Factors influencing hydroquinone degradation in aqueous solution using a modified microelectrolysis method

Tong Li, Tingting Li, Houfeng Xiong and Donglei Zou

ABSTRACT

The discharge of hydroquinone (HQ), an important chemical raw material, to natural waters poses different ecological threats to aquatic organisms. In this study, we investigated the removal performance of traditional and modified microelectrolysis methods in aqueous solutions. The traditional microelectrolysis packing was modified by adding manganese (Mn), zinc (Zn), and copper (Cu) powder as additives. The factors affecting the removal performance of HQ, such as catalytic metal type, mass fraction of additive, reaction time, and initial pH, were examined. The results showed that the Mn modified packing exhibited the best performance compared to Zn and Cu powder. The removal rate of HQ using Mn modified packing can reach 94% after 4 h. In addition, 9% of Mn packing has a higher removal rate than other mass fractions. The acidic solution pH shows a more favorable degradation than a neutral and alkaline solution. The intermediates of HQ degradation by modified microelectrolysis were identified and then the pathway of HQ degradation was proposed. Our result indicates that Mn as catalytic metal holds promising potential to enhance HQ removal in water using the microelectrolysis method.

KEYWORDS | hydroquinone, manganese, mechanism, microelectrolysis

INTRODUCTION

Hydroquinone (HQ) is an important chemical raw material in the manufacture of anthraquinone, azo dye, cosmetics, and photographic developer in the photosensitive material industry (Hu & Lu et al. 2009; Vilius & Chen et al. 2014). Meanwhile, HQ is widely applied as inhibitor, rubber antioxidant, and food antioxidant. Therefore, it exists widely in industrial effluents, such as the waste from oil refineries, rubber, and pharmaceutical industries (Zou & Ma et al. 2014). Owing to its high-potential for toxic effect on aquatic organisms and persistence in water, the discharge of HQ to natural water causes different threats to human health and the ecological environment (Yıldız & Gönülşen et al. 2005). Therefore, there is an urgent need to treat HQ in wastewater.

To date, the treatment technologies of HQ in wastewater include activated carbon adsorption, electrochemical oxidation, ozone oxidation, sequencing batch reactor, photocatalysis, and Fenton reaction (Zazo & Casas et al. 2005; Suresh 2011; Etesami & Karoonian et al. 2013). However, these methods are often very costly and the operation conditions of these methods are relatively complex. Compared to these methods, microelectrolysis has many advantages, such as simple operation, sufficient decolorization, environmental friendliness, and low cost. Microelectrolysis also features no chemical addition and energy input to the system, as in the cases of coagulation and electrolysis (Wu & Kong et al. 2005; Yang 2009; Ruan & Liu et al. 2010; Ren & Wu et al. 2011). This technology has been widely used in the pre-treatment of industrial wastewater, such as petrochemical, acrylic fiber, olive mill, electroplating, and pharmaceutical wastewater (Yang & Xu et al. 2004; Cheng & Xu et al. 2007; Qin & Li et al. 2011; Lai & Zhou et al. 2012).

The basic principle of the microelectrolysis method involves the microelectrolysis reaction between iron and activated carbon, the main components that cause an electrolytic reaction (Lai & Zhou et al. 2012). Wastewater serves as the electrolyte solution during the microelectrolysis process. In addition, there are many other decontamination effects including electrochemical reaction, oxidation-reduction, physical adsorption and flocculation (Yang & Xue et al. 2009; Lai & Zhou et al. 2012). When a
mixture of iron and activated carbon is in contact with wastewater, macroscopic galvanic cells are formed between the particles of iron and carbon. Meanwhile, microscopic galvanic cells are also formed in the interior of the iron powder because of cementite (Lai & Zhou et al. 2012). Products released from the galvanic cell reaction include the hydroxyl radical (OH), Fe (II), and hydrogen peroxide (H$_2$O$_2$), all of which have high reactivities to degrade contaminants (Yang 2009). The electrode reaction is as follows (Ren & Wu et al. 2011):

$$\text{Fe} - 2e \rightarrow \text{Fe}^{2+}$$  \hspace{1cm} \text{E}^0(\text{Fe}^{2+}/\text{Fe}) = -0.44\text{V}(\text{anode}) \quad (1)$$

