peanut shell were studied. In addition, after the above adsorption research, the application of B@M in MCW was studied. The main contents included effects of different dosages of B@M and recycled B@M on adsorption of Pb(II), plant growth, plant biomass, tissue Pb(II) concentration and tissue Pb(II) accumulation.

2. Material and methods

2.1. Preparation of biochar and characterization

The peanut shell collected from Shaoxing City, Zhejiang Province, China was used as the original material. After washing with deionized water, the peanut shells were dried in nature to remove the deionized water. The biochar was burned under oxygen-limited conduction at a pyrolysis temperature of 523 K for 2 h, and after natural cooling, it was pulverized and screened. Clay mineral montmorillonite was added to the biochar in a weight ratio

![Fig. 1. Preparation of B@M, removal Pb(II) and application in MCW.](image)
of 1:1.5, stirred in a deionized water environment for 2 h at 4,500 rpm with a magnetic agitator, and dried at 378 K. Then we can get the modified biochar (B@M).

The surface morphology of B@M was observed by scanning electron microscope (SEM); the elemental analysis was carried out by an elemental analyzer. The specific surface area and microporous structures were determined by the specific surface area (N₂-BET) and porosity tester; the surface functional groups were qualitatively analyzed by FTIR and the crystal structure and phase were determined by X-ray diffractometer (XRD).

2.2. Adsorption experiment of Pb(II)

To analyze the effect of contact time and solution pH values on the adsorption, adding 50 mg absorbent into the 100 mL 50 mg L⁻¹ Pb(II) solution at 150 rpm (T = 298 K). The solution pH values were adjusted to 2.0–6.0 by using low concentration HCl or NaOH solutions. Within the specified time, the adsorbed solution was filtered and separated. The samples were taken in a 25 mL colorimetric tube, and a certain amount of 8-hydroxyquinoline (HOx) solution, sodium hydroxide solution, sodium sulfite solution, T(DBHP)P solution and emulsifier OP solution were added in sequence, and deionized water was added to the calibration line. The final step was to shake. The concentration of Pb(II) was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin-Elmer Plasma 3200, Waltham, Massachusetts, USA) [17,19]. At 479 nm, the absorbance at the corresponding time was measured by a 1 cm colorimetric dish with a similar reagent blank as the reference. Finally, the difference in concentration before and after adsorption was compared. In addition, all chemicals used were of analytical grade and dissolved in deionized water during the study. After the adsorption of Pb(II) ions, the recycled B@M desorption by 1 M HNO₃ was measured by an elemental analyzer. The specific surface area and porosity tester; the surface functional groups were qualitatively analyzed by FTIR and the crystal structure and phase were determined by X-ray diffractometer (XRD).

2.3. Experiment in microcosms of constructed wetlands

2.3.1. Experimental design

The experiment was carried out in the greenhouse of Environmental Science Department, Shaoxing University, China (29°59′N, 120°34′E). The average daily temperature of the greenhouse was in the range of 20°C–23°C and at around 20°C (night), and the humidity was maintained at 65%–80%. In early April, cultivate seedlings of Iris tectorum begun, and then uniform and vigorous seedlings were transferred from the nursery to microcosms of constructed wetlands (MCWs, length × width × height = 50 cm × 38 cm × 18 cm per plastic tub, Fig. 2) after two weeks. A foam planting bed (42 cm length × 31 cm width × 8 cm height) was used to keep the seedlings in each microcosm. Water or nutrient solution of 15 L was supplied to each microcosm. To ensure the growth of the plants, an air pump was used to supply oxygen to the root zone. After 6 d, microcosms were placed into six treatments: T₁: plants only, no Pb(II), T₂: plants containing 100 μM Pb(II) but no biochar, T₃: plants containing 100 μM Pb(II) and 0.5 g B@M, T₄: plants containing 100 μM Pb(II) and 1.0 g B@M, T₅: plants containing 100 μM Pb(II) and 4.0 g B@M, and T₆: plant containing 100 μM Pb(II) and 1.0 g regenerated B@M (the recycled B@M desorption by 1 M HNO₃). T₇ was the control treatment, and T₈ was utilized to distinguish the toxic effect of Pb(II). T₉, T₁₀ and T₈, T₉ were used to study the effects of different dosages of B@M and recycled B@M on Pb(II) adsorption and plant growth, respectively. The B@M samples were loaded into perforated cloth bags and placed in simulated constructed wetlands. The nutrient solution and tap water was renewed every 3 d, and a 100 μM PbCl₂ solution was added to the tap water of the T₄ to T₆ treatments. Packing of B@M was replaced with a new one with each water replacement. Wastewater samples of T₁ to T₄ were collected before and after each replacement of nutrient solution, respectively. All treatments were performed five times.

