Adsorption Removal of Humic Acid from Micro-Polluted Water Using in Situ Manganese Dioxide

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Abstract

The adsorption removal of humic acid (HA) from micro-polluted water using manganese dioxide (MnO₂) formed in situ, which was prepared through the oxidation of MnSO₄ with K₂MnO₄, was investigated through batch experiments including kinetics, thermodynamics and isothermal adsorption models with online dosing mode. The results of analysis by the UV₅₀₀ and permanganate index CODₘₐ₅ methods indicates that HA removal reach 29.82% and 49.99%, respectively at amount of in situ MnO₂ 8 mg/L and contact time 2h. The kinetics data proves a closerfit to the pseudo-second order model. The isotherm data can be fit with Langmuir isotherm model, and maximum adsorption capacity achieved 27.20 mg/g which is near to the experimental value 26.38 mg/g. Moreover, the thermodynamic analysis shows the HA adsorption on in situ MnO₂ is a spontaneous and exothermic process. The excellent adsorption performance and low cost of the in situ MnO₂ can be considered as one of the effective options to remove HA from micro-polluted water.

Keywords: In situ MnO₂; Humic acid; Online dosing mode; Adsorption

Introduction

Humic acid (HA) is the primary organic compound in natural water, and the molecular weight of HA is between 300 and 3000. The HA content represents 60–90% of the total organic matter in water, and it exists in the form of colloidal particles in water [1,2]. Meanwhile, HA is one of the primary potential hazards in water [3,4].

Recently, studies on using environmental materials, which widely exist in nature, as adsorbents to remove pollutants from water have drawn great attention. Among these studies, progress has been made in applying manganese dioxide (MnO₂) as environmental materials [5,6]. The natural forms of MnO₂ include δ-MnO₂, γ-MnO₂, etc, and the properties of different forms of MnO₂ are also different. Researches on using MnO₂ for removing pollutants from water have mainly focused on oxidation and adsorption. Stone reported the redox reaction between a small molecular organic compound and MnO₂ [7]. The organic compound was adsorbed on the surface of MnO₂ to form a complex, and the chemical reaction process on the surface of MnO₂ was the rate-controlling step. Liu and Tang studied the effect of mineral MnO₂ on the removal of a dye (F, B) [8]. Their results showed that both illumination and a low pH could promote the degradation of the dye. Other researchers have also publicized the synergistic effect of MnO₂ on the oxidation and adsorption for heavy metal ions in water, such as chromium (Cr) and arsenic (As) [9,10].

On the subject of the adsorption of MnO₂, some research presented the effects of MnO₂ on the removal of uranium (VI) and thallium (I) ions under different conditions [11,12]. Bernard et al. [13] studied the primary factor that affected the adsorption of organic pollutants (e.g., HA, tannic acid, etc.) onto MnO₂ was the electrophoreticity of the surfaces of organic compounds. In addition, MnO₂ tended to adsorb organic pollutants with a positive surface charge. On the other hand, the results obtained from Liu et al. showed that δ-MnO₂ tended to adsorb HA with large molecular weights [14].

In situ MnO₂ is generated from K₂MnO₄ at the instant when K₂MnO₄ is reduced. The particles of in situ MnO₂ are small in size, and have a large specific surface area. Moreover, in situ MnO₂ is more active and has stronger adsorption ability compared with mineral MnO₂ [15,16]. Currently, studies on in situ MnO₂ have primarily focused on the removal of heavy metals from water, such as cadmium (Cd), strontium (Sr), and lead (Pb). However, there are few studies on using in situ MnO₂ to remove natural organic contaminants from micro-polluted water. Therefore, the aim of this study is to investigate the adsorption performance and behavior of HA on in situ MnO₂ using the on-line adding mode. The effects of different factors on the adsorption were studied. The adsorption process is described by different kinetic and isotherm models and thermodynamics to identify the adsorption mechanism. The results give us a better understanding of the adsorption behavior of HA onto in situ MnO₂.

