Enhanced Cr(VI) reduction and removal by Fe/Mn oxides biochar composites under acidic simulated wastewater

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Research Article

Abstract

Chromium (Cr(VI)) has attracted extensive attention because of its toxicity, which can cause severe damage to the ecosystem and human. In this paper, adsorbed Fe/Mn ions *Bacillus cereus* ZNT-03, lotus seeds, and graphene oxide were co-cultured as raw materials. Fe/Mn oxides biochar composite (FMBC) was prepared to treat Cr(VI) by one-step pyrolysis. FMBC has high-density micropores, and the average pore size is about 0.82 nm. Given the content of Fe (3.07 mg g^{-1}), Mn (2.56 mg g^{-1}), and N (3.04%) in the FMBC, Fe(II), Mn(II), and N-containing functional groups could be served as electron donors to reduce Cr(VI). The removal of Cr(VI) is monolayer chemisorption and pH-dependent. The maximum adsorption capacity of FMBC was 21.25 mg g^{-1}. Cr(VI) is reduced and adsorbed on FMBC by physical adsorption, reduction, complexation, electrostatic attraction, and co-precipitation. The contribution ratio of reduction mechanism to Cr(VI) is 72.25%. The packed column and regeneration experiments indicated that FMBC had high adsorption performance and excellent adsorption stability even after soaking in acidic simulated wastewater after 180 days (pH 1.5). These results indicate that FMBC can provide rapid reduction and efficient adsorption for Cr(VI), making it possible to apply in water treatment.

Introduction

Chromium (Cr(VI)) is seriously dangerous to hazard human health. Cr(VI) could trigger cancer by breaking DNA double bonds in human lung cell and inhibiting DNA repairs (Browning et al. 2016). The main route of human exposure to Cr(VI) is through contaminated drinking water. The maximum concentration of Cr(VI) is 0.05 mg L^{-1} in potable water permitted by WHO. With the growth of industry and economy, large amounts of Cr(VI)-containing effluent is released. Metallurgical, electroplating, printing, and dyeing factories are the primary source of Cr(VI) pollution in solution (Gao et al. 2019). Because of multiple negative effects, Cr(VI) in the water must be thoroughly treated before being discharged.

Different methods to treat Cr(VI) in solution have been used, including adsorption, reduction, membrane separation, and precipitation (Koushkbaghi et al. 2016). The adsorption has gotten a lot of attention, because of its advantages of high efficiency, simple operation, and wide applicability. Biochar derived from low-cost agricultural wastes are often used as heavy metal adsorbent due to excellent characteristics such as cost-effective and environmentally friendly. (Chen et al. 2018; Liu et al. 2021). Biochar is a porous carbon substance with a large specific surface area formed by pyrolysis of biomass. However, biochar has an weak adsorbing to HCrO$_4^-$ oxygen anion due to the surface negative charge (Zhu et al. 2020). Furthermore, it is difficult to reduce HCrO$_4^-$ to Cr(III). Therefore, improving reduction and adsorption ability of biochar is a major challenge.

Iron-based materials with adsorption and reduction properties are often employed to remove Cr(VI). Surface hydroxylation of iron oxide biochar containing -OH functional groups could improve adsorption capacity for Cr(VI) (Chen et al. 2018). Zhong et al. (2018) reported that the Cr(VI) adsorption ability of biochar with loading iron oxide could be improved, because Fe$_3$O$_4$ provided active