2.3.2. Plant analysis and measurement of Pb(II) in wastewater

After five weeks of sowing, plant samples were harvested from each microcosm to measure plant height and root length. Wash the roots and shoots of the plants with tap water. The samples were then dried in an oven at 65°C until completely dry and weighed. To determine Pb(II) contents in plant tissue, the plant samples were ground using an electric grinder. After digesting with a 0.5 g ground material with a mixture of HNO₃ – HClO₄ (3:1), Pb(II) content was measured by flame AAS (Varian AA240FS) [29]. Plant Pb(II) accumulation (pool) was obtained by Pb(II) tissue concentrations by plant tissue biomass.

The concentration of Pb(II) in water samples of T₁ to T₆ was determined by ICP-AES (Perkin-Elmer Plasma 3200, Waltham, Massachusetts, USA). Removal rate (%) of Pb(II) was calculated as ((input–output)/input) × 100%.

2.4. Data processing and statistical analysis

2.4.1. Adsorption experiment

The adsorption removal rate and adsorption capacity of Pb(II) in water by B@M were expressed by qₑ and R, respectively.
\[ R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \]  
\[ q_e = \left(C_0 - C_t\right) \frac{V}{m} \]

where \( C_0 \) was the initial concentration of heavy metal Pb(II) in solution (mg L\(^{-1}\)); \( C_t \) was the concentration of Pb(II) in solution at \( t \) time (mg L\(^{-1}\)); \( C_e \) was the concentration of Pb(II) in solution at adsorption equilibrium (mg L\(^{-1}\)); \( V \) was the volume of Pb(II) solution (L); \( m \) was the dosage of biochar (g).

In order to avoid experimental errors, three parallel groups were established in the experiment, and the data results were processed independently and repeatedly. Experimental deviations were less than 5%. Finally, the average value was used as the measurement result. Data processing was carried out with Microsoft Excel 2007 and Origin 7.0.

2.4.2. MCW experiment

Statistical analysis of MCW experiment was performed with SPSS 18.0. Means were compared by the analysis of standard error (SE). Differences were considered significant at \( p < 0.05 \) based on one-way analysis of variance (ANOVA).

3. Results and discussion

3.1. Characterization of adsorbents

Table 1 was the pore structure of the studied samples by BET. As shown in Table 1, the surface area, total pore volume, and average pore width of B@M observably increased by more than 2 times, 6 times, and 3 times, respectively, that of the biochar. These indicated that montmorillonite prominent improves biochar performance. Fig. 3 shows the surface morphology and elemental composition of B@M by SEM and energy-dispersive X-ray spectroscopy (EDS). It can be seen that the surface of B@M was covered with small particles with irregular porous structure, which improved the adsorption capacity. The contact between metal ions and absorbent provided more space by the roughness of the surface and edge of the absorbent [30].

Figs. 3a and b show that when montmorillonite was mixed with biochar, montmorillonite adhered to the surface of biochar and provided sufficient morphology for the adsorption of Pb(II). The transmission electron microscopy (TEM) image (Fig. 3c) shows that the surface of B@M was massive, and there were flocculent substances on the surface.

In the EDS of Fig. 4, biochar’s main elements C and O were 68.5% and 31.4%. It also can directly see that those mineral elements of Al, Si, Ca and Fe came from montmorillonite (Figs. 4b and c). After adsorption, the Pb element adhered to B@M (Fig. 4d). It showed that Pb(II) has been

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Total pore volume (cm(^3) g(^{-1}))</th>
<th>Average pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B@M</td>
<td>6.18</td>
<td>0.020</td>
<td>12.7</td>
</tr>
<tr>
<td>Biochar</td>
<td>2.79</td>
<td>0.003</td>
<td>3.94</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>31.3</td>
<td>0.073</td>
<td>9.33</td>
</tr>
</tbody>
</table>

Fig. 3. Characterizations of the B@M (a and b) SEM images and (c) TEM image.
adsorbed on the surface of B@M (Fig. 4d). The composition elements of biochar were similar to other biochars, which indicated that the biochar prepared at 523 K has successfully become an adsorbent [31].

From the FTIR diagram (Fig. 5), it can be revealed by the surface functional groups of adsorbents. In general, the characteristic peak around 1,180–3,698 cm$^{-1}$ indicated that there are a series of absorption peaks in the adsorbents, such as –COOH, –OH in water molecules [32,33]. When band at near 1,137 cm$^{-1}$, it represented the stretching vibration of mostly C–O (including alcohols, ethers, phenols, etc.); when peak at about 1,460 cm$^{-1}$, it was the stretching vibration of C–H; when the characteristic peak at around 1,700 cm$^{-1}$ assigned to the stretching vibration of C=O; when peak at 3,500–3,700 cm$^{-1}$, it was the stretching vibration peak of associating –OH.

The addition of montmorillonite to biochar, significantly increased the adsorption peak of 2,100 cm$^{-1}$, most of them were triple bonds, while the association of –OH, C–O and –COOH groups increased. The heavy metal would be complex with the surface groups of adsorbents. The reaction process was expressed by the following two equations [34].

$$nC – COOH + Pb^{2+} + H_2O \rightarrow nC – COOPb^{+} + H_3O^+ \quad \text{(A)}$$

$$nC – OH + Pb^{2+} + H_2O \rightarrow nC – OPb^{+} + H_3O^+ \quad \text{(B)}$$

According to the X-ray diffraction pattern (Fig. 6), the diffraction peaks near 20 = 11° and 24.5° indicated the formation of biochar [35], and the diffraction peak at 20 = 35° was presumed to be calcium carbonate crystal face. At the same time, it showed that no new material is produced in the synthesis process. The four new peaks at 20 = 5.85°, 19.72°, 26.63° and 61.76° came from montmorillonite, which were d(001), d(021), d(130) and d(060) of montmorillonite [36]. The quartz diffraction peak of biochar samples appeared at 20 = 26°, which indicated the existence
of SiO$_2$ in montmorillonite [37]. The SiO$_2$ in the adsorption materials was helpful to the adsorption of heavy metals [38].

3.2. Effect of solution pH value on adsorption of Pb(II)

The solution pH was an important factor affecting the adsorption of heavy metal ions. Under acidic conditions, plenty of hydrogen ions can inhibit the adsorption of Pb(II) by biochar [39]; once pH > 6.0, pH was greater than 6.0, Pb(II) existed in the form of Pb(OH)$_2$, from ionic state to colloidal state [40]. This also confirmed the conclusion of previous studies that the best pH of removal Pb(II) was between 4.5 and 5.5 [41,42]. This work also proved that in the pH = 5.0, the adsorption of Pb(II) reached the highest point (Fig. 7). Pb(II) existed in the form of a free state when pH < 6.0. Meanwhile, the pH of the original solution was about 5.0, so the subsequent experiment did not need to adjust the pH of the original solution.

3.3. Effect of adsorbed time

From Fig. 8 it is obvious that the adsorption reaction reached equilibrium within 40 min. Meanwhile, the adsorption capacity of B@M (61.5 mg g$^{-1}$) was better than the biochar (35.5 mg g$^{-1}$) and montmorillonite (54.4 mg g$^{-1}$). It indicated that B@M showed a better adsorption capacity of 61.5 mg g$^{-1}$.

3.4. Adsorption kinetics of Pb(II) on B@M

The adsorption mechanism of Pb(II) in solution was studied by fitting experimental data with two models: pseudo-first-order and pseudo-second-order.

$$q_t = q_0 (1 - e^{-kt})$$

(3)
\[ \frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{q_e} \]  

(4)

where \( t \) was the adsorption time (min); \( k_1 \) was pseudo-first-order model rate constant (min\(^{-1}\)); \( k_2 \) was pseudo-second-order model rate constant (min\(^{-1}\)); \( q_t \) and \( q_e \) were the amount of Pb(II) adsorbed per unit mass (mg g\(^{-1}\)) at \( t \) time and adsorption equilibrium, respectively. According to the above formulas, in the adsorption process, the important factor affecting the adsorption effect is the adsorption time [15]. Through the preliminary experiment, it was found that the adsorption equilibrium of Pb(II) on 90 min was achieved by the biochar with peanut shell as raw material, thus the final sampling time was set at 90 min.