Experimental

Materials

All the reagents used were analytical grade. The concentration of stock solution K₂MnO₄ and MnSO₄ was 4.6 mmol/L and 6.9 mmol/L, respectively. The raw water from East Lake of Wuhan, China was used in this investigation.

Adsorption batch experiments

100 mL of raw water were added into conical flasks of 250 mL. Equivalent amounts of MnSO₄ solution and K₂MnO₄ solution were added...
into each conical flask successively. The conical flasks were then sealed and stirred at the speed of 200 r/min and temperature 298K for a certain time. \(U_{254}\) and \(C_{OD}\) of each filtrate (0.45 μm pore filter) were measured. The effects of adsorption time, amount of \(\textit{in situ} \ MnO_2\), and solution pH on the adsorption were studied.

The kinetics studies were investigated with sorbent dosages 8 mg/L, initial COD\(_{in}\) (4.31 mg/L, 13.02 mg/L) and temperatures 298K with contact time ranging from 0 to 4.0h, and samples were taken at regular intervals from the reaction solution and filtered (0.45 μm pore filter) for \(U_{254}\) and \(C_{OD}\) analysis.

The adsorption isotherm experiments were studied by varying the initial HA concentration from 5.0 to 11.0 mg/L at temperatures 298K, 308K, and 318K.

All samples were prepared in duplicate, and average values of the replicated measurements were reported in all experiments. The amount of adsorbed HA, \(q\) (mg/g) was calculated using equation:

\[
q = \frac{V(C_0 - C_e)}{M}
\]

Where \(q\) is the amount of adsorbed HA, \(C_0\) is the initial HA concentration, \(C_e\) is the equilibrium HA concentration, \(V\) is the volume of the solution and \(M\) is the mass of the \(\textit{in situ} \ MnO_2\).

The HA removal efficiency (%) was considered in percent as

\[
\text{Removal} (%) = 100 - \frac{C_e}{C_0} \times 100
\]

**Analytical methods and instruments**

X-ray diffraction (XRD) were performed to confirm the crystal structure and identity using X-ray Diffracto meter (Rigaku D/MAX-RB, Japan) with Cu Ka radiation in the 2θ ranges of 5°–80° at a scan rate of 1°/min. The surface structures of samples were determined using scanning electron microscopy method (SEM, JSM-5610LV, and Japan). The characterization of the samples were carried out at their optimal working conditions.

A glass pH electrode (PHS-25, China) was used for pH measurement. The permanganate index was calculated as the chemical oxygen consumption using potassium permanganate solution as the oxidant, which is denoted as COD\(_{in}\) in accordance with the standards [17]. The UV\(_{254}\) absorbance was defined as the absorbance of some organic matter in water in the presence of ultraviolet light with a wavelength of 254 nm. UV\(_{254}\) can reflect the content of natural organic matter such as HA, molecules that consists of conjugated double bonds, and aromatic compounds with C=O functional groups. The UV\(_{254}\) was measured using a UV-1600 UV/V is spectrophotometer.

**Results and Discussion**

**XRD and SEM**

The XRD pattern of the \(\textit{in situ} \ MnO_2\) is shown in Figure 1. The diffraction peak of the \(\textit{in situ} \ MnO_2\) is relatively weak and wide, which indicates low crystalline structure. Analyzing the XRD pattern as a whole, only one peak is apparent, which suggests that the purity of the \(\textit{in situ} \ MnO_2\) was relatively high. Given that the diffraction peak is at 2θ = 37.17°, a comparison with powder diffraction patterns indicates that the nature of the manganate dioxide is \(\gamma\)-MnO\(_2\) [18].

Figure 2 shows the SEM image of the \(\textit{in situ} \ MnO_2\). It can be observed that the \(\textit{in situ} \ MnO_2\) particles are amorphous in nature, with a maximum diameter of approximately 120 nm. With an aging time of 30 min, the \(\textit{in situ} \ MnO_2\) is observed to coagulate into clusters. There is a tendency of increasing aggregation with increasing concentration of the \(\textit{in situ} \ MnO_2\).