chemisorption/reduction sites for Cr(VI). In addition, iron oxide composite with ferromagnetism can quickly and effectively separate. Manganese oxide as Cr(VI) scavenger has a high affinity to Cr(VI), providing an effective way to remove Cr(VI). Polymetallic materials have synergistic adsorption and reduction effect, which can considerably enhance Cr(VI) treatment (Zhang et al. 2017). Particularly, iron-manganese binary oxides can increase electron transport capacity (Li et al. 2017). Fe-Mn oxides composites have large surface area and excellent mechanical properties, making it obtain larger adsorption capacity. Manganese oxide and iron oxide modified biochar composites can significantly enhance Cr(VI) adsorption, and the maximum adsorption capacity is 30.83 mg g^{-1} (Yang et al. 2020). There are still some disadvantages in stability and preparation of iron/manganese oxide modified biochar composites. Lin et al. (2019) used chemical impregnation with a high iron concentration solution to prepare Fe-Mn biochar composites. However, chemical impregnation is ineffective, cumbersome, and may cause secondary pollution. Metal oxides have a strong tendency to aggregate in preparation, which significantly inhibits their reactivity and mass transfer kinetics. Although stable suspensions of metal oxides in the laboratory can be formed, it is difficult to avoid aggregation under field conditions (Schrick et al. 2004). In addition, metal oxides are mainly distributed on the surface of composites, which are unstable and easy to collapse under acidic condition. Therefore, a stable and uniformly distributed metal oxide biochar composite need to be prepared to Cr(VI) reduction and adsorption.

Metal resistance microorganisms can change and reduce metal ions by biological oxidation and reduction. Metal resistance microorganisms have the advantages of strong metabolic activity, low cost and environmentally friendly to adsorb metal ions (Zeeshanur, 2020). In this study, Fe and Mn resistance *Bacillus cereus* ZNT-03 was isolated from heavy metal-contaminated soil, and it could strongly adsorb Fe(II) and Mn(II). *Bacillus cereus* ZNT-03 was used as a Fe/Mn ion carrier to improve Fe/Mn loading and dispersion in composites preparation. Therefore, *Bacillus cereus* ZNT-03 as Fe/Mn ions carrier was co-cultured with lotus seeds and GO as raw materials. The raw materials were pyrolyzed to prepare Fe/Mn oxides biochar composite. Cr(VI) was reduced and removed from solution by Fe/Mn oxides biochar composites of one-step synthesis. The objectives of this study are to (1) prepare Fe/Mn oxides biochar composites; (2) characterize Fe/Mn oxides biochar composites; (3) clarify the removal mechanisms of Cr(VI) by Fe/Mn oxides biochar composites; (4) verify the possibility of application of Fe/Mn oxides biochar composites.

Materials And Methods

Materials

Lotus seeds were gathered in Xiangtan (Hunan Province, China). All chemicals (analytical grade) including $FeSO_4 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$, $K_2Cr_2O_7$, H_2SO_4, H_3PO_4, NaOH, and HCl were obtained from Sinopharm Chemical Reagent Co., Ltd (Tianjin China). The solutions were prepared using deionized water. GO was produced by oxidizing graphite with H_2SO_4, HNO_3, and $KMnO_4$ according to the Hummers method (Zhu et al. 2015).

Bacillus cereus ZNT-03 was isolated from heavy metal-contaminated soil in Xiangtan (Hunan Province, China). 1 g soil was diluted in 1 mL sterile water. 1 g mL^{-1} soil solution was diluted to 10^{-5} g L^{-1} by gradient dilution. And then 100 μL of 10^{-5} g L^{-1} soil solution was transferred to beef extract peptone medium for culturing over 24 h at 298 K. The individual microorganism was purified and preserved. All operations were performed in an aseptic environment. Microorganism was identified by China Center for Type Culture Collection (Wuhan University) and named *Bacillus cereus* ZNT-03.

Preparation of FMBC

Fe/Mn metal oxides biochar composite was prepared as follows: *Bacillus cereus* ZNT-03 was cultured in the beef extract peptone medium for 24 h at 298 K, and then Fe(II) and Mn(II) solutions were added for another 24 h to obtain the adsorbed Fe(II) and Mn(II) *Bacillus cereus* ZNT-03. And then *Bacillus cereus* ZNT-03 was collected. *Bacillus cereus* ZNT-03 was washed with sterile water three times. *Bacillus cereus* ZNT-03 and Lotus seeds were co-cultured for 6 h at the beef extract peptone medium. 50 mg L^{-1} GO was added and continued cultured for another 18 h. The raw materials were collected, and then dried in oven. All the above operations were performed under aseptic conditions. Raw materials were pyrolyzed under nitrogen protection at 873 K for 2 h. Fe/Mn oxides biochar composite was named FMBC.

Characterization of FMBC

The C, H, and N elements of FMBC were determined by an elemental analyzer (Elementar Analysensysteme GmbH). Specific surface areas (S_{BET}) were measured by Micromeritics 2020 HD88. The Fourier transform infrared Nicolet 5700 spectrophotometer was used to analyze functional groups of FMBC. The elements including Fe, Mn, and Cr were measured by XPS (Thermo Fisher Scientific). Morphologies and surface elements distributions were observed by Zeiss Smart EDX. Fe/Mn oxide phases were observed by an X-ray diffractometer (M21X, MAC Science Ltd.). The total Cr concentrations were measured by an atomic absorption spectrometer (Agilent 200 Series AA). The concentration of Cr(VI) was detected via a UV-Vis spectrometer (Agilent Cary 60).

Batch experiments

To study the kinetics and isotherms adsorption, the experiments were performed at different temperatures and a rotation speed of 150 rpm in different concentrations of Cr(VI). NaOH and HCl were used to adjust the pH of solutions. To further analyze the relationship of Cr morphology during the adsorption, 1 mg mL^{-1} FMBC and Cr(VI) oscillated at 150 rpm and 298 K for 24 h at an initial pH value of 1.5. Regeneration experiments were performed under the different Cr(VI) concentrations at pH 1.5 using 1 mg mL^{-1} FMBC. The Cr(VI)-loaded FMBC were eluted with NaOH (Gupta and Mondal 2020).

Packed column experiment

The total volume and the inner diameter of the packed column are 10 mL and 1 cm, respectively. The column was filled with FMBC. Two ends of the packed column are loaded with 2 mm thick quartz cotton

to prevent leakage of FMBC. The flow rate of the first cycle and the third cycle is 10 mL min⁻¹ under simulated wastewater. The flow rate of the first cycle and the second cycle is 10 mL min⁻¹ and 1.5 mL min⁻¹ under Cr(VI)-containing wastewater. The simulated wastewater was prepared with coexisting ions SO_4^{2-}, NO_3^-, PO_4^{3-}, Cu(II), and Ni(II) (Zhao et al. 2018).

Results And Discussion

Growth curve of resistant *Bacillus cereus* ZNT-03

In the study, *Bacillus cereus* ZNT-03 was used as Fe(II) and Mn(II) carrier for FMBC preparation. *Bacillus cereus* ZNT-03 was cultured under the medium containing 1 g L⁻¹ Fe(II) and 5 g L⁻¹ Mn(II), respectively (Fig. S1). *Bacillus cereus* ZNT-03 entered logarithmic phase after 6 h. Then *Bacillus cereus* ZNT-03 grew in stabilization phase from 12 to 36 h. *Bacillus cereus* ZNT-03 growth cannot be affect by Mn(II). The lag phase of *Bacillus cereus* ZNT-03 was delayed under the condition of 1 g L⁻¹ Fe(II), due to *Bacillus cereus* ZNT-03 being suppressed. However, Fe(II) and Mn(II) in the medium cannot be detected under the stabilization phase of *Bacillus cereus* ZNT-03, which suggested that *Bacillus cereus* ZNT-03 can effectively adsorb Fe(II) and Mn(II).

Morphology analysis

The surface morphology and porosity of FMBC were analyzed (Fig. 1). FMBC has abundant structural pores, which are similar to the honeycomb shape (Fig. 1a). It can also be observed that the pores vary in size, which may reflect the evolution of volatiles and carbon consumption at the rising temperature. Flaky folds were observed, suggesting the existence of GO (Fig. 1b). *Bacillus cereus* ZNT-03 are oval and rich in Fe and Mn elements after high-temperature pyrolysis (Fig. S2a). The uniform distribution of *Bacillus cereus* ZNT-03 could improve the physicochemical properties of FMBC (Fig. 1c). The distributions of Fe and Mn elements on SEM mapping are consistent with O elements (Fig. 1e), indicating that Fe/Mn oxides were formed. As shown in Fig. 1d, *Bacillus cereus* ZNT-03 entered into the pores of lotus seeds which could enhance the stability of the Fe/Mn oxides. GO and *Bacillus cereus* ZNT-03 could provide additional adsorption sites and increase specific surface area of FMBC after being pyrolyzed.

Elemental analysis results showed that FMBC contains 66.22% C, 2.38% H, and 3.04% N (Table S1). The contents of Fe and Mn are 2.56 mg g⁻¹ and 3.07 mg g⁻¹, indicated FMBC was prepared successfully by co-culturing the *Bacillus cereus* ZNT-03, GO, and lotus seeds. FMBC contains the high content of N element originating from *Bacillus cereus* ZNT-03, which is beneficial to Cr(VI) reduction and removal (Geng et al. 2018). The surface morphology of lotus seeds was preserved and FMBC was endowed with magnetism after pyrolysis.

The adsorption-desorption curve of N_2 presented type IV (Fig. S3a), which proved the material was a porous composite (Xu et al. 2018). The hysteresis ring could be observed at the intermediate pressure end, caused by the condensation and accumulation of N_2 in the pore. That reveals the presence of high-

density micropores. The average pore size is about 0.82 nm (Fig. S3b). The pore volume and specific surface area of FMBC are 0.142 cm^3 g^{-1} and 165.204 m^2 g^{-1}. These results revealed that FMBC possesses a large specific surface area and high-density micropores. Mass transfer process of Cr from aqueous phase to solid sorbent is related to the porosity of sorbent. The rich pore structure of FMBC will provide more channels for solute diffusion (Chu et al. 2018).

The crystal structure properties of FMBC were detected by XRD (Fig. S4). Different Fe/Mn oxide crystals were observed (JCPDS 75–1609), including $MnFe_2O_4$ (diffraction peaks at 42.6° and 56.2°), MnO (diffraction peaks at 40.5° and 58.6°), MnO_2 (diffraction peaks at 28.4° and 45.5°), Fe_3O_4 (diffraction peaks at 30.1° and 75.2°), and Fe_2O_3 (diffraction peaks at 35.4° and 23.2°). Thus, it can be concluded that Fe/Mn oxides were successfully formed on FMBC. An abundance of metal oxides could provide more adsorption sites, implying that FMBC has a high redox capacity for Cr(VI).

Adsorption kinetics and isotherms

Adsorption kinetics and isotherms of FMBC for Cr(VI) at pH 1.5 were shown in Fig. 2. Fig. 2(a) showed the kinetics of Cr(VI) removal. During the first two hours, Cr(VI) adsorption is rapid, indicating that FMBC had a large surface area and any amount of functional groups. At the initial absorption period, Cr(VI) was reduced rapidly by Fe/Mn oxides and functional groups. Subsequently, the absorption rate of Cr(VI) by FMBC declined, which may be because more active sites were occupied by Cr(VI) and Fe/Mn oxide was consumed. Kinetics parameters (k_1, k_2, k_t, Q_e, and R^2) are listed in Table S2. Adsorption behavior is more consistent with the pseudo-second-order adsorption model, illustrating that adsorption was mainly controlled by chemisorption (Lu et al. 2012). Therefore, the redox rate and absorption sites of FMBC are hinges to limit Cr(VI) removal.

To describe the adsorption properties and simulate isotherms, Langmuir and Freundlich models were utilized.(Fig. 2b). The absorption capacity of FMBC for Cr(VI) increased with the Cr(VI) initial concentration increasing. Absorption capacity increased because more adsorption sites on FMBC surface are utilized by Cr(VI). The q_{max} of FMBC is 21.25 mg g^{-1} at 298 K. The isotherm parameters are listed in Table S3. Compared with Freundlich model (R^2=0.91), illustrated that Cr(VI) adsorption fitted Langmuir model (R^2=0.97) better. The results show that the adsorption behavior of FMBC is mainly monomolecular adsorption (Lv et al. 2020). This may be adsorption sites are uniformly distributed on FMBC surface and a position is occupied by metal ions, no further adsorption can occur at the site (Agrafioti et al. 2014). As the temperature rises, the adsorption efficiency was increased. Because the pore size expands and the surface activation increases, the mass transfer resistance in the boundary layer reduces (Asl et al. 2013). However, the adsorption capacity of FMBC decreases at 308 K. This is because metal oxides on FMBC surface could be dissolved under acid and high-temperature conditions.

Influence of pH on Cr(VI) adsorption by FMBC

The pH_{zpc} of FMBC was 8.45 (Fig. S5). FMBC possesses a positive charge at pH from 1 to 6, which is beneficial to attracting negatively charged Cr(VI) species and promoting Cr(VI) species diffusion into FMBC. pH values of 1-6 were analyzed on Cr(VI) adsorption by FMBC (Fig. 3). Removal efficiency at pH 1 and 2 is higher than other pH values. Cr(VI) removal efficiency decreased from 100% at pH 2 to 40.99% at pH 3. At low pH, the adsorption capacity of FMBC is higher, mainly because FMBC has a higher reduction ability (Fei et al. 2022). With increasing pH, the changes of Cr(VI) species were from $HCrO_4^-$ to CrO_4^{2-} or $Cr_2O_7^{2-}$, the affinity of FMBC for Cr(VI) decreases (Huang et al. 2016). FMBC is deprotonated gradually, which repels CrO_4^{2-} and $Cr_2O_7^{2-}$. Meanwhile, the competition between hydroxyl ions and Cr(VI) on the adsorption site exists, which can lead to a lower Cr(VI) removal rate. Lower removal rates were observed at higher pH, mainly because the reduction ability decreases significantly at pH 4-6 (Fei et al. 2022). Although pH increasing is harmful to Cr(VI) reduction, electrostatic attraction and complexation still allow Cr(VI) to interact with functional groups or metal oxides.

Fig. 4 depicts the variations in Cr species concentration. Cr(VI) is rapidly reduced at 10 mg L^{-1}, followed by the concentrations of different Cr species closing to 0 mg L^{-1}, which is related to the ability of rapid reduction and adsorption by FMBC. Subsequently, Cr(VI) removal rate is gradually decreased until 12 h. The high concentrations show the same trend, but the final equilibrium concentration increases as the initial concentration increases. Cr(III) is from Cr(VI), indicating that Cr(VI) could be reduced by FMBC. In the adsorption process, Cr(VI) is reduced by FMBC and then bonded to functional groups and Fe/Mn oxide through complexation and electrostatic attraction (pan et al. 2013).

Cr(III) adsorption by FMBC was further studied. Cr(III) adsorption capacity of FMBC increases with the pH increasing from 1 to 6 (Fig. S6). The removal rate reaches 100% at pH 3. Under the condition of low pH, FMBC has a positive charge, which has an influence on Cr(III) adsorption due to the charge repulsion. The negative charges on the composite increase with the increase of pH. Therefore, more Cr(III) is attached to the FMBC by electrostatic adsorption. As the pH increases, Cr(III) is easily hydrolyzed to produce Cr(III)-hydroxyl ions including $Cr(OH)_2^+$, $Cr_2(OH)_4^{2+}$, and $Cr_3(OH)_5^{4+}$. The adsorption affinity of Cr(III)-hydroxyl ions is greater than Cr(III) (Tong et al. 2011). Furthermore, the O-containing functional groups can form complexes with Cr(III) on the FMBC (pan et al. 2013). In a word, the reduction decreased, but the adsorption of FMBC to Cr(III) is enhanced with the increase of pH. FMBC possesses a high capability of Cr(VI) reduction and adsorption.

Effect of NaCl on Cr(VI) adsorption

Different NaCl concentrations on Cr(VI) treatment was studied. The results are shown in Fig. S7. NaCl concentration is negatively correlated with adsorption efficiency. NaCl had no effect at doses of 0.001 mol L^{-1}. However, Cr(VI) removal efficiency was reduced from 100% to 68% at 1.0 mol L^{-1} NaCl. Cl^- and Na^+ can strongly compete with Cr(VI) for sorption sites at higher NaCl concentrations. Under a high concentration of background ions, the activity of Cr(VI) is weakened, and the effective collision between

Cr(VI) and adsorbent is reduced (Bai and Abraham 2003). Besides, the electrostatic interaction between Cr(VI) and FMBC was weakened also. Thus, the adsorption efficiency of FMBC is reduced.

