Simultaneous removal of Sb(III) and Cd(II) in water by adsorption onto a MnFe$_2$O$_4$–biochar nanocomposite†

Yu-Ying Wang, a,b Hai-Yang Ji, a,c Hao-Hao Lu, a,b Yu-Xue Liu, a,b Rui-Qin Yang, d,e Li-Li He a,b and Sheng-Mao Yang b,c

In this study, a jacobsite–biochar nanocomposite (MnFe$_2$O$_4$–BC) was fabricated and used to simultaneously remove Sb(III) and Cd(II) from water via adsorption. The MnFe$_2$O$_4$–BC nanocomposite was prepared via a co-precipitation method and analyzed using various techniques. The results confirm the successful decoration of the biochar surface with MnFe$_2$O$_4$ nanoparticles. The maximum Sb(III) removal efficiency was found to be higher from bi-solute solutions containing Cd(II) than from single-solute systems, suggesting that the presence of Cd(II) enhances the removal of Sb(III). The Langmuir isotherm model describes well Sb(III) and Cd(II) removal via adsorption onto the MnFe$_2$O$_4$–BC nanocomposite. The maximum adsorption capacities are 237.53 and 181.49 mg g$^{-1}$ for Sb(III) and Cd(II), respectively, in a bi-solute system. Thus, the prepared MnFe$_2$O$_4$–BC nanocomposite is demonstrated to be a potential adsorbent for simultaneously removing Sb(III) and Cd(II) ions from aqueous solutions.

1. Introduction

The introduction of antimony (Sb) and cadmium (Cd) into the environment, mainly from anthropogenic activities like mining and industrial work, has created global concern. Sb, a hazardous substance, may lead to pneumoconiosis and have carcinogenic effects on human health. The maximum permissible Sb concentrations in drinking water are 5, 6 and 10 μg L$^{-1}$, as established by China, the United States Environmental Protection Agency and the European Union, respectively. Moreover, there are two inorganic species (Sb(III) and Sb(IV)) of Sb in aquatic systems. Of these, Sb(III) is more toxic than Sb(IV) by a factor of ten. Cd is one of the most toxic heavy metals, and has received significant attention in recent years. Cd is ubiquitous, and over-exposure to Cd can cause bone and kidney damage. According to guidelines from the World Health Organization, the maximum contaminant level (MCL) of Cd(II) in drinking water should be limited to 3 μg L$^{-1}$. Alarmingly, Sb and Cd generally coexist in many sources, such as tailing heaps, water, and sediments. For instance, combined Sb and Cd pollution is frequently observed in Xikuangshan, because of the concomitant presence of Cd in Sb-containing ores. Moreover, Sb and Cd are the most abundant heavy metal contaminants threatening some cities in the Guangxi province of China. The coexistence of Sb and Cd might pose a higher risk to human health and ecological safety than their individual presence. In addition, the processes required for the simultaneous removal of Sb and Cd might also differ from those used for removal from systems containing only Sb or Cd. Despite this, investigations into the simultaneous removal of Sb(III) and Cd(II) are rare.

It is widely known that adsorption technologies are promising for the elimination of contaminants from aqueous solutions. Biochar is an inexpensive carbon-rich material that might widely be used in adsorbent systems, and is produced through the pyrolysis of biomass under oxygen-free or oxygen-limited conditions. Biochar has a large specific surface area and porous structure, as well as abundant surface functional groups and mineral components; thus, it is a potential adsorbent for pollutants. Because most biochar presents a predominantly net negatively charged surface, its ability to remove aqueous Sb, which is in anionic form, may be relatively weak. Therefore, several methods have been developed to modify biochar to enhance its anion adsorption capabilities. Biochar modified with iron oxide or manganese oxide has been reported to show strong ability in removing Sb from aqueous solutions. For instance, Xu et al. investigated the capabilities for and
mechanisms involved in the removal of Sb(III) using Fe–Mn binary oxides, ferric hydroxide, and manganese dioxide.\(^4\) Bai et al. investigated potential oxidation and adsorption pathways for Sb(III and V) species in the presence of Mn(II) and Mn-oxidizing bacteria, with or without Fe(II), and found that in situ formed biogenic Mn oxide and Fe–Mn oxides could effectively remove Sb.\(^5\) Qi and Pichler studied the sequential and simultaneous adsorption of Sb(III and V) on ferrihydrite, and demonstrated that ferrihydrite is an effective adsorbent for Sb(III and V) in single and binary systems, with a higher efficiency toward Sb(III) than Sb(V).\(^6\) However, despite the evident potential interference of Sb(III) into the adsorption of Cd(II) and the coexistence of Sb(III and V) in water samples, the adsorption behavior of this important binary system on Fe and Mn modified biochar has not been reported to date.

In this study, a jacobsite–biochar nanocomposite (MnFe\(_2\)O\(_4–BC\)) was synthesized and used to evaluate the co-adsorption performance of Sb(III and V) and Cd(II). The effects of various experimental conditions, such as solution pH, contact time, initial concentration, and coexisting ions, on their adsorption were investigated. A possible mechanism for Sb(III and V) and Cd(II) adsorption on the MnFe\(_2\)O\(_4–BC\) nanocomposite is also proposed. Thus, our results may contribute to the development of decontamination technologies targeting Sb(III)/Cd(II) polluted solutions.

