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## Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: Adsorption behavior and mechanism

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### Abstract

Hydrous manganese dioxide (HMO) synthesized by redox of potassium permanganate and hydrogen peroxide was used as an adsorbent for Pb(II) removal. The specific surface area, pore volume and BJH pore diameter of the HMO were 79.31 m<sup>2</sup>/g, 0.07 cm<sup>3</sup>/g and 3.38 nm, respectively. The adsorption equilibrium at 298 K could be well described by the Langmuir isotherm equation with  $q_{\max}$  value of 352.55 mg/g. The negative values of  $\Delta G$  and the positive values of  $\Delta H$  and  $\Delta S$  indicated the adsorption process was spontaneous and endothermic. The pseudo second-order equation could best fit the adsorption data. The value of the calculated activation energy for Pb(II) adsorption onto the HMO was 38.23 kJ/mol. The uptake of Pb(II) by HMO was correlated with increasing surface hydroxyl group content and the main adsorbed speciation was PbOH<sup>+</sup>. The final chemical state of Pb(II) on the surface of HMO was similar to PbO. HMO was a promising candidate for Pb(II) removal from aqueous solution.

**Key words:** adsorption; mechanism; heavy metal; manganese dioxide

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### Introduction

Lead (Pb(II)) is extensively used in our daily life. Unfortunately, waste streams containing different levels of Pb(II) are often encountered in industries. Due to its high toxicity and non-biodegradability (Liu et al., 2008), Pb(II) pollution and its control have received great attention in recent years. Various processes have been employed to remove Pb(II) from solutions. Among the techniques, the adsorption method is commonly adopted due to its high efficiency, cost effectiveness and easy implementation. As a result, a great deal of natural and synthetic materials were developed and used as adsorbents for Pb(II) removal (Kozar et al., 1992; Inglezakis et al., 2002; Costodes et al., 2003; Agrawal et al., 2005; Han et al., 2007; Zhao et al., 2009; Dong et al., 2000; Wang et al., 2007; Oubagaranadin and Murthy, 2009; Kang et al., 2010; Shihabudheen et al., 2010; Xiong et al., 2011).

Among these Pb(II) scavengers, manganese oxides stood for the negative surface charge, large surface area, micro- or meso-porous structure and high affinity for heavy metal ions (Perret et al., 2000; Agrawal et al., 2005; Han et al., 2006; Xu et al., 2006; Liu et al.,

2008; Dong et al., 2010; Qin et al., 2011; Tiwari et al., 2011), especially, the hydrous manganese oxide (HMO) was regarded as an economic and selective sorbent for Pb(II) removal. Su et al. (2010) evaluated the properties of HMO as a sorbent for Pb(II) removal and observed that the extraction of Pb(II) could be enhanced by the synergetic effects of electrostatic interaction and inner-sphere complex formation. Su et al. (2009) also combined nanosized HMO within a porous polystyrene cation exchanger D-001, which resulted in a decrease of Pb(II) from 1.0 to below 0.01 mg/L. Moreover, an *in-situ* formed HMO, namely manganese dioxide formed *in-situ* (MOF), was found to have a great potential application in Pb(II) treatment. The mechanism of Pb(II) uptake by MOF was related to the formation of the inner-sphere complex (Qin et al., 2011). The available studies have investigated the performance of the HMO, but the mechanism of Pb(II) adsorption by HMO are not unanimous and much efforts needed to further explore the co-relation between HMO and the target heavy metals.

In the current study, the HMO was prepared using a new method and the adsorption behaviors of Pb(II) on HMO were evaluated. In addition, the adsorption mechanism was determined.

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## 1 Material and methods

### 1.1 Hydrous manganese oxide preparation

The HMO was synthesized by *in-situ* reduction of  $\text{KMnO}_4$  by  $\text{H}_2\text{O}_2$  using the cetyltrimethylammonium bromide (CTAB) as the template. The procedures were as following: 1.2 g CTAB and 1.816 g  $\text{KMnO}_4$  were dissolved in 60 and 30 mL of de-ionized water, respectively. Then the solution of  $\text{KMnO}_4$  and 30 mL  $\text{H}_2\text{O}_2$  (30%) were dropped slowly into the CTAB solution simultaneously under magnetic stirring. The  $\text{HNO}_3$  (1 mol/L) solution was added during the reaction to keep the solution pH at  $7.0 \pm 0.2$ . After reaction, the formed suspension was continuously stirred for 0.5 hr and aged at room temperature for 3 hr. The suspension was washed with ethanol and de-ionized water till no obvious bubbles. After filtration, the wet paste was dried at  $60^\circ\text{C}$  till a constant weight. The dried material appeared in the form of fine powder and was passed through a 200 mesh sieve for future use. All reagents used in this study were of analytical grade and were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd (China).

