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

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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 and employed as an efficient adsorbent for Cr(VI). The maximum adsorption capacity is 80.58 mg/g obtained by Hexanediamine modified biochar (MFBAP), which is nearly twice that of the pristine biochar (42.47 mg/g). BET demonstrated that Hexanediamine and Melamine could enhance the S_{BET} of biochars, while L-Glutathione could reduce its S_{BET} , which SEM images could support this conclusion. Adsorption kinetics and isotherms studies showed that the Cr(VI) adsorption process of MFBAP followed Elovich kinetic model and Langmuir isotherm, which means that it was mainly a chemical adsorption process. The characterization results proved that -NH_2 derived from amines play 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_{BET} and excellent recyclability, which is a promising candidate for solving the problem of invasive plants and wastewater treatment.

1 Introduction

Alternanthera philoxeroides(AP), a weed belonging to Amaranthaceae, originated in South America and was introduced into China as horse feed in the 1930s, which was listed as an invasive plant worldwide (Du et al. 2020). It has strong ecological adaptability and reproductive diffusion ability (Li et al. 2013). In the Sichuan Province of China, the distribution area of AP was more than 1.2 million hm^2 . At present, the treatment methods of AP mainly include chemical methods (spraying herbicides) and physical methods (mechanical or manual cutting). However, these methods are very restricted and will consume a lot of manpower and financial resources. Currently, the world is advocating the concept of waste recycling, therefore it's imperative to explore a method that can not only cope with the problem of invasive plants but also make the most of them to safeguard the environment.

Biochar has been proven to be an excellent adsorbent for pollutants. It has a wide range of sources and simple preparation methods. Therefore, many studies on the properties of biochar have been born(Hai et al. 2014). However, it is far from enough to only use biochar for the adsorption of pollutants (Liu et al. 2020). It involves many problems, such as difficult recovery, low adsorption efficiency and weak reusability (Gopinath et al. 2021). Therefore, the modification of biochar has become a research hotspot in recent years (Nguyen et al. 2021), such as acid-base, chemical, physical and magnetic modification, which can improve the shortcomings of biochar. According to past studies, numerous researchers (Table 1) have discovered that AP can be pyrolyzed at high temperatures to produce biochar applied for the treatment of heavy metals and organic pollutants. For example, Yu Yang et al. (Yang et al. 2014) pyrolyzed AP at 600 °C for 3 h and successfully prepared biochar which possesses specific surface area (S_{BET}) of 690.31 m^2/g and rich functional groups such as free carboxyl/hydroxyl and it was certificated that its adsorption ability on Pb (II) could reach 257.12 mg/g. Employing AP as raw material, Xian Fa Li et al. (Li et al. 2017) prepared biochar by K_2CO_3 one-step mixed activation method, which extremely beefs up its specific surface area(1799.8 m^2/g). But the temperature they used to prepare biochars was too high, which is not conducive to energy conservation, and a fatal disadvantage of biochar is that it is difficult to recover in aqueous solution (Rajapaksha et al. 2016).

In this paper, utilizing AP as raw material, a green and simple method referred to as hydrothermal carbonization (HTC) was used to prepare magnetic biochar with different S_{BET} and excellent adsorption capacity for Cr(VI). This work also provides an insight into the treatment of invasive plants and the application of waste biomass.

Table 1
Application of *Alternanthera philoxeroides* as biochar

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. 2017)
350–650	2 h	HNO ₃ H ₂ SO ₄	Pb(II)	(Wang et al. 2019)
350	2 h	Bentonite	Cd(II)	(Jing et al. 2020)
600	1 h	NaOH	Ibuprofen	(Yuanda et al. 2021)

2 Materials And Methods

2.1 Materials and chemicals

AP were collected from Chengdu University of Technology, and were 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 FeCl₃·6H₂O were obtained from Shanghai Chemical Industry Park (Shanghai, China), Melamine and L-Glutathione were purchased from Chengdu Area Of The Industrial Development Zone Xindu Mulan (Chengdu, China). K₂Cr₂O₇ was got from Chengdu Jinshan Chemical Reagent Co., Ltd.