2. Materials and methods

2.1 Materials

All chemical reagents used in this study were of analytical reagent (AR) grade. Stock solutions of 1000 mg L\(^{-1}\) Sb(III) (KSB\(_C\),\(_4\)H\(_4\)O\(_7\)) and Cd(II) (Cd(NO\(_3\))\(_2\)·2H\(_2\)O) were prepared with deionized water. The required concentrations for working solutions were obtained through diluting the Sb(III) and Cd(II) stock solutions.

2.2 Preparation of MnFe\(_2\)O\(_4–BC\)

The biochar used in this study was obtained from tea branches through a typical slow pyrolysis process.\(^7\) Briefly, a tea branch was loaded into a programmable tube furnace and pyrolyzed under anaerobic conditions at 500 °C at a heating rate of 25 °C min\(^{-1}\) for 90 min. After carbonization, the biochar was cooled naturally to room temperature to obtain the pristine BC samples used in the experiments. The MnFe\(_2\)O\(_4–BC\) nanocomposite was prepared via a co-precipitation method. Briefly, 8.34 g (0.3 M) of FeSO\(_4–7H_2O\) was dissolved in 100 mL of deionized water, and 1 g of the prepared BC was added to obtain suspension A. Then, 1.58 g (0.1 M) of KMnO\(_4\) was dissolved in 100 mL of deionized water under vigorous stirring to obtain solution B. Finally, solution B was added to suspension A under continuous stirring. During the reaction, an appropriate amount of NaOH solution was added to maintain the pH of the solution at about 10. The resulting slurry was aged at room temperature for 3 h, then centrifuged and washed with deionized water to remove excess salt. After that, the product was vacuum dried overnight at 25 °C.

2.3 Characterization

pH Values were measured using a pH meter (Mettler Toledo FE28), supplied with a combined electrode. Field emission electron microscopy (FESEM) images of BC and MnFe\(_2\)O\(_4–BC\) were gained using a field emission electron microscope (Hitachi S-4800). Fourier transform infrared spectra (FT-IR) were recorded using a Nicolet 380 spectrometer. An X-ray diffractometer (Bruker D8 Advance) was used to collect X-ray diffraction (XRD) patterns of the samples. The specific surface area was measured using a Nova 2000e surface area analyzer (Quantachrome, USA). A Thermo Scientific K-Alpha spectrometer was used to obtain X-ray photoelectron spectra (XPS) of MnFe\(_2\)O\(_4–BC\) after adsorption.

2.4 Adsorption experiments

All adsorption experiments were carried out in triplicate at 298 K, and averaged values of the results are reported. The influence of the pH of the initial solution, adsorption kinetics, adsorption isotherms, ionic strength, and competing ions on Sb(III and V) and Cd(II) adsorption were analyzed. The influence of pH on the adsorption abilities of BC and MnFe\(_2\)O\(_4–BC\) was examined over the pH range of 3–7. Acidic pH was mainly selected because Cd(OH)\(_2\) has relatively low solubility in basic media. HCl and/or KOH were used to adjust the pH of solutions.

Kinetic experiments were carried out at room temperature. Mixed solutions consisting of 50 mL of Sb(III and V) (50 mg L\(^{-1}\) were added to a 100 mL conical flask, and the pH of the resulting solution was adjusted to an optimum pH value using 0.1 mol L\(^{-1}\) HCl and/or KOH. Then, 50 mg of BC or MnFe\(_2\)O\(_4–BC\) was added to the solutions. The conical flasks were shaken using a thermostatically controlled shaker (ZWYR-2102C) at 120 rpm for different time intervals (10, 30, 60, 180, 300, 540, 720, and 1440 min).

Sb(III) and Cd(II) adsorption isotherms were obtained for Sb(III and V) and Cd(II) mixed solutions (50 mL) in 100 mL conical flasks via batch tests. The initial concentration of the mixture was varied from 25 to 300 mg L\(^{-1}\). 50 mg of BC or MnFe\(_2\)O\(_4–BC\) was added to the conical flask after the pH of the solution was adjusted to an optimum pH value. The pH of the solution was adjusted by adding 0.1 mol L\(^{-1}\) HCl and/or KOH. Then, the conical flasks were shaken using a thermostatically controlled shaker at 120 rpm at room temperature for 24 h.

The influence of ionic strength on the removal of Sb(III and V) and Cd(II) was also investigated by adjusting the ionic strength of solution to 0, 0.001, 0.005, 0.01, 0.05, 0.1 and 0.5 M, using KCl.

The effects of five common coexisting cations, K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), PO\(_4^{3−}\), and NO\(_3^{−}\), were also investigated by adding 0.01 M KCl, CaCl\(_2\), MgCl\(_2·6H_2O\), NH\(_4\)H\(_2PO_4\), and KNO\(_3\) to mixed solutions containing 50 mg L\(^{-1}\) Sb(III and V) and Cd(II) in separate conical flasks. After the adsorption experiments, all samples were filtered, and then the filtrates were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Prodigy). The removal efficiencies (U, %) and equilibrium adsorption amounts of Sb(III and V) (q\(_e\), mg g\(^{-1}\)) were calculated using the following equations:

\[ q_e = \frac{C_0 - C_e}{m} \\
\]
exhibited in Fig. 1b. The band in the range of 3000 cm⁻¹ suggests that the BC sample contains carbon, oxygen, and hydrogen (C–H, C=O, and OH groups). The peak located at about 245 cm⁻¹ is typical of amorphous carbon dihydroxylation. 

