Adsorption of Hg(II) from aqueous solution using functionalized hydrogel loaded with hydrous manganese dioxide particles

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ABSTRACT

In this paper, a high performance adsorbent (hydrous manganese oxides onto acylamino and hydroxyl functionalized hydrogel) containing manganese oxide was prepared by the cross-linking polymer; the novel composite adsorbent has an excellent adsorption for Hg(II) removal. The adsorbent was characterized by scanning electron microscopy and Fourier transform infrared analysis, the hydrogel adsorbent had a typical three-dimensional network structure, and manganese oxides particles were dispersed into the channel and pores structure. The adsorption of Hg\(^{2+}\) in water was tested by using the adsorbent. The results show that the adsorption isotherms were fitted well with Langmuir model, and the maximum Hg\(^{2+}\) adsorption capacity was 0.654 mmol g\(^{-1}\)\(C_0\) (131.2 mg g\(^{-1}\)\(C_0\)). The adsorption kinetics followed a pseudo-second-order equation, and the adsorption equilibrium can be reached in the first 120 min. The optimum pH of adsorption was determined to be 8.0. The desorption efficiency of 94% can be reached using 0.7 mol L\(^{-1}\) HCl as the regeneration agent. The results suggest that this material can be a promising adsorbent for Hg\(^{2+}\) removal in several industrial processes.

Key words | adsorption, composite adsorbent, Hg\(^{2+}\), manganese oxide

INTRODUCTION

For decades, mercury pollution has been arousing much attention because of its high toxicity and long-term existence in aqueous solution. Once released into the environment, mercury can accumulate in the food chain and cause neurological, nephrological, reproductive, and genetic disorders in humans (Valentino et al. 1995; Mearns et al. 2015). Consequently, it is essential to develop effective and economical methods to remove mercury from contaminated water.

Several methods concentrated on the removal of Hg(II) from wastewater have been reported, including chemical precipitation (Blue et al. 2010), ion exchange (Chiarle et al. 2000; Dong et al. 2011), membrane separation (Urgun-Demirtas et al. 2012) and adsorption (Natale et al. 2011; Khaloo et al. 2012). Among them, adsorption is an easy, economical and promising method for wastewater purification due to its high selectivity, simplicity of design and separation of various pollutants. The adsorbent plays a key role in the adsorption process.

Metal oxides exhibit high adsorption capacity, metal ions affinity, and the possibility of removing metals in trace concentration (GallegosGarcia et al. 2012). Manganese oxides are considered to be one of the most promising adsorbents for the removal of aqueous trace heavy metals such as Hg, Cd, Cr, Pb and As from drinking water as well as wastewater (Gadde & Laitinen 1988). The manganese oxides particles possess large surface area and adsorption capacity in nano scale level. However, nano-manganese oxides are prone to aggregation in aqueous solution, and the particles diameter approximately increased to 200 nm after aggregation. The increase of particles diameter lowers the heavy metals adsorption capacity of nano-manganese oxides. Thus, many organic framework materials such as resin (Donia et al. 2008), chitosan (Zhou et al. 2009) and silica gel (Chen et al. 2012) have been developed as the supporter for nano-manganese oxides particles recently. However, to our best knowledge, the adsorption of Hg by hydrogel supported with nano-manganese oxides has rarely been reported.

Through the literature review results, there are advantages and disadvantages of various adsorbents in the adsorption of heavy metal ions in water, as shown in Table 1. The chemical stability of the hydrogel is better than other adsorbents; it also has good selective adsorption

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to $\text{Hg}^{2+}$, and the number of recyclings is large after analyzing and separating, while the strength of the mechanism is better because of its net structure. It has important practical significance to study this type of adsorbent.

In this study, we investigated the adsorption behavior of $\text{Hg(II)}$ on composite adsorbent, which was prepared by loading of hydrous manganese oxides onto acylamino and hydroxyl functionalized hydrogel (HMO-AHFH). The adsorption equilibrium and kinetics and the effects of solution pH and coexisting cations on the adsorption process were studied in detail, and the mechanism of adsorption was further discussed.

**ADSORPTION MECHANISM**

The hydrogel was formed by the polymerization of hydroxyl groups of acrylamide and acrylic acid, and the hydrated manganese oxide particles were dispersed in the polymer. It is a new kind of composite polymer emulsion with excellent properties. The adsorption properties of the hydrogel are both inorganic and organic. The inorganic colloid is mainly carried out in two ways. $\text{Hg}^{2+}$ in the water can be directly adsorbed by ion exchange with the hydroxyl group in the colloid. $\text{Hg}^{2+}$ also can be hydrolyzed beforehand, and then capture the $\text{OH}$ in the surface of colloidal polymer to form hydroxyl complex. The adsorption process is as follows:

$$\begin{align*}
\text{Hg}^{2+} + n\text{H}_2\text{O} & \rightleftharpoons \text{Hg(OH)}_n^{(2-n)+} + n\text{H}^+ \\
\equiv \text{AOH} + \text{Hg(OH)}_n^{(2-n)+} & \rightleftharpoons \text{AHg(OH)}_{n-1}^{(2-n)+} = (1)
\end{align*}$$

In terms of organic colloid, the groups ($-\text{OH}$, $\text{C}=$ $\text{O}$, $\text{NH}_2$) in the polymer can be protonated under certain conditions, so it can exchange adsorption with heavy metals.

In the case of hydroxyl group of acrylamide monomer, the reaction is as follows:

$$\begin{align*}
\text{H}_2\text{C} - \text{N} - \text{OH} + \text{Hg}^{2+} & \rightleftharpoons \text{H}_3\text{C} - \text{N} - \text{OH} + 2\text{H}^+ \\
& \equiv \text{AOH} + \text{Hg(OH)}_2^{+} + 2\text{H}^+ = (2)
\end{align*}$$

**MATERIALS AND METHODS**

**Materials**

All reagents used in the experiment were analytical reagent grade and used without further purification. N-hydroxymethyl acrylamide (HMAm) and 2-hydroxyethyl acrylate (HEA) were purchased from Sigma-Aldrich Co. $\text{HgCl}_2$ was used to prepare the aqueous solution.

**Preparation of adsorbents**

4.57 g of HMAm, 36.96 mL of HEA and 100 mL of Milli-Q water were mixed in an amber laboratory bottle. The mixture was deaerated by purging with nitrogen gas, then placed in an insulation barrel at $-78 \degree C$ using dry ice and alcohol to keep the temperature constant. The mixture was irradiated to 20 KGY by $\gamma$-rays for 24 h. The obtained AHFH product was washed with Milli-Q and was dried at 50 $\degree C$ in a vacuum drying oven, and cut into cubes for use.

After that, 1.0 g of AHFH was added into 100 mL $\text{MnSO}_4\cdot\text{H}_2\text{O}$ solution (0.1 mol L$^{-1}$), then oscillated at 150 r/min, 50 $\pm$ 2 $\degree C$ for 12 h in an orbital shaker. Then, the $\text{MnSO}_4\cdot\text{H}_2\text{O}$ solution was discarded by filtration, and the residual AHFH solid was immersed into 50 mL $\text{KMnO}_4$ solution (0.1 mol L$^{-1}$) and stirred for 2 h. Finally, the product (HMO-AHFH) was washed with Milli-Q water until the effluent did not present a pink color, and dried at 50 $\degree C$.  

