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A novel manganese-oxide/biochar composite for efficient removal of lead(II) from aqueous solutions

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Abstract Biochar (BC) derived from pyrolysis of plant biomass can be used as an inexpensive adsorbent for removal of aqueous heavy metals. In the present study, amorphous hydrous manganese oxide was loaded onto BC to fabricate a novel manganese-oxide/biochar (Mn/BC) composite for further enhancing lead(II) removal by sorption from water. Mn/BC was characterized by X-ray diffraction, scanning electron microscope, and specific surface area analysis. After impregnation with 3.65 % Mn, BC raised the removal efficiency of lead(II) from 6.4 to 98.9 % at pH 5.00. This improvement is attributed to the increase in surface hydroxyls and the decrease in pH_{PZC} (pH at the point of zero charge) of carbon. The maximum monolayer adsorption of lead(II) on Mn/BC at 298 K was five times that on BC. The smaller pseudo-second-order rate constant of Mn/BC compared with that of BC indicated that the sorption rate of Mn/BC is faster than that of BC. The calculated thermodynamic parameters implied that the sorption of lead(II) is a spontaneous and endothermic process. The results suggest that Mn/BC composite is a promising adsorbent for the efficient removal of lead(II) from water.

Keywords Biochar · Removal · Sorption · Manganese oxide · Lead(II)

Introduction

A "green" porous carbon (biochar) has been recently prepared and applied in carbon sequestration to address global warming (Chen et al. 2012; Fraser 2010). This carbon-rich material is produced from the fast thermal decomposition of biomass at oxygen-limited conditions without any steam and/or chemical activation (Wang et al. 2013; Qiu et al. 2009a) and features higher productivity with less energy consumption compared with commercial activated carbon (AC) (Cao et al. 2009). As a more economical carbonaceous adsorbent, biochar (BC) may be a potential AC substitute for the removal of contaminants from wastewater (Kong et al. 2011).

Biochar has a smaller surface area and less porosity than AC but also features more surface oxygen-containing functional groups (Chun et al. 2004). These characteristics indicate that BC is more suitable for removing heavy metal pollutants (HMPs) than hydrophobic organic pollutants. Recent studies have confirmed more effective removal or immobilization of Pb(II), Cd(II), Cu(II), and Ni(II) by BC compared with AC (Uchimiya et al. 2011; Qiu et al. 2008). However, the reported sorption capacity of HMPs on BC is not adequately high for actual wastewater treatment applications. To enhance the uptake of HMPs on BC, two improved approaches are applied to functionalize the surface of BC: (1) chemical modification (oxidation) to increase the surface acidity of BC and (2) introduction of metal oxides onto BC to increase surface hydroxylation. The traditional chemical oxidation method (e.g., by HNO₃) has apparent negative effects on BC characteristics, including destruction of the rigid matrix structure, decrease in carbon content, and reduction in surface area (Considine et al. 2001). In comparison, loading of hydrated metal oxides onto carbons is a moderate way to effectively raise



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HMP sorption by enhancing electrostatic interactions between the charged HMP species and the hydroxylated metal oxide surface (Vasudevan et al. 2001).

Hydrous manganese oxide (HMO) is applied more widely than hydrous Fe or Al oxides due to its stronger affinity for HMPs (Wang et al. 2007). However, the micron-scale size of HMO particles is difficult to use in continuous-flow water treatment devices. In addition, HMO colloids easily agglomerate in waters exposed to solution chemistry conditions. Finally, HMO particles dispersed in aqueous solutions are not easy to collect for regeneration. To overcome these disadvantages and expand the application of HMO in dynamic wastewater treatment, many researchers have considered impregnating amorphous HMO onto various layered and porous structural materials [e.g., montmorillonite (Thipnakarin et al. 2006), zeolite (Han et al. 2006a), polymer resin (Su et al. 2009)]. Carbonaceous materials are the ideal support media for increasing the stability of HMO against aggregation and enhancing its sorption affinity for HMPs (Wang et al. 2007; Fan and Anderson 2005). As BC is a more environmentfriendly and less expensive carbon source compared with AC and carbon nanotubes, it may be more suitable for use as an HMO support. The number of acid groups per unit surface area of BC is higher than that of AC, implying that BC can provide more surface sites (e.g., carboxyl groups) for combination with Mn(II) and further reaction with oxidants (e.g., potassium permanganate, sodium hypochlorite). Thus, more HMO can disperse and deposit on BC surfaces.

