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Removing dye Rhodamine B from aqueous medium via wet peroxidation with V-MCM-41 and H₂O₂

Deyong Wu, Mingce Long, Chao Chen, Yahui Wu, Weimin Cai, Jiangya Zhou and Dawei Ding

ABSTRACT

A new heterogeneous Fenton-like system, consisting of V-MCM-41 catalyst and hydrogen peroxide, was proved to be effective in removing recalcitrant dye Rhodamine B (RhB) in aqueous solutions. V-MCM-41 was prepared following a direct hydrothermal procedure with tetraethyl silicate and ammonium metavanadate as precursor. The mesoporous structure has been characterized by XRD, and the specific surface area was determined as $x \text{ m}^2 \text{ g}^{-1}$ according to BET method. The catalytic reaction can proceed in a relatively wide pH range from acidic to alkaline. And the visible light irradiation cannot promote the reaction process. In addition, the mechanism implication for V-MCM-41 as a Fenton-like catalyst has been discussed.

Key words | fenton-like reaction, heterogeneous, MCM-41, mesoporous, visible light

INTRODUCTION

A large portion of industrial wastewater including resistant-biodegradable pollutants such as dyeing wastewater must be removed by physicochemical methods. In the past decades, advanced oxidation processes (AOPs) have been emerged and accepted as efficient ways for the degradation of biorefractory organic pollutants (Hislop & Bolton 1999; Fernandez et al. 2000; Feng et al. 2004; Gulkaya et al. 2006; Mijangos et al. 2006; Song et al. 2008). Fenton process, as one of the advanced oxidation processes, has been widely used for wastewater treatment. Recently modified photo-Fenton reaction has also been developed quickly, such as utilizing UV to accelerate the activation of H₂O₂ (Hislop & Bolton 1999), or visible light to photoactivate dyes for promoting the degradation of organic pollutants (Fernandez et al. 2000). However, there are some drawbacks in homogeneous Fenton system (Feng et al. 2004), such as the low utilization of H₂O₂, requirement of a narrow pH range (pH < 4), formation of the sludge containing of iron at the end of the process. To overcome these drawbacks, heterogeneous Fenton process has intrigued much more interests in recent years. Various supports used in heterogeneous Fenton reactions have been reported, such as clay (Li et al. 2006), carbon (Ramirez et al. 2007), zeolite (Kusic et al. 2006), and so on. However, owing to iron leaching, contemporary heterogeneous reagents are easy to lose catalytic activity, especially, in acidic wastewater. Moreover, a separation system is required to remove the ferric ion remaining in the treated wastewater, thus the overall process becomes complicated and uneconomical.
In this context, on the one side, many researchers have been interested in designing new heterogeneous Fenton systems with highly efficient and durable. On the other side, they have turned to investigate other transition metals such as Co, Cu, Au and so on as Fenton-like reagent. Han et al. (2008) investigated Au/hydroxyapatite as a Fenton-like reagent for phenol peroxidation, which showed higher stability and activity than the conventional iron exchanged zeolite (Fe/ZSM-5) (Han et al. 2008). Chen et al. (2007) studied the fiber-supported cobalt phthalocyanine with H₂O₂ on degradation of dyes, which had good stability, and a wide suitable pH range (Chen et al. 2007). Lam et al. (2007) reported that MCM-41-supported copper catalyst was effective in mineralizing Orange II in a wide pH range via the photo-Fenton-like process (Lam et al. 2007). MCM-41 molecular sieve has a mesoporous structure with a large surface area and uniform pore-size (Zhao & Lu 1998). Due to its mesoporous structure and high adsorption capacity, MCM-41 has been widely used in various fields, including enzyme immobilization (Diaz & Balkus 1996), drug delivery system (Vallet et al. 2001) and benzene adsorption (Zhao & Lu 1998). Moreover, the replaced metal ions in the MCM-41 structure can be served as active center and exhibit selectively catalytic performance (Marino et al. 2008).

Vanadium-substituted MCM-41 was reported on the structure and the catalytic activity on the oxidation of alcohol and aromatics (Chen & Lu 1999; Lim & Haller 2002). However it is worthy to note that the application of V-MCM-41 as Fenton-like catalyst has rarely been revealed. Herein we present the description of the Fenton-like reaction by vanadium-MCM-41 and H₂O₂ for the degradation of the model pollutant RhB in aqueous media. This research provides a new potential approach in the efficient treatment of dye effluent.

