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## Heterogeneous Fenton-like degradation of 4-chlorophenol using iron/ordered mesoporous carbon catalyst

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### ABSTRACT

Ordered mesoporous carbon supported iron catalysts (Fe/OMC) were prepared by the incipient wetness impregnation method and investigated in Fenton-like degradation of 4-chlorophenol (4CP) in this work. XRD and TEM characterization showed that the iron oxides were well dispersed on the OMC support and grew bigger with the increasing calcination temperature. The catalyst prepared with a lower calcination temperature showed higher decomposition efficiency towards 4CP and H<sub>2</sub>O<sub>2</sub>, but more metals were leached. The effect of different operational parameters such as initial pH, H<sub>2</sub>O<sub>2</sub> dosage, and reaction temperature on the catalytic activity was evaluated. The results showed that 96.1% of 4CP and 47.4% of TOC was removed after 270 min at 30°C, initial pH of 3 and 6.6 mmol/L H<sub>2</sub>O<sub>2</sub>. 88% of 4CP removal efficiency was retained after three successive runs, indicating Fe/OMC a stable catalyst for Fenton reaction. 4CP was degraded predominately by the attack of hydroxyl radical formed on the catalyst surface and in the bulk solution due to iron leaching. Based on the degradation intermediates detected by high performance liquid chromatography, possible oxidation pathways were proposed during the 4CP degradation.

## Introduction

Chlorophenols (CPs) are a particular group of priority toxic pollutants listed by the US Environmental Protection Agency in the Clean Water Act. They have been used in many industries such as preservative agents for wood and synthesis intermediates in the manufacturing of herbicides. They are resistant and hardly biodegradable, which pose a great threat to the human beings (Pera-Titus et al., 2004).

In recent years, advanced oxidation processes (AOPs) based on the generation of hydroxyl radical, a very powerful oxidizing agent, are reported as effective processes for treatment of organic pollutants (Brillas et al., 2009). Among these technologies, oxidation with Fenton's

reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) is a promising method due to its efficiency, low cost and simplicity. However, the traditional Fenton process based on homogeneous ferrous or ferric salts is limited with several disadvantages, including narrow range of pH (2–4) and the production of high amounts of sludge after disposal (Thi et al., 2011). To overcome these drawbacks, the heterogeneous Fenton process with Fe-based catalysts containing Fe oxides or supported Fe oxides has been developed. So far, the catalyst supports such as zeolites (Fajerwerg and Debellefontaine, 1996), mesoporous silica (Shukla et al., 2010),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Bautista et al., 2011), clay mineral (Aşçı, 2013), carbon aerogel (Duarte et al., 2009) and activated carbon (Duarte et al., 2011) have been reported. Among these supports, the carbon materials usually have high surface areas and abundant pore structures, which favor the adsorption and catalytic degradation of the contaminants.

Because of its large specific surface area and low

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price, activated carbon is frequently used as the catalyst support. However, its widespread use is restricted due to micropore size. Compared with microporous activated carbon, mesoporous carbons (MCs) have recently aroused great attention due to their large pore size and uniform pore structure (Liang et al., 2008). Hu et al. (2012) employed magnetic Fe<sub>3</sub>O<sub>4</sub>/ordered mesoporous carbon CMK-3 composite for adsorption of phenol and regenerated the adsorbents by dry oxidation. Kong et al. (2012) synthesized coordinatively unsaturated manganese monoxide-containing mesoporous carbon catalyst which demonstrated a high activity over a wide pH range in the wet peroxide oxidation of phenol. Chun et al. (2012) developed a magnetite-loaded mesocellular carbonaceous material. It exhibited superior activity as both a Fenton catalyst and an adsorbent for removal of phenol and arsenic. However, few reports studied the OMC-based catalyst for the heterogeneous Fenton-like oxidation of chlorophenols.

In this work, ordered mesoporous carbon supported iron catalysts (Fe/OMC) were synthesized by the incipient wetness impregnation method and applied to Fenton-like degradation of 4-chlorophenol (4CP). The influence of catalyst calcination temperature and working parameters such as initial pH, H<sub>2</sub>O<sub>2</sub> concentration, and reaction temperature was assessed. Stability and reusability of the Fe/OMC catalyst was also tested. Possible pathways were proposed according to the identification of reaction intermediates.

## 1 Materials and methods

### 1.1 Materials

All chemicals used in this study are at least analytical reagent. HNO<sub>3</sub>, NaOH, H<sub>2</sub>O<sub>2</sub>, HCl, HF, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 4CP, tetraethyl orthosilicate (TEOS), potassium oxalate titanium, phenol and formaldehyde solution were obtained from Xilong Chemical Company in China. Triblock copolymer Pluronic F127 (MW=12,600, PEO<sub>106</sub>PPO<sub>70</sub>PEO<sub>106</sub>) was supplied by Sigma-Aldrich. 4-chlorocatechol, 4-chlororesorcinol, catechol, hydroquinone, and benzoquinone were supplied by Alfa-Aesar. All chemicals were used as received without further purification.

### 1.2 Preparation of OMC and Fe/OMCs

OