Amine-functionalized magnetic biochars derived from invasive plants *Alternanthera philoxeroides* for enhanced efficient removal of Cr(VI): performance, kinetics and mechanism studies

Xin Luo1 · Haiying Du1 · Xiaochao Zhang1 · Yuhang Yang1

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**Abstract**

In this study, novel magnetic biochars derived from *Alternanthera philoxeroides* and modified by different amines (hexanediamine, melamine, and L-glutathione) were successfully prepared by hydrothermal carbonization and employed as an efficient adsorbent for Cr(VI). When pH = 2.0, T = 25 °C, c₀ = 100 mg/L, and the dosage of biochars is 0.05 g, the maximum adsorption capacity of Cr(VI) by pristine biochar (BAP) was 42.47 mg/g and modified biochars (MFBAP, MEBAP, LBAP) was 80.58, 62.26, and 55.66 mg/g, respectively. It was found that hexanediamine and melamine could enhance the \( S_{\text{BET}} \) of biochars, while L-glutathione could reduce its \( S_{\text{BET}} \), which could be supported by BET measurement and SEM images. Adsorption kinetics and isotherm studies showed that the Cr(VI) adsorption process of MFBAP followed Elovich kinetic model and Langmuir isotherm, respectively, which means that it was mainly a chemical adsorption process. The characterization results proved that -NH₂ derived from amines plays a significant role in removing Cr(VI), which is mainly degraded by complexation reaction, electrostatic interaction, and reduction. In sum, the biochar modified by amines has excellent Cr(VI) adsorption performance, highly enhanced \( S_{\text{BET}} \), and excellent recyclability, which is a promising candidate for solving the problem of invasive plants and wastewater treatment.

**Keywords** Adsorption · Cr(VI) · Invasive plants · Kinetics · Magnetic biochar · Reduction

**Introduction**

Plant invasion has had a far-reaching impact all over the world and attracted extensive public attention (Bolpagni 2021). Biological invasion is one of the five global environmental problems in the twenty-first century (Galasso et al. 2018). It has adverse effects on species, communities, and ecosystems (Paini et al. 2016). *Alternanthera philoxeroides* (AP), a weed belonging to Amaranthaceae, is one of the 100 most invasive species in the world (Du et al. 2021). The mass propagation of AP will reduce the productivity of crops and cause economic losses (Chen et al. 2013). At present, the methods of controlling invasive plants mainly include artificial elimination, chemical control (Yuan et al. 2021), and biological control (You et al. 2018). However, these methods are very restricted and will consume a lot of manpower and financial resources.

Heavy metal wastewater has become a problem that cannot be ignored in the development of science and technology (Akram et al. 2017). Heavy metals cannot be degraded in the environment and can be continuously concentrated through the food chain, which poses a serious threat to the ecological environment and human health (Liu et al. 2011). The absence of an effective treatment process exposes individuals to potential health risks (Badawi et al. 2022). The heavy metals in water mainly come from human activities, mainly including, lead, cadmium, chromium, nickel, and copper (Ren et al. 2011). Among them, the environmental threshold of Cr(VI) is small (Jiang et al. 2019), the toxicity is huge, and it is carcinogenic after entering the human body, causing irreversible damage to human organs and the nervous system (Xie et al. 2017). The adsorption process...
is a chemical technique and is considered among the most promising routes for the removal of dyes, solvable organic contaminants, and toxic compounds from wastewater (Badawi and Zaher 2021). At present, adsorbents mainly include agriculture waste adsorbents, industrial waste adsorbents, natural materials, and nanomaterials (Badawi et al. 2021). However, these materials are either expensive or the adsorption efficiency is too low (Bora et al. 2021). It is necessary to develop cheap and efficient adsorbents.

Biochar, which has been proven to be an excellent adsorbent for pollutants, has a broad application prospect in the field of heavy metal sewage purification (Tan et al. 2015). Therefore, many studies on the properties of biochar have been born (Pan et al. 2021; Pandey et al. 2020). However, it is far from enough to only use biochar for the adsorption of pollutants. It involves many problems, such as difficult recovery (Yi et al. 2020), low adsorption efficiency, and weak reusability (Akhil et al. 2021). Therefore, the modification of biochar has become a research hotspot in recent years (Ding et al. 2016; Dissanayake et al. 2020), chemical (Zhou et al. 2018), physical (Duan et al. 2021), and magnetic modification (Bacelo et al. 2020). Chemical and magnetic modification can fully improve the shortcomings of biochar. Amino-functionalized biochar can improve the amino groups on the surface of biochar, which have a strong chelating affinity with heavy metal ions and can capture heavy metal ions by forming stable chelates or strong electrostatic interaction (Yang and Jiang 2014, Zhou et al. 2017). Yang et al. (Yang and Jiang 2014) prepared amino-functionalized biochar as a high-efficient and selective adsorbent for Cu(II) by nitration and reduction. They found that the Cu(II) could combine with the amino groups through strong complexation. Ekanayake et al. (Ekanayake et al. 2022) evaluated and compared the efficacy of Cr(VI) removal by amino-modified and pristine biochar derived from an invasive plant Mimosa pigra and found that the maximum removal efficiency could reach 76%. It can be seen from Table 1 that biochar derived from AP has been proved to be an excellent material for environmental remediation. Utilizing AP to prepare biochar to remove Cr(VI) in aqueous solution may be a win–win solution. It cannot only save production costs but also improve the biological value of invasive plants and make them widely used in the fields of environmental remediation (Feng et al. 2021).