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Table 1: Comparison of $\text{Hg(II)}$ adsorption capacities of HMO-AHFH and other adsorbents

| Adsorbent                        | Adsorption capacity (mg. g$^{-1}$) | Conditions | Reference                                      |
|----------------------------------|-----------------------------------|------------|-----------------------------------------------|
| Titanate nanotubes               | 140                               | pH 10      | Ladeira & Ciminelli (2004), Lópezmuñoz et al. (2016) |
| Magnetic cobalt ferrite-reduced graphene oxide nanocomposites | 157.9                             | pH 4.6, 25 $\degree C$ | Zhang et al. (2014) |
| Resin loaded magnetic $\beta$-cyclodextrin bead | 88.43                             | pH 7.1, 50 $\degree C$ | Cui et al. (2015) |
| Organo-clay minerals             | 54.7                              | pH 4       | Phothitonmongkol et al. (2009)                |
| Manganese dioxide nanowhiskers   | 199.53                            | pH 5.5     | Lisha et al. (2010)                          |
Batch adsorption test

Hg(II) batch adsorption experiments were performed in 250 mL glass conical flasks containing 100 mL aqueous solution. The solution pH was adjusted with HNO₃ and NaOH solution to pH 5.5 (±0.2). The flasks were shaken at 160 ± 5 rpm in an orbital shaker at 30 ± 2 °C for certain periods. Suspensions were centrifuged afterwards at 4,000 rpm for 5 min, and the supernatants were determined by XGY-1011A atomic fluorescence spectrometer to evaluate the Hg(II) concentration. In addition the batch adsorption experiments were performed by varying effects of initial Hg(II) concentration (5–60 mg L⁻¹), contact time (0.5–8 h), initial pH (2.5–8.0) and ionic strength (0.01–0.2 M) in a similar manner as introduced above to determine interactions between Hg(II) and adsorbents. Effect of contact time on Hg(II) uptake was studied for 30 mg L⁻¹ Hg(II). The samples were collected at specific time intervals for residual Hg(II) analysis.

The equilibrium adsorption amounts of Hg(II) were calculated by the following formula:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

where \( q_e \) (mmol/g) is the amount of Hg(II) adsorbed per unit amount of adsorbents at equilibrium; \( C_0 \) (mmol/L) and \( C_e \) (mmol/L) are the initial and equilibrium concentration of Hg(II), respectively; \( V \) (L) is the volume of aqueous solution, and \( m \) (g) is the weight of adsorbents.

Hg(II) desorption

Desorption experiments were carried out using HCl solution at different concentrations (0.01–1.00 mol L⁻¹). The adsorbent was firstly reacted with 30 mg L⁻¹ Hg(II) at pH 5.5 (±0.2). Subsequently, the mixture was centrifuged and the supernatant was discarded, then the residual solid was washed with Milli-Q water, and the centrifugation process above was repeated several times to remove excess salts. The acid solution was added into the absorbent loaded with Hg(II) to initiate the desorption process. These desorption experiments were performed under the conditions of adsorbent dosage 0.02 g, desorption reagent 10 mL and desorption time 30 min. The suspensions were shaken for 30 min, then centrifuged. The concentration of Hg(II) in the supernatants was tested. The desorption efficiency was calculated by the following equation:

\[ R = \frac{C_f \times V_f}{C_0 V_0} \]  

where \( R \%) \) is the desorption rate of Hg(II); \( C_0 \) (mmol/L) and \( C_f \) (mmol/L) are the initial and desorption concentration of Hg(II), respectively; \( V_0 \) (L) and \( V_f \) (L) are the initial and desorption volume of Hg(II), respectively.

RESULTS AND DISCUSSION

Characterization of the adsorbents

The scanning electron microscopy (SEM) images of AHFH and HMO-AHFH samples are shown in Figure 1. As can be clearly seen from Figure 1(a), AHFH has a typical three-dimensional network structure. For HMO-AHFH, the manganese oxide particles were dispersed into the channels and pores of AHFH; the shape of the colloid which is not doped with manganese oxide particles is round or oval, belonging to the micron particle size range. After adding manganese oxide particles, the surface morphology changed obviously, belonging to the nanometer grade material.