### 1.2 Analysis and characterization

The adsorbent was characterized using X-ray powder diffraction (XRD, PANalytical Co.), scanning electron microscopy (SEM, S-3000N Hitachi Co.) and nitrogen adsorption-desorption isotherms measurement by Brunauer Emmett Teller method (ASAP 2000, Micromeritics Co.).

The X-ray photoelectron spectroscopy (X-ray) photoelectron spectroscopy (XPS) measurements were carried out with an imaging photoelectron spectrometer (Kratos AXIS Ultra, UK), using the aluminum anode X-ray source with a monochromator ( $\text{Al } K\alpha$ ,  $h\nu = 1486.71 \text{ eV}$ ) or a dual anode ( $\text{Al/Mg}$  target). The X-ray source was run at a power of 225 W (15 kV and 15 mA). A hemispherical analyzer was employed with a multi-channel detector and scintillator fluorescence plate CCD imager. Wide-scan spectra were collected in the range from 0 to 1100 eV with pass energy of 160 eV. The high-resolution scans were conducted according to the peak being examined with pass energy of 40 eV. All binding energy values ( $E_b$ , eV) were determined with respect to C 1s line (284.6 eV) originating from adventitious carbon. The XPS results were collected in binding energy forms and fitted using the software of Vision (PR2.1.3) and Casa XPS (2.3.12Dev7).

### 1.3 Isothermal study

In the adsorption isotherm study, 0.01 g adsorbents were added into 100 mL solutions with different initial Pb(II) concentrations (12.59 to 53.96 mg/L). The solution pH and ionic strength were controlled at 4.0 and 0.001 mol/L  $\text{NaNO}_3$ . The isotherm study was conducted at 298, 308 and 318 K with an air bath. The flasks were shaken at 140 r/min for 48 hr. The solution pH was kept at  $4.0 \pm 0.2$ .

The uptake of Pb(II) at time  $t$  ( $q_t$ ) was calculated by Eq. (1):

$$q_t = \frac{V(C_0 - C_t)}{W} \quad (1)$$

where,  $C_0$  (mg/L) and  $C_t$  (mg/L) are the initial and equilibrium Pb(II) concentrations in solution, respectively,  $V$  (L) is the solution volume, and  $W$  (g) is the amount of adsorbent.

The adsorption data were fitted by the Langmuir (Eq. (2)) and the Freundlich (Eq. (3)) isotherms.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = k_F C_e^{1/n} \quad (3)$$

where,  $q_e$  (mg/g) is the equilibrium Pb(II) adsorption capacity,  $C_e$  (mg/L) is equilibrium concentration of Pb(II),  $q_{\max}$  (mg/g) is the maximum adsorption capacity,  $K_L$  (L/mg) is the Langmuir equilibrium constant,  $K_F$  is the Freundlich constant, and  $n$  is the Freundlich exponent.

### 1.4 Batch adsorption experiments

For kinetics study, 0.08 g adsorbents were added into 800 mL solutions with Pb(II) concentration of 25.22, 30.32 and 35.93 mg/L, respectively. The pH was kept at  $4.0 \pm 0.2$  and the mixture was shaken at 140 r/min. The samples were taken at different time intervals, filtered through a  $0.45 \mu\text{m}$  film and analyzed for the Pb(II) concentrations by an atomic absorption spectrophotometer (AA-6300, Shimadzu, Japan).

The pseudo second-order (Eq. (4)) model was used to investigate the adsorption behavior.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where,  $K_2$  is the pseudo second-order rate constant and  $t$  (min) is time.