Regeneration

The regenerated FMBC was used to remove Cr(VI) (Fig. S8). After four cycles, the removal efficiency of FMBC remains 100% at 8 mg L^{-1} Cr(VI) solution. However, after four cycles with a 15 mg L^{-1} Cr(VI) solution, the Cr(VI) removal effectiveness dropped from 100% to 56%. This may be because the complexation between functional groups and Cr is tight. Cr cannot be eluted in micropore. Meanwhile, shocking and repeated washing bring the loss of metal oxides on FMBC surface. Besides, the reduction of FMBC is not regenerated. Despite the fact that adsorption efficiency decreases after four cycles, FMBC still has the potential for recycling.

Characteristics analysis

The FTIR spectra of the FMBC is shown in Fig. 5. The main characteristic bands were assigned as follows: The -OH and Fe(OH)$_2$ can be detected for the characteristic peaks at 3440 cm^{-1} and 1438 cm^{-1} (Sun et al. 2017; Xu et al. 2019). The tensile vibration of -CH$_2$ is represented at 2843 cm^{-1} and 2916 cm^{-1} (Yu et al. 2015). C=O extension of aldehydes or ketones is responsible for the peaks at 1618 cm^{-1} (Gan et al. 2015). N-H is connected with 1555 cm^{-1} characteristic peak (Zeng et al. 2021). C-O is confirmed by the peaks of 1153 cm^{-1} and 1252 cm^{-1} (Chen et al. 2015). -CNH is linked to the characteristic peak at 1072 cm^{-1} (Zhu et al. 2018). Fe-OH (Fe$_2$O$_3$) and FeOOH are associated with the characteristic peaks at 430 cm^{-1} and 876 cm^{-1}, whereas Mn-OH and MnO$_2$ are associated with the peak at 515 cm^{-1} (Yang et al. 2020; Liu et al. 2021). FMBC has abundant functional groups, which indicates that the composite is successfully prepared. Besides, functional groups also can increase the hydrophilicity of FMBC. The difference in peak positions at the FMBC were little before and after adsorption, which reflects the stability of the FMBC. The reduction reaction between Cr(VI) and Fe(OH)$_2$ occurs, resulting the peak of 1438 cm^{-1} disappeared. A new peak of 785 cm^{-1} was generated after adsorption. The characteristic peaks fluctuation at 785 cm^{-1} indicated that Cr-O is formed after Cr(VI) adsorption (Du et al. 2019). Cr is pretty consistent with O elements, indicating complexation occurs between Cr(VI) or Cr(III) and O-containing functional groups (Fig. S2b).

C 1s, O 1s, N 1s, Fe 2p, Mn 2p, and Cr 2p of XPS spectra are depicted (Fig. 6). Fig. 6a shows the C 1s spectra at 283.41 eV, 284.49 eV, and 288.17 eV, which associated with C=C, C-C, and C=O (Chen et al. 2020; Zou et al. 2021). The little difference of C element before and after adsorption indicates the stability of FMBC (Table S4). The O 1s spectra presented four peaks at 530.0 eV, 531.24 eV, 531.66 eV, and 534.93 eV (Fig. 6b), respectively. A peak at 530.0 eV is characteristic of oxygen in metal oxide (O^{2-}) (Zhang et al. 2020). Other peaks at 531.24 eV, 531.66 eV, and 534.93eV suggest the presence of C=O, Fe-O, and O-H, respectively (Lesiak et al. 2018; Li et al. 2020). The O 1s changed before and after adsorption, indicating that chemical reaction occurred between O-containing functional groups and Cr(VI). Fig. 6c

shows the N 1s spectra at 399.4 eV, 397.4 eV, and 396.4 eV, which associated with pyrrolic N, Fe-N$_x$, and pyridinic N. (He et al. 2017; Lu et al. 2019). N-doped FMBC destroys the inert structure of sp2-hybridized carbon and improves electron transfer, resulting in more active sites in the carbon matrix. Moreover, the chemical reactivity of composites can be effectively adjusted by introducing N element. The contents of Fe-N$_x$ and pyridinic N cannot be observed after adsorption, implying that Fe-N$_x$ and pyridinic N could provide electrons (Xu et al. 2020). The high N element of FMBC (3.04%) showed a high Cr(VI) capacity and excellent reused capacity. Pyridinic N can promote the free-flowing π-electrons transfer of sp2 carbon atoms in biochar matrix, which benefit to adsorb Cr(VI) and promote the Cr(VI) reduction.