**MATERIAL AND METHODS**

**Catalyst preparation**

All chemicals were reagent grade and used without further purification. V-MCM-41 catalyst used in this work was prepared following a direct hydrothermal synthesis procedure. In the preparation, tetraethyl silicate was used as the silica source, cetyltrimethylammonium bromide (CTAB) as the template, and ammonium metavanadate as the vanadium source. The molar composition of the final mixture was Si: V: CTAB: H₂O = 1: 0.02: 0.015: 140. A typical procedure was described as follows: organic template CTAB was dissolved in deionized water with stirring, and then cooled down to room temperature. NH₄VO₃ was firstly dissolved in deionized water, and then 1.0 mol L⁻¹ NaOH was added dropwise until the solution clear (solution A). The solution A was stirred at 313 K in a water bath until it was clear, and then cooled down to room temperature. NH₄VO₃ was firstly dissolved in deionized water, and then 1.0 mol L⁻¹ NaOH was added dropwise until the solution clear (solution B). Solution B and tetraethyl silicate were slowly added into solution A with stirring at the same time. The pH of mixture was rapidly adjusted to about 11 with 1.0 mol L⁻¹ NaOH. After stirring for 2 h at room temperature, the final mixture was poured into a Teflon-lined stainless-steel autoclave, and aged at 373 K for 72 h. The reaction products were filtered, washed with deionized water, and dried in air at 373 K. The dried products were calcined at 823 K for 6 h with a rate of 1 K/min to obtain the resulted product V-MCM-41. MCM-41 molecular sieve was made using the similar steps as above, only without ammonium metavanadate.

**Catalyst characterization**

The mesoporous sieves were characterized by X-ray diffraction (XRD) and nitrogen physisorption. The crystal structures of the catalyst powders were determined by powder X-ray diffraction (XRD, D/Max-2200/PC, Rigaku Corporation, Japan) with Cu Kα radiation. A scanning speed of 0.5° per minute was used. Adsorption and desorption isotherms of nitrogen were obtained at 77 K on NOVA1000 Sorptomatic apparatus (Quantachrome Corporation, USA). Before measurement, the samples were out gassed in a vacuum at 323 K, 373 K, 423 K, 473 K, 523 K and 573 K for 10 min, 10 min, 10 min, 10 min, 10 min and 30 min respectively.

**Catalytic test**

The model pollutant was a typical recalcitrant dye Rhodamine Bextra (RhB), whose structure was shown in Figure 1. The dosage of catalyst was 0.4 g L⁻¹, and the RhB and H₂O₂
concentrations were fixed at 0.02 mmol L\(^{-1}\) and 4 mmol L\(^{-1}\), respectively. The original pH of 0.02 mmol L\(^{-1}\) RhB solution was about 6.15, and the different initial pH was adjusted by the 1.0 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution or 1.0 mol L\(^{-1}\) NaOH solution. All experiments were carried out under constantly stirring in order to make the catalysts good dispersion. Before reaction, the suspension containing V-MCM-41 or MCM-41 and RhB solution was stirred in dark for 30 min to achieve adsorption equilibrium. Then H\(_2\)O\(_2\) was added to the solution and start the degradation reaction. Samples were taken at regular time intervals and separated by centrifugation at 5,000 rpm. The concentration of RhB was monitored by spectrophotometry with a UNICO 7,200 Spectrophotometer. A 1,000-W Xe lamp with a cutoff filter removing any irradiation below 400 nm has been employed as the source of visible light.