To investigate the effects of pH, 100 mL of 50.29 mg/L Pb(II) solutions at various initial pH (2.0–6.0) were prepared in conical flasks. After 0.01 g adsorbent added into the solutions, the flasks were shaken at 140 r/min for 48 hr. The solution pH was measured and adjusted accordingly during the experiments using 0.1 mol/L  $\text{HNO}_3$  or 0.1 mol/L NaOH.

To determine the effects of ionic strength, 100 mL of 36.12 mg/L Pb(II) solutions at ionic strength ranged from 0 to 0.2 mol/L were prepared with  $\text{NaNO}_3$  in conical flasks. After 0.01 g adsorbent added into the solutions, the flasks were shaken at 140 r/min for 48 hr. The solution pH was kept at  $4.0 \pm 0.2$ .

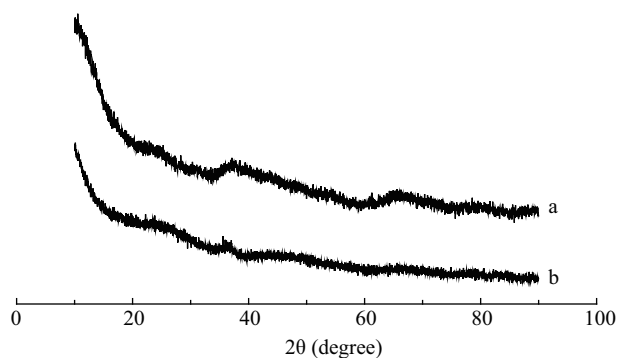
## 2 Results and discussion

### 2.1 Characterization of HMO

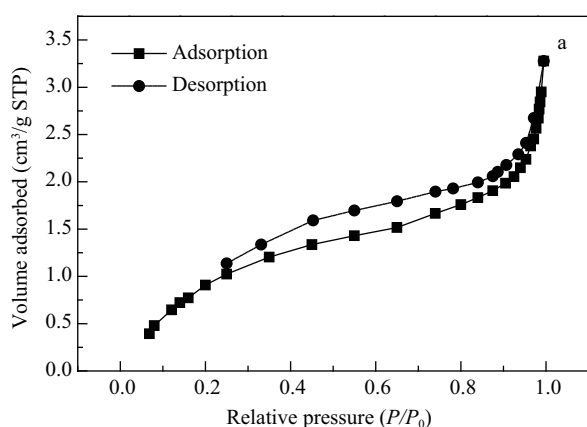
The HMO before and after Pb(II) adsorption are analyzed by the wide-angle XRD and the results are shown in

**Fig. 1.** Except for two broad bands, there were no obvious crystalline peaks detected from the prepared HMO, which demonstrated the amorphous characterization of the synthesized HMO. The result was in agreement with the characterization of the synthetic amorphous  $\delta$ -MnO<sub>2</sub> (Wang et al., 2007; Eren et al., 2009; Tiwari et al., 2011).

The nitrogen adsorption-desorption isotherms for the HMO are shown in **Fig. 2a**. The isotherms of HMO exhibited a typical type IV isotherm according to the



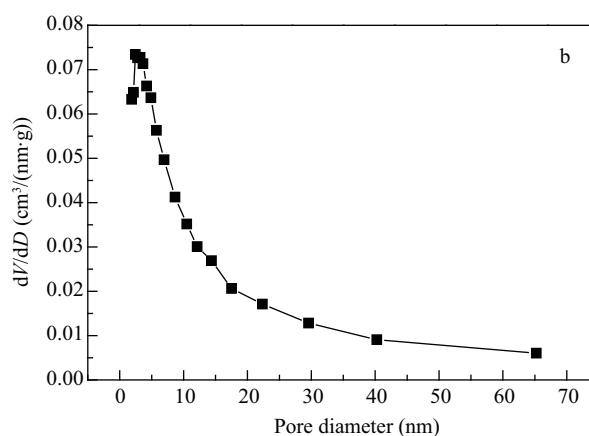
**Fig. 1** XRD patterns of hydrous manganese dioxide (HMO) samples: before (line a) and after (line b) Pb(II) adsorption.