The Fourier transform infrared (FTIR) spectra were used to analyze the presence of main adsorption functional groups. The FTIR spectra of the samples are presented in Figure 2. The broad band between 3,000 and 3,600 cm⁻¹ is related to the –OH stretching vibration of adsorbed water molecules. The band at 1,662 cm⁻¹ was attributed to the stretching vibration of C = O and C-N groups. The band at 1,407 cm⁻¹ was assigned to the stretching vibration of C = O and deformation vibration of OH. The band at 1,013 cm⁻¹ was attributed to the stretching vibration of –OH. Compared with AHFH, the band shapes of HMO-AHFH were similar, and no new adsorption peak was observed, indicating that the material structure did not change after HMO combination. Additionally, for AHFH, the band at 1,407 cm⁻¹ was moved for 22 cm⁻¹ toward the infrared region after HMO combination. In the vicinity of 1,662 cm⁻¹, a pair of scissors peak is the same as the result of the hydration of manganese oxide particles dispersed in the colloidal space; the original hydroxyl functional groups change the distance between the molecules, and the resulting stress changes. It was due to hydrous manganese dioxides binding with –OH group.

The Brunauer–Emmett–Teller (BET) analysis of the HMO-AHFH is shown in Figure 3. The nanometer particles have high specific surface area (numerical value 69.4 m²/g) and large pore size. The water soluble manganese oxide particles are dispersed in the three-dimensional lattice space.
Adsorption isotherm

To evaluate the adsorption capacity of HMO-AHFH for Hg(II), the equilibrium adsorption isotherms are of fundamental importance. The Langmuir isotherm models were used to analyze the isotherm constants and predict the maximum Hg(II) adsorption capacity. These models assume monolayer adsorption onto a homogeneous surface with a finite number of identical sites. It can be written in a form:

\[ q_e = \frac{Q_{\text{max}} K_a C_e}{1 + K_a C_e} \]  

where \( Q_{\text{max}} \) is the maximum adsorption capacity (mmol·g\(^{-1}\)), \( q_e \) is the equilibrium adsorption amount (mmol·g\(^{-1}\)), \( C_e \) is the equilibrium adsorbate concentration (mmol·L\(^{-1}\)) and \( K_a \) is the isotherm constant.

As shown in Figure 4, HMO-AHFH had higher adsorption capacity for Hg(II) than AHFH. The equilibrium data were analyzed by Langmuir isotherm models. Fitting determination coefficients (R\(^2\)) for both HMO-AHFH and AHFH are larger than 0.97, indicating that the Langmuir isotherm models are suitable for describing the adsorption behavior of Hg(II) on HMO-AHFH and AHFH. The fitting \( Q_{\text{max}} \) values of AHFH and HMO-AHFH were 0.109 mmol·g\(^{-1}\) and 0.654 mmol·g\(^{-1}\) (131.2 mg·g\(^{-1}\)), respectively.

The estimated \( q_m \) value was compared with that of some other reported adsorbents. It revealed that HMO-AHFH could be an efficient adsorbent for Hg(II) removal from water, although the efficiency comparison with other adsorbents is somewhat difficult due to difference of the experimental conditions used. However, it is obvious that HMO-AHFH is a better adsorbent for removal of Hg(II) than many others, excepting ferrite-reduced
graphene oxide nanocomposites and manganese dioxide nanowhiskers.

**Adsorption kinetics**

To describe the mechanism of the adsorption process of Hg(II) onto HMO-AHFH, the dependence of the Hg(II) adsorbed amount on reaction time was studied at initial Hg(II) concentration $30 \text{ mg·L}^{-1}$, pH $5.5 \pm 0.2$, $30 \pm 2 \text{ °C}$, and sorbent dose $2 \text{ g·L}^{-1}$.

Results (Figure 5(a)) reveal that a rapid uptake within the first 120 min was achieved. Then the uptake is stabilized after the first 240 min of agitation time, implying that the equilibrium has been reached.