In addition, the XRD pattern of BC has a peak at 29.5°, which is attributed to CaMg(CO₃)₂/dolomite. For MnFe₂O₄–BC, new diffraction peaks are observed at 29.76°, 35.05°, 42.59°, 56.26°, and 61.68°, corresponding to d values of 3.00 Å, 2.56 Å, 2.13 Å, 1.64 Å and 1.50 Å, respectively, which are indexed to MnFe₂O₄, with JCPDS card no. 742403. This result suggests that MnFe₂O₄ nanoparticles have been loaded on the surface of the biochar. The corresponding FT-IR spectra of BC and MnFe₂O₄–BC are exhibited in Fig. 1b. The band in the range of 3000–3445 cm⁻¹ may be due to the stretching vibrations of the O–H groups of water. The peaks at about 1424 cm⁻¹ for BC and at 1454 cm⁻¹ for MnFe₂O₄–BC in the FT-IR spectra were assigned to –CH₂ groups, while the peak at about 1604 cm⁻¹ represents the aromatic C=–C and C=O stretching vibrations. These organic functional groups may be attributed to the lignin structure of tea branches. Compared to the FT-IR spectrum of BC, new peaks at approximately 578 cm⁻¹ and 420 cm⁻¹ appear in the FT-IR spectrum of MnFe₂O₄–BC. These two peaks can be identified as the infrared absorption peaks of MnFe₂O₄. Bujoreanu et al. showed that the IR peaks between 600 and 400 cm⁻¹ for MnFe₂O₄ mainly depend on the vibrations of the octahedral group. Therefore, the results from the FT-IR spectrum are consistent with the XRD results presented in Fig. 1a, and further confirm the successful loading of MnFe₂O₄ nanoparticles on BC.

The morphologies of BC and MnFe₂O₄–BC were characterized using FESEM, and representative images are shown in Fig. 1c and d. As shown in Fig. 1c, BC derived from tea branches is composed of irregular sheets, with some small granules attached to the sheet surface. The corresponding energy-dispersive X-ray (EDX) spectroscopic analysis (inset of Fig. 1c) suggests that the BC sample contains carbon, oxygen, and a small quantity of potassium. Moreover, FESEM/EDX analyses of MnFe₂O₄–BC suggest that MnFe₂O₄ particles are present on the biochar surface (Fig. 1d). The SEM image clearly shows that many small aggregates/particles are present on the surface of MnFe₂O₄–BC (Fig. 1d). The EDX analysis of MnFe₂O₄–BC indicates that these nanoparticles contain carbon, oxygen, iron, and manganese, as well as small amounts of sodium, chlorine, potassium, and calcium (Fig. 1d, inset). Carbon, sodium, chlorine, potassium, and calcium originate from biochar, whereas oxygen, iron, and manganese originate from MnFe₂O₄. Thus, the results of XRD, FT-IR, and FESEM characterization clearly demonstrate that MnFe₂O₄ particles are successfully loaded onto the surface of the pristine biochar.

3. Results and discussion

3.1 Characterization of the MnFe₂O₄–BC nanocomposite

Fig. 1a depicts XRD patterns of BC and MnFe₂O₄–BC. The broad peak located at about 24° in the XRD pattern of BC represents a typical amorphous carbon diffraction pattern. In addition, the XRD pattern of BC has a peak at 29.5°, which is attributed to CaMg(CO₃)₂/dolomite. For MnFe₂O₄–BC, new diffraction peaks are observed at 29.76°, 35.05°, 42.59°, 56.26°, and 61.68°, corresponding to d values of 3.00 Å, 2.56 Å, 2.13 Å, 1.64 Å and 1.50 Å, respectively, which are indexed to MnFe₂O₄, with JCPDS card no. 742403. This result suggests that MnFe₂O₄ nanoparticles have been loaded on the surface of the biochar. The corresponding FT-IR spectra of BC and MnFe₂O₄–BC are exhibited in Fig. 1b. The band in the range of 3000–3445 cm⁻¹ may be due to the stretching vibrations of the O–H groups of water. The peaks at about 1424 cm⁻¹ for BC and at 1454 cm⁻¹ for MnFe₂O₄–BC in the FT-IR spectra were assigned to –CH₂ groups, while the peak at about 1604 cm⁻¹ represents the aromatic C=–C and C=O stretching vibrations. These organic functional groups may be attributed to the lignin structure of tea branches. Compared to the FT-IR spectrum of BC, new peaks at approximately 578 cm⁻¹ and 420 cm⁻¹ appear in the FT-IR spectrum of MnFe₂O₄–BC. These two peaks can be identified as the infrared absorption peaks of MnFe₂O₄. Bujoreanu et al. showed that the IR peaks between 600 and 400 cm⁻¹ for MnFe₂O₄ mainly depend on the vibrations of the octahedral group. Therefore, the results from the FT-IR spectrum are consistent with the XRD results presented in Fig. 1a, and further confirm the successful loading of MnFe₂O₄ nanoparticles on BC.