RESULTS AND DISCUSSION

Catalysts characterization

The small-angle XRD patterns of the V-MCM-41 and MCM-41 catalysts were showed in Figure 2. An intense diffraction peak (100) together with several weak peaks, characteristic of the hexagonal ordered mesoporous MCM-41 structure, was obviously visible in the V-MCM-41 XRD patterns. This indicated clearly that the as-prepared V-MCM-41 has the same mesoporous structure as MCM-41. In addition, no characteristic peaks of vanadium oxides were found in the broad-angle XRD patterns, suggesting that no bulk vanadium oxides are present in the catalyst. That is to say, the vanadium atoms have been incorporated into the framework of MCM-41 catalyst or highly dispersed on the wall. According to Bragg's Equation \(2d \sin \theta = \lambda\), where \(\lambda = 0.15418\) nm for the Cu K\(_{a}\) line, \(d(100)\) of V-MCM-41 and MCM-41 were 3.65 nm and 5.32 nm obtained from the first peak at 2.42\(^\circ\) and 1.66\(^\circ\) in the XRD pattern respectively. According to the Equation \(a_0 = \frac{\sqrt{3}}{2}d_{100}\), the cell unit dimension \(a_0\), distance of the adjacent pore center, were calculated as 4.21 nm and 6.14 nm respectively. Assuming pore wall thickness of 1.0 nm of sample, the pore diameters of V-MCM-41 and MCM-41 can be calculated as 3.21 nm and 5.14 nm, respectively.

The sorption isotherms of nitrogen reported here were determined at 77 K by using a conventional volumetric technique. Preliminary work involved the investigation of the reproducibility of the nitrogen isotherm after out gassing at a temperature of 623 K. Excellent agreement was obtained, as indicated in Figure 3(a), and the stability of the adsorbent was also demonstrated. A linear increase of adsorbed volume at low pressures \((P/P_0, 0.24)\) was followed by a steep increase in nitrogen uptake, which was due to capillary condensation inside the mesopores (Grun et al. 1999). The long plateau of nitrogen adsorption at \(P/P_0 > 0.35\) was a clear indication that pore filling was restricted to the narrow range of \(P/P_0 = 0.24-0.35\). The isotherm can be classified as a type IV, the same as that of MCM-41 (Figure 3b), which is a typical style for the mesoporous solids (Chen & Lu 1999).

By the BET(Brunauer-Emmett-Teller) method, the specific surface area of V-MCM-41 and MCM-41 can be
obtained as 1357 m$^2$ g$^{-1}$ and 1123 m$^2$ g$^{-1}$, and the specific pore volume as 1.101 cm$^3$ g$^{-1}$ and 0.9916 cm$^3$ g$^{-1}$, respectively. Application of the BJH (Barrel-Joyner-Halenda) method to calculate the pore size distribution was not suitable due to the instability of the liquid nitrogen meniscus inside the mesopores (Grun et al. 1997). A summary of all parameters for MCM-41 and V-MCM-41 obtained by nitrogen sorption and X-ray diffraction has been shown in Table 1.

**Table 1 | Properties of catalysts**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Specific pore volume$^*$ (cm$^3$ g$^{-1}$)</th>
<th>Pore diameter $4V_p/a_s$ (nm)</th>
<th>Pore diameter (XRD)$^\dagger$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-MCM-41</td>
<td>1357</td>
<td>1.101</td>
<td>3.25</td>
<td>3.21</td>
</tr>
<tr>
<td>MCM-41</td>
<td>1123</td>
<td>0.9916</td>
<td>3.53</td>
<td>5.14</td>
</tr>
</tbody>
</table>

$^*$According to the BET plot.
$^\dagger$Using the $d_{100}$ value and assuming pore wall thickness of 1.0 nm of sample.

V$_p$: specific pore volume, $a_s$: specific surface area.

Catalytic activity of catalysts

**Effect of vanadium elements**

The different catalysts, V-MCM-41 and MCM-41, were adopted with H$_2$O$_2$ for the degradation of the dye RhB. The results were shown in Figure 4. Because of its huge surface area, V-MCM-41 or MCM-41 has a strong surface adsorption, thus the adsorption equilibrium can be achieved in a relatively short time. Our blank tests suggested that the adsorption equilibrium can be achieved in 30 min in the suspension both for V-MCM-41 and MCM-41, and the adsorption ability was as much as 15.83 mg/g catalysts. Moreover, it was found that after adsorption equilibrium, the concentration of RhB showed no reduction in the presence of MCM-41 and H$_2$O$_2$ (Figure 4). It meant that the silica mesoporous structure is noneffective for the activation of the hydrogen peroxide. However, the RhB decreased in presence of V-MCM-41 and H$_2$O$_2$, more than 38.7% had been degraded in 60 min. This suggested the transition metal vanadium played an important role in the activity of catalyst, and this new system acted as a Fenton-like process to decompose pollutants.