In this study, utilizing AP as raw material, a green and simple method referred to as hydrothermal carbonization (HTC) was used to prepare three kinds of amino-functionalized magnetic biochars with different $S_{\text{BET}}$ and excellent adsorption capacity for Cr(VI). The biochars were characterized by FT-IR, SEM, BET measurement method, X-ray diffraction, and analytical methods. Adsorption kinetics and capacity of the biochars for Cr(VI) were studied under different experimental conditions (i.e., contact times, pH, and initial Cr(VI) concentrations). Additionally, the adsorption isotherms and kinetics parameters were evaluated using the experimental data, and the mechanism of adsorption of Cr(VI) by biochars was explored through XPS analysis. This work also provides an insight into the treatment of invasive plants, the application of waste biomass as well as heavy metal wastewater.

### Materials and methods

#### Materials and chemicals

The biomass, AP, was collected from Chengdu University of Technology and was washed with deionized water for 3 times and dried at 80 °C for 24 h, subsequently crushed and ground to particle size, passed through a 60-mesh sieve, and then bagged for standby. Hexamethylenediamine (HDA) and FeCl$_3$·6H$_2$O were obtained from Shanghai Chemical Industry Park (Shanghai, China), melamine and L-glutathione were purchased from the Chengdu area of the Industrial Development Zone Xindu Mulan (Chengdu, China). K$_2$Cr$_2$O$_7$ was obtained from Chengdu Jinshan Chemical Reagent Co., Ltd.

| Pyrolytic temperature (°C) | Residence time | Reagent | Contaminants | References |
|----------------------------|----------------|---------|--------------|------------|
| 600                        | 3 h            | -       | Pb(II)       | (Yang et al. 2014) |
| 300, 450                   | 2 h            | H$_2$O$_2$ | Metformin Hydrochloride | (Huang et al. 2016) |
| 500–900                    | 1–4 h          | -       | -            | (Li et al. 2017b) |
| 350, 650                   | 2 h            | HNO$_3$ | Pb(II)       | (Wang et al. 2019) |
|                            |                | H$_2$SO$_4$ |              |            |
| 350                        | 2 h            | Bentonite | Cd(II)      | (Jing et al. 2020) |
| 600                        | 1 h            | NaOH    | Ibuprofen    | (Du et al. 2021) |
Characterization

X-ray diffraction (XRD) analyzes (D8-ADVSNCE, China), Fourier transform infrared spectroscopy (FT-IR) analyzes (IS-10, China), scanning electron microscope-energy-dispersive spectrometer (SEM–EDS) analyzes (Phenom Pharos, Netherlands), X-ray photoelectron spectroscopy (XPS) analyzes (AXIS Supra, Japan), and Brunauer–Emmett–Teller (BET) analyzes (Micromeritics, ASAP2460, USA) were used to characterize the structure of the biochar. The magnetic properties of MFBAP were investigated with vibrating sample magnetometer (VSM) (LakeShore 7404, USA). The zeta potentials of MFBAP were measured at different pH by Zetasizer Nano ZS (ZEN3690, Malvern, UK).

Preparation of pristine biochar and modified biochars

Schematic representation of preparation for four kinds of biochars is shown in Scheme 1. To obtain pristine biochar (BAP), 4.5 g crushed AP was added to a beaker containing 38 mL of deionized water; then, the suspension liquid was stirred vigorously (500 rpm) at 25 °C for 1 h. After that, the mixture was transferred into a 100-mL Teflon-lined autoclave which then was placed into the oven at 210 °C for 12 h. After natural cooling, pour out the supernatant and wash the remaining substances with deionized water several times and dry at 70 °C for 24 h.

The preparation of modified biochar is mainly based on previous studies (Cai et al. 2019). Take HAD-modified biochar (MFBAP) for example, 38 mL of deionized water was added into a beaker containing 4.5 g crushed AP, 2.7 g FeCl₃·6H₂O, and 2.8 g of HDA; subsequently the suspension liquid was stirred vigorously (500 rpm) at 25 °C for 1 h. After that, the mixture was transferred into a 100-mL Teflon-lined autoclave which then was placed into the oven at 210 °C for 12 h. After natural cooling, pour out the supernatant and wash the remaining substances with deionized water several times and dry at 70 °C for 24 h to obtain MFBAP. Similarly, melanin-modified biochar (MEBAP) and L-glutathione-modified biochar (LBAP) were prepared by the above method as well, which just altered HDA to melamine or L-glutathione.