The adsorption kinetics equation can be expressed as

$$q_e = k_t t^m$$

Equation (5) can be expressed in linearized form as

$$\ln q_e = \ln K_t + m \ln t$$

where $q_e$ is the amount of Hg(II) adsorbed onto HMO-AHFH at reaction time $t$ (mmol·g$^{-1}$), $t$ is the contact time (min), $m$ and $k_t$ are the constants.

The linearization plot of $\ln q_e$ versus $\ln t$ can reveal the rate limiting step of Hg(II) adsorption process. For pore diffusion to be the rate limiting step, the value of $m$ should have been 0.5 (Kundu & Gupta 2007). A plot of $\ln q_e$ versus $\ln t$ (Figure 5(b)) shows that the adsorption kinetics can be divided into two linear phases: rapid removal phase and relative steady phase. However, in the first fast removal phase, the value of $m$ was 0.306, which was lower than the 0.5, which implies that pore diffusion is not the rate limiting step. Therefore, the rate limiting step may be film diffusion.

**Effect of pH**

In the case of Hg(II) sorption behavior, the pH is an important parameter because the variation of proton concentration can strongly modify the chemical speciation of adsorbates as well as surface charge of sorbents. Hence, batch equilibrium experiments were carried out with a range of pH from 2.5 to 8.0.

Figure 6 demonstrates the amount of Hg(II) adsorbed under various initial pH conditions, and shows the increase
in Hg(II) adsorbed with rising pH from 2.5 to 8.0 and reaching a maximum at 8.0.

The variation of the adsorption capacities with pH could be reasonably explained on the basis of the surface charge of the adsorbent and the proton competition for binding sites.

At low pH values, the Hg(II) adsorption is inhibited, possibly due to the competition between Hg(II) ions and protons. Furthermore, the –OH groups of loaded manganese dioxides catch more positive charges at low pH values, and the electrostatic repulsions between adsorbates and Hg(II) ions could suppress the adsorption process. With the increase of solution pH, the competition of protons and the electrical repulsion force become weaker; thus the adsorption of metal ions increased. Similar trends were also reported for the adsorption of Hg(II) onto other adsorbents such as resin loaded magnetic β-cyclodextrin bead (Cui et al. 2015), mercaptoethylamine (Tran et al. 2015) and magnetic CoFe2O4-reduced graphene oxide (Zhang et al. 2014).

Hg(II) desorption

The desorption and regeneration property of the adsorbent was studied to make the sorption process more economical. HCl solutions with various concentrations (0.05 mol L\(^{-1}\) to 1.00 mol L\(^{-1}\)) were used to desorb the adsorbed Hg(II) from the HMO-AHFH. Figure 7 shows the effect of HCl concentration on Hg(II) desorption. A higher desorption efficiency was obtained at higher HCl concentration. It is observed that 0.7 mol L\(^{-1}\) could desorb more than 94% adsorbed Hg(II). As discussed before, under the acidic circumstances, the surface of HMO-AHFH would be protonated and the coordination between Hg(II) and surface –OH groups would be suppressed. These results were consistent with the research of the pH effect on the adsorption capacity. The good reproducibility suggested that HMO-AHFH is an economical and efficient adsorbent for Hg(II) polluted water purification.

CONCLUSIONS

The composite adsorbent (HMO-AHFH) with three-dimensional network structure was prepared for Hg(II) removal by dispersion of manganese oxides into AHFH. The prepared polymer composite adsorbent has good chemical stability and high mechanical strength, which can effectively degrade Hg\(^{2+}\) in the water.

The isotherm data were in accord with the Langmuir isotherm model with maximum adsorption capacities of 131.2 mg g\(^{-1}\). The optimum pH of adsorption was determined to be 8.0. The desorption efficiency of 94% can be reached using 0.7 mol L\(^{-1}\) HCl as the regeneration agent. Therefore, the prepared novel adsorbent HMO-AHFH could be considered as a promising absorbent for Hg(II) removal.

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