The morphologies of BC and MnFe₂O₄–BC were characterized using FESEM, and representative images are shown in Fig. 1c and d. As shown in Fig. 1c, BC derived from tea branches is composed of irregular sheets, with some small granules attached to the sheet surface. The corresponding energy-dispersive X-ray (EDX) spectroscopic analysis (inset of Fig. 1c) suggests that the BC sample contains carbon, oxygen, and a small quantity of potassium. Moreover, FESEM/EDX analyses of MnFe₂O₄–BC suggest that MnFe₂O₄ particles are present on the biochar surface (Fig. 1d). The SEM image clearly shows that many small aggregates/particles are present on the surface of MnFe₂O₄–BC (Fig. 1d). The EDX analysis of MnFe₂O₄–BC indicates that these nanoparticles contain carbon, oxygen, iron, and manganese, as well as small amounts of sodium, chlorine, potassium, and calcium (Fig. 1d, inset). Carbon, sodium, chlorine, potassium, and calcium originate from biochar, whereas oxygen, iron, and manganese originate from MnFe₂O₄. Thus, the results of XRD, FT-IR, and FESEM characterization clearly demonstrate that MnFe₂O₄ particles are successfully loaded onto the surface of the pristine biochar.

3.2 Effects of solution pH

The surface charge of BC and MnFe₂O₄–BC, the degree of ionization, and the species ions, Sb(III) and Cd(II), can be affected by the pH of solution. Therefore, the effects of solution pH on the adsorption of Sb(III) and Cd(II) ions onto BC and MnFe₂O₄–BC were examined. Considering metal hydrolysis and precipitation, the experiments were carried out at pH values between 3 and 7. Obviously, the adsorption of Sb(III) by BC was found to be sensitive to variations in solution pH, which generally improved with an increase in pH from 3.0 to 7.0 (Fig. 2a). This could be because biochar contains surface functional groups such as –COOH and –OH (Fig. 1b). The dissociation of these organic functional groups increases upon increasing the pH of the solution, and these functional groups may interact with Sb(III) and Cd(II) ions to form surface complexes. However, the influence of pH on the removal of Sb(III) by MnFe₂O₄–BC was minimal, whereas the adsorption of Cd(II) by MnFe₂O₄–BC increased with pH. This suggests that the mechanism of Sb(III) adsorption onto MnFe₂O₄–BC is different from that using BC. Based on the uptake by BC and MnFe₂O₄–BC, pH 7.0 was chosen as the optimal pH value for Sb(III) and Cd(II) adsorption in subsequent experiments.

3.3 Adsorption kinetics of a bi-solute (Sb + Cd)

To study the kinetics of adsorption of Sb(III) and Cd(II) on BC and MnFe₂O₄–BC, the adsorption processes were investigated with respect to contact time. The experimental data were fitted with the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model is given by the equation:

\[
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{1}{q_e} \frac{t}{C_0}
\]

where \(q_t\) is the amount of metal adsorbed at time \(t\) (mg/g), \(k_1\) is the pseudo-first-order rate constant (min⁻¹), \(q_e\) is the amount of metal adsorbed at equilibrium (mg/g), and \(C_0\) is the initial metal concentration (mg/L).

The pseudo-second-order kinetic model is given by the equation:

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]

where \(k_2\) is the pseudo-second-order rate constant (g/mg min⁻¹).

The values of \(k_1\) and \(k_2\) were determined from the linear plots of the pseudo-first-order and pseudo-second-order kinetic models, respectively. The correlation coefficients (R²) were calculated to determine the best-fit model. The results showed that the pseudo-second-order kinetic model fitted the experimental data better than the pseudo-first-order kinetic model, indicating that the adsorption process is controlled by chemical sorption.
using pseudo-first-order and pseudo-second-order kinetic models, which can be expressed as follows:

\[
\log\left(\frac{q_e - q_t}{q_e - q_i}\right) = \log \frac{q_e}{k_1 t + 1} \quad (3)
\]

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

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) represent the amount of target ions adsorbed at equilibrium and at time \( t \), respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the adsorption rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

The kinetic curves are shown in Fig. 2c and d. For BC, the adsorption of Sb(III) is rapid in the first 3 h, and then becomes slower and reaches equilibrium after 12 h (Fig. 2c). In contrast, the adsorption of Cd(II) is slow and reaches equilibrium after 12 h (Fig. 2c). Moreover, the removal of Sb(III) and Cd(II) through adsorption onto pristine BC is poor. Fig. 2d shows that the removal of both Sb(III) and Cd(II) using MnFe\(_2\)O\(_4\)–BC is rapid in the first 1 h and then becomes slow. Adsorption equilibrium is
gradually achieved within 5 h for both Sb(III) and Cd(II). This is because there are abundant available sites on the biochar surface during the initial rapid adsorption stage. As adsorption proceeds, Sb(III) and Cd(II) accumulate on the surface of the biochar, resulting in a decrease in the adsorption rate. Moreover, the removal of Sb(III) and Cd(II) using MnFe₂O₄–BC is nearly complete, and is much higher than that facilitated by pristine BC. The pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data (Fig. 3). The corresponding parameters and correlation coefficients are listed in Table 1. It is clear that the correlation coefficient ($R^2$) of the pseudo-second-order model is closer to 1 and is higher than that of the pseudo-first-order model. Moreover, the theoretical $q_{e,calc}$ values for both Sb(III) and Cd(II), calculated from the pseudo-second-order model, are closer to the experimental values ($q_{e,exp}$). Therefore, the adsorption behavior of Sb(III) and Cd(II) in binary solution is well described using pseudo-second-order kinetics, which suggests that the adsorption mechanism involves chemisorption.²⁵

Fig. 2 The effects of pH on the removal of Sb(III) and Cd(II) from a binary system using (a) BC and (b) MnFe₂O₄–BC at room temperature for 24 h; the removal of Sb(III) and Cd(II) from a binary system at pH 7.0 using (c) BC and (d) MnFe₂O₄–BC at room temperature, after different contact times; and the effects of initial concentration on the removal of Sb(III) and Cd(II) from a binary system at pH 7.0 using (e) BC and (f) MnFe₂O₄–BC.