$$2\text{H}^+ + 2e \rightarrow \text{H}_2$$  \hspace{1cm} \text{E}^0(\text{H}^+/\text{H}_2) = 0.00\text{V}(\text{cathode, without oxygen}) \quad (2)$$

$$\text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O}$$  \hspace{1cm} \text{E}^0(\text{O}_2) = 1.22\text{V}$$ (cathode, with oxygen and in acid solution) \quad (3)$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^-$$  \hspace{1cm} \text{E}^0(\text{O}_2/\text{OH}^-) = 0.41\text{V}$$ (cathode, with oxygen, in neutral to alkaline solution) \quad (4)$$

It is noted that H$_2$O$_2$ is also generated at the cathode in acid condition. The amount of H$_2$O$_2$ is increased under the influence of Fe$^{2+}$ in acidic solution. OH and Fe$^{3+}$ are then generated as products of the Fenton reaction. OH acts as a non-selective, strong oxidant to oxidize the organic pollutants in wastewater (Ren & Wu et al. 2011). In addition, coagulation by Fe (III)-hydroxides also occurs in the system. The hydroxides are released by oxidation and precipitation of Fe$^{2+}$ from the anode and they can capture pollutants from the solution (Ren & Wu et al. 2011).

However, as a pre-treatment technology for industrial wastewater, traditional microelectrolysis does not always exhibit high-removal performance for organic pollutants (Yang & Xu et al. 2004; Cheng & Xu et al. 2007; Lai & Zhou et al. 2012). Since manganese (Mn), zinc (Zn), and copper (Cu) metals have high-catalytic activity (Lu & Yang et al. 2014; Chen & He et al. 2014), the purpose of this study is to modify traditional microelectrolysis packing by adding different amounts of Mn, Zn, and Cu as additives. We investigated the degradation kinetics of HQ with different parameters using modified packing. In addition, the mechanism of HQ degradation during microelectrolysis has been explored in the present study.

**Materials and Methods**

**Chemicals**

HQ purchased from Beijing Chemical Works (Beijing, China) was used as received. Activated carbon powder, iron powder, Mn powder, Zn powder, and Cu powder (Tianjin Guangu Chemical Research Institute, Tianjin, China) were of analytical grade. Methyl alcohol, acetic acid, and dichloromethane (Shanghai Xingke Biochemistry Ltd., Shanghai, China) were of chromatographic grade. Clay was in 100 sieve mesh.

**Chemical analysis**

The aqueous concentration of HQ was analyzed using high-performance liquid chromatography (HPLC; Agilent 1100) with a C18 column. The mobile phase was 50% (methanol): 50% (0.2% acetic acid) and flow rate was 1.0 mL min$^{-1}$. The wavelength of 277 nm was set for the HQ detection. Intermediates of HQ during microelectrolysis were analyzed using gas chromatography-mass spectrometry (GC-MS) with an SE-54 capillary column (50 m × 0.53 mm × 1.0 μm). The column temperature started at 60 °C for 2 min and then ramped up to 300 °C for 10 min with an increased temperature rate of 20 °C·min$^{-1}$. The carrier gas was helium with the flow rate of 1 mL·min$^{-1}$. Full-scan mode was used for intermediate product identification.

**Characterization**

The morphology and structure of the packing were observed by scanning electron microscopy (SEM, HITACHI SU8000). X-ray diffraction (XRD) patterns were recorded from 20 to 80° (2θ) with Cu-Kα radiation (λ = 0.154 nm). All measurements were carried out at room temperature (25 ± 2 °C).

**Preparation of microelectrolysis packing**

Four different kinds of microelectrolysis packing were prepared in this study, including one traditional and three modified packing types. The specific preparation methods were as follows. First, the traditional packing was made of iron powder, activated carbon powder and clay at the mass ratio of 6:1:3. Then, these powders were mixed thoroughly. Second, the mixture was swung with water to form granular packings. We dripped some water into the mixture and swung the mixture circularly to generate...
small granular packings. Then, we continued to drip water onto the surface of the small granular packings and swung them in the powder. We repeated the above process to make the particles bigger and bigger. The diameter of the granular packings ranged from 3 to 10 mm. Third, the packings were heated in the oven under 50°C. Finally, the packings were put into a muffle furnace at 300°C for 2 h. On the basis of the traditional packing, iron powder was partly replaced by three different additives (i.e., Zn, Cu, and Mn powder), respectively. Then, three different modified packings were prepared.