**Effect of adsorption time**

Figure 3 displays the effect of time on adsorption of HA at a fixed initial UV\(_{254}\) 0.52 and initial COD\(_{in}\) 13.02 mg/L with sorbent dosages 8 mg/L at 298K. As the adsorption time increased, HA removal by UV\(_{254}\) and COD\(_{in}\) methods increased. When the adsorption process continued for 2h, HA removal by UV\(_{254}\) and COD\(_{in}\) methods were 24.00% and 44.69%, respectively. However, HA removal by COD\(_{in}\) method remained the same after 2 h, therefore, when the adsorption process continued for 2 h the adsorption of HA on \(\textit{in situ} \ MnO_2\) reached equilibrium.

According to adsorption theory, during the initial adsorption stage, there was no HA on the surface of and inside \(\textit{in situ} \ MnO_2\); however, the HA content in the solution was at its highest, and thus, HA could be rapidly adsorbed onto the surface of \(\textit{in situ} \ MnO_2\). As time increased, more HA was adsorbed on to \(\textit{in situ} \ MnO_2\) thus, the removal rates of HA also gradually increased. When all of the adsorption sites of \(\textit{in situ} \ MnO_2\) were saturated and in adsorption/desorption dynamic equilibrium, the adsorption capacity of \(\textit{in situ} \ MnO_2\) for HA would no longer increase as time increased, and thus, HA removal remained the same.

**Effect of amount of \(\textit{in situ} \ MnO_2\)**

As shown in Figure 4, when more \(\textit{in situ} \ MnO_2\) was added, HA removal exhibited a clear trend, in which they first increased and then leveled off; when the amount of added \(\textit{in situ} \ MnO_2\) was 8 mg/L, HA removal by UV\(_{254}\) and COD\(_{in}\) methods leveled off, which were 29.82% and 49.99%, respectively.

The curve is divided into three stages. During the first stage, the added amount of \(\textit{in situ} \ MnO_2\) was 0 – 6 mg/L and its content was low; therefore, the generated MnO\(_2\) could rapidly disperse into the solution.

In addition, the interaction between MnO₂ particles was relatively weak, and the HA content was relatively high at this time; thus, the adsorbent was “surrounded” by the adsorbate, and the adsorbent could fully adsorb the adsorbate. Consequently, as the amount of in situ MnO₂ increased, the removal of HA by UV₂₅₄ and CODₘₙ methods increased linearly. During the second stage, the concentration of in situ MnO₂ increased from 6 mg/L to 10 mg/L. HA removal continued to increase, though at a slower rate, which might be due to the increasing concentration of in situ MnO₂, which would generate a certain interaction between MnO₂ particles that affects the adsorption effect. During the third stage, the content of in situ MnO₂ increased from 10 mg/L to 20 mg/L, whereas HA removal did not increase significantly, instead tending to level off for the reason that polymerization between MnO₂ particles could occur with the continuously increasing concentration of in situ MnO₂. Thus, with increasing concentration, the number of the adsorption sites of in situ MnO₂ did not increase, and continuously increasing the amount of adsorbent had no impact on the adsorption effect.

**Effect of solution pH**

As shown in Figure 5, when the pH = 2.0, HA removal by UV₂₅₄ and CODₘₙ methods were 49.59% and 47.52%, respectively, which were higher than those under the alkaline condition. When the pH = 4.0, HA removal decreased rapidly. However, HA removal by UV₂₅₄ and CODₘₙ methods increased when the pH increased to 6.0 and above 6.0.