3.4 Bi-solute (Sb + Cd) adsorption isotherms
The results of experiments employing various initial concentrations of Sb(III) and Cd(II) ions at the optimized pH of 7 with a contact time of 24 h are shown in Fig. 2e and f, respectively. The adsorption capacities for both Sb(III) and Cd(II) increased...
significantly with an increase in the initial concentration of Sb(III) and Cd(II) from 100 to 500 mg L\(^{-1}\). The experimental data were fitted with Langmuir and Freundlich isotherm models.\(^{26,27}\) The linear forms of the Langmuir and Freundlich isotherms are given by eqn (5) and (6), respectively:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \(C_e\) (mg L\(^{-1}\)) is the equilibrium concentration of Sb(III) or Cd(II), and \(q_e\) (mg g\(^{-1}\)) represents the amount of adsorbed Sb(III) or Cd(II) per unit mass of biochar. \(q_{\text{max}}\) (mg g\(^{-1}\)) indicates the adsorption capacity, whereas \(K_L\) (L mg\(^{-1}\)) is the Langmuir affinity constant. For the Freundlich isotherm, \(K_F\) signifies the adsorption affinity, while \(n\) is an indicator related to the heterogeneity of the adsorbent surface.

The fits to the Langmuir and Freundlich models are shown in Fig. 4, and the isotherm parameters are listed in Table 2. For the adsorption of Sb(III) using BC, the Freundlich model provides a better fit for the experimental data than the Langmuir model (Fig. 5a), whereas the adsorption isotherms from Cd(II) are better fitted using the Langmuir model (Fig. 5b). This suggests that Sb(III) adsorption on pristine biochar is a multilayer adsorption process, whereas Cd(II) follows a monolayer.
adsorption process. Moreover, the maximum adsorption capacities calculated from the Langmuir model for BC in the biosolute system are 199.60 and 145.13 mg g\(^{-1}\) for Sb(III) and Cd(II) ions, respectively. Nevertheless, a different scenario is observed for MnFe\(_2\)O\(_4\)–BC. As shown in Fig. 4c and d and Table 2, the Langmuir isotherms correlate better than the Freundlich ones with the experimental data for both Sb(III) and Cd(II). This implies that Sb(III) and Cd(II) likely form monolayers on MnFe\(_2\)O\(_4\)–BC. In addition, the calculated maximum adsorption capacity, \(q_{\text{max}}\) values from the Langmuir model are 237.53 mg g\(^{-1}\) for Sb(III) and 181.49 mg g\(^{-1}\) for Cd(II), which are higher than the values obtained for BC. The maximum adsorption capacities for Sb(III) and Cd(II) are compared with those reported in the literature (Table 3). The adsorption capacity of MnFe\(_2\)O\(_4\)–BC is also higher than that of pyrochar derived from swine manure, a mercapto-functionalized hybrid sorbent, hematite modified magnetic nanoparticles, graphene, biochar derived from Sida Hermaphrodita, titanian nanotubes, chitosan crosslinked with epichlorohydrin–triphosphate, and manganese dioxide. Therefore, the MnFe\(_2\)O\(_4\)–BC composite prepared in this study is a possible efficient adsorbent for the removal of Sb(III) and Cd(II).

For comparison, the influence of ionic concentration on the removal of either Sb(III) or Cd(II) was investigated for single solute solutions. However, only 11.4% of Sb(III) was absorbed by BC when the initial Sb(III) concentration was 25 mg L\(^{-1}\). This is because the surface of pristine biochar (BC) has a predominantly net negative charge (as shown in Fig. 1b), and therefore the removal of Sb(III) was limited. The Sb(III) adsorption isotherms for BC are not shown. The effect of the initial Sb(III) or

### Table 2 Langmuir and Freundlich parameters for Sb(III) and Cd(II) adsorbed using BC and MnFe\(_2\)O\(_4\)–BC in a binary system