2.2 Characterization

X-ray diffraction (XRD) analyzes (D8-ADVSANCE), Fourier transform infrared spectroscopy (FT-IR) analyzes (IS-10), Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) analyzes (Phenom LE), X-ray photoelectron spectroscopy (XPS) analyzes (AXIS Supra) and Brunauer Emmett Teller (BET) analyzes (Micromeritics, ASAP2460) were used to characterize the structure of the biochar.

2.3 Preparation of BAP, MFBAP, MEBAP and LBAP

The preparation of 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 at 25 °C for 1h. After that, the mixture was transferred into a 100 mL Teflon-lined autoclave which then was placed into the oven at 210 °C for 12h. After natural cooling, pour out the supernatant and washed the remaining substances with deionized water several times and dried at 70 °C for 24h. Schematic representation of preparation for MFBAP is shown in Scheme. 1. MEBAP and LBAP were prepared by this method as well, which just altered HDA to Melamine or L-Glutathione. Similarly, BAP was prepared in the absence of FeCl₃·6H₂O and HDA during the hydrothermal reaction.

2.4 Sorption experiments

2.829 g K₂Cr₂O₇ 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, and then 0.05 g biochar was added. The conical flask was placed in a thermostatic oscillation, which the experimental conditions were 24 h, 25 °C, 150 r·pm⁻¹. To explore the adsorption isotherms, 0.05 g adsorbent was employed to treat Cr(VI)

ions solution (pH = 2) 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/L) and removal efficiency (%) were obtained as follows:

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

1

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

2

Where c_0 and c_e are the initial and equilibrium concentration of Cr(VI), respectively; V is the volume of Cr(VI) solution and m is the mass of adsorbent.

2.5 Regeneration and recycling experiment

0.2 g biochar was added into 200 mL Cr(VI) solution (100 mg/L, pH = 2) and placed in a constant temperature vibrator at 25 °C and 150 r·pm⁻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.

2.6 The coexisting cations interference study

Different concentrations of anions (Cl⁻, NO₃⁻, SO₄²⁻, HPO₄²⁻) and cations (Cu²⁺, Ca²⁺, Ni²⁺, Cd²⁺) were added to 100mL Cr(VI) solution(100 mg/L, pH = 2) and shook in a thermostatic oscillator for 24 h at 25 °C, then calculate the residual Cr(VI) in the solution.

3 Results And Discussions

3.1 Characterizations of biochar

3.1.1 XRD and FT-IR

The XRD results are shown in Fig. 1(a), 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 JCPDSCard 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 γ-Fe₂O₃ (Xiao et al. 2019), which indicated that γ-Fe₂O₃ particles were embedded in the pristine biochar.

The FT-IR patterns of four biochars were shown in Fig. 1(b). It can be seen that the biochar, before and after modification, had the homologous peaks shape except for BAP which not possessed a peak at 582 cm⁻¹ that was assigned to stretching vibration of Fe-O (Cai et al. 2019). Besides, seven main functional groups are contained on it, 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} , 1058 cm^{-1} . Furthermore, it is convincing that adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is the reason why the surface of biochar can form iron oxide which is consistent with the XRD results.

3.1.2 SEM

Figure 2(a) 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. 2(b-c). These particles are mainly composed of $\gamma\text{-Fe}_2\text{O}_3$, 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 are 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 $\gamma\text{-Fe}_2\text{O}_3$. 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. 2(d) that the skeleton structures of the LBAP were conspicuous. However, its gap between the skeleton structures is blocked, which this phenomenon was explained that L-Glutathione could hinder the formation of the circular skeleton structures and blocked 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, 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. 2(e-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 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.

3.2 BET

Table 2
The pore structure parameters of BAP, MFBAP, MEBAP and LBAP.

Sample	S_{BET} (m^2/g)	Average pore size (nm)	Average mesoporous volume (nm)	Pore volume (cm^3/g)
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

Their N_2 adsorption/desorption isotherms are displayed in Fig. 4(a). It can be seen from Table 2 that the four biochars all show a pseudo-type IV curve. The S_{BET} of the biochar were $5.6308 \text{ m}^2/\text{g}$ (BAP), $11.8252 \text{ m}^2/\text{g}$ (MFBAP), $7.0464 \text{ m}^2/\text{g}$ (MEBAP), $3.4583 \text{ m}^2/\text{g}$ (LBAP), respectively, which means HAD and ME modification can improve S_{BET} . The outcome may owe to the process of manufacturing modified biochar, which was produced by mixing biomass with FeCl_3 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_{BET} , average pore size, average micropore volume as well as pore volume. The S_{BET} of MFBAP is almost twice that BAP and the pore volume is almost four times. More importantly, it can be seen that the S_{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_{BET} and pore volume. These results all were corresponding with the previous results of SEM images partially. In this study, the S_{BET} of the four biochar is not large, but previous studies (Yi et al. 2019a) have shown that the adsorption capacity of magnetic biochar to degrade Cr(VI) does not depend on its S_{BET} . In other words, the S_{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.