In the present work, we focus on the fabrication and application of BC-supported HMO for the removal of Pb(II) from aqueous solutions. The objectives of the study are to determine the ability of HMO–BC composites for enhanced Pb(II) uptake and explore the kinetic and thermodynamic sorption mechanisms of Pb(II) on the HMO-loaded BC.

Materials and methods

Materials

Analytical grade reagents of potassium permanganate, manganese nitrate, and lead nitrate were purchased from Shanghai Chemical Reagent Company (China). Peeled pine wood (*Pinus massoniana*) was cut into small pieces ($3 \text{ mm} \times 3 \text{ mm} \times 8 \text{ mm}$) and then placed in a ceramic pot. Pyrolysis of the air-dried wood was conducted in a muffle furnace at 100 °C for 1 h and then at 700 °C for 3 h. The collected BC products were milled to pass through a 0.18-mm sieve prior to sorption experiments.



Preparation of HMO-loaded BC

Hydrous-manganese-oxide-loaded BC was prepared by a conventional wet impregnation method. BC (10.0 g) was added to 200 mL of manganese nitrate solutions with different concentration (0.002, 0.01, and 0.05 mol/L) and shocked at 150 rpm for 12 h. The filtered Mn(II)-impregnated BC samples were washed several times to remove uncombined Mn(II) cations on their surface and then transferred to 200 mL of potassium permanganate solution (0.033 mol/L). The mixtures were further stirred for 24 h at 25 °C. The chemical reactions involved can be described as follows:

$$2 \bigcirc -\text{COOH} + \text{Mn}^{2+} \implies (\bigcirc -\text{COO})_2 \text{Mn} + 2\text{H}^+$$
(1)

 $(\bigcirc -COO)_2 Mn + MnO_4^- + H^+ \longrightarrow \bigcirc -COOH + HMO_4^-$

Note: \bigcirc = Biochar matrix

After drying in a vacuum at 60 °C overnight, Mn-impregnated BCs were obtained and designated as Mn/BC-0, Mn/BC, and Mn/BC-2, which correspond to the solution concentrations of manganese nitrate (0.002, 0.01, and 0.05 mol/L, respectively). The surface area and porosity of all of the samples were measured by nitrogen sorption at 77 K using a Micromeritics ASAP-2020 accelerated surface area and porosimetry analyzer (USA). Data were analyzed by the Brunauer–Emmett–Teller (BET) and *t* plot methods. X-ray powder diffraction (XRD) patterns of BC and HMOloaded BCs were obtained on an X'Pert PRO X-ray diffractometer (PANalytical, Holland) at 40 kV/40 mA using CuK α radiation ($\lambda = 0.154$ nm). XRD patterns were recorded by step scanning from 10° to 80° (2 θ angular range) with the sample spinning at 2 r/s.

Determination of manganese content on BC

Hydrous-manganese-oxide-loaded BCs (0.010 g) were added into digestion bottles containing a mixture of 10 mL of HNO₃ (67 %), 2 mL of H₂O₂ (30 %), 2 mL of HClO₄ (70 %), and 2 mL of HF (40 %). All samples were digested in a microwave digestion instrument (800 W; 200 °C; 800 psi; 60 min). The decomposed solution was evaporated to less than 1 mL and then mixed with 0.5 mL HNO₃. The total volume of the solution was increased to 25 mL with distilled water. The manganese content (Mn %) of the HMO-loaded BCs (Mn/BC-0, Mn/BC, and Mn/BC-2) was determined from flame absorption measurements obtained using a PerkinElmer[®] AAnalystTM 800 atomic absorption spectrometer (USA) at a wavelength of 279.5 nm. To evaluate the effect of the Mn % loading on Pb(II) removal, the equilibrium sorption of 50 mg/L Pb(NO₃)₂ (50 mL) was determined in 100 mL conical flasks with HMO-free BC and HMO-loaded BC (0.050 g each).