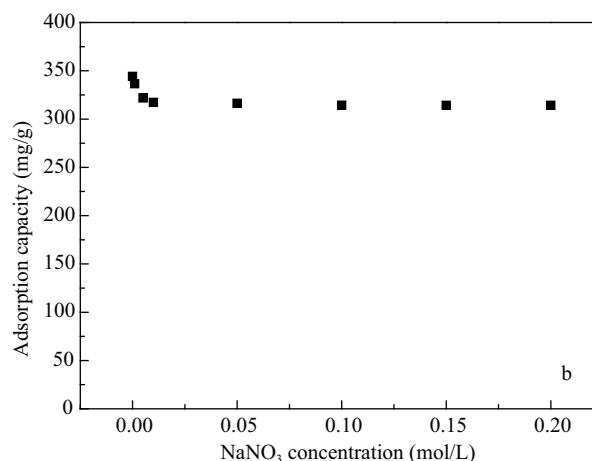
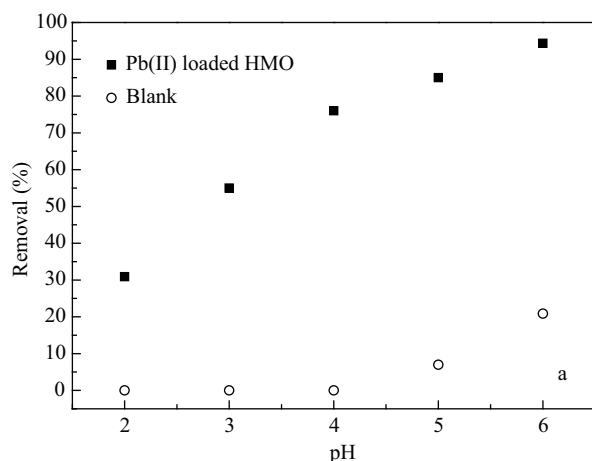
IUPAC classification with a nitrogen hysteric loop. This implied that the pores comprising the HMO were mostly mesoporous or macroporous (Huo et al., 1995; Morishige et al., 2003). The volume adsorbed for the isotherms increased obviously at a relative pressure ( $P/P_0$ ) of 0.3, indicating capillary condensation of nitrogen within the uniform mesoporous structure (Feng et al., 1997; Matos et al., 2003; Morishige et al., 2003). The synthesized HMO possessed specific surface area of 79.31 m<sup>2</sup>/g, pore volume of 0.07 cm<sup>3</sup>/g and BJH pore diameter of 3.38 nm. The pore size distribution analysis (**Fig. 2b**) indicated that the HMO had a narrow range of pore sizes (peak at 2.45 nm), which provided evidence for the mesoporosity of the framework of HMO.

## 2.2 Effects of pH and ionic strength

The effect of solution pH on Pb(II) removal is illustrated in **Fig. 3a**. It was clear that the uptake of Pb(II) was strongly affected by solution pH. At the initial Pb(II) concentration of 50.29 mg/L, the Pb(II) removal efficiency of HMO increased sharply from 30.90% to 94.35% with the pH rising from 2.0 to 6.0. The results of the blank



**Fig. 2** Nitrogen adsorption-desorption isotherms of the HMO (a) and pore size distribution for HMO (b).



**Fig. 3** Effect of pH (a) and ionic strength (b) on Pb(II) adsorption. Initial Pb(II) concentration 50.29 mg/L (a) and 35.95 mg/L (b), HMO 100 mg/L, 298 K, pH 4.0 for (b).

experiment indicated that over 20% of Pb(II) precipitated at pH 6.0 and there was little Pb(II) precipitated at solution pH less than 4.0. At pH over 5.0, the precipitation of Pb(II) expedited the removal of Pb(II). But to evaluate the adsorbing process, all the following batch adsorbing experiments were conducted at pH 4.0 to avoid the effect of Pb(II) precipitation.

The effects of ionic strength on Pb(II) adsorption onto HMO at pH 4.0 were determined. As shown in Fig. 3b, the increasing ionic strength (0.001 to 0.01 mol/L of NaNO<sub>3</sub>) caused little decrease in Pb(II) uptake by HMO from 344.17 to 314.22 mg/g. With the ionic strength increasing from 0.01 to 0.20 mol/L of NaNO<sub>3</sub>, only a negligible decrease of Pb(II) uptake by HMO was detected. These results indicated that the adsorption of Pb(II) on HMO was ionic strength independent and the adsorption mechanism of Pb(II) was inner-sphere complexation rather than ion exchange (Hayes et al., 1988; Zhao et al., 2010). The similar results also obtained for the removal of Pb(II) by manganese-modified natural sand, manganese oxide-coated bentonite and zeolite (Eren et al., 2009, 2011; Tiwari et al., 2011).