3.3 Adsorption kinetics and isotherms

Table 3
Kinetic parameters of Cr(VI) adsorption by BAP, MFBAP, MEBAP, 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	β_E	α_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
Isotherm parameters of Cr(VI) adsorption by BAP, MFBAP, MEBAP, 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

The study of adsorption kinetics and isotherms are of great significance to determine the adsorption efficiency in practical application (Tao et al. 2018). The pseudo-first-order, 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 (Wei et al. 2020) and two isotherm models (Zhang et al. 2020) are described by equations (1)-(5):

$$\text{Pseudo-first-order: } q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (1)$$

$$\text{Pseudo-second-order: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

$$\text{Elovich: } q_t = \frac{1}{\beta_E} \ln \alpha_E \beta_E + \frac{1}{\beta_E} \ln t \quad (3)$$

$$\text{Langmuir: } q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (4)$$

$$\text{Freundlich: } q_e = k_F c_e^{\frac{1}{n}} \quad (6)$$

Where q_e and q_t (mg/g) 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 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$) models, respectively. α_E and β_E are the initial adsorption rate ($\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) and desorption rate ($\text{g} \cdot \text{mg}^{-1}$) 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. 4(c). 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. 4(d). 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) 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, equal adsorption energies and few interactions between adsorbed species (Liabc et al. 2019). Hence, Cr(VI) is mainly adsorbed to the surface of biochar through various chemical reactions.

3.4 Effect of pH

pH can affect the speciation of Cr(VI) and the surface charge of the biosorption in aqueous solution, therefore it has a vital impact on Cr(VI) removal (Qiu et al. 2020). The effect of the initial pH of the solution on adsorption is shown in Fig. 4(b). It can be seen that it is more efficient for MFBAP to remove Cr(VI) than BAP and the adsorption capacity of BAP and MFBAP for Cr(VI) becomes lower gradually with the increase of pH value (2–8). When pH = 2, the adsorption capacity reaches the maximum value, which are 80.58 mg/g and 43.21 mg/g respectively. Meanwhile, the minimum adsorption capacity was observed at pH = 8 (13.89 mg/g and 11.70 mg/g). Research (Liabc et al. 2019) found that Fe_2O_3 can be protonated as FeOH^+ that could be the active centers of Cr(VI) adsorption under lower initial pH, which is beneficial to adsorption of biochars.

These results proved that high pH value is unfavorable to the removal of Cr(VI) by MFBAP and BAP.

3.5 Effect of the coexisting cations.

The actual wastewater exists various kinds of ions, therefore the effects of different anions (Cl^- , NO_3^- , SO_4^{2-} , HPO_4^{2-}) and cations (Cu^{2+} , Ca^{2+} , Ni^{2+} , Cd^{2+}) on the adsorption capacity of MFBAP were studied in Fig. 4(e-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 Cd^{2+} , which lays a certain foundation for the study of 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 the 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-ions interference ability to some extent.

3.6 Regeneration performance of biochar

Regeneration performance of adsorbent materials is very important for evaluating the feasibility of practical and large-scale applications (Fomina & Gadd 2014). The recycling experiment of MFBAP after five times of adsorption/desorption was studied. The results are shown in Fig. 5. 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.

Table 5
Comparison of Cr(VI) adsorption capacities with other adsorbents.