| Sample       | Ion      | \(K_L\) (L mg\(^{-1}\)) | \(q_{\text{max}}\) (mg g\(^{-1}\)) | \(R^2\) | \(K_F\) (mg g\(^{-1}\) (L mg\(^{-1}\))\(^{1/n}\)) | \(n\) | \(R^2\) |
|--------------|----------|--------------------------|---------------------------------|--------|---------------------------------|------|--------|
| BC           | Sb(III)  | 0.00789                   | 199.60                          | 0.912  | 4.803                           | 1.66 | 0.973  |
| BC           | Cd(II)   | 0.0109                    | 145.13                          | 0.990  | 4.038                           | 1.66 | 0.947  |
| MnFe\(_2\)O\(_4\)–BC | Sb(III)  | 0.0316                    | 237.53                          | 0.969  | 17.89                           | 2.04 | 0.673  |
| MnFe\(_2\)O\(_4\)–BC | Cd(II)   | 0.00605                   | 181.49                          | 0.960  | 49.34                           | 4.62 | 0.900  |
Cd(II) concentration on Sb(III) or Cd(II) removal was investigated over the range of 25–500 mg L⁻¹. As shown in Fig. S1a and b, the adsorption efficiency qe increased with the initial ionic concentration for both BC and MnFe₂O₄-BC, with the latter displaying relatively higher adsorption capacity for each ion. The corresponding adsorption isotherms and isotherm parameters for BC and MnFe₂O₄-BC are shown in Fig. S2 and Table S1, respectively. For both BC and MnFe₂O₄-BC, the regression coefficients for the Langmuir adsorption isotherms were higher than those for the Freundlich adsorption isotherms. From the Langmuir adsorption isotherms, the calculated value of the adsorption capacity of BC for Cd(II) is 99.40 mg g⁻¹, whereas the adsorption capacities of MnFe₂O₄-BC for Sb(III) and Cd(II) are 159.48 and 122.10 mg g⁻¹, respectively. Therefore, the removal of Sb(III) and Cd(II) using both BC and MnFe₂O₄-BC obeys the Langmuir adsorption isotherm, indicating a monolayer adsorption process. In addition, the maximum Sb(III) adsorption capacity (qₘₐₓ) of the system in the absence of Cd(II) is lower than that observed in the presence of Cd(II), for both BC and MnFe₂O₄-BC. This result indicates that Cd(II) promotes the removal of Sb(III) using both BC and MnFe₂O₄-BC. Meanwhile, the presence of Sb(III) also promotes the removal of Cd(II). Therefore, MnFe₂O₄-BC is highly promising for the simultaneous removal of Sb(III) and Cd(II), especially in a bi-solute system.

3.5 Effects of ionic strength
The influence of ionic strength on the removal of Sb(III) and Cd(II) using MnFe₂O₄-BC was evaluated, and the results are shown in Fig. 5a. KCl was selected to adjust the ionic strength of the solution to 0, 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 mol L⁻¹. Apparently, the ionic strength did not have an obvious effect on the removal of Sb(III) and Cd(II) using MnFe₂O₄-BC. Only when the KCl concentration reached 0.5 mol L⁻¹ did the removal of Sb(III) and Cd(II) using MnFe₂O₄-BC slightly decrease. This is because K⁺ and Cl⁻ create sterically hindered conditions for Sb(III) and Cd(II), and act as competitors for the surface adsorption sites on MnFe₂O₄-BC, leading to a reduction in the adsorption capacity. Therefore, the above results indicate that the fabricated MnFe₂O₄-BC could effectively remove Sb(III) and Cd(II) from water even at ionic strengths of 100 mM.

3.6 Effects of competing ions
Five common ions (K⁺, Ca²⁺, Mg²⁺, NO₃⁻, and PO₄³⁻) were chosen to investigate the effects of competing ions on Sb(III) and Cd(II) adsorption using MnFe₂O₄-BC. As shown in Fig. 5b, none of these five ions have a remarkable effect on the uptake of Sb(III) and Cd(II) under the experimental conditions. Specifically, the presence of K⁺, Mg²⁺, and NO₃⁻ did not have any noticeable influence on the removal of Sb(III) and Cd(II). In fact, Ca²⁺ could promote the adsorption of Sb(III), while the uptake of Cd(II) was found to decrease in the presence of Ca²⁺ (Fig. 5b). In addition, PO₄³⁻ slightly reduced the uptake of both Sb(III) and Cd(II) under the experimental conditions. These results confirm that Sb(III) and Cd(II) could be effectively removed using MnFe₂O₄-BC, despite the presence of competing ions.

3.7 Reusability studies
Reusability is a desirable trait for an effective absorbent. In our experiments, 0.1 mol L⁻¹ HCl was chosen as the desorbent. To
study the reusability of MnFe$_2$O$_4$–BC, adsorption–desorption cycles were repeated five times with the same MnFe$_2$O$_4$–BC sample. As shown in Fig. 5c, the removal percentages of both Sb(III) and Cd(II) decreased gradually. For the first three cycles, the removal percentage of Sb(III) changed very little. From the third to the fourth cycle, however, there was a decrease of about 20% in the amount of adsorbed Sb(III). Moreover, the removal of Sb(III) ions still reached 60% after the fifth cycle. However, in the case of Cd(II), the situation was different. From the first to the second cycle, the removal percentage of Cd(II) dropped sharply to 53%, and then it declined gradually from the second to the fifth cycle. In the fifth cycle, the removal percentage of Cd(II) ions was found to be ~40%. Thus, the reusability is not satisfactory with regards to Cd(II). This might be because Sb(III) and Cd(II) in solution compete for the adsorption sites on the surface of the MnFe$_2$O$_4$–biochar nanocomposite. Further, the adsorption capacity of the MnFe$_2$O$_4$–biochar nanocomposite for Sb(III) is better than for Cd(II). Therefore, the reusability is not good for Cd(II) compared to Sb(III).