The adsorption kinetics of Pb(II) on the biochar, montmorillonite and B@M were evaluated by the pseudo-first-order model and pseudo-second-order model. All the metal parameters are shown in Table 2. Compared to the pseudo-first-order model, the pseudo-second-order model had a better correlation which fitted the experimental data (\( R^2 = 0.999 \)). Besides, the experiment \( q_t \) value was much closer to the calculated \( q_t \) value. Generally, the pseudo-second-order model represented the chemisorption involving valency forces [43]. Thus, this represented that the chemical process might control the overall rate of Pb(II) in the adsorption process [41].

For many adsorption, the intraparticle diffusion model was used to describe the rate-controlling step of the adsorption and analyze the existence of this process [37,44]. The related formula can be written as:

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

(5)

where \( K \) is intraparticle diffusion model rate constant (mg g\(^{-1}\) min\(^{0.5}\)); \( C \) is intraparticle diffusion model rate intercept, the rate constant; \( t \) is the adsorption time (min); \( q_t \) is the amount of Pb(II) adsorbed per unit mass (mg g\(^{-1}\)) at \( t \) time.

As shown in Fig. 9, the fitting curve exhibits a multi-segment linear relationship. The first stage was the rapid adsorption process mainly occurs on the surface of biochar in the pre-adsorption period; in the second stage, the adsorption rate decreased significantly. The \( K \) value and \( C \) value of B@M (\( k_1 > k_2, C_1 > C_2 \)) shown in Table 3, indicates that the adsorption was rapid in the first stage due to B@M’s large surface area. With the passage of adsorption time, the adsorption sites on the surface of biochar decreased and the adsorption efficiency decreased. Because the curve cannot pass through the origin (\( C \neq 0 \)), suggesting that the intraparticle diffusion was not the only rate of the control procedure. Hence, it could still have a considerable effect on the adsorption rate [34].

3.5. Adsorption isotherm

The adsorption isotherms of Langmuir and Freundlich were selected to study the adsorption isotherms.

**Langmuir equation:**

\[ C_\infty = \frac{1}{k_L q_m} \left( \frac{C}{q_e} \right) \]  

\[ R^2 = \frac{k_L q_m}{1 + k_L C} \]  

(6)

**Freundlich equation:**

\[ \ln q_e = \ln k_F + \frac{1}{n} \ln C \]  

(7)

Among them, \( C_\infty \) is the solution concentration at adsorption equilibrium (mg L\(^{-1}\)); \( q_e \) – the adsorption amount at equilibrium) (mg g\(^{-1}\)); \( q_m \) – the maximum dosage of adsorbents (mg g\(^{-1}\)); \( k_L \) – Langmuir constant, which is related to the affinity between absorbents and adsorbents. \( k_F \) is the Freundlich constant, which is related to the adsorption capacity of the adsorbents, and \( n \) was the parameter related to the interaction strength between the adsorption molecules and the surface of the adsorbents.

The adsorption isotherms of Pb(II) by B@M are shown in Fig. 10. As shown in Fig. 10, the Pb(II) adsorption capacity of

![Fig. 9. The intraparticle diffusion curve of Pb(II) by B@M.](image)

---

**Table 2**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{\text{exp}} )</th>
<th>( q_e )</th>
<th>( k_1 )</th>
<th>( R^2 )</th>
<th>( q_e )</th>
<th>( k_2 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B@M</td>
<td>61.5</td>
<td>20.0</td>
<td>0.047</td>
<td>0.98</td>
<td>63.3</td>
<td>0.005</td>
<td>0.99</td>
</tr>
<tr>
<td>Biochar</td>
<td>35.5</td>
<td>9.04</td>
<td>0.007</td>
<td>0.94</td>
<td>37.2</td>
<td>0.005</td>
<td>0.99</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>54.5</td>
<td>24.6</td>
<td>0.046</td>
<td>0.99</td>
<td>57.1</td>
<td>0.004</td>
<td>0.99</td>
</tr>
</tbody>
</table>
B@M increased with the increase of adsorption equilibrium concentration and temperature. The parameter of adsorption isotherm of Pb(II) adsorption are listed in Table 4. The data fitting results of adsorption isotherm model indicated that the Langmuir model was considered to be more reliable due to it has higher $R^2$ values (0.98–0.99). In addition, Langmuir model described that the maximal adsorption capacity ($q_m$) of B@M (20°C) < B@M (30°C) < B@M (40°C), which showed that this adsorption was an endothermic process.