Sorption experiments

K₂Cr₂O₇ (2.829 g) was dissolved in deionized water to obtain Cr (VI) standard solution with a concentration of 1000 mg/L. The pH of Cr(VI) solution was adjusted by 0.1 M HCl and NaOH. The initial pH of 100 mg/L Cr (VI) solution was adjusted to 2.0, and then 0.05 g biochar was added. The conical flask was placed in a thermostatic oscillation, in which the experimental conditions were 24 h, 25 °C, and 150 r·pm⁻¹. To explore the adsorption isotherms, 0.05 g adsorbent was employed to treat Cr(VI) ions solution (pH=2.0) with initial Cr(VI) ions concentrations varied from 20 to 500 mg/L. During the adsorption process, the concentration of residual Cr(VI) ions was measured at various times to obtain the adsorption kinetics.

The concentration of chromium solution was measured by 1,5-diphenylcarbazide method. The adsorption capacity (mg/g) and removal efficiency (%) were obtained as follows:

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

(1)

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\[ R = \frac{c_0 - c_e}{c_0} \times 100\% \]  

where \( c_0 \) and \( c_e \) (mg/L) are the initial and equilibrium concentration of Cr(VI), respectively; \( V \) (mL) is the volume of Cr(VI) solution; and \( m \) (g) is the mass of the adsorbent.

**Regeneration and recycling experiment**

Biochar of 0.2 g was added into 200 mL Cr(VI) solution (100 mg/L, pH = 2.0) and placed in a constant temperature vibrator at 25 °C and 150 rpm\(^{-1}\) for 24 h. After adsorption, the Cr-loaded biochar was washed several times with deionized water and dried. Added Cr-loaded biochar into 100 mL 0.1 M NaOH solution in a beaker under thermostatic oscillation, the conditions are similar to those above. After desorption, the biochar is washed with deionized water and dried for the next adsorption experiment.

**The coexisting cations interference study**

Different concentrations of anions (Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), HPO\(_4^{2-}\)) and cations (Cu\(^{2+}\), Ca\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\)) were added to 100 mL Cr(VI) solution (100 mg/L, pH = 2.0) and shook in a thermostatic oscillator for 24 h at 25 °C, then calculate the residual Cr(VI) in the solution.

**Results and discussions**

**Characterizations of biochar**

**XRD and FT-IR**

The XRD results are shown in Fig. 1a, BAP, MFBAP, MEBAP, and LBAP have similar peak shapes. The diffraction pattern of four biochars shows diffraction peaks at 14.8° (110) and 24° (002), which can be distinguished as carbon with JCPDS Card No. 50–0926 and JCPDS Card No. 46–0944, indicating that they were made of amorphous carbon (Cai et al. 2019), the other peaks of BAP belonged to the crystal form of whewellite. In addition, by comparing the PDF card (JCPDS Card No.391346), the new characteristic peaks of MFBAP, MEBAP, and LBAP at 30.2° (220), 35.5° (311), 43.2° (400), 57.3° (511), and 62.9° (440) were discovered to be the crystal form of \( \gamma \)-Fe\(_2\)O\(_3\) (Xiao et al. 2019), which indicated that \( \gamma \)-Fe\(_2\)O\(_3\) particles were embedded in the pristine biochar. After adsorption, some characteristic peaks of BAP weaken or even disappeared, while the characteristic peaks of modified biochar hardly change, indicating that the crystal form of BAP has been damaged to some extent after adsorption.

The FT-IR patterns of four biochars before and after adsorption are shown in Fig. 1b. It can be seen that the biochar, before and after modification, had the homologous peak shape except for BAP which did not possess a peak at 582 cm\(^{-1}\) that was assigned to the stretching vibration of Fe–O (Cai et al. 2019). Besides, seven main functional groups are found to exist on the surface of biochars, such as -OH stretching vibration of carboxy and hydroxyl group, C = O bending vibration, aromatic C = C, N–C = O stretching vibration, -COOH flexural vibration or conjugated C-N stretching vibration, alcoholic CO- stretching vibration (Jiang et al. 2017; Li et al. 2016; Sun et al. 2011) for the 4 samples which characteristic absorption peaks are at 3384 cm\(^{-1}\), 2858 cm\(^{-1}\), 1628 cm\(^{-1}\), 1452 cm\(^{-1}\), 1368 cm\(^{-1}\), and 1058 cm\(^{-1}\). It was also found that the peaks of four biochars were reduced and even disappeared after adsorption, which means that the functional group was involved in the adsorption process. Furthermore, it is convincing that adding FeCl\(_3\)·6H\(_2\)O is the reason why the surface of biochar can form iron oxide which is consistent with the XRD results.