### 2.3 Adsorption isotherms

Adsorption isotherms are important for the description of the interaction of Pb(II) with HMO and critical in optimizing the use of the adsorbent. The adsorption isotherm of Pb(II) on the adsorbent are shown in Fig. 4. The adsorption data are fitted by the Langmuir and Freundlich equation and the calculated parameters are summarized in Table 1. It was shown that the Langmuir equation could well describe the adsorption isothermal behaviors with high correlation coefficients at different adsorption temperatures ( $R^2 = 0.993\text{--}0.997$ ). The maximum Pb(II) adsorption capacities ( $q_{\max}$ ) were 352.55, 432.62 and 473.62 mg/g at 298, 308 and 318 K, respectively, which was accordance with the experimental determined adsorption capacity ( $q_{\text{exp}}$ ) of HMO.

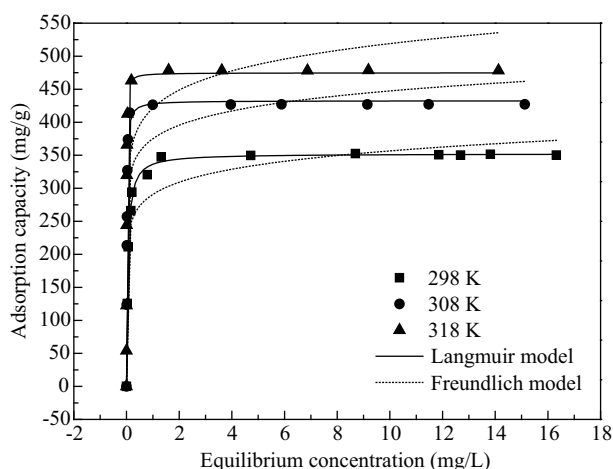


Fig. 4 Adsorption isotherms of Pb(II) at different temperatures. HMO 100 mg/L, pH 4.0.

### 2.4 Thermodynamic studies

The thermodynamic analysis of Pb(II) adsorption on adsorbent with experimental data of different temperatures was conducted. The change in the enthalpy ( $\Delta H$ ), Gibbs free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) were calculated according to the following Eq. (5):

$$\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

where,  $R$  (8.314 J/(mol·k)) is the universal gas constant and  $T$  (K) is the solution temperature.

The plot of  $\ln(q_e/C_e)$  versus  $1/T$  according to Eq. (5) was a straight line and the values of  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of the line.  $\Delta G$  could be calculated using Eq. (6):

$$\Delta G = -RT \ln\left(\frac{q_e}{C_e}\right) \quad (6)$$

A positive value of the  $\Delta H$  (205.41 kJ/mol) indicated that the adsorption of Pb(II) on the adsorbent was endothermic. The positive value of  $\Delta S$  (749.33 J/mol) reflected the randomness at the solid/liquid interface during the adsorption of Pb(II) on HMO. It was supported by the increasing adsorption of Pb(II) with the increase in temperature. The values of  $\Delta G$  at 298, 308 and 318 K were  $-17.35$ ,  $-26.41$  and  $-32.34$  kJ/mol, respectively. The negative  $\Delta G^0$  value increased with an increase in temperature, indicating that the spontaneous nature of adsorption was proportional to the temperature.