### 3.8 Adsorption mechanism

The surface states of MnFe$_2$O$_4$–BC after the adsorption of Sb(III) and Cd(II) were studied using FT-IR and XPS to ascertain the mechanism of Sb(III)/Cd(II) adsorption on MnFe$_2$O$_4$–BC. FT-IR and full-range XPS spectra of MnFe$_2$O$_4$–BC after adsorption are shown in Fig. 6a and b, respectively. Compared to the IR spectrum of the original MnFe$_2$O$_4$–BC sample (Fig. 1b), a less intense band at ~3400 cm$^{-1}$ is observed in the spectrum of MnFe$_2$O$_4$–BC after the adsorption of Sb(III) and Cd(II). This may be attributed to the deprotonation of hydroxyl groups associated with Fe on the MnFe$_2$O$_4$–BC surface upon the adsorption of Sb(III) and Cd(II). The vibration peaks at 1604 cm$^{-1}$ and 1454 cm$^{-1}$, which are ascribed to the vibrations of C=O and C–O, shifted to 1590 cm$^{-1}$ and 1430 cm$^{-1}$ after Sb(III) and Cd(II) adsorption, suggesting that Sb(III) and Cd(II) may interact with the C=O/C=O and C–OH groups in the MnFe$_2$O$_4$–BC samples. Moreover, the chemical composition of MnFe$_2$O$_4$–BC after Sb(III) and Cd(II) co-adsorption was studied by XPS. Peaks corresponding to O 1s, C 1s, N 1s and Sb 3d are clearly identified in the survey scan spectrum (Fig. 6b). The presence of Sb(III) and Cd(II) in the resultant product further verifies the co-adsorption of Sb(III) and Cd(II) onto MnFe$_2$O$_4$–BC. In addition, the binding energies (BE) of Sb(III) and Cd(II) adsorption on MnFe$_2$O$_4$–BC shown an indicative Sb(III) binding energy for Sb 3d$^{3}/2$ at 539.6, 539.8, and 540.2 eV, respectively.$^{14-16}$ Our XPS spectra of Sb(III)-adsorbed MnFe$_2$O$_4$–BC showed an indication Sb(III) binding energy for Sb 3d$^{3}/2$ at ~540.2 eV, indicating the presence of Sb(III) on the MnFe$_2$O$_4$–BC surface after adsorption. This indeed demonstrates that Sb(III) is chemically adsorbed on the MnFe$_2$O$_4$–BC surface.

#### Table 3: A comparison of the adsorption capacities of MnFe$_2$O$_4$–BC for Sb(III) and Cd(II) with those of other reported adsorbents

| Adsorbents | Concentration range (mg L$^{-1}$) | pH | Sb(III) Adsorption capacity (mg g$^{-1}$) | Cd(II) Adsorption capacity (mg g$^{-1}$) | Ref. |
|------------|----------------------------------|----|-----------------------------------------|-----------------------------------------|-----|
| Pyrochar from swine manure | 0.1–100/0.3–150 | 6 | 13.09 | 81.32 | 28 |
| Mercapto-functionalized hybrid sorbent | 100–800 | 5 | 108.8 | — | 29 |
| Hematite modified magnetic nanoparticles | 1–20 | 4.1 | 36.7 | — | 30 |
| Graphene | 1–10 | 11 | 8.506 | — | 31 |
| Biochar derived from Sida hermaphrodita | 5–500 | 6 | — | 35.71 | 32 |
| Titanate nanotubes | 25–300 | 57 | — | 65.97 | 33 |
| Chitosan crosslinked with epichlorohydrin-triphosphate | 100–400 | 5.6 | — | 83.75 | 34 |
| Manganese dioxide | 0.05–0.7 | — | — | 176 | 35 |
| Metal-organic frameworks (MOFs) | 10–250 | — | — | 225 | 37 |
| MnFe$_2$O$_4$–BC | 25–500 | 7 | 237.53 | 181.49 | This work |

---

**Fig. 6** (a) FT-IR spectrum and (b) XPS spectrum of MnFe$_2$O$_4$–BC after Sb(III) and Cd(II) co-adsorption.
oxidation mechanism may very well explain the higher Sb(III) adsorption on MnFe₂O₄-BC than on pristine BC.

4. Conclusions

In this study, a jacobsite–biochar nanocomposite (MnFe₂O₄–BC) was successfully fabricated and its adsorption performance for the removal of Sb(III) and Cd(II) was evaluated. The MnFe₂O₄–BC samples exhibited excellent adsorption capabilities and could simultaneously remove Sb(III) and Cd(II) from water. The ionic strength of the solution and coexisting ions did not have an obvious influence on the removal of Sb(III) and Cd(II) using MnFe₂O₄–BC, under the examined conditions. Moreover, MnFe₂O₄–BC could be used repeatedly. Therefore, the MnFe₂O₄–BC fabricated in our study is a promising adsorbent for the simultaneous removal of Sb(III) and Cd(II) from water.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Natural Science Foundation of Zhejiang (LQ17D020002, LY16D010004), the Key Research and Development Projects in Zhejiang Province (2015C03020), and the Zhejiang Provincial Collaborative Innovation Center of Agricultural Biological Resources Biochemical Manufacturing/ Zhejiang Provincial Key Lab for Chem & Bio Processing Technology of Farm Products open fund (2016KF0116).