**SEM**

Figure 2a shows that BAP displayed neat and porous structures with no Fe existing on its smooth surface. Unlike BAP, MFBAP, MEBAP, and LBAP present a rough surface in which many irregular particles are uniformly contained in Fig. 2b–c. These particles are mainly composed of \( \gamma \)-Fe\(_2\)O\(_3\),
which has been confirmed by previous XRD results. In addition, MFBAP and MEBAP show a circular structure, and under the same scale, the diameter of their circular structures is much larger than BAP, which is also far from the structures of BAP. Hence, it can be proved that the introduction of HAD and melamine can dramatically alter the surface and porous structure of pristine biochar so that the porous structure can transform and extend into a kind of circular structure on which the surface is covered with a myriad of \( \gamma \)-Fe\( _2 \)O\(_3\). This permits better mass transfer and diffusion of constituents into the inner iron nanoparticles (Badawi et al. 2021). The possible reason is that adding HDA and ME can increase the pH of the reaction solution, which makes the decomposition of lignin or cellulose in AP more thorough during the HTC process (Wang et al. 2018), and thus leaving a large number of circular structures. In addition, it can be observed notably from Fig. 2d that the skeleton structures of the LBAP were conspicuous. However, the gap between the skeleton structures is blocked; this phenomenon was explained that L-glutathione could hinder the formation of the circular skeleton structures and block the pore channel during the HTC process, which is why the \( S_{BET} \) and pore volume (Table 2) decreased after being modified by coating L-glutathione onto pristine biochar. The different structures of the four materials account for the dissimilarity of BAP, MFBAP, MEBAP, and LBAP for adsorption efficiency of Cr(VI) in a way.

In addition to studying the typical SEM appearance of four kinds of biochar, the surfaces before and after adsorption were also researched. As is shown in Fig. 2e–h, it is found that the surface of four kinds of biochar has changed dramatically before and after adsorption. The surface of BAP has become rough and uncomely, indicating that its surface had been seriously damaged after adsorption. Followed by

| Sample  | \( S_{BET} \) (m\(^2\)/g) | Average pore size (nm) | Average mesoporous volume (nm) | Pore volume (cm\(^3\)/g) |
|---------|-----------------|-----------------|-----------------|-----------------|
| Before adsorption BAP | 5.6308 | 17.5925 | 19.8232 | 0.0248 |
| MFBAP | 11.8252 | 30.6540 | 35.1388 | 0.0906 |
| MEBAP | 7.0464 | 17.2099 | 13.7804 | 0.0303 |
| LBAP | 3.4583 | 15.7163 | 27.4638 | 0.0136 |
| After adsorption BAP | 8.7136 | 18.5442 | 17.5984 | 0.0404 |
| MFBAP | 17.6486 | 24.2337 | 23.6759 | 0.1069 |
MFBAP, MEBAP, and LBAP, despite their surfaces having also been damaged to some extent, it can be seen from SEM images that their surfaces are much less damaged than BAP. Therefore, it can be said that the introduction of amines could enhance the external resistance of biochar.

The elemental composition of the surface of BAP and MFBAP after adsorption was analyzed by SEM–EDS in Fig. 3. It can be seen that the surface of MFBAP is loaded with a ton of Cr(VI) ions, and its load scale and quantity are more tremendous than that of BAP. The Cr(VI) loaded on the surface of BAP accounts for 19.24%, which is lower than 21.44% of that MFBAP, demonstrating that the Cr(VI) loading performance of MFBAP has been strengthened. In addition, the N content of MFBAP also increased by 3.05% relative to BAP, which also shows that the introduction of HDA increases a large number of N-containing functional groups on the surface of MFBP. The Fe peak in the EDS spectrum of MFBAP further proves that Fe is successfully introduced into biochar by HTC.

BET

Their N_2 adsorption/desorption isotherms are displayed in Fig. 4a. It can be seen from Table 2 that the four biochars all show a pseudo-type IV curve. The S\textsubscript{BET} of the biochars were 5.6308 m\textsuperscript{2}/g (BAP), 11.8252 m\textsuperscript{2}/g (MFBAP), 7.0464 m\textsuperscript{2}/g (MEBAP), and 3.4583 m\textsuperscript{2}/g (LBAP), respectively, which means HAD and ME modification can improve S\textsubscript{BET}. The outcome may owe to the process of manufacturing modified biochar, which was produced by mixing biomass with FeCl₃ and amines, and the pore structures of pristine biochar were changed during the HTC process. Among them, MFBAP is the highest in terms of S\textsubscript{BET}, average pore size, and average micropore volume as well as pore volume. The S\textsubscript{BET} of MFBAP is almost twice that of BAP and the pore volume is almost four times. The increased S\textsubscript{BET} and pore volume of MFBAP also reflected the uniformly distributed nature of γ-Fe₂O₃ particles (Deng et al. 2020), which would favor its applications in adsorption. More importantly, it can be seen that the S\textsubscript{BET} and pore volume of LBAP is the lowest, which was again proved that L-glutathione can block the pores of biochar, reducing its S\textsubscript{BET} and pore volume. These results all were corresponding with the previous results of SEM images partially. In this study, the S\textsubscript{BET} of the four biochar is not large, but previous studies (Yi et al. 2019) have shown that the adsorption capacity of magnetic biochar to degrade Cr(VI) does not depend on its S\textsubscript{BET}. In other words, the S\textsubscript{BET} of magnetic biochar is not the key factor to determine the adsorption capacity, which means that the
removal mechanism of Cr(VI) onto MFBAP relies mostly on functional groups.

It was also discovered that the SBET of BAP and MFBAP was enhanced after adsorption. This is because after the adsorption under acidic conditions (pH = 2, 100 mg/L Cr(VI)), some impurity particles attached to the pores were eluted and the pore structures became sparse (Pan et al. 2021).