### 2.5 Adsorption kinetics

Figure 5 shows the adsorption kinetics of Pb(II) on the adsorbent. It clearly indicated that with the increase of initial Pb(II) concentration the uptake of Pb(II) also increased. Although the initial Pb(II) concentrations were different, the rate of adsorption had no clear difference in the initial phase. In the slower uptake phase, the percentage

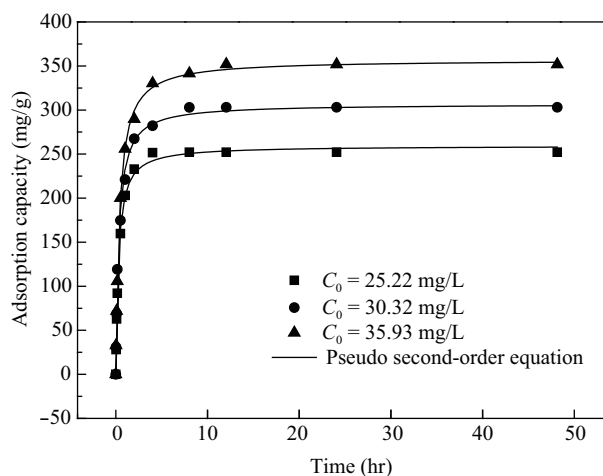


Fig. 5 Adsorption kinetics of Pb(II) at different concentrations. HMO 100 mg/L, 298 K, pH 4.0.

**Table 1** Isotherm parameters and  $q_{\text{exp}}$  for the adsorption system

Temperature (K)	$q_{\text{exp}}$ (mg/g)	Langmuir model			Freundlich model		
		$K_L$ (L/mg)	$q_{\text{max}}$ (mg/g)	$R^2$	$K_F$ ((mg/g)(L/mg) <sup>1/n</sup> )	$n$	$R^2$
298	352.49	20.88	352.55	0.997	291.60	0.089	0.883
308	427.19	88.05	432.62	0.995	375.06	0.076	0.814
318	478.65	202.35	473.62	0.993	428.72	0.087	0.790

of Pb(II) adsorption rose with the increasing agitation time and increasing initial Pb(II) concentration. Finally, the adsorption attained equilibrium at 6 hr or 8 hr for the initial Pb(II) concentrations of 25.22 or 30.32 and 35.93 mg/L, respectively. In general, the percentage of Pb(II) removal increased rapidly up to approximately 80% in 4 hr, thereafter rose slowly before attaining a constant value. The  $q_{\text{exp}}$  of HMO was 252.20, 303.14 and 351.94 mg/g at the initial Pb(II) concentrations of 25.22, 30.32 and 35.93 mg/L, respectively.

The pseudo second-order equation was used to investigate the adsorption behavior of the adsorbent. The plots are also shown in Fig. 5 and the calculated results are shown in Table 2. To the pseudo second-order equation, the calculated  $q_e$  were in accordance with the  $q_{\text{exp}}$  at the same temperature. All of the correlation coefficient values ( $R^2$ ) were over 0.996. This suggested that the Pb(II) adsorption on the HMO might involve chemisorption based on the assumption of the pseudo second-order equation.

## 2.6 Adsorption activation energy

To deepen the understanding of adsorption mechanism of Pb(II) on the HMO, the rate constants acquired according to the pseudo second-order equation at different temperatures were used to fit the parameters of the Arrhenius equation. The linear form of the Arrhenius equation is expressed as:

$$K_2 = k \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where,  $K_2$  is the rate constant value at different temperature obtained from pseudo second-order equation for the metal adsorption,  $k$  (g/(mg·hr)) is the temperature independent factor,  $E_a$  (kJ/mol) is the activation energy of the adsorption of Pb(II) onto the HMO.

According to the above procedure, the adsorption experiments were conducted with Pb(II) solution of 57.18 mg/L at 298, 308 and 318 K and the contact time was maintained at 48 hr. A plot of  $\ln K_2$  versus  $1/T$  yielded a straight line and  $E_a$  was calculated from the slope. The value of the  $E_a$  for Pb(II) adsorption onto the HMO was 38.23 kJ/mol, which suggested that chemical adsorption process dominate the adsorption process of the Pb(II) onto the surface of HMO (Onyango et al., 2004; Tahir and Rauf, 2003; Özcan et al., 2007; Unuabonah and Adebowale, 2007).