As shown in Table 5, the obtained thermodynamic parameters can describe the thermodynamic of adsorption [37]. The values of $\Delta G^\circ$ were negative values, indicating that the adsorption process was spontaneous. And the values of $\Delta G^\circ$ became more negative, suggesting that B@M has more adsorption capacity at the higher temperature. The $\Delta H^\circ$ ($\Delta H^\circ > 0$) mean that the adsorption of B@M was an endothermic process. And B@M and Pb(II) had a strong interaction in the adsorption process. According to the positive values of $\Delta S^\circ$, B@M had an endothermic affinity for Pb(II).

### 3.6. Reusability

To test the reusability of B@M for removal Pb(II) in solution, the adsorption and desorption experiments were carried out for five times. The B@M was rinsed by 100 mL of 0.1 mol L$^{-1}$ NaOH, then rinsed by 100 mL of 0.01 mol L$^{-1}$ HCl for 30 min, and washed with distilled water again for 5 min. Thus treated B@M was used as adsorbents for the recycling experiments. The repeated reusability of B@M is shown in Fig. 11. From Fig. 11 it can be concluded that the removal rate of Pb(II) decreased from 61.5% to 49.2% during five adsorption and desorption experiments. It shows that the chemical stability of B@M was very well.

### 3.7. Application in microcosms of constructed wetlands

A case study of microcosms of constructed wetlands (MCW) was performed to evaluate the applicability of B@M. The effects of different dosages of B@M and recycled B@M on adsorption of Pb(II) ion, plant growth, plant biomass, tissue Pb(II) concentration and tissue Pb(II) accumulation were investigated.

As shown in Table 6 and Fig. 12, among the six different treatment, T$_1$ (the control, no Pb(II) addition) plants had the best growth, with the highest plant height, root length, aboveground biomass, underground biomass and R/S rate, because they were not subjected to Pb(II)-stress. It can be seen from T$_3$, T$_4$ and T$_5$, with the increasing addition of B@M, Pb(II) content in both aboveground and underground parts of plants significantly reduced ($P < 0.05$).

### Table 3

Parameter of intraparticle diffusion for Pb(II) on B@M (pH = 5.0 ± 0.2; $C_0$ = 10 mg L$^{-1}$; m(adsorbent) = 0.05 g)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$k_1$</th>
<th>$C_1$</th>
<th>$R^2$</th>
<th>$k_2$</th>
<th>$C_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B@M</td>
<td>3.49</td>
<td>40.5</td>
<td>0.99</td>
<td>1.35</td>
<td>56.1</td>
<td>0.99</td>
</tr>
</tbody>
</table>

### Table 4

Parameters of adsorption isotherm of Pb(II) adsorption (pH = 5.0 ± 0.2; m(adsorbent) = 0.05 g)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>$k_L$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>58.5</td>
<td>0.06</td>
<td>0.99</td>
<td>0.62</td>
</tr>
<tr>
<td>30</td>
<td>64.5</td>
<td>0.12</td>
<td>0.98</td>
<td>0.45</td>
</tr>
<tr>
<td>40</td>
<td>68.0</td>
<td>0.22</td>
<td>0.99</td>
<td>0.32</td>
</tr>
</tbody>
</table>

### Table 5

Thermodynamic parameters for Pb(II) adsorption on B@M

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>K</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.60</td>
<td>–1.22</td>
<td>19.230</td>
<td>–2.81</td>
</tr>
<tr>
<td>30</td>
<td>3.06</td>
<td>–2.81</td>
<td>15.8</td>
<td>19.2</td>
</tr>
<tr>
<td>40</td>
<td>6.13</td>
<td>–4.41</td>
<td>15.8</td>
<td>19.2</td>
</tr>
</tbody>
</table>

**Fig. 10.** Removal effect of Pb(II) by B@M at different reaction temperatures.

**Table 6**

Parameters of adsorption isotherm of Pb(II) adsorption (pH = 5.0 ± 0.2; m(adsorbent) = 0.05 g)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>$k_L$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>58.5</td>
<td>0.06</td>
<td>0.99</td>
<td>0.62</td>
</tr>
<tr>
<td>30</td>
<td>64.5</td>
<td>0.12</td>
<td>0.98</td>
<td>0.45</td>
</tr>
<tr>
<td>40</td>
<td>68.0</td>
<td>0.22</td>
<td>0.99</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Table 5**

