



## Research paper

# A novel strategy for preparation of an effective and stable heterogeneous photo-Fenton catalyst for the degradation of dye



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## ABSTRACT

A novel strategy was applied in the synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> pillared bentonite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent) by intercalating Fe<sup>3+</sup> into bentonite in the presence of the surfactant CTAB as an expanding agent and template agent. Then  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent catalyst was used as a heterogeneous catalyst for photo-Fenton degradation of organic contaminants. CTAB can promote the formation of crystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in the process of calcination. In addition, the CTAB also significantly increased the surface area of the composites. Only the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> pillared bentonite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent) could be obtained under the same conditions without CTAB. The as-obtained composites were well characterized by various techniques to study their morphological, structural and magnetic properties. The specific surface area of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent catalyst increased from 29 to 117 m<sup>2</sup>/g compared to bentonite. The saturated magnetization (Ms) values of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent was 10 emu/g. The effects of various reaction parameters such as H<sub>2</sub>O<sub>2</sub> dosage, initial pH value,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent dosage on the degradation of RhB were studied. Under the best conditions (0.2 g/L of catalyst, 10 mM of H<sub>2</sub>O<sub>2</sub>), the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent catalyst displayed to possess superior degradation ability to Rhodamine B (RhB) comparing the results with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent. The catalyst showed efficient for the degradation of other organic dyes as well. After five reaction cycles the catalyst still showed high photocatalytic activity (91%), which showed that the magnetic catalyst possessed very stable, highly reactive, and easy to separate by an external magnetic field. Hence, this facile and high efficiency method may be extended to fabricate other types of magnetic materials.

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## 1. Introduction

Dye pollutants used in textile industries were major sources of environmental contamination (Rapsomanikis et al., 2014; Sun et al., 2015). Dye pollutants caused the utmost concern because of their nearly ubiquitous use, lasting color and poorly biodegradable by traditional aerobic wastewater treatment (Chen et al., 2015a, 2015b). Most of them have complex chemical structure, which make them stable and recalcitrant to oxidant and resistant to be bleached by sunlight (Qin et al., 2014). In order to eliminate the negative environmental impact of dye, a wide range of chemical and physical methods have been developed, such as adsorption (Qin et al., 2014), ion-exchange (Choi et al., 2007), photocatalysis (Papoulis et al., 2010; Wu et al., 2015) and ozonation (Zhou et al., 2015).

Among the methods used for removal pollutants, advanced oxidation processes (AOP) that have been defined as promising alternatives based on the generation of highly reactive transitory species (OH, O<sub>2</sub>) to initiate non-selective oxidation destruction of organic pollutants (Garrido-

Ramírez et al., 2013). The Fenton reaction (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup> + Fe<sup>3+</sup>) has attracted widely attention among the AOPs due to reaction's strong oxidative capacity for the degradation of organic contaminants (Wang et al., 2014). The Fenton reaction was a potentially convenient, economical, and environmentally friendly method for wastewater treatment (Ma et al., 2015). The Fenton process uses Fe<sup>2+</sup> as the catalyst to generate highly reactive hydroxyl radicals (OH) from hydrogen peroxide (Garrido-Ramírez et al., 2010). Fenton reaction can be written in its general form (Kouraichi et al., 2015):



However, several drawbacks of the homogenous Fenton process limit the scale-up of its application, including the narrow acidic pH range, high cost of H<sub>2</sub>O<sub>2</sub>, and the accumulation of iron-containing sludge, which are regarded as a secondary pollution involving the loss of catalyst (Dorrajji et al., 2015). To overcome these drawbacks, many efforts have been made to develop heterogeneous Fenton and photo-Fenton catalysts, including the immobilization of Fe ions, Fe clusters,

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or iron oxides (Lan et al., 2015). To date, various supports have been used to prepare heterogeneous Fenton catalysts, such as resin (Shu et al., 2010), zeolites (Navalon et al., 2010), silica (Panda et al., 2011), clay (Daud and Hameed, 2011; Liu et al., 2015), activated carbon (Duarte et al., 2013). Bentonite was found by its unique characteristics, abundant, natural, environmentally benign as well as low cost to make it has the suitable choice as catalyst support (Xu et al., 2013). It was reported that Fe-pillared bentonite can exhibit high catalytic activity and good long-term stability for degradation of RhB in heterogeneous Fenton system (Hou et al., 2011). However, in some reports, the organic modifiers can change the surface properties of the clays from hydrophilic to hydrophobic, which significantly enhance their affinity for organic contaminants (Li and Wu, 2010; Stathatos et al., 2012). The surface modification of the clays by organic cations leads to an increase in adsorption capacity (Anirudhan and Ramachandran, 2015). Therefore, organic-inorganic complex modified bentonite have attracted great attention to improve swelling properties, enhance hydrogel strength, and reduce production cost of corresponding superabsorbents (Bulut et al., 2009). For example, Chen et al. (2013) reported CTAB as expanding agents in the TiO<sub>2</sub> pillared montmorillonites and these can control the size of the pillars. Ma and Zhu (2006) reported that the modified bentonite, with both Fe polycations and CTMAB, was an effective sorbent for simultaneous removal of phenanthrene and phosphate from water. In addition, it is well known that magnetic nanoparticles became very interesting and economically viable because they allow easier and more convenient processes for separation and recycling of photocatalysts by applying an external magnetic field (Liu et al., 2012; Zhang et al., 2015). Therefore, there has been a growing interest in magnetic iron-based materials pillared organobentonite (Sun et al., 2011). Wu et al. (2013) synthesized of Organo-bentonite-Fe<sub>3</sub>O<sub>4</sub> poly by solution copolymerization technique. Ma et al. (2005) successfully prepared of stable adduct  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/CTAB/Clay with sandwich-like architecture and at the same time it also proved that the periodic nanostructures can be created by using inorganic or organic matter intercalation. Although much research has focused on the magnetic organobentonite-iron oxides, little attention has investigated its performance as the heterogeneous Fenton catalyst. In addition, to the best of our knowledge, most studies on the magnetic organobentonite-iron oxides report the form of Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> methods in the surface of organobentonite that are difficult and complex.