**Effect of Visible Light Irradiation**

Generally in Fenton or Fenton-like reaction, the utilization efficiency of H$_2$O$_2$ is low. Ultraviolet irradiation has been...
introduced to assist Fenton treatment of organic pollutants, for it can accelerate the decomposition of H\textsubscript{2}O\textsubscript{2} and increasing the quantum efficiency of the intermediate Fe(OH)\textsuperscript{2+} according to Equation (1):

\[
\text{Fe(OH)}^{2+} \xrightarrow{hv} \text{Fe}^{2+} + \cdot\text{OH} \tag{1}
\]

where the production of hydroxyl radical has been enhanced. However, solar irradiation with a large amount of visible light is an ideal and cheap source of light. Therefore recently researchers have exerted much effort on developing novel heterogeneous Fenton-like system which can be accelerated by the visible light irradiation (Fernandez et al. 2000).

To investigate the effect of visible light on the V-MCM-41/H\textsubscript{2}O\textsubscript{2}/RhB solution, we carried out some control experiments both in the dark and upon visible light radiation. The results (Figure 5) showed that there was almost no conversion of RhB after running for 120 min in the presence of exclusively V-MCM-41 or H\textsubscript{2}O\textsubscript{2} solution. These results suggested that: (1) the V-MCM-41 catalyst and H\textsubscript{2}O\textsubscript{2} all are indispensable for degradation of RhB; (2) dissolved oxygen in water cannot be activated by V-MCM-41. It also showed that the concentration of RhB declined quickly with time in the dark as well as upon visible light. There was no obvious difference on the degradation dynamic. It indicated that visible light has negligible effect on the oxidation of RhB in presence of both H\textsubscript{2}O\textsubscript{2} and V-MCM-41. Therefore the intermediate species during the Fenton-like reactions cannot be promoted and the production of hydroxyl radicals cannot be improved under the visible light irradiation.

### Influence of pH

The effect of solution pH on the decomposition of RhB was investigated in a set of experiments where the initial pH of the solution was adjusted to 2.68, 3.14, 6.15 and 9.07, and the results were summarized in Figure 6. Clearly, the reaction can proceed in a wide pH range from acidic to alkaline in the V-MCM-41/H\textsubscript{2}O\textsubscript{2} catalytic system. This result was distinct from the traditional Fenton system, where the oxidation can only take place at a narrow pH range (pH \(< 4\)), because iron precipitation as hydroxides may be produced at pH above 4 (Mijangos et al. 2006). But there are no precipitates for element vanadium even in strong alkaline ambience. In the test, better catalytic effect on the degradation of RhB was displayed at pH about 3, about 55% RhB has been removed in 60 min, which is similar with the results obtained in many literatures (Feng et al. 2004; Mijangos et al. 2006). Although the catalytic activity of this Fenton-like system decreased with the pH increasing, which must be attributed to the oxidation potential of hydroxyl radical decreasing (Modirshahla et al. 2007). Anyway, the catalyst still exhibited activity when the initial pH up to 9.02.
Mechanism implication for V-MCM-41 as a Fenton-like Catalyst

In the homogeneous Fenton system or in heterogeneous Fenton reactions, oxidation and removal of organic pollutants depends on the formation of hydroxyl radicals, which can oxidize and mineralize almost all the organic molecules because of its high oxidation potential \(E^o = +2.8\) V (Satoh et al. 2007). In the Fenton or Fenton-like process, highly reactive hydroxyl radicals are produced by the activation of hydrogen peroxide with iron or other transition metal species (Kwan & Voelker 2003).