Sorption kinetics

Preliminary kinetic experiments showed that Pb(II) sorption onto HMO-free BC and HMO-loaded BC reaches apparent equilibrium within 20 h. To determine sorption kinetics, ~0.005 g of BC and Mn/BC were added to 21-mL glass tubes. The sorption of Pb(II) in 0.0050 samples was measured at various time intervals by rotating with lots of Pb(NO₃)₂ solutions (20 mL, 50 mg/L) in a 0.01 mol/L NaNO₃ background electrolyte at 25 °C.

Equilibrium sorption

Pb(II) uptake was measured by the batch equilibration method. In brief, BC (~ 0.05 g) and HMO-loaded BC $(\sim 0.01 \text{ g})$ were mixed with 20 mL of Pb(NO₃)₂ solution (10-100 mg/L) in 21-mL glass tubes with 0.01 mol/L NaNO₃ to increase the ionic strength. All tubes were capped and rotated end-over-end at 40 rpm for 48 h at 10, 25, and 40 °C, respectively. The solution pH was adjusted by addition of HNO₃ (0.01 mol/L) and NaOH (0.01 mol/L) solution as necessary. The concentrations of Pb(II) in filtrates were analyzed using the flame atomic absorption spectrometer at a wavelength of 283.3 nm. The amount of Pb(II) adsorbed by the carbons was calculated by conducting mass balance measurements of the solute before and after the test. All sorption experiments were performed in triplicate, and the data are expressed as mean values with maximum relative standard deviations (RSDs) lower than ± 2.1 %. Blank tests did not show any Pb(II) sorption on tube walls during the experiments.

Results and discussion

Screening of HMO-loaded BC for efficient removal of Pb(II)

To assess the effect of HMO coating on the nature and sorption of BC, a series of Mn/BC samples was prepared by impregnating carbon with different amounts of Mn (0.88, 3.65, and 9.96 %). The X-ray diffraction patterns of BC and HMO-loaded BC are shown in Fig. 1. The original BC exhibited broad peaks at around 0.388 and 0.208 nm, which are assigned to *hkl* 002 and overlapping



Fig. 1 XRD spectra of BC and HMO-loaded BC

101 and 100 planes, respectively (Keiluweit et al. 2010). For HMO-loaded BCs, the obvious decrease in the peak at 0.388 nm and disappearance of the peak at 0.208 nm indicates effective HMO loading on the BC surface. The emergence of new peaks (d = 0.245 and 0.143 nm) in all of the Mn/BC samples over the whole range of 2 θ degrees implies that HMO particles precipitate on the carbon surface, as is typical of δ -MnO₂ (Pretorius and Lindner 2001). A similar result was found by Lenoble et al. (2004), who successfully loaded δ -MnO₂ on the surface of polystyrene resin.

Selected physicochemical properties of HMO-free and all of the HMO-loaded BCs are listed in Table 1. The HMO-free BC is characterized with a BET surface area of 369 m²/g, a micropore surface area of 203 m²/g, and total pore and micropore volumes of 0.200 and 0.090 cm³/g, respectively. These porous properties suggest that the original BC is an appropriate support for HMO loading. The larger the amount of Mn impregnated on the BC surface, the larger the amount of Pb(II) sorbed on the resulting material (Table 1). A minimal loading of Mn (0.88 %) increased the Pb(II) removal efficiency of the resulting BC material from 6.4 to 41.9 %. However, the excess coating with HMO leads to obvious pore blockage. For example, loading of HMO with 9.96 % Mn (i.e., Mn/BC-2) resulted in a significant decrease in the surface area and pore volume of the resulting material by 82.1 and 72.5 %, respectively. In comparison, the Mn/BC adsorbent impregnated with 3.65 % Mn yielded the optimal HMO-BC composite, which has excellent removal efficiency of Pb(II) (Table 1). The SEM images demonstrate that micron-sized HMO particles are highly dispersed on the surface of BC after deposition of 3.65 % Mn onto the carbon support (Fig. 2). The concentration of surface hydroxyl groups also increased from 0.06 to 0.20 mmol/g (Table 1). This higher hydroxyl density results in the lower pH_{PZC} value (pH at the point of zero charge) of BC, which is favorable for Pb(II) sorption.