The pH affected the adsorption of HA on in situ MnO₂ by two aspects: on one hand, the pH variation changes the surface properties of in situ MnO₂, which in turn, affects the adsorption effect. On the other hand, the pH variation changes the existing forms of HA in the solution. When pH >6.0, HA existed in ionic forms (HA⁻ and A²⁻) in water; in situ MnO₂ could adsorb HA through van der Waals forces, hydrophobic interaction, and hydrogen bond interaction. The removal of HA was approximately 40% under this condition. When pH<4.0, HA existed in the form of HA molecules in water. Because HA is difficult to dissolve in water, the interaction between in situ MnO₂ and HA molecules was weakened, and therefore, under this acidic condition, the adsorption effect of in situ MnO₂ on HA decreased. In addition, under an acidic condition, the yield of MnO₂ also decreased, which decreased the amount of the adsorbent. When the pH = 2.0, the removal of HA were higher than those under the alkaline condition, due to the fact that under the strong acidic condition (pH<3.8), in situ MnO₂ was a strong oxidant and thus, could oxidize HA.

**Adsorption kinetics**

Adsorption kinetic models can be useful to determine the mechanism of adsorption and the efficiency of the adsorbents for the removal of pollutants. In this study, for the interpretation of the kinetic batch experimental data three different kinetic models were used: (1) the pseudo-first order kinetic model (Equation 3) [19-21], (2) the pseudo-second order kinetic model (Equation 4) [20,22,23] and (3) the intraparticle diffusion model (Equation 5) [20,24].

The pseudo-first order kinetic could be shown by Equation 3:

$$\ln(q_t - q_e) = k_1 t$$

Where, $q_t$ (mg/g) and $q_e$ (mg/g) are the amounts of HA adsorbed on in situ MnO₂ at equilibrium and adsorbed, respectively. $K_1$ (1/h) is the pseudo-first order rate constant. $K_1$ and $q_e$ were determined from the slope and intercept of the linear plot of ln($q_t - q_e$) against $t$, respectively. The pseudo-second order kinetic model can be expressed as [25]:

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

$$h = k_2 q_e^2$$  

Where $q_t$ is the amount sorbed at equilibrium (mg/g), $k_2$ is the equilibrium rate constant of pseudo-second order (g/mg h), and $h$ is the initial adsorption rate (mg/g h). These constants can be determined by plotting $t/q_t$ against $t$.

The intraparticle diffusion kinetic (Weber-Morris diffusion model) is shown by the following equation [26]:

$$q_t = k_3 t^{1/2} + C$$
Where, $K_d$ (g/mg h) is the rate constant of the interparticle diffusion kinetic model. The value of $C$ and $K_d$ are obtained from the intercept and slope of the linear plotted of $q_e$ against $t^{1/2}$, respectively.

It can be seen from the Figure 6 that the adsorption capacity of $in situ$ MnO$_2$ increased as the initial concentration of HA increased. When the initial HA concentration increased from 4.31 mg/L to 13.02 mg/L, the $q_e$ of HA adsorption on $in situ$ MnO$_2$ increased accordingly from 24.08 mg/g to 27.52 mg/g.

The adsorption of HA on $in situ$ MnO$_2$ is classified into three stages: rapid adsorption stage, slow adsorption stage, and adsorption equilibrium stage. The rapid adsorption stage refers to the period that was within 30 min after $in situ$ MnO$_2$ was added, where $q_e$ reached 73.96% of the $q_m$. At this stage, $in situ$ MnO$_2$ was just added into the HA solution, and there were large amounts of adsorption sites on the surface of $in situ$ MnO$_2$. Additionally, the amount of HA in the solution was at its greatest. The second stage was the slow adsorption stage, at which time, large amounts of HA molecules had already been adsorbed onto the surface of $in situ$ MnO$_2$, though adsorption had not reached equilibrium. $in situ$ MnO$_2$ continued to adsorb HA in the solution; however, the adsorption rate was far slower than that during the first stage. The third stage was the equilibrium adsorption stage; when the adsorption process continued for more than 1 h (Figure 6), large amounts of HA had been adsorbed onto the surface of $in situ$ MnO$_2$. Additionally, adsorption had essentially reached equilibrium. Therefore, the adsorption of HA on $in situ$ MnO$_2$ was in adsorption/desorption dynamic equilibrium during this stage, and hence, the adsorption capacity would no longer increase as the adsorption time increased.