Raw material	Adsorption capacity (mg/g)	reference
Eichhornia crassipes	120	(Zhang et al. 2015a)
Astragalus membranaceus	23.85	(Shang et al. 2016)
Enteromorpha prolifera	88.17	(Chen et al. 2018)
Phoenix tree leaves	27.2	(Shi et al. 2018)
Melia azedarach wood	25.27	(Zhang et al. 2018)
Pine sawdust	25.25	(Li et al. 2019)
Loofah	30.14	(Xiao et al. 2019)
Steel pickling waste liquor	43.12	(Yi et al. 2019a)
Water hyacinth	43.48	(Yu et al. 2018)
Bamboo	38	(Huang et al. 2018)
Sugarcane bagasse	43.12	(Yi et al. 2019b)
This study	81.31	-

3.7 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 were displayed in Fig.6. 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 2p_{1/2} and Cr 2p_{2/3} of Cr(III), while the peaks at 585.4 eV and 578.2 eV are ascribed to the Cr 2p_{1/2} and Cr 2p_{2/3} 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%), N 1s (2.84%) after adsorption. 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, -NbN- and N-H respectively. Apparently, the three peaks of N 1s 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). Simultaneously, Cr(VI) exists as the form of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ under acidic conditions (Saha & Orvig 2010, Zhang et al. 2017), under which the amino-functional groups $-\text{NH}_2$ could be protonated to $-\text{NH}_3^+$ as well as $-\text{OH}$ and $-\text{COOH}$, which also could be protonated to $-\text{OH}_2^+$ and $-\text{COOH}_2^+$. Therefore, part of the process for the mechanisms of Cr(VI) can be portrayed as follows (Mohan & Pittman 2006):

Except for these three peaks, Fe 2p can also be observed in XPS survey spectra, which demonstrated the preparation of magnetic biochar was successful. 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 = C and C-N bonds (Li et al. 2019, Zhang et al. 2015a), respectively. Compared with C1s before and after adsorption, it was found that the C-O peak became weak, while the C = C peak increased, suggesting that functional groups participated in the process of Cr(VI) adsorption. In fact, some active functional groups, such as C = 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:

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 ($-\text{NH}_3^+$, $-\text{OH}_2^+$, $-\text{COOH}_2^+$), 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). (4) Ion exchange, where Cr(VI) was adsorbed onto active sites of the MFBAP.

4 Conclusions

In this work, it found that different amines can change the morphology of biochar to increase or decrease its S_{BET} . Biochar derived from AP was feasible for Cr(VI) removal. Even if the pore size of LBAP was blocked, its adsorption capacity for Cr(VI) was still higher than that of BAP, which is attributed to the amino groups on the surface of the modified biochar. Through the modification of different amines, it is found that HDA has the best adsorption effect on biochar, and the maximum adsorption capacity calculated by Langmuir is 90.6798 mg/g. After five times of adsorption/desorption, the adsorption capacity can still reach more than 30 mg/g and has anti-ion interference ability. The optimum adsorption pH is 2. The adsorption mechanism of Cr(VI) by MFBAP is mainly electrostatic interaction, ion exchange, complexation and reduction. In conclusion, this method can not only solve the problem of invasive plants but also be used as environmental remediation materials for the adsorption of heavy metals.

Declarations

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

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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Scheme

Scheme 1 and 2 are available in Supplemental Files section.

Figures

Figure 1

(a) XRD graphs and (b) FT-IR spectra of BAP, MFBAP, MEBAP and LBAP.

Figure 2

SEM images of (a) BAP, (b) MFBAP, (c) MEBAP and (d) LBAP before adsorption, and (e) BAP, (f) MFBAP, (g) MEBAP and (h) LBAP after adsorption.

Figure 3

(a) and (b) elemental mapping of spatial distributions of C, O, N and Cr in BAP and MFBAP after adsorption. (c) and (d) EDS spectra of BAP and MFBAP after adsorption

Figure 4

(a) N_2 adsorption-desorption isotherms of BAP, MFBAP, MEBAP, LBAP; (b) effect of pH; (c) adsorption kinetics curves; (d) adsorption isotherms; (e) and (f) effect of the competitive ions.

Figure 5

Regeneration performance of biochar

Figure 6

(a) XPS survey spectra of MFBAP before and after adsorption of Cr(VI); (b) Cr 2p XPS spectra of MFBAP; C 1s and N 1s XPS spectra of MFBAP before adsorption of Cr(VI) (d) and (e); and (d) (f) C 1s and N 1s XPS spectra of MFBAP after adsorption of Cr(VI).

Supplementary Files

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- [Scheme1.png](#)
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