	Mn % ^a	$S_{\text{BET}}^{\text{b}}$ (m ² /g)	$S^{\rm c}_{ m micro}$ (m ² /g)	$V_{\text{total}}^{\text{d}}$ (cm ³ /g)	$V_{\rm micro}^{\rm e}$ (cm ³ /g)	Surface hydroxyl (mmol/g)	$\mathrm{pH}_{\mathrm{PZC}}^{\mathrm{f}}$	Removal efficiency ^g (%)
BC	0	369 ± 3.5	203 ± 2.6	0.200 ± 0.013	0.090 ± 0.006	0.06 ± 0.00	4.5 ± 0.1	6.4
Mn/BC1	0.88 ± 0.03	361 ± 2.9	209 ± 2.5	0.194 ± 0.010	0.094 ± 0.005	ND	ND	41.9
Mn/BC	3.65 ± 0.11	194 ± 1.8	74 ± 0.7	0.141 ± 0.011	0.030 ± 0.002	0.20 ± 0.01	3.2 ± 0.1	98.9
Mn/BC2	9.96 ± 0.30	66 ± 1.0	34 ± 0.5	0.055 ± 0.008	0.015 ± 0.001	ND	ND	100

Table 1 Selected physicochemical properties of biochar (BC) and Mn/BC

ND not determined

^a The percentage content of Mn on BC

^b BET surface area

^c t Plot micropore area

^d Single point sorption total pore volume of pores

^e t Plot micropore volume

f pH of zero net charge point

^g Removal efficiency of Pb(II) onto BC and HMO-loaded BC at 298 K (pH 5.00, the initial concentration of Pb(II) = 80 mg/l)



Table 2 Chemical speciation of Pb(II) in 0.01 mol/L NaNO_3 solution under the different pH at 25 $^\circ\text{C}$

pН	Pb ²⁺ (%)	PbNO ₃ ⁺ (%)	Pb(NO ₃) ₂ (aq) (%)	PbOH ⁺ (%)
1.73	92.252	7.652	0.097	0
2.18	91.613	8.278	0.109	0
2.72	91.298	8.586	0.116	0
3.15	91.209	8.672	0.117	0
3.93	91.153	8.714	0.118	0.014
4.43	91.118	8.718	0.118	0.045
4.65	91.089	8.716	0.118	0.075
4.80	91.06	8.714	0.118	0.105
5.00	91.002	8.709	0.118	0.167



Fig. 2 SEM images of a BC and b Mn/BC

Effect of pH

The solution pH influences both the Pb(II) species and the surface net charges on Mn/BC, which, in turn influences Pb(II) sorption. The speciation of Pb(II) in water with a ionic strength from 0.01 mol/L NaNO3 at different equilibrium pH can be described by MINTEQA2 model calculations (Qiu et al. 2008). At pH < 3.15, three Pb(II) species [Pb²⁺, PbNO₃⁺, and Pb(NO₃)₂(aq)] are present in solution (Table 2). When the pH is increased from 3.93 to 5.00, an additional species (PbOH⁺) emerges. In the range of acidic pH (1.73-5.00), Pb(II) exists predominantly as Pb^{2+} (>91 %) and $PbNO_3^+$ (>7.5 %) cations and no Pb(II) hydroxide precipitate forms. Other Pb(II) species, including $Pb(NO_3)_2(aq)$ and $PbOH^+$, present in solution can be ignored. This finding indicates that the uptake of Pb(II) by Mn/BC depends completely on the effective combination of Pb^{2+} and $PbNO_3^+$ cations on the surface binding sites.