Pseudo-first order kinetics (Figure 7a) and pseudo-second order kinetics (Figure 7b) were used to fit the process of the adsorption of HA on $in situ$ MnO$_2$. Table 1 lists the obtained related parameters. The values of $R^2$ from the pseudo-second order kinetics were 0.9999 and 0.9891 at different initial COD$_{Mn}$, and the adsorption process of HA on $in situ$ MnO$_2$ fitted more with the pseudo-second order kinetics compared with the pseudo-first order kinetics. The $q_e$ obtained from the pseudo-first order kinetics was 7.70 mg/g and 15.52 mg/g at different initial COD$_{Mn}$. However, the $q_e$ obtained from the pseudo-second order kinetics was 24.01 mg/g and 27.20 mg/g, respectively. From the comparison with the $q_e$ obtained from the experiment values (24.08 mg/g and 26.38 mg/g), it was more reasonable to use pseudo-second order kinetics to describe the adsorption process of HA on $in situ$ MnO$_2$.

An internal mass-transfer model, the Webber-Morris model, was used to further analyze this adsorption process. In the Webber-Morris pore diffusion model, if pore diffusion is a rate-controlling process, then $q_t$ and $t^{1/2}$ should satisfy a linear relationship, where the straight line passes through the origin point [25,27]. Figure 7c shows the relationship and fitting curves of $q_t$ and $t^{1/2}$. The values of $R^2$ of the adsorption process with different HA concentrations obtained from Webber-Morris model were 0.8044 and 0.9271 (Table 1). In addition, the straight line did not pass through the origin, which indicates that the internal diffusion process was not the only rate-controlling process; but there might be other rate-controlling processes [27].

### Adsorption isotherms

Langmuir and Freundlich, isotherms models are applied in this study. Langmuir isotherm is assumed that adsorption is a monolayer adsorption and the maximum adsorption occurs when molecules adsorbed on the surface of sorbent form a saturated layer. The Langmuir equation is

$$ q_m = \frac{q_m b C_e}{1 + b C_e} \quad 7 $$

Where $q_m$ is the amount sorbed at equilibrium (mg/g), $C_e$ is the equilibrium concentration (mg/L), $q_m$ is the maximum adsorption capacity (mg/g), and $b$ is the adsorption intensity or Langmuir coefficient related to the affinity of the binding site (L/mg).

The Freundlich isotherm can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and is expressed by the following equation:

$$ q_e = K_f C_e^{1/n} \quad 8 $$

Where $K_f$ and $1/n$ are the constants that are related to the adsorption capacity and the adsorption intensity, respectively. This equation can be rearranged in the linear form by taking the logarithm of both sides as

$$ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad 9 $$
The values of $K_e$ and $1/n$ can be calculated by plotting $\ln q_e$ against $\ln C_e$. As shown in Figure 8, the adsorption capacity of in situ MnO$_2$ increased as the initial concentration of HA increased. When the initial concentration of HA increased to 10 mg/L, the adsorption capacity of in situ MnO$_2$ slowly leveled off.

Figures 9a and 9b represent the Langmuir and Freundlich adsorption isotherm curves of HA on in situ MnO$_2$ at temperatures 298K, 308K, and 318K. Table 2 shows the parameters of the curves. The values of correlation coefficients $R^2$ show the adsorption behavior of HA on in situ MnO$_2$ fits more with the Langmuir model than Freundlich model, which is consistent with the conclusion obtained from the study by Zhang [28].

It can be seen from Table 2 that when using the Langmuir isothermal adsorption model, the maximum adsorption capacity of in situ MnO$_2$ for HA ($q_m$) decreased as the temperature increased; at 298K, $q_m$ was as high as 161.03 mg/g; however, when the temperature reached 318K, $q_m$ was only 36.66 mg/g because adsorption is an exothermic process, and temperature increases can cause the adsorption/desorption equilibrium to shift towards the desorption direction.