HQ degradation experiment

A certain mass of each packing was weighed and transferred into four beakers. Then, 120 mL DI water containing HQ (1,000 mg·L⁻¹, initial pH = 3) was added into the four beakers. After that, the mixture was oscillated at 25°C. By doing this, HQ reacted with the packings for several hours to determine the removal rate of HQ. The residual concentration of HQ was measured every hour by HPLC. Changes of solution pH were also monitored every hour. At the same time, intermediates of HQ degradation were analyzed during the reaction. We also changed the mass fraction of the additive and initial pH of the HQ solution, and repeated the experiment above.

The activated carbon in the packings adsorbs HQ from wastewater. To make sure that microelectrolysis degraded the HQ and was not just a simple case of adsorption, an adsorption control experiment was conducted. Activated carbon was put into a beaker, and the mass of the carbon was equal to that in the microelectrolysis packings. Then, 120 mL DI water containing HQ (1,000 mg·L⁻¹, initial pH = 3) was added into the beaker. The mixture was oscillated at 25°C, and the residual concentration of HQ was measured every hour by HPLC.

All the experiments were carried out at least in triplicate.

RESULTS AND DISCUSSION

Effect of packing mass on HQ removal rate

We investigated the effect of packing mass in aqueous solution on HQ removal performance. Different masses of traditional packing were added into 120 mL DI water containing HQ (1,000 mg·L⁻¹, initial pH = 3). As shown in Figure 1, the HQ removal rate rises gradually with the increase of packing mass. When the mass is less than 3.3 g, the HQ removal rate increases significantly with packing mass. After that, the HQ removal rate changes little. It is because more galvanic cells are generated in the solution if more packing is added. The HQ removal rate also rises correspondingly. However, an excess of packing often produces large amounts of Fe²⁺. The excessive Fe²⁺ can reduce the concentration of OH⁻ and influence HQ degradation (Wang & Chu et al. 2014). Therefore, the optimal packing mass is selected at 3.3 g for the rest of the experiments.

Effect of additive type on HQ removal rate

Because microelectrolysis exhibited high-removal performance in the acidic solution (Ren & Wu et al. 2011), the initial pH was adjusted to 3. The initial concentration of HQ was 1,000 mg·L⁻¹. The mass fraction of additive in each kind of modified packing was 12%. It can be seen from Figure 2 that the packings tested have HQ-removal performance to different extents. The removal rate of HQ using traditional packing is about 10% higher than that by simple activated carbon adsorption. This result suggests that not only adsorption, but also degradation reactions, exist during the process. Compared to traditional packing, the removal performance of HQ by Mn modified packing exhibits the best performance. The electrode potentials of Mn, Zn, Fe, Cu, and H are −1.18 V, −0.76 V, −0.44 V, +0.34 V and 0.00 V, respectively. Fe acts as reductant and H⁺ acts as oxidant in traditional packing and Cu modified packing. In Mn modified packings, Mn acts as reductant and Fe²⁺ acts as oxidant. Analogously, in Zn modified packing, Zn
acts as reductant and \( \text{Fe}^{2+} \) acts as oxidant. It can be seen that the potential difference between Mn and Fe is the highest, while the potential difference between Zn and Fe is the lowest. Therefore, the experimental results in Figure 2 show the superiority of Mn and the inferiority of Zn. The removal rate of HQ using Mn modified packing can reach 94% after 4 h, whereas it is 52% for the traditional packing. Therefore, this study selected Mn modified packing for the rest of the experiments.

**Effect of the mass fraction of Mn on HQ removal rate**

We tested the effect of the mass fraction of Mn (i.e., 3, 6, 9, and 12%) on HQ removal performance. The initial pH of HQ was 3 and the initial concentration was 1,000 mg L\(^{-1}\). As shown in Figure 3, the best removal performance was observed at 9% of Mn. The removal effect of packing added to the system at 9–12% of Mn was almost the same. The similar removal rates indicate that at 9% of Mn, the packing is saturated. The reason is because the quantity of Fe/Mn redox couples is not enough if the content of Mn in packing is less than 9%. Therefore, increasing Mn content can improve HQ removal performance. The removal rate can reach 98.55% after 4 h using 9% of Mn modified packings. But compared with HQ content, the quantity of Fe/Mn redox couples is too much if the content of Mn goes up to 12%. Therefore, packing containing 9–12% of Mn obtain a similar HQ removal rate.