Thermodynamic parameters for Pb(II) adsorption on B@M

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>K</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.60</td>
<td>–1.22</td>
<td>19.230</td>
<td>–2.81</td>
</tr>
<tr>
<td>30</td>
<td>3.06</td>
<td>–2.81</td>
<td>15.8</td>
<td>19.2</td>
</tr>
<tr>
<td>40</td>
<td>6.13</td>
<td>–4.41</td>
<td>15.8</td>
<td>19.2</td>
</tr>
</tbody>
</table>
while the plant height and root length, aboveground and underground biomass of plants significantly increased ($P < 0.05$). This shows that B@M has a certain ability to remove Pb(II) from wastewater of MCW, and could reduce the stress of heavy metals on plant growth [18,19,45,46], and the effect was much more obvious with the more addition of B@M. The other studies also showed that biochar is a safeguard against the harmful effects of pollutants [17,19].

According to the results in Fig. 13, treatment T1 (without adding B@M) also had 11% removal rate of Pb(II), indicating that plants have certain heavy-metal removal ability in water [18,19,26,45]. However, compared with T1, the removal rate of Pb(II) in MCW was effectively improved after adding B@M. Meanwhile, with the increasing addition of B@M (T3, T4, and T5), the removal rate of Pb(II) in MCW was significantly increased ($P < 0.05$), with the removal rate of 31.3%, 48.3%, and 86.1%, respectively. This showed that adding B@M had a good effect on removing Pb(II) from MCW.

In order to study the reproducibility of B@M, the adsorbed B@M was cleaned with 1 M HNO3 for several times and then air-dried to continue to be put into the MCW (T6). Compared with T4 and T6, the results showed that the B@M after regeneration had no significant difference in the removal rate of Pb(II) in MCW, which indicated that B@M had good reproducibility. In conclusion, adding B@M had a good effect on removing Pb(II) from MCW. Also, B@M can weaken the stress of Pb(II) on aquatic plants, reduce the content of Pb(II) in plants, and achieve good growth. Therefore, B@M can be used as a new substrate material for CWs and Pb(II) adsorbent.

### 4. Conclusions

It was found that B@M have a good adsorption capacity of Pb(II) (61.5 mg g$^{-1}$) because the surface was rough, the functional groups were rich. The adsorption process of

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Plant height (cm)</th>
<th>Root length (cm)</th>
<th>Aboveground biomass (g plant$^{-1}$)</th>
<th>Underground biomass (g plant$^{-1}$)</th>
<th>R/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>43.8 ± 4.22a</td>
<td>18.5 ± 2.12a</td>
<td>7.06 ± 1.11a</td>
<td>6.87 ± 1.89a</td>
<td>0.97</td>
</tr>
<tr>
<td>T2</td>
<td>31.6 ± 3.21c</td>
<td>12.3 ± 1.85c</td>
<td>3.26 ± 1.01c</td>
<td>2.35 ± 0.89c</td>
<td>0.72</td>
</tr>
<tr>
<td>T3</td>
<td>34.4 ± 2.75bc</td>
<td>13.0 ± 1.54c</td>
<td>3.68 ± 0.89bc</td>
<td>2.89 ± 0.89bc</td>
<td>0.79</td>
</tr>
<tr>
<td>T4</td>
<td>37.0 ± 4.21b</td>
<td>14.8 ± 2.17b</td>
<td>4.23 ± 0.48b</td>
<td>3.23 ± 0.85b</td>
<td>0.76</td>
</tr>
<tr>
<td>T5</td>
<td>43.0 ± 3.17a</td>
<td>17.9 ± 1.02a</td>
<td>6.96 ± 0.91a</td>
<td>6.16 ± 1.02a</td>
<td>0.88</td>
</tr>
<tr>
<td>T6</td>
<td>36.1 ± 1.75b</td>
<td>14.1 ± 2.03b</td>
<td>4.19 ± 0.81b</td>
<td>3.18 ± 0.79b</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Values were means ± SE. The same lowercase letters in a line indicate non-significant differences among plants in different treatments.
Pb(II) was according to the pseudo-second-order model and Langmuir adsorption model. The results of MCWs showed that with the increased amount of B@M, the removal rate of lead in MCWs increased significantly. It showed that B@M had good reproducibility and can reduce the stress of Pb(II) in plants of MCWs. Therefore, B@M can be used as a new substrate material and heavy metal Pb(II) adsorbent for constructed wetlands.

CRediT authorship contribution statement


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References