The binding energy of Mn 2p peaks at 640.5 eV and 651.3 eV are Mn(IV), matching well with the characteristic peak of MnO$_2$ (Fig. 6d). And peaks at 644.2eV and 655.9 eV are corresponding to the binding energy of Mn(II), which is fitting well with the characteristic peak of MnFe$_2$O$_4$ (Zhang et al. 2019). Mn(II) offers electrons for Cr(VI) and Cr(VI) was reduced, then Mn oxide is consumed during adsorption. The binding energy of Fe 2p at 724.2 eV and 710.4 eV are Fe(III), and peaks at 729.4 eV and 716.6 eV are Fe(II) (Zhu et al. 2020). Before and after adsorption, the chenges of Fe vary slightly, showing that Fe is involved in reduction process, but maintains the stability of the material (Fig. 6e). A new peak corresponding to Cr was observed on FMBC after adsorption. The Cr(VI) peaks of Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ are 589.2eV and 577.5 eV (Fig. 6f), respectively (Cai et al. 2021). The peaks of Cr(III) are 586.6 eV and 576.3 eV corresponded to Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$, which indicated that Cr(III) compound consists of Cr(OH)$_3$ and Cr$_2$O$_3$ (Diao et al. 2018). 72.25% Cr(III) and 27.75% Cr(VI) were represented by the XPS scan of Cr 2p analysis, indicating a significant contribution of reduction rather than direct adsorption. The presence of Cr-O was consistent with FTIR analysis results, further indicating that the main mechanism of FMBC in Cr(VI) adsorption is reduction.

Packed column adsorption using FMBC

Fig. 7 shows the penetration curve using a packed column under acidic simulated wastewater. At the beginning of the adsorption experiment, Cr(VI) cannot be detected in effluent. Until 1900 BV, the removal rate was still 100%. The concentration of Cr(VI) increases slowly after 1900 BV. The Cr(VI) can be permitted by the National Standard of the People's Republic of China in industrial wastewater is 0.2 mg L^{-1}. When Cr(VI) concentration is greater than 0.2 mg L^{-1}, the cycle number of the packed column is 2300 BV (23 L). The penetration curve grows slowly with the increase of water inflow, and it takes a long time to exceed the discharge standard at the same flow rate. The increase in the penetration curve is because the reduction rate of FMBC reduces as water input increases, and adsorption sites on FMBC were occupied. The slow growth rate of the penetration curve could be owing to high adsorption capacity of FMBC. The used FMBC in the packed column was desorbed with 1 mol L^{-1} NaOH solution as eluent. And when it reached 150 BV (1.5 L), Cr(VI) cannot be detected. FMBC is washed with deionized water for further use. Cr(VI) can be detected in the effluent of the packed column after 1000 BV, and the discharge standard is exceeded until 1300 BV in the third cycle. 2400BV is the first time that the Cr(VI)-containing wastewater concentration reaches 0.2 mg L^{-1}, which is consistent with the simulated wastewater. In

addition, effluent concentration of Cr(VI) in the second cycle can be effectively reduced by reducing effluent flow rate. Compared with Cr(VI)-containing wastewater without coexisting ions SO_4^{2-}, NO_3^-, PO_4^{3-}, Cu(II), and Ni(II), results showed that coexisting ions have little effect on Cr(VI) reduction and removal. In addition, Cr(VI) removal efficiency can be increased by regulating effluent flow rate. The contact time of solution in the packed column is prolonged and the removal efficiency is increased. To verify the reduction and adsorption capacity of FMBC, FMBC was soaked in acid for more than 180 days. Results showed that FMBC still had good magnetic and adsorption properties (Fig. S9). Therefore, FMBC can provide rapid reduction and efficient adsorption for Cr(VI), making it possible to apply in real water treatment.