**Effect of reaction time on HQ removal rate**

The length of reaction time has a significant influence on the HQ removal rate (Yang & Xu et al. 2004; Cheng & Xu et al. 2007; Lai & Zhou et al. 2012). As shown in Figures 2 and 3, the removal rate of HQ rises rapidly within the first 2 h,
because there are abundant galvanic cells in the aqueous solution. However, the removal rate rises slowly after 2 h and it begins to stabilize after 4 h. Thus, the optimal reaction time of this experiment is selected at 4 h in the study.

**Effect of the initial pH on HQ removal rate**

Initial pH is another important factor which affects the removal rate. Electrolysis occurs mainly in the acidic condition. It is generally accepted that microelectrolysis also has a higher reactivity at a lower pH. However, there exists an optimal pH range for specific wastewater (Qin & Li et al. 2014). The initial pH of the HQ solution was adjusted to 1, 2, 3, 4, 5, or 6. As shown in Figure 4, when the initial pH is 3, the removal rate can reach 95.55% after 4 h.

Because of the consumption of H\(^+\) and the generation of Fe(OH)\(_2\), Fe(OH)\(_3\), and other products, the solution pH changed constantly during the reaction, as shown in Figure 5. It can be seen that the solution pH changes from acidic to neutral by using traditional packing and modified packing with Zn and Cu. For modified packing with Mn, the pH value rises gradually from 1. However, the pH still remains acidic because of the excess H\(^+\) in the solution. When the initial pH is 3, 5, or 6, the pH value of the mixture can rise to more than 8.5 in 15 min and reach the peak after 30 min. After that, the pH becomes neutral gradually. This is because Mn in packing can result in the following reactions in acidic conditions:

\[
\text{Mn} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2 \quad E_0(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V} \quad (5)
\]

With a low-electrode potential Mn \((E_0(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V})\) can react with H\(^+\) rapidly in the acidic solution raising the pH value to neutral or weak alkaline quickly. Since OH\(^-\) has been generated at the cathode by microelectrolysis reactions in neutral or weak alkaline solution, these OH\(^-\) can combine with Mn\(^{2+}\), Fe\(^{2+}\), and Fe\(^{3+}\) to generate Mn(OH)\(_2\), Fe(OH)\(_2\), and Fe(OH)\(_3\), respectively. Next, Fe(OH)\(_2\) is oxidized to Fe(OH)\(_3\) and forms flocs, and then precipitates out of the solution. Meanwhile, Mn(OH)\(_2\) can be oxidized to MnO\(_2\) and Mn\(_3\)O\(_4\) because Mn(OH)\(_2\) is not stable in an oxidation environment (Zhou 2008). Therefore, the pH value of the system decreases gradually. The reactions are as follows:

\[
\begin{align*}
2\text{Mn(OH)}_2 + \text{O}_2 & \rightarrow 2\text{MnO}_2 + 2\text{H}_2\text{O} \quad (6) \\
6\text{Mn(OH)}_2 + \text{O}_2 & \rightarrow 2\text{Mn}_3\text{O}_4 + 6\text{H}_2\text{O} \quad (7)
\end{align*}
\]

### Intermediates and mechanism of HQ degradation

Table 1 summarizes the fragments of degradation intermediates. Five compounds are identified in Figure 6.

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Signal of ions</th>
<th>Compound name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>Hydroquinone</td>
</tr>
<tr>
<td>2</td>
<td>108</td>
<td>Benzoquinone</td>
</tr>
<tr>
<td>3</td>
<td>116</td>
<td>Maleic acid</td>
</tr>
<tr>
<td>4</td>
<td>104</td>
<td>Malonic acid</td>
</tr>
<tr>
<td>5</td>
<td>59</td>
<td>Acetic acid</td>
</tr>
</tbody>
</table>

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**Figure 4** | Effect of initial pH on HQ removal rate with 9% Mn.