There are some researches on the vanadium (III or V)/H\(_2\)O\(_2\) Fenton-like system. Generally the homogeneous reaction of peroxovanadium species and the radical chain mechanism can be described briefly as follows: \(\text{V}^{3+}\) can be oxidized by H\(_2\)O\(_2\) to V(IV) species, further to V(V) species, highly reactive hydroxyl radicals are simultaneously produced; Meanwhile, V(V) species can be changed to V(IV) species with the help of intermediate product HOO\(^{·}\). The brief mechanism can be displayed by Equations (2–7) (Bonchio et al. 1994; Du & Espenson 2005):

\[
\begin{align*}
\text{V}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{VO}^{2+} + \cdot\text{OH} + \text{H}^+ \\
\text{VO}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{VO}_2^- + \text{H}^+ + \cdot\text{OH} \\
\text{VO}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{OVOOH}^{+} + \text{H}^+ \\
\text{OVOOH}^- & \rightarrow \text{VO}_2^- + \cdot\text{OH} \\
\text{H}_2\text{O}_2 + \cdot\text{OH} & \rightarrow \text{HO}^- + \text{H}_2\text{O} \\
\text{VO}_2^- + \text{HO}^- + \text{H}^- & \rightarrow \text{VO}^{2+} + \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

According to the above mechanism, inter-conversion among the different vanadium species can be realized, and highly reactive hydroxyl radicals also can be produced during these Fenton-like reactions. Based on these reactions, the following hydroxyl radical formation mechanism via V-MCM-41 and H\(_2\)O\(_2\) can be proposed as follows:

Catalyst - \(\text{V}^{5+} + \text{H}_2\text{O}_2\) \(\rightarrow\) Catalyst - \(\text{[VOOH]}^{4+} + \text{H}^+\) \(\quad\) (8)

Catalyst - \(\text{[VOOH]}^{4+}\) \(\rightarrow\) Catalyst - \(\text{V}^{4+} + \cdot\text{HO}^-\) \(\quad\) (9)

Catalyst - \(\text{V}^{4+} + \text{H}_2\text{O}_2\) \(\rightarrow\) Catalyst - \(\text{V}^{5+} + \cdot\text{OH} + \text{OH}^-\) \(\quad\) (10)

Catalyst - \(\text{V}^{5+} + \text{HO}^-\) \(\rightarrow\) Catalyst - \(\text{V}^{4+} + \text{O}_2 + \text{H}^+\) \(\quad\) (11)

Catalyst - \(\text{V}^{4+} + \cdot\text{OH}\) \(\rightarrow\) Catalyst - \(\text{V}^{5+} + \text{OH}^-\) \(\quad\) (12)

where the vanadium in V-MCM-41 is present as \(-\text{V}^{(IV)}\) or \(-\text{V}^{(IV)}\text{O}\) (Parvulescu et al. 2003). When the H\(_2\)O\(_2\) is present in the solution, recycles between V(V) and V(IV) and production of the active radicals \(\cdot\text{OH}\) and \(\text{HOO}^-\) can be realized. Subsequently, the RhB can be oxidized and degraded by these radicals. Although the recycle of V(V) is possible on the Fenton-like reactions, dynamically the step is not fast enough, therefore the removal rate of the RhB concentration is decreased slowly.

It is well known that Fenton reaction cannot progress in the alkaline solution because of the iron precipitates as hydroxides. The V-MCM-41 served as heterogeneous Fenton-like catalyst take effect in a wide pH range as proved in our work. As a heterogeneous Fenton system, the main cost is the consumption of H\(_2\)O\(_2\), which is a very cheap chemical. Therefore the operation cost must be economic. It is claimed that the V-MCM-41 catalyst is a promising catalytic material for the Fenton-like degradation of resistant-biodegradable pollutants, especially in high pH reaction medium. Future studies should go along if there are novel system based on transition metal substitute MCM-41 can destroy more biorefractory organic pollutants.

CONCLUSIONS

The V-MCM-41 catalyst with typically mesoporous structure and a large surface area \((1557 \text{ m}^2 \text{ g}^{-1})\), synthesized by a direct hydrothermal procedure, has been employed as Fenton-like reagent together with H\(_2\)O\(_2\) for the degradation of RhB dye pollutant. The results demonstrated that 55% RhB has been removed after 120 min in presence of V-MCM-41 and H\(_2\)O\(_2\). Moreover, the best pH for the reaction system is about 3.0. The rate of RhB degradation decreased with increasing pH. However, it is also activity in the RhB degradation at pH as high as 9.0. In addition, the visible light irradiation had negligible effect on the degradation of RhB. The new Fenton-like system, consisting of V-MCM-41 catalyst and hydrogen peroxide is promising to be an alternative of AOPs.

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REFERENCES