Fig. 4 a N₂ adsorption–desorption isotherms of BAP, MFBAP, MEBAP, LBAP; b effect of pH (c₀ = 100 mg/L, T = 25 °C, t = 24 h, dose of adsorbent = 0.05 g); c adsorption kinetics curves (c₀ = 100 mg/L, pH = 2.0, T = 25 °C, dose of adsorbent = 0.05 g); d adsorption isotherms (T = 25 °C, pH = 2.0, t = 24 h, dose of adsorbent = 0.05 g); e and f effect of the competitive ions (c₀ = 100 mg/L, T = 25 °C, pH = 2.0, t = 24 h, dose of adsorbent = 0.05 g)
Adsorption kinetics and isotherms

In order to evaluate adsorption as a unit operation, it requires consideration of two important physicochemical aspects of the process, the kinetics and the equilibrium of adsorption (Bayramoglu and Arica 2008). The pseudo-first-order and pseudo-second-order models and Elovich were used to study the adsorption kinetics of Cr(VI) on biochar, and the adsorption isotherms of Cr(VI) on biochar were simulated by Langmuir and Freundlich model. The three kinetics models (Xiang et al. 2020) and two isotherm models (Zhang et al. 2020) are described by Eqs. (3)–(7):

\[ q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (3) \]

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4) \]

\[ q_t = \frac{1}{b_E} \ln \alpha_E \beta_E + \frac{1}{b_E} \ln t \quad (5) \]

\[ q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (6) \]

\[ q_e = k_F c_e^{1/n} \quad (7) \]

where \( q_e \) and \( q_t \) are the adsorption amounts of Cr(VI) by biochars at equilibrium and time \( t \), respectively. \( k_1 \) and \( k_2 \) are the corresponding adsorption rate constants of the pseudo-first-order (h\(^{-1}\)) and pseudo-second-order (g·mg\(^{-1}\)·h\(^{-1}\)) models, respectively. \( \alpha_E \) and \( \beta_E \) are the initial adsorption rate (mg·g\(^{-1}\)·h\(^{-1}\)) and desorption rate (g·mg\(^{-1}\)) constants, respectively. \( q_m \) (mg/g) is the maximum monolayer adsorption capacity, \( k_L \) and \( k_F \) is the Langmuir and Freundlich isotherm constant, respectively. \( n \) is the measure of adsorption intensity.

The experimental results of kinetics are shown in Fig. 4c. The adsorption of Cr(VI) by four kinds of biochar is rapid, which reached 59.45% (MFBAP), 45.73% (BAP), 35.26% (MEBAP), and 51.29% (LBAP) within 120 min. When adsorption reached 800 min, the adsorption capacity of the four biochars reached equilibrium. The reason why the adsorption equilibrium took a long time is that the active surface sites of biochar were occupied by Cr(VI), which made the binding sites on the material surface decrease rapidly (Zhang et al. 2015a). As illustrated in Table 3, it is the MFBAP that possessed the maximum adsorption capacity of 80.58 mg/g, which is higher than that of the BAP (42.47 mg/g) and that of the MEBAP and LBAP (62.26 mg/g and 55.66 mg/g). The adsorption data were further fitted by the pseudo-first-order model and the pseudo-second-order model. The fitting degree of kinetic was judged by the correlation coefficients (\( R^2 \)). The pseudo-second-order model is better fitted to BAP (\( R^2 = 0.9763 \)) and MEBAP (\( R^2 = 0.9765 \)), indicating that the adsorption of Cr(VI) by BAP and MEBAP is mainly a chemical adsorption process (Liu et al. 2017). Meanwhile, the Elovich model was found to better fit MFBAP (\( R^2 = 0.9889 \)) and LBAP (\( R^2 = 0.9851 \)), demonstrating that the MFBAP and LBAP have a variety of adsorption mechanisms for Cr(VI).

The adsorption isotherm parameters and the fitting results of the two models are shown in Table 4 and Fig. 4d. At low concentration, the adsorption capacity of the four biochar increased extremely and as the concentration gradually raised, their adsorption capacity approached saturation. Besides, it could be negligible for the residual Cr(VI)

### Table 3 Kinetic parameters of Cr(VI) adsorption by BAP, MFBAP, MEBAP, and LBAP

| Sample | \( q_e \) (mg/g) | Pseudo-first-order | Pseudo-second-order | Elovichs |
|--------|-----------------|-------------------|---------------------|----------|
|        | \( R^2 \) | \( Q_e \) (mg/g) | \( k_1 \times 10^3 \) | \( R^2 \) | \( Q_e \) (mg/g) | \( k_2 \times 10^3 \) | \( R^2 \) | \( \beta_E \) | \( \alpha_E \) |
| BAP    | 42.4740 | 0.9563 | 40.5171 | 4.97 | 0.9763 | 46.2992 | 0.1405 | 0.9559 | 0.1405 | 1.5309 |
| MFBAP  | 80.5804 | 0.9315 | 71.7952 | 9.31 | 0.9749 | 80.3924 | 0.1669 | 0.9889 | 0.0768 | 4.6688 |
| MEBAP  | 62.2600 | 0.9669 | 61.6264 | 2.91 | 0.9765 | 74.8279 | 0.0415 | 0.9118 | 0.0986 | 1.3514 |
| LBAP   | 55.6647 | 0.9179 | 50.0845 | 6.98 | 0.9634 | 55.6755 | 0.1886 | 0.9851 | 0.1116 | 2.6622 |