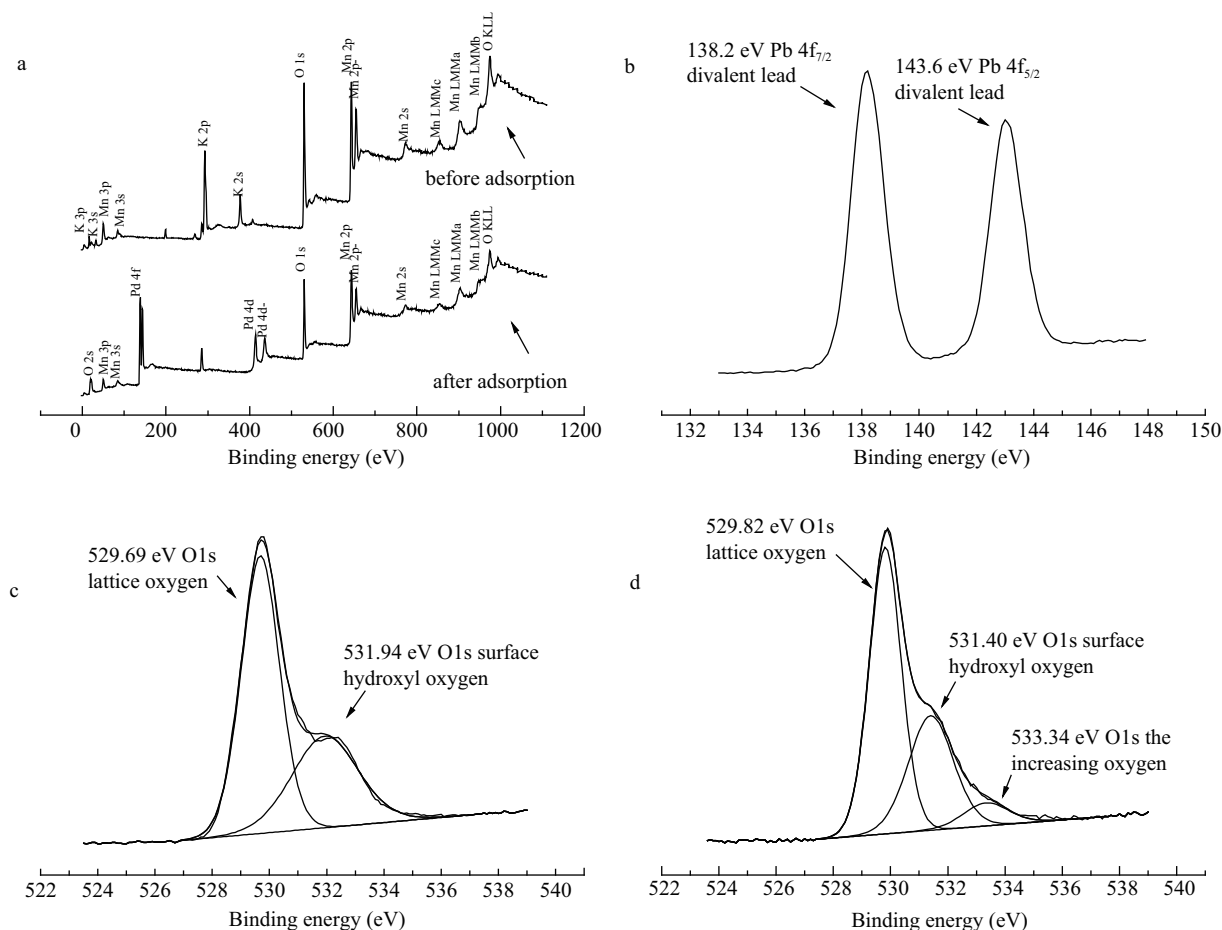
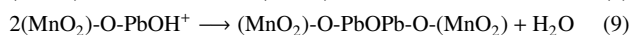
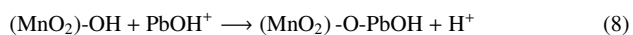
## 2.7 Adsorption mechanism