References

1. Z. Wu, M. He, X. Guo and R. Zhou, *Sep. Purif. Technol.*, 2010, **76**, 184–190.
2. S. Guo, P. Jiao, Z. Dan, N. Duan, G. Chen and J. Zhang, *Chem. Eng. J.*, 2017, **317**, 999–1011.
3. M. Krachler, H. Emons and J. Zheng, *Trends Anal. Chem.*, 2001, **20**, 79–90.
4. W. Xu, H. Wang, R. Liu, X. Zhao and J. Qu, *J. Colloid Interface Sci.*, 2011, **363**, 320–326.
5. X. Guo, K. Wang, M. He, Z. Liu, H. Yang and S. Li, *J. Environ. Sci.*, 2014, **26**, 1549–1556.
6. B. Belhalfaoui, A. Aziz, E. H. Elandaloussi, M. S. Ouali and L. C. De Ménorval, *J. Hazard. Mater.*, 2009, **169**, 831–837.
7. D. Sud, G. Mahajan and M. P. Kaur, *Bioresour. Technol.*, 2008, **99**, 6017–6027.
8. M. He, *Environ. Geochem. Health*, 2007, **29**, 209–219.
9. S. Fu and C. Y. Wei, *J. Soils Sediments*, 2013, **13**, 106–116.
10. J. Lehmann, J. Gaunt and M. Rondon, *Mittig. Adapt. Strat. GL.,* 2006, **11**, 395–419.
11. Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen and L. Yang, *Chem. Eng. J.*, 2014, **240**, 574–578.
12. A. Mukherjee, A. R. Zimmerman and W. Harris, *Geoderma*, 2011, **163**, 247–255.
13. Y. Yao, B. Gao, M. Zhang, M. Inyang and A. R. Zimmerman, *Chemosphere*, 2012, **89**, 1467–1471.
14. Y. Bai, W. A. Jefferson, J. Liang, T. Yang and J. Qu, *J. Environ. Sci.*, 2017, **54**, 126–134.
15. P. Qi and T. Pichler, *Chemosphere*, 2016, **145**, 55–60.
16. Y. Y. Wang, H. H. Lu, Y. X. Liu and S. M. Yang, *RSC Adv.*, 2016, **6**, 83534–83546.
17. X. Xiao, B. L. Chen and L. Z. Zhu, *Environ. Sci. Technol.*, 2014, **48**, 3411–3419.
18. R. Azargohar, S. Nanda, J. A. Kozinski, A. K. Dalai and R. Shutarto, *Fuel*, 2014, **125**, 90–100.
19. Y. Y. Wang, H. H. Lu, Y. X. Liu and S. M. Yang, *Colloids Surf., A*, 2016, **509**, 550–563.
20. Z. Droussi, V. D’orazio, M. R. Provenzano, M. Hafidi and A. Ouattane, *J. Hazard. Mater.*, 2009, **164**, 1281–1285.
21. B. Chen, Z. Chen and S. Lv, *Bioresour. Technol.*, 2011, **102**, 716–723.
22. A. Han, J. Liao, M. Ye, Y. Li and X. Peng, *Chin. J. Chem. Eng.*, 2011, **19**, 1047–1051.
23. V. M. Bujoreanu, E. Segal, M. Brezeanu, R. Salmon, J. J. Videau and C. Gheorghies, *Thermochim. Acta*, 1996, **288**, 221–237.
24. Y. S. Ho and G. McKay, *Water Res.*, 2000, **34**, 735–742.
25. H. Liu, C. Wang, J. Liu, B. Wang and H. Sun, *J. Environ. Manage.*, 2013, **128**, 727–734.
26. I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1361–1403.
27. H. M. F. Freundlich, *Z. Phys. Chem.*, 1906, **57**, 385–470.
28. L. Han, H. Sun, K. S. Ro, K. Sun, J. A. Libra and B. Xing, *Bioresour. Technol.*, 2017, **234**, 77–85.
29. H. T. Fan, W. Sun, B. Jiang, Q. J. Wang, D. W. Li, C. C. Huang, K. J. Wang, Z. G. Zhang and W. X. Li, *Chem. Eng. J.*, 2016, **286**, 128–138.
30. C. Shan, Z. Ma and M. Tong, *J. Hazard. Mater.*, 2014, **268**, 229–236.
31. Y. Q. Leng, W. L. Guo, S. N. Su, C. L. Yi and L. T. Xing, *Chem. Eng. J.*, 2012, **211**, 406–411.
32. A. Bogusz, P. Oleszczuk and R. Dobrowolski, *Bioresour. Technol.*, 2015, **196**, 540–549.
33. T. Wang, W. Liu, L. Xiong, N. Xu and J. Ni, *Chem. Eng. J.*, 2013, **215**, 366–374.
34. R. Laus and V. T. de Fávere, *Bioresour. Technol.*, 2011, **102**, 8769–8776.
35. Q. D. Qin, Q. Q. Wang, D. F. Fu and J. Ma, *Chem. Eng. J.*, 2011, **172**, 68–74.
36. R. Delobel, H. Baussart, J. M. Leroy, J. Grimblot and L. Gengembre, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 879–891.
37. H. Xue, Q. H. Chen, F. L. Jiang, D. Q. Yuan, G. X. Lv, L. F. Liang, L. Y. Lia and M. C. Hong, *Chem. Sci.*, 2016, **7**, 5983–5988.