As reported in some literatures the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase was prepared easily using cationic surfactant cetyltrimethylammonium bromide (CTAB) (Liu et al., 1999; Ramezanzadeh et al., 2015). In this study, we designed a simple method for the preparation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent with the addition of CTAB surfactant. CTAB not only acts as expanding agent of the layered clay to control the size of pillars, but also serves as a template to control the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. 1). The heterogeneous catalyst  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent was then applied for degradation of RhB under ultraviolet light with aqueous H<sub>2</sub>O<sub>2</sub>. The attempt was to determine whether the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent catalyst could promote the degradation rate and better than the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent. Meanwhile, the effects of different operating parameters such as catalyst addition, initial pH, catalyst dosage, and H<sub>2</sub>O<sub>2</sub> dosage were optimized in detail. Finally, the stability of the catalyst and the degradation of different organic dyes including methylene blue (MB) and methyl orange (MO) was studied.

## 2. Materials and methods

### 2.1. Materials

The bentonite (Na<sup>+</sup>-Mt, 98%) used in this study came from Huzhou, Zhejiang, P.R. China. The cation exchange capacity of bentonite was determined to be 0.8 meq/g. Ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, w/w) were purchased from Chengdu Kelong Chemical Reagent Company. Rhodamine B (RhB) was procured from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>) was bought from ShengAo Chemical Reagent Company (Tianjin, China). Cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Solarbio. Chemicals used in the experiment were analytical grade and were used without any further purification. Deionized water was used throughout the whole experiment.

### 2.2. Preparation of $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent

#### 2.2.1. The preparation of polymeric hydroxyl iron pillared agent

Iron pillaring agent was prepared as follows: Na<sub>2</sub>CO<sub>3</sub> solution (0.5 M, 20 mL) dropwise into a Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution (0.2 M, 50 mL) under vigorous stirring for 2 h at 60 °C until the molar ratio of [Na<sup>+</sup>]/[Fe<sup>3+</sup>] became 1:1. Then the solution was aged for 24 h.

#### 2.2.2. The preparation of $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent

1 g bentonite and 0.2 g CTAB was dispersed in 50 mL deionized water under vigorous stirring at 60 °C for 2 h. Continue to maintain the temperature, add the pillaring solution to the suspension under stirring to obtain a Fe/bentonite ratio of 10 mmol/g in accordance to previously published results (Chen and Zhu, 2007). Then the suspension was aged for 24 h. Afterwards, the precipitate was separated by centrifuging and washed with deionized water several times. Finally the product dried in air at 60 °C and calcined at 400 °C for 3 h. Then, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent catalyst was obtained.

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent was also prepared using above procedures but without CTAB.

### 2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained from 1° to 70° of 2 $\theta$  using a Bruker D8 X-ray diffractometer with a Cu K $\alpha$  radiation (40 kV, 40 mA) at a scanning speed of 6°/min. The microstructure of samples was observed with a scanning electron microscopy (SEM JSM-6490LV) and transmission electron microscopy (TEM Tecnai G2 F20). N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K on a Quantachrome Autosorb 3-B apparatus. The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) methods at 77 K (ASAP 2020 V USA) and DR method respectively. The magnetic property (M-H curve) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent was also examined at room temperature on a SQUID magnetometer made by quantum design corporation.

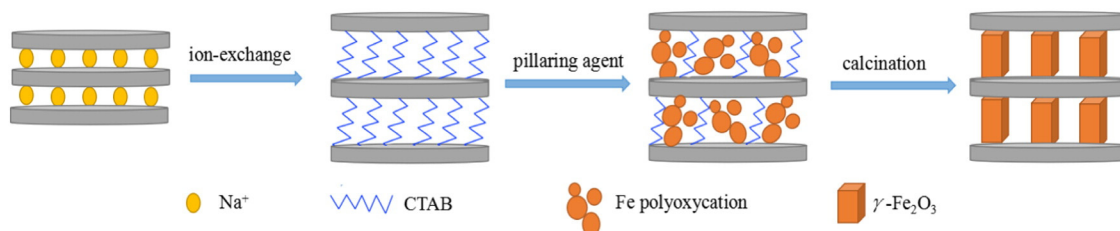


Fig. 1. The formation process of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P-Bent material.

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