The surface elemental compositions and the existing chemical speciation of the elements of HMO before and after Pb(II) adsorption were further analyzed by XPS method and the spectra of the virgin and Pb-loaded of HMO are shown in Fig. 6. The strong peaks attributed to Mn and O were present in the XPS wide-scan spectrum of HMO before Pb(II) adsorption, while the strong peak of Pb appeared after Pb(II) adsorption in Fig. 6a. This confirmed the uptake of Pb(II), but the chemical speciation of Pb needed further detection. The high-resolution XPS spectra of Pb 4f obtained after Pb(II) adsorption is presented in Fig. 6b. The characteristic conjugated peaks of Pb(II) appeared clearly. The peak at 138.2 eV was assigned to Pb 4f<sub>7/2</sub> and the peak at 143.6 eV was assigned to Pb 4f<sub>5/2</sub>. The chemical valence of Pb on the HMO could be determined to be divalent thereafter. The binding energies of Mn were 642.1 and 642.3 eV before and after interaction of Pb(II) and the HMO. It was reported that the binding energies of Mn 2p<sub>3/2</sub> in MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> were 641.0, 641.5, 641.9 and 642.6 eV, respectively (Katsoyiannis and Zouboulis, 2004; Qin et al., 2011). In view of the typical reported spectra of the tetravalent Mn (Wagner, 1990; Han et al., 2006), the chemical valence of Mn in the HMO before and after Pb(II) adsorption could be assigned to Mn(IV) (Sagheer and Zaki, 2000). The high-resolution XPS spectra of O 1s were shown in Fig. 6c and d. The lower binding energy at 529.69 eV was the characteristic spectra of oxygen in the manganese oxides, which was assigned to the lattice oxygen. The broad band at 531.94 eV could be assigned to the oxygen of the metal surface hydroxyl group. The ratio of the integral area of the lattice oxygen and the total oxygen decreased from 63.65% to 59.58% before and after Pb(II) adsorption which indicated that the surface hydroxyl group content increased with the uptake of Pb(II).

On the other hand, the aqueous speciation of Pb was determined by the hydrolysis constant. The main speciation of Pb in the single element solution system at pH 4.0 would be Pb(II). While the pH value at surface was usually 1–2 unit higher than that of the bulk solution (Zhan and Zhao, 2003), the main speciation of Pb might turn into PbOH<sup>+</sup> under the experimental condition. According to the principle of ion-exchange and above results, the major pathways involved in the uptake of Pb(II) by HMO at pH 4.0 might be concluded in Reactions (8) and (9).

**Table 2** Experimental adsorption capacity and kinetic parameters for the adsorption systems

Temperature (K)	$C_0$ (mg/L)	$q_{exp}$ (mg/g)	Pseudo second-order equation		
			$K_2$ (g/(mg·min))	$q_e$ (mg/g)	$R^2$
298	25.22	252.20	$2.29 \times 10^{-4}$	259.43	0.996
298	30.32	303.14	$1.71 \times 10^{-4}$	310.58	0.996
298	35.93	351.94	$1.21 \times 10^{-4}$	356.86	0.996
298	57.18	353.21	$1.18 \times 10^{-4}$	362.98	0.996
308	57.18	406.59	$2.02 \times 10^{-4}$	411.42	0.997
318	57.18	439.76	$3.23 \times 10^{-4}$	442.08	0.996

**Fig. 6** XPS spectra of adsorbent. (a) XPS wide scan of the HMO; (b) XPS detailed spectra of Pb 4f<sub>7/2</sub> after Pb(II) adsorption; (c) XPS detailed spectra of O 1s before Pb(II) adsorption and (d) XPS detailed spectra of O 1s after Pb(II) adsorption.

According to Reaction (9), the final product of Pb(II) on the surface of HMO would be similar with the PbO and the high resolution XPS spectrum of O1s at 533.40 eV agreed with the value reported for PbO (Costodes et al., 2003).

### 3 Conclusions

The newly synthesized HMO was mesoporous  $\delta\text{-MnO}_2$ . Langmuir isotherm equation could fit well for the exper-

imental results and the maximum equilibrium adsorption capacity of HMO for Pb(II) were 352.49, 427.19 and 478.65 mg/g at 298, 308 and 318 K, respectively. The negative values of  $\Delta G$  and the positive values of  $\Delta H$  and  $\Delta S$  indicated the adsorption process was spontaneous and endothermic in the environment. Chemical adsorption process dominated the adsorption process. The uptake of Pb(II) was correlated with the increasing of the surface hydroxyl group content. The increased surface hydroxyl groups banded together with Pb(II) and the main speciation of Pb adsorbed by HMO was  $\text{PbOH}^+$ . The final chemical speciation of Pb(II) on the surface of HMO was similar with the compound of PbO.



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