Fig. 3 pH-dependant uptake of Pb(II) on BC and Mn/BC at 298 K

After impregnating BC with 3.65 % Mn, the pH_{PZC} (pH at the point of zero charge) of the carbons decreased from 4.5 to 3.2, indicating the presence of more hydroxyl groups on the HMO-loaded surface. Early literatures show that the pH_{PZC} values of amorphous HMO in solution are 2.4 (Eren et al. 2009) or 3.0 (Liu et al. 2009), which is also close to the pH_{PZC} of Mn/BC (3.2). The similarity of the pH_{PZC} of the coated HMO on the carbon surface and the colloidal HMO in aqueous solution suggests that immobilization of HMO may not impact the sorption affinity of HMO for HMPs.

The pH dependence of the surface charges on Mn/BC is due to the exchange of H⁺ ions in aqueous solution, which can be illustrated as follows.

$$\bigcirc -Mn - OH + H_2O \longrightarrow \bigcirc -Mn - OH_2^+ + OH^- \quad (pH < pH_{PZC})$$
(3)

○-Mn-OH → **○**-Mn-O⁻ + H⁺ $(pH > pH_{PZC})$

Note: **()** = HMO-loaded biochar matrix

(4)

When $pH < pH_{PZC}$, hydroxyl groups on the Mn/BC surface are essentially protonated, resulting in a positively net charged surface. By contrast, deprotonation of the surface hydroxyl groups results in a negative net charge on the carbon surfaces (Han et al. 2006b).

The dependence of the uptake of Pb(II) by Mn/BC on the solution pH is shown in Fig. 3. The equilibrium sorption capacity exponentially increased by 8.32 times when the solution pH was raised from 1.73 to 5.00. This finding indicates that Pb(II)-free cations in water can be appropriately adsorbed at high pH, while sorbed Pb(II) on Mn/ BC can be desorbed at low pH. At equilibrium $pH < pH_{PZC}$, electric repulsion between cationic Pb(II) species and positively charged carbon surfaces weakens the sorption affinity of Pb(II) to Mn/BC, the main driving force



100

80

60

40

20

4

3

2

1

0

-1

100

50

0

0

ťqt

qt (mg/g)

(b)

In (qe-qt)

Fig. 4 a Sorption kinetics of Pb(II) on BC and Mn/BC at pH 5.00; the kinetic rates were modeled using b the pseudo-first-order model (PFOM) and c the pseudo-second-order model (PSOM)

2000

t (min)

1000

of which is cation exchange between the protonated Mn/ BC and cationic Pb(II) species (Qiu et al. 2008). When $pH > pH_{PZC}$, electrostatic interactions between $Pb^{2+}/$ $PbNO_3^+$ cations and the negative charge sites of Mn/BC play a dominant role in Pb(II) sorption. The corresponding sorption mechanism is illustrated as follows.

$$2 \bigcirc -Mn - O^{-} + Pb^{2+} \longrightarrow \bigcirc -Mn - O - Pb - O - Mn - \bigcirc (5)$$

$$\bigcirc -Mn - O^{-} + Pb(NO_3)^{+} \longrightarrow \bigcirc -Mn - O - Pb(NO_3)$$
(6)



Mn/BC

3000

	$q_{e,\exp}$	PSOM				PFOM			
	(mg/g)	$q_{e,\mathrm{cal}}\(\mathrm{mg/g})$	Δq (%)	k ₂ (g/mg min)	R^2	$q_{e,\mathrm{cal}} \ (\mathrm{mg/g})$	Δq (%)	$k_1 \pmod{(\min^{-1})}$	R^2
BC	24.25 ± 0.34	21.79	1.01	4.53×10^{-4}	0.9437	12.32 ± 0.08	49.20 %	1.00×10^{-3}	0.5066
Mn/BC	93.36 ± 1.12	91.74	1.74	1.94×10^{-4}	0.9925	39.78 ± 0.16	57.39 %	1.60×10^{-3}	0.7585

Table 3 Kinetic parameters of pseudo-second-order model (PSOM) and pseudo-first-order model (PFOM) for sorption of Pb(II) on biochar (BC) and Mn/BC at 313K

