

Technical Note

# Catalytic degradation of Orange II by UV-Fenton with hydroxyl-Fe-pillared bentonite in water

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## Abstract

Although homogeneous photo-Fenton system is a very efficient method for organic wastewater treatment, it suffers from costly pH adjustment as well as difficult separation of catalysts from aqueous in practical application. Through cation exchange reaction, hydroxyl-Fe-pillared bentonite (H-Fe-P-B) was successfully prepared as a solid catalyst for UV-Fenton to degrade non-biodegradable azo-dye Orange II. Compared with raw bentonite, the content of iron, interlamellar distance and external surface area of H-Fe-P-B increased remarkably. H-Fe-P-B had good photosensitivity and catalyst reactivity. And the catalytic activity of H-Fe-P-B for  $\text{H}_2\text{O}_2$  came from hydroxyl-Fe between sheets rather than  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  in tetrahedral or octahedral sheets of bentonite. In UVA- $\text{H}_2\text{O}_2$  system,  $\text{H}_2\text{O}_2$  could destroy the azo bond of excited Orange II molecules but could not effectively mineralize it. After 120 min treatment, 83% discoloration was obtained while only 2% of TOC was removed. When H-Fe-P-B was used as catalyst, a significant degradation of Orange II was observed at the same condition as UVA- $\text{H}_2\text{O}_2$  system. Almost 100% discoloration and more than 60% TOC removal of Orange II could be achieved after 120 min treatment. Because of the strong surface acidity and the electronegativity of H-Fe-P-B, the pH range of this catalyst in the Orange II discoloration could be extended up to 9.5. And this catalyst showed good stability during Orange II degradation in water in wide range of pH (3.0–9.5). These results indicated that the H-Fe-P-B was a promising catalyst for UV-Fenton system. © 2006 Elsevier Ltd. All rights reserved.

*Keywords:* UV-Fenton; Bentonite; Azo-dye; Hydroxyl radical; Degradation; Wastewater

## 1. Introduction

Photo-Fenton process, which could generate hydroxyl radical with powerful oxidizing ability (standard oxidation potential of 2.80 V), has been reported for degradation of organic contaminations in water (Pignatello et al., 1999; Moraes et al., 2004), including non-biodegradable dyes (Bandara et al., 1996; Herrera et al., 1999; Chen et al., 2002).

In homogeneous photo-Fenton system, the catalysts of iron ions are dissolved in water. Although these homogeneous catalysts are generally very efficient for such reactions, their separation and reuse are rather difficult at the

end of treatment. The removal of iron ions from the treated water needs a large amount of chemicals and manpower, which will increase the cost of treatment. And the production of ferric hydroxide sludge may create other environmental problem (Catrinescu et al., 2003; Feng et al., 2004a,b). Furthermore, the pH of solution should be adjusted between 2 and 4 beforehand to carry out the Fenton pretreatment, and the acidification is more costly than the energy and oxidant used in Fenton degradation (Cheng et al., 2004; Parra et al., 2004a; Gumy et al., 2005). The tight range of pH and the difficult separation of catalysts from solution limit further application of homogeneous photo-Fenton system in wastewater treatment.

To overcome these drawbacks, in recent years, much attention has been focused on development of heterogeneous catalyst for Fenton or photo-Fenton process (Catrinescu et al., 2003; Cheng et al., 2004; Feng et al.,

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2004a,b; Parra et al., 2004a,b; Gumy et al., 2005; Noorjahan et al., 2005). The catalyst loaded with irons can be reused for further runs and extend the range of pH for Fenton oxidant (Catrinescu et al., 2003; Cheng et al., 2004; Feng et al., 2004b; Parra et al., 2004a,b; Gumy et al., 2005). For example, Parra et al. (2004b) used Nafion membrane as a support for the preparation of Fe/histidine/Nafion catalyst. The pH range of this catalyst in the Orange II discoloration could be extended up to 10.2. And this catalyst showed good long-term stability of activity during Orange II degradation. However, the Nafion membrane is too expensive to be used for a practical application (Feng et al., 2004a). The ideal heterogeneous catalyst should be cheap, suitable for wide range of pH, as well as has good catalytic activity, low catalyst leaching and good photosensitivity. Selection of catalyst supports is the most important during the preparation of heterogeneous catalyst. The Fe-pillared clay may be one of promising heterogeneous catalyst because of its unique characteristics, abundance and low cost. Through cation exchange reaction, the hydroxyl-Fe polycation could intercalate bentonite and be fixed as pillars to form hydroxyl-Fe-pillared bentonite (Kloprogge, 1998; Sze et al., 2004). After calcinations at a high temperature, the hydroxyl-Fe species will be converted to oxide pillars through dehydration and dehydroxylation process (Sze et al., 2004). At the same time, the hydroxyl-Fe-pillared bentonite is converted to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-pillared bentonite. Compared with raw bentonite, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-pillared bentonite presents large micropore volume and specific surface area as well as more special catalytic activity (Kloprogge, 1998; Feng et al., 2004a,b; Sze et al., 2004). For example, Feng et al. (2004a,b) successfully prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-pillared bentonite as a heterogeneous catalyst for UV-Fenton to discolor and mineralize non-biodegradable azo-dye Orange II. To synthesize  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-pillared bentonite, the hydroxyl-Fe-pillared bentonite has to be treated with calcinations at 350 °C for 24 h, which will increase the cost of catalyst preparation. It was reported that the pillared clay contained of Fe<sup>3+</sup> could also show significant catalytic activity for hydrogen peroxide to degrade organic pollutant (Catrinescu et al., 2003; Guélou et al., 2003). For example, Catrinescu et al. (2003) have successfully developed Fe-exchanged Al-pillared synthetic beidellite for the wet hydrogen peroxide oxidation of phenolic aqueous wastes. In his study, COD removal efficiency of 88% was obtained, and the range of pH values for Fenton-type oxidation could be extended by using this catalyst with low leaching of catalyst. The hydrolysis products of iron ions, such as Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> and so on, have high photochemistry activity (Lunar et al., 2000; Park et al., 2002). So the hydroxyl-Fe-pillared bentonite may also have high photochemistry activity and could be used as a new and cheap catalyst for photo-Fenton.

In the present paper, the interest has been focused on the UV-Fenton process for degradation of azo-dye with hydroxyl-Fe-pillared bentonite as catalyst. The effect of initial pH on UV-Fenton process as well as the stability of

catalyst was studied in detail. And the catalytic activity of raw bentonite was also detected to discuss the catalytic ability of different iron configurations in hydroxyl-Fe-pillared bentonite. Orange II was employed as a model compound of azo-dye, which is non-biodegradation and used extensively in textile industry.

## 2. Experiment

### 2.1. Materials

The bentonite used was primarily Ca<sup>2+</sup>-montmorillonite from Inner Mongolia Autonomous Region, China. Its chemical formula was Ca<sub>0.39</sub>Na<sub>0.02</sub>K<sub>0.02</sub>(Si<sub>7.91</sub>Al<sub>0.09</sub>)(Al<sub>2.51</sub>Fe<sub>0.45</sub>Mg<sub>1.10</sub>)O<sub>20</sub>(OH)<sub>4</sub>*n*H<sub>2</sub>O and its cation-exchange capacity (CEC) was 108.4 mM 100 g<sup>-1</sup>. Bentonite was mechanically grinded with a mortar and pestle to less than 200-mesh (0.074 mm). Orange II purchased from Shanghai Chemical Reagent Company was of chemical reagent grade and used without further purification. H<sub>2</sub>O<sub>2</sub> (30% in H<sub>2</sub>O), Na<sub>2</sub>CO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, KI, NaOH and HCl were of analytical grade and obtained from Shanghai Chemical Reagent Company.

### 2.2. Synthesis and characterization of Hydroxyl-Fe-pillared bentonite

The hydroxyl-Fe-pillared bentonite catalyst was prepared by pillaring the bentonite through cation exchange process. Firstly, Na<sub>2</sub>CO<sub>3</sub> was added slowly as a powder into the solution of Fe(NO<sub>3</sub>)<sub>3</sub> under magnetic stirring and N<sub>2</sub> atmosphere, until the molar ratio of [Na<sup>+</sup>]/[Fe<sup>3+</sup>] became 1:1. Then the solution was aged at 60 °C for 1 d. Secondly, the intercalant solution was added to the clay suspension under stirring. The final [Fe<sup>3+</sup>]/clay ratio was equal to 10 mol kg<sup>-1</sup> of dry clay. The product was then filtered, washed with deionized water several times. Then the hydroxyl-Fe-pillared bentonite was dried at 105 °C overnight, ground to less than 200-mesh (0.074 mm). The *d*<sub>001</sub>-spacing was measured by XRD analysis on a (Rigaku) D/max-2550 diffractometer. Specific surface area was determined by N<sub>2</sub> adsorption (BET method) on a NOVA2000e instrument. The samples were degassed at 473 K for 3 h before the adsorption and the external and micropore surface area determined with the *t*-plot method. The element content of raw bentonite and solid catalyst was analyzed by X-ray fluorescence (XRF) spectrometer (ZSX100e). The UV-Vis absorption spectra were measured by Shimadzu UV-2401 double-beam digital spectrophotometer equipped with conventional components of a reflectance spectrometer (diffuse reflectance of BaSO<sub>4</sub>/diffuse reflectance of sample).

### 2.3. Degradation of azo-dye Orange II

The experiments were carried out in a photocatalytic oxidation reactor which was shown in Feng's experiments

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