The adsorption mechanisms of FMBC

FMBC possesses a porous structure, and Fe/Mn oxides are uniformly distributed on FMBC. The mass transfer of Cr species from aqueous phase to solid sorbent site depends on the porosity of sorbent. Physical adsorption of Cr species occurs in porous structures (Liu et al. 2021). Adsorption kinetics and isotherms illustrated Cr(VI) adsorption was monolayer chemisorption. At low pH, Fe(II), Mn(II), and N-containing functional groups can donate electrons for Cr(VI) reduction, and electrons can be quickly transported through Fe/Mn oxides and GO (Fig. 8). The XPS scan of Cr 2p indicated that most of Cr(VI) was reduced into Cr(III). Cr(III) can be absorbed on FMBC via complexation between Cr(III) and -COOH, -OH, and $-NH_2$ (He et al. 2020). The contribution of Cr(VI) reduction is greater than direct Cr(VI) adsorption, indicated reduction is the main adsorption mechanisms. Compared with pyrogenic carbon (Table S5), the reducing capacity of Fe/Mn oxides biochar composite is stronger (Zhao et al. 2020). Because electron transfer is direct and faster between Fe/Mn oxides and Cr(VI) (Zhang et al. 2020). Given the content of Fe, Mn, and N in FMBC, Fe(II), Mn(II), and N-containing functional groups may be served as electron donors to transfer electrons. FMBC is rich in -COOH, -OH, and N-containing functional groups. The complexation between Cr(VI) and these functional groups on FMBC surface is convenient for the electrons transportation to Cr(VI). In addition, Cr(VI) could be directly anchored on FMBC surface by electrostatic attraction (Huang et al. 2016). SEM mapping revealed that parts of Fe/Mn oxides fall off from FMBC at low pH, suggesting that Fe/Mn oxides involved in the dissolution, reaction, and reprecipitation processes (Fei et al. 2022). Besides, Fe/Mn oxides can bind to Cr by complexation and co-precipitation (Zhao et al. 2020). In conclusion, the adsorption mechanisms of FMBC for Cr(VI) involve physical adsorption, reduction, complexation, electrostatic attraction, and co-precipitation.

Conclusions

The Fe/Mn oxides biochar composites was prepared by the pyrolysis of lotus seeds, graphene oxide, and the adsorbed Fe/Mn ions *Bacillus cereus* ZNT-03, as a cheap adsorbent to treat Cr(VI) in the water. SEM results show that the distribution of Fe/Mn oxides on FMBC is uniform. The packed column experiment demonstrated that FMBC has significant advantages in fast redox and high adsorption capacity. Even after soaking in an acidic solution (pH 1.5) after 180 days, FMBC still retains strong magnetism,

reduction, and adsorption capacity. Therefore, FMBC could be a sustainable material for large-scale applications in Cr(VI) wastewater treatment and remediation.

Declarations

CRediT authorship contribution statement

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Data Availability

All data generated or analyzed during this study are included in this published article and its supplementary information files.

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Figures

Figure 1

SEM images (a-e) and SEM mapping (f) (C, O, Mn, Fe) of FMBC before Cr(VI) adsorption

Figure 2

(a) Kinetics models of Cr(VI) adsorption using FMBC; (b) Isotherm models of Cr(VI) adsorption using FMBC (dosage = 1 g L^{-1}; T = 298 K; pH = 1.5)

Figure 3

Effects of pH on the adsorption of Cr(VI) by FMBC (C_0 = 15 mg L^{-1}; dosage = 1 g L^{-1}; T = 298 K)

Figure 4

Changes in Cr species at different Cr(VI) concentrations (a) 10 mg L^{-1} Cr(VI); (b) 25 mg L^{-1} Cr(VI); (c) 50 mg L^{-1} Cr(VI) (dosage = 1 g L^{-1}; T = 298 K; pH = 1.5)

Figure 5

FTIR spectra of FMBC before and after Cr(VI) adsorption

Figure 6

XPS survey spectra (C 1s, O 1s, N 1s, Mn 2p, Fe 2p, and Cr 2p) of FMBC (a-f)

Figure 7

Packed column adsorption (C_0 =1 mg L^{-1}; T = 298 K; pH = 1.5; V = 10 mL min^{-1}; (Insert : C_0 = 1 mg L^{-1}; T = 298 K; pH = 1.5; V_{first} = 10 mL min^{-1}; V_{second} = 1.5 mL min^{-1}))

Figure 8

Removal mechanisms of Cr(VI) by FMBC

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