Sorption kinetics

To evaluate differences in Pb(II) sorption kinetic rates on BC and Mn/BC and describe the kinetic sorption process, a pseudo-first-order model (PFOM) and a pseudo-secondorder model (PSOM) were employed (Fig. 4). The PSOM assumes that the rate-limiting step is chemical sorption involving valence forces through the sharing or exchange of electrons between the sorbent and sorbate (Ho and McKay 1999). By contrast, the PFOM uses the sorption capacity of sorbents as basis for predicting the rate of sorption (Oiu et al. 2009b). The two kinetic models are presented as follows (Sharaf and Hassan 2013):

$$PFOM: \ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \tag{7}$$

$$PSOM: \ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t$$
(8)

where q_t and q_e (mg/g) are the uptake of Pb(II) at time t (min) and equilibrium, respectively, and k_1 and k_2 are the first-order (1/min) and second-order (g/mg min) rate constants, respectively. The calculated kinetics parameters are presented in Table 3. Clearly, the PSOM fits the sorption data of BC and Mn/BC well, as evidenced by the higher R^2 values (the square of the regression coefficient) of PSOM compared with PFOM.

To quantitatively compare the applicability of these two models, the normalized standard deviation Δq (%) was calculated using the following formula (Lv et al. 2007).

$$\Delta q \ (\%) = 100 \times \sqrt{\frac{\sum \left[(q_{e,\exp} - q_{e,\text{cal}})/q_{e,\exp}\right]^2}{n-1}} \tag{9}$$

where $q_{e,exp}$ and $q_{e,cal}$ (mg/g) are the experimental and calculated equilibrium sorption of Pb(II) on carbons, respectively, and n is the number of measurements. The smaller Δq values of BC and Mn/BC from PSOM (1.01 and 1.74 %) compared with those from PFOM (49.20 and 57.39 %) further indicate that the sorption of Pb(II) may be better described by PSOM kinetics (Sölener et al. 2008). Generally, a larger k_2 value means a slower sorption rate (Maliyekkal et al. 2006; Fan et al. 2003). The k_2 value of Mn/BC $(1.94 \times 10^{-4} \text{ g/mg min})$ in this experiment was





Fig. 5 Langmuir and Freundlich adsorption isotherm of Pb(II) on BC at 298 K and onto Mn/BC at 283, 298, and 313 K, respectively (pH 5.00)

2.33 times lower than that of BC (4.53 \times 10⁻⁴ g/mg min), indicating that the sorption rate of Mn/BC is faster than that of BC. Table 1 shows that the micropore area of Mn/BC $(74 \text{ m}^2/\text{g})$ accounts for only 38.1 % of the total surface area of the resulting material. Thus, most of the sorption sites on Mn/BC may be in mesopore and macropore regions that are easily accessible for Pb(II) sorption. By contrast, the micropore areas of original BC accounted for over 50 % of the total surface area of the material. Therefore, the sorption rate of Pb(II) on BC must be slower than that on Mn/ BC because most of the Pb(II) cations must diffuse into the micropore regions to combine with sorption sites. Similar findings were showed in the previous study, which found that micropores of Mn-impregnated AC derived from Typha orientalis do not contribute to the sorption of neutral red dye (Zhang et al. 2008). Moreover, the faster sorption rate of Mn/BC compared with that of original BC may be attributed to the higher availability of sorption sites on the surface of Mn/BC. This explanation is in agreement with other reports (Guo et al. 2011; Reddad et al. 2002).

Sorption isotherms

The sorption isotherms of Pb(II) on BC at 298 K and Mn/ BC at three different temperatures are shown in Fig. 5. The sorption capacities of Pb(II) on Mn/BC increased markedly with the increase in environmental temperature, indicating

Table 4 Langmuir and Freundlich parameters for sorption of the biochar (BC) and Mn/BC

Adsorbents	Langmuir model			Freundlich model		
	KL	$q_{ m m}$	R^2	K _F	1/ <i>n</i>	R^2
BC (298 K)	0.57 ± 0.13	18.13 ± 0.94	0.9639	7.77 ± 1.01	0.235 ± 0.043	0.9268
Mn/BC (283 K)	7.45 ± 2.28	62.77 ± 1.89	0.9672	45.80 ± 2.61	0.091 ± 0.017	0.9753
Mn/BC (298 K)	34.3 ± 7.76	91.98 ± 2.05	0.9830	67.18 ± 4.19	0.093 ± 0.018	0.9660
Mn/BC (313 K)	5.92 ± 1.85	121.8 ± 5.82	0.9436	77.76 ± 6.63	0.138 ± 0.026	0.9407

a typical chemical sorption process between the adsorbate and adsorbent (Aksu 2002). The experimental data were analyzed using the Langmuir and Freundlich models, which are expressed as follows:

Langmuir model:
$$q_e = \frac{q_{\rm m} K_{\rm L} C_e}{1 + K_{\rm L} C_e}$$
 (10)

Reundlich model: $q_e = K_F C_e^{1/n}$ (11)

where q_e (mg/g) is the equilibrium sorption of Pb(II), $q_{\rm m}$ (mg/g) is the maximum Pb(II) sorption corresponding to complete monolayer coverage, $K_{\rm L}$ (l/mg) denotes the affinity of binding sites and $K_{\rm F}$ and 1/n indicate the sorption capacity and intensity, respectively (Shuang et al. 2012). The equilibrium data fit the Langmuir model well, thus implying that sorbed Pb^{2+} and $PbNO_{3+}$ cations form monolayer coverage on the carbon surface. The sorption data of Mn/BC also fit the Freundlich model well, which is likely due to the heterogeneous nature of surface sites of Mn/BC involved in the Pb(II) uptake (Reddad et al. 2002). The fitted values of the Langmuir and Freundlich parameters are presented in Table 4. The maximum monolayer sorption (q_m) of Mn/BC at 298 K was five times larger than that of BC, which can be attributed to the larger number of surface hydroxyl groups and lower pH_{PZC} of Mn/BC. These findings indicate that the Mn/BC composite fabricated in the present study is an effective adsorbent for Pb(II) removal from aqueous solutions.

To further evaluate the sorption mechanism of Pb(II) on Mn/BC, sorption thermodynamics under different temperatures (283, 298, and 313 K) was studied. According to the Van't Hoff equation, the thermodynamic parameters (ΔH , ΔG , and ΔS) can be calculated using the sorption equilibrium constant ($K_{\rm F}$) obtained from the Freundlich isotherm (Wu et al. 2011) (Table 5).

$$\ln K_{\rm F} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{12}$$

$$\Delta G = -RT \ln K_{\rm F} \tag{13}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{14}$$

where ΔH is the change in enthalpy (kJ/mol), ΔS is the change in entropy (J/mol K), ΔG is the change in standard

Table 5 Thermodynamic parameters for sorption of Pb(II) on Mn/BC

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	$\Delta S (J/mol K)$
283	-9.00 ± 0.14	13.10 ± 0.75	78.27 ± 3.31
298	-10.60 ± 0.15	13.10 ± 0.75	78.92 ± 3.02
313	-11.33 ± 0.23	13.10 ± 0.75	78.22 ± 3.29

Gibbs free energy (kJ/mol), *T* (K) is the absolute temperature (K) and *R* is the gas constant (8.314 J/mol K). The negative values of ΔG at three temperatures verify the spontaneous nature of sorption of Pb(II) on Mn/BC. Moreover, the decrease ΔG value with the increase in solution temperature suggests that adsorption was more spontaneous at high temperature (Table 5). The positive value of ΔH (13.10 ± 0.75 kJ/mol) indicates that the sorption reaction is endothermic in nature. The positive value of ΔS shows the increasing randomness of sorbates and solutes during the sorption processes, which may be due to the sorbed Pb²⁺ and PbNO₃⁺-hydrated cations may displace a considerable number of water molecules (Lin and Teng 2002).

Conclusion

The present study demonstrated that the loading of HMO onto BC markedly increases Pb(II) uptake from aqueous solutions. In comparison with the original BC, the HMO–BC composite impregnated with 3.65 % Mn not only showed enhanced adsorption capacity for Pb(II) but also indicated an accelerated sorption rate for Pb(II). An increase in pH enhanced electrostatic interactions between Pb(II) and the Mn/BC surface. The negative value of ΔG and positive value of ΔH indicated that the Pb(II) sorption process is spontaneous and endothermic. Therefore, HMO-loaded BC is an effective adsorbent for removing Pb(II) from water.

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