**Figure 5** | Changes of solution pH during the reaction.

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401 T. Li et al. | Hydroquinone degradation using modified microelectrolysis method | Water Science & Technology | 71.3 | 2015

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Chromatographic peak 1 represents HQ and peak 2 represents benzoquinone. It can be seen that HQ is gradually oxidized to benzoquinone. Therefore, the solution changes from colorless to yellow. As shown in Figure 6, the benzene ring breaks into maleic acid (chromatographic peak 3) after 2 h. Then, malonic acid (chromatographic peak 4) and acetic acid (chromatographic peak 5) are generated in the system after 3 h.

The mechanism of HQ degradation can be preliminarily determined through the analysis of intermediates. First, HQ is oxidized to benzoquinone by the effect of microelectrolysis reactions. Meanwhile, MN oxides can improve the removal rate of HQ because MN oxide is a kind of mineral composition that has high reactivity, and is one of the strongest oxidants in nature (Xu & Zhang et al. 2013). Another study shows that MN oxide can participate in the oxidation and reduction of many organic and inorganic compounds in the environment (Shin & Cheney 2004; Lin & Liu et al. 2009). Then, in the effect of OH, benzoquinone is degraded to maleic acid, malonic acid, and monocarboxylic acid. The probable pathway of HQ degradation is shown in Figure 7.

### Packing characterization

The characterization of packing structures was performed by SEM and XRD. As the SEM micrographs show in Figure 8, activated carbon and iron are dispersed evenly (Figure 8(a)). As a result, galvanic cells are formed between the particles of iron and carbon when HQ wastewater is in contact with the packing. Homoplastically, MN is dispersed evenly in the mixture of activated carbon and iron (Figure 8(b)). The size of MN particles is smaller than iron particles.

Figure 9 illustrates: the XRD patterns of traditional packing (a), Mn modified packing before reaction (b), and Mn modified packing after reaction for 4 h (c). It can be seen that there are sharp and strong peaks of iron at \(2\theta = 44.7^\circ\) and short peaks of carbon at \(2\theta = 26.6^\circ\) in the XRD patterns of all samples. There are also peaks of MN at \(2\theta = 42.3^\circ\) in the patterns of Mn modified samples. Owing to the calcination at 300 C, Fe, and Mn in the packings are partly oxidized by oxygen. Hence, there is a little \(\text{Fe}_3\text{O}_4\) in traditional packing, and \(\text{Fe}_3\text{O}_4\), \(\text{MnO}_2\), and \(\text{Mn}_3\text{O}_4\) in Mn modified packing. The peak intensity of Fe, Mn, and \(\text{Fe}_3\text{O}_4\) decreases after the microelectrolysis reaction (Figure 9(c)). However, the peak intensity of \(\text{MnO}_2\) and \(\text{Mn}_3\text{O}_4\) are essentially unchanged. This indicates that \(\text{MnO}_2\) and \(\text{Mn}_3\text{O}_4\) are generated from the oxidation of \(\text{Mn(OH)}_2\) in the microelectrolysis reaction.
In this study, the treatment of HQ using four different microelectrolysis packing types was investigated, and the mechanism of HQ degradation was analyzed. Among three different modified packing types, the addition of Mn powder could greatly improve the removal rate of HQ because MnO₂ and Mn₃O₄ generated during the reaction could adsorb and degrade HQ. During the modified microelectrolysis process, the removal rate of HQ was strongly affected by many factors, such as mass fraction of additive, reaction time, and initial pH. When the initial concentration of HQ was 1,000 mg·L⁻¹, the optimal reaction conditions were as follows: the mass fraction of Mn was 9%, and the initial pH was 3, and the reaction time was 4 h. The removal rate of HQ could reach 98.55% under optimal conditions. According to the results of GC-MS, HQ was first oxidized to benzoquinone and then was gradually oxidized into organic acids. This study has provided a modified microelectrolysis method to improve the removal effect of HQ. The microelectrolysis method has been exhibited with a high removal for HQ under acidic conditions at bench scale. However, reducing pH to acidity on full-scale wastewater treatment plants is not economically desirable. A systematic study on increasing the removal performance of HQ using the microelectrolysis method under neutral conditions is one of our future research goals.
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