### Table 4 Isotherms parameters of Cr(VI) adsorption by BAP, MFBAP, MEBAP, and LBAP

| Sample | \( q_e \) (mg/g) | Langmuir | Freundlich |
|--------|-----------------|----------|-----------|
|        | \( R^2 \) | \( Q_e \) (mg/g) | \( k_L \) | \( R^2 \) | \( n \) | \( k_F \) |
| BAP    | 42.4740 | 0.9921 | 46.1405 | 0.6031 | 0.9522 | 8.6398 | 25.0175 |
| MFBAP  | 80.5804 | 0.8979 | 90.6798 | 0.3817 | 0.8719 | 6.4624 | 39.4584 |
| MEBAP  | 62.2600 | 0.9476 | 66.5468 | 0.7089 | 0.8917 | 8.2141 | 34.6154 |
| LBAP   | 55.6647 | 0.9231 | 59.1987 | 0.8952 | 0.8806 | 9.3205 | 33.2846 |
concentration after adsorption by MFBAP as the initial concentration in the solution is relatively low. Langmuir and Freundlich are the most common models used to describe the adsorption characteristics between adsorbent and Cr(VI). The Langmuir correlation coefficients of the BAP, MFBAP, MEBAP, and LBAP ($R^2 = 0.9921, 0.8979, 0.9476, 0.9231$) are higher than those of Freundlich ($R^2 = 0.9522, 0.8719, 0.8917, 0.8806$), and the values of $q_m$ calculated by the Langmuir isotherm are quite close to experimental values $q_e$, indicating that Langmuir has a better fitting effect on the four biochar and the adsorption process of Cr(VI) onto four biochars was monolayer adsorption with uniform binding sites and equal adsorption energies and few interactions between adsorbed species (Li et al. 2020). Hence, Cr(VI) is mainly adsorbed to the surface of biochar through various chemical reactions.

**Effect of pH**

In general, the medium pH has the highest effect on the removal performance of the adsorbents and shows a significant role in the ionization of useful groups on the sorbent surfaces; therefore, it has a vital impact on Cr(VI) removal (Arica et al. 2019). The effect of the initial pH of the solution on adsorption is shown in Fig. 4b. It can be seen that it is more efficient for MFBAP to remove Cr(VI) than other biochars and the adsorption capacity of biochars for Cr(VI) becomes lower gradually with the increase of pH value (2.0–8.0). When pH = 2.0, the adsorption capacity reaches the maximum value. Meanwhile, the minimum adsorption capacity was observed at pH = 8.0. It means that acidic conditions favored the efficient removal of Cr(VI) mainly by alleviating surface passivation (Deng et al. 2020). Cr(VI) exists in the form of anion under acidic conditions (Li et al. 2017a); therefore, it is likely that electrostatic attraction occurred under this condition, which makes Cr(VI) adsorbed in large quantities. Besides, Fe$_2$O$_3$ can be protonated as FeOH$^+$ that could be the active centers of Cr(VI) adsorption under lower initial pH (Li et al. 2020), which is beneficial to the adsorption of biochars.

**Effect of the coexisting cations**

The actual wastewater contains various kinds of ions; therefore, the effects of different anions ($\text{Cl}^−, \text{NO}_3^−, \text{SO}_4^{2−}, \text{HPO}_4^{2−}$) and cations ($\text{Cu}^{2+}, \text{Ca}^{2+}, \text{Ni}^{2+}, \text{Cd}^{2+}$) on the adsorption capacity of MFBAP are studied in Fig. 4e–f. Several anions had little effect on the adsorption effect; however, cations exerted great influence on adsorption capacity. The disturbance capability of the coexisting cations on the adsorption capacities of MFBAP was as follows: $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+}$ due to that their affinity to compete for the active site of the MFBAP is related to the valence, hydration state, and chemical structure of ions (Dong et al. 2018). For the above results, it can also be said that MFBAP has a partial adsorption ability on these cations in a way due to the competition mechanism, especially had a high affinity for $\text{Cd}^{2+}$, which lays a certain foundation for the study of $\text{Cd}^{2+}$ adsorption by HAD-modified magnetic biochar. At the same time, a previous study has shown that the reason why Ca$^{2+}$ can affect adsorption is that Ca$^{2+}$ can occupy the active adsorption sites on the surface of biochar. The above results show that MFBAP has an anti-ion interference ability to some extent.

**Regeneration performance and VSM analysis of MFBAP**

The use of an adsorbent in wastewater treatment depends not only on the adsorptive capacity but also on how well the adsorbent can be regenerated and reused (Arica et al. 2017). Regeneration performance of adsorbent materials is very important for evaluating the feasibility of practical and large-scale applications (Fomina and Gadd 2014). The recycling experiment of MFBAP after five times of adsorption/desorption was studied. The results are shown in Fig. 5a.