### Adsorption thermodynamics

To shed light on the HA adsorption on in situ MnO$_2$, the adsorption free energy ($\Delta G^0$), standard enthalpy ($\Delta H^0$) and standard entropy ($\Delta S^0$) were also calculated from the adsorption of HA on in situ MnO$_2$ at various temperatures. Based on thermodynamic theory, the basic relationship is shown as the following Equations 10 and 11, respectively:

$$\ln \frac{Q}{C_e} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

Where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature (K). Thus, $\Delta H^0$ and $\Delta S^0$ were obtained from the slope and intercept of the line plotted by $\ln(Q/C_e)$ versus $1/T$, respectively.

Figure 10 show the relationship curves of $\ln q_e/C_e$--$q_e$ and the obtained thermodynamic parameters were listed in Table 3. The free energy ($\Delta G^0$) of the adsorption at all temperatures in the current study was negative, indicating that the adsorption process was spontaneous. The negative enthalpy change ($\Delta H^0$) suggested that the adsorption of HA on in situ MnO$_2$ was an exothermic reaction, which was in accord with the decreasing adsorption capacity associated with increasing adsorption temperature. Also, the negative values of entropy ($\Delta S^0$) proposed decreased randomness at the solid-solution interface during the adsorption HA onto in situ MnO$_2$ surface, and the negative entropy indicated that the mobility of HA onto the surface of in situ MnO$_2$ became more restricted as compared with that of aqueous solution. It also showed that the driving force of HA adsorption on in situ MnO$_2$ was due to an enthalpy change rather than an entropy effect.

### Conclusions

In situ MnO$_2$ exhibits a good adsorption effect on HA in micro-polluted water. When the added amount of in situ MnO$_2$ is 8mg/L and the adsorption time is 2 h, the removal of HA by UV$_{254}$ and COD$_{in situ}$ methods can reach 29.36% and 49.99%, respectively. The adsorption kinetics of HA onto in situ MnO$_2$ can be well described by the pseudo-secondorder reaction model. Furthermore, the Langmuir model appears to fit the experimental data better than the Freundlich models for describing the adsorption behavior of HA from water on in situ MnO$_2$. The adsorption thermodynamics results suggest that the process of HA adsorption on

![Figure 8: Adsorption capacities vs. initial HA concentration (pH = 8.0; adsorption time 2 h; amount of in situ MnO$_2$ 8mg/L)](image)

**Figures 9:**

(a) Linearized Langmuir isotherm curves; (b) Linearized Freundlich isotherm curves

**Table 1:** The parameters of pseudo-first-order, pseudo-second-order and Weber-Morris diffusion model kinetics

<table>
<thead>
<tr>
<th>Initial COD$_{in situ}$ (mg/L)</th>
<th>pseudo-first-order</th>
<th>pseudo-second-order</th>
<th>Weber-Morris diffusion model</th>
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<tbody>
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<td>$q_m$ (mg/g)</td>
<td>$k_1$ (1/h)</td>
<td>$R^2$</td>
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<td></td>
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</table>

in situ MnO₂ is a spontaneous and exothermic process. Because of low cost, eco-friendly, non-toxicity and adsorption capacity of in situ MnO₂, this novel adsorbent can be considered as one of the effective options to remove HA from micro-polluted water. Moreover, this study can provide scientific bases for the processes that use enhanced coagulation to remove HA from micro-polluted water.

Even so, some directions and research need to be carried out in future, these issues include: (1) influences of the nature micro-polluted water and the HA rich surface waters for the in situ MnO₂, (2) evaluation of natural organic matter (NOM) removal and disinfection by-product (DBPs) control by in situ MnO₂, (3) feasible technological strategies using in situ MnO₂ to enhance the removal of NOM and to minimize DBPs formation, (4) assessment of a plant-scale application of in situ MnO₂ combined with coagulant to enhance coagulation on the removal of NOM.

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References