![Fig. 5](image-url)
It can be seen from the figure that the adsorption capacity of MFBAP after regeneration decreased a lot, and the final adsorption capacity is still 33.68 mg/g after 5 cycles, which is better than many other adsorbents reported in the literature (Table 5), demonstrating that the adsorbent has preferable adsorption potential, which could be applied in large scale for real wastewater treatment Fig. 6.

The characteristic of the VSM curve determines the practicability of ferromagnetic materials (Xiao et al. 2019). The VSM curve of MFBAP is presented in Fig. 5b. The obtained curve shows the normal S-type hysteresis curve with a saturation magnetization of 28.767 emu/g. The coercivity at room temperature is about zero, which can be attributed to the superparamagnetic property. There will be no residual magnetic moment when the magnetic field is removed, which is conducive to easy and rapid magnetic separation. Therefore, the external magnetic field can be used to separate and recover biochar to achieve the recovery effect and greatly reduce the energy consumption in the process of Cr(VI) adsorption and desorption.

**Cr(VI) removal mechanisms**

In order to understand the valence state of elements on the surface of biochar and whether the functional groups on the surface of biochar are involved in the reaction, and most importantly, the mechanisms of Cr(VI) adsorption, XPS was used to study the chemical changes of the surface of biochar before and after Cr(VI) adsorption and explain the mechanism of Cr(VI) removal. The results are displayed in Fig. 7. A new double peak appears in the spectrum after adsorption, which was confirmed to be the photoelectron peak of Cr 2p, indicating that the phenomenon of Cr(VI) ions adsorption onto MFBAP took place. The peaks at 585.20 and 574.5 eV attributed to the Cr 2p1/2 and Cr 2p3/2 of Cr(III), while the peaks at 585.4 eV and 578.2 eV are ascribed to the Cr 2p1/2 and Cr 2p3/2 of Cr(VI), respectively, indicating that on the surface of MFBAP after adsorption, there are two forms of chromium: Cr(III) and Cr(VI), and therefore it is the biochar that converted Cr(VI) to Cr(III) by reduction. The other significant peaks represent C 1s (83.25%), O 1s (12.73%), and N 1s (4.02%) before adsorption, and C1s (80.06%), O 1s (17.11%), and N 1s (2.84%) after adsorption. Except for these three peaks, Fe 2p can also be observed in XPS survey spectra, which demonstrated the preparation of magnetic biochar was successful. Comparing the XPS spectra before and after adsorption, it can be found that the N/C atomic ratio decreases after Cr(VI) was adsorbed by biochar, indicating that the amino groups participated in the reaction and were consumed in the adsorption process. In the XPS spectrum of N 1s before adsorption, the peak at 397.70, 396.5, and 398.4 eV were identified as N–C, N–H, and N–N, respectively.

![Fig. 6](image-url) The zeta potentials of MFBAP at different pH values

| Raw material                     | Adsorption capacity (mg/g) | pH | Cr(VI) concentration (mg/L) | Reference          |
|----------------------------------|----------------------------|----|------------------------------|--------------------|
| Eichhornia crassipes             | 120                        | 2  | 150                         | (Zhang et al. 2015a) |
| Astragalus membranaceus         | 23.85                      | 2  | 50                          | (Shang et al. 2016) |
| Enteromorpha prolifera          | 88.17                      | 2  | 100                         | (Chen et al. 2018) |
| Phoenix tree leaves             | 27.2                       | 1  | 50                          | (Shi et al. 2018)  |
| Melia azedarach wood            | 25.27                      | 3  | 100                         | (Zhang et al. 2018) |
| Pine sawdust                    | 25.25                      | 2  | 50                          | (Li et al. 2019)   |
| Loofah                          | 30.14                      | 2  | 40                          | (Xiao et al. 2019) |
| Steel pickling waste liquor     | 43.12                      | 2  | 100                         | (Yi et al. 2019)   |
| Water hyacinth                  | 43.48                      | 2  | 100                         | (Yu et al. 2018)   |
| Bamboo                          | 38                         | 3  | 50                          | (Huang et al. 2018) |
| This study                      | 81.31                      | 2  | 100                         | -                  |
-NbN- and N–H, respectively. Apparently, the three peaks of N 1 s became weaker after adsorption, which means the amino-functional groups of MFBAP were consumed after participating in the degradation of Cr(VI) adsorption. In other words, the amino-functional groups are the significant adsorption mechanism of Cr(VI). The reduction of Cr(VI) to Cr(III) requires the participation of electron donors, and amino, carboxyl, and hydroxyl groups have been reported as electron donors for the reduction of Cr(VI) (Bayramoglu and Arica 2008, Bayramoglu and Arica 2011). The N1s peak shifted to higher binding energy after adsorption, which further showed that the amino-functional groups on the surface of biochar participated in the Cr(VI) reduction process. In fact, -NH- can provide electrons for the reduction process of Cr(VI) to Cr(III) and make itself oxidized to —NH= (Chen and Li 2022, Wang et al. 2022), so is C-O, which could be oxidized to C=O (Ding et al. 2021). The peaks of 284.8 eV and 286.06 eV, 284.2 eV and 286.7 eV were assigned to the C–C, C-O, C=O, and C-N bonds (Li et al. 2019), respectively. Compared with C1s before and after adsorption, it was found that the C-O peak became weak, while the C=O peak increased, suggesting that functional groups participated in the process of Cr(VI) adsorption. Cr(VI) exists as the form of HCrO₄⁻ and Cr₂O₇²⁻ under acidic conditions (Saha and Orvig 2010, Zhang et al. 2017). The zero point of zeta potential (pHₚzc) for MFBAP was at pH between 7 and 8, which means that when the solution pH < pHₚzc, the hydrated surface of MFBAP was protonated, which
made the MFBAP surface potential electropositive (Zhang et al. 2015a); thus, HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ were electrostatically adsorbed to the surface; meanwhile, with the gradual increase of pH, the OH$^-$ in the aqueous solution gradually reduced the surface positive charge of biochar and competed with Cr(VI) for adsorption, resulting in the reduction of the adsorption capacity of Cr(VI) (Qiua et al. 2020). Besides, some active functional groups, such as C$\equiv$C and C–OH, which can be called Lewis base, can provide electrons for Cr(VI) in the adsorption process to reduce into Cr(III) (Hai et al. 2014; Zhang et al. 2015b). Therefore, the reduction process of Cr(VI) should be as follows:

\[
\text{HCrO}_4^- + 7\text{H}^+ + 3e^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}
\]

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Simultaneously, the amino-functional groups -NH$_2$ could be protonated to -NH$_3^+$ under acidic conditions as well as -OH and -COOH, which also could be protonated to -OH$_2^+$ and -COOH$_2^+$. Therefore, part of the process for the mechanisms of Cr(VI) can be described as follows (Mohan and Pittman 2006):

Part of Cr (VI) is directly complexed on the surface of biochars as the form of Cr (VI), and the rest of Cr (VI) is reduced to Cr (III) by N-containing functional groups (-NH$_3^+$) and O-containing functional groups (C-O and -OH) on the biochar surface under acidic conditions. As is shown in Scheme 2, the main interaction mechanisms of the removal of Cr(VI) include four key steps: (1) complexation, where functional groups on biochar can be protonated at low pH to form positively charged sites (-NH$_3^+$, -OH$_2^+$, -COOH$_2^+$), which Cr(VI) can be easily bound to the electropositive surface of biochar and form complexes with the functional groups; (2) electrostatic interaction, where the surface of the modified biochar material has a positive charge (H$^+$) when the pH is low, and Cr(VI) in the valence state of negative ions can be trapped on the surface of the adsorbent material; (3) reduction, where some active functional groups can act as Lewis bases to provide electrons for the reduction of Cr(VI); and (4) ion exchange, where Cr(VI) was adsorbed onto active sites of the MFBAP.

**Conclusions**

1. In this paper, amino-functional groups derived from hexanediamine, melamine, and L-glutathione were introduced on the surface of magnetic biochars derived from AP in the process of hydrothermal carbonization and employed as an excellent adsorbent to remove Cr(VI). Compared with other biomass materials, modified biochars had the characteristics of efficient adsorption and can achieve the effect of “making waste from waste,” which has a certain reference value for invasive plant derivative materials to remove heavy metals or organic pollutants.

2. It was found that BAP displayed neat and porous structures, while MFBAP, MEBAP, and LBAP present a rough surface in which γ-Fe$_2$O$_3$ particles were uniformly contained, which means that different amines can change the morphology of biochar, which is an ideal adsorption active site for Cr(VI). Meanwhile, hexanediamine and melamine could enhance the $S_{BET}$ of biochar, while L-glutathione was on the contrary.

3. Optimum conditions for removal of Cr(VI) by biochars: pH = 2.0, $c_0 = 100$ mg/L, $t = 24$ h, $T = 25$ °C. The maximum theoretical adsorption capacity of modified biochars is 90.68 mg/g (MFBAP), 66.55 mg/g (MEBAP), and 59.20 mg/g (LBAP), which is much greater than
BAP (46.14 mg/g). Besides, MFBAP followed Elovich kinetic model and Langmuir isotherm and after five times of adsorption/desorption, the adsorption capacity can still reach more than 30 mg/g and has anti-ion interference ability. The adsorption mechanism of Cr(VI) by MFBAP is mainly electrostatic interaction, ion exchange, complexation, and reduction through XPS analysis.

4. In view of biochars being in the experimental stage, the following aspects can be considered in industrial application in the future: combining biochars with new materials in various fields to design high-performance three-dimensional new composites. Although the modified biochars can improve the adsorption efficiency, it still has some flaws, such as poor dispersion and easy agglomeration. Therefore, it is of great significance to develop a cheap and efficient preparation process for adsorbents.

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Author contribution DHY and ZXC contributed to the study conception and design. Material preparation was performed by LX, and data collection and analysis were performed by LX and YYH. The first draft of the manuscript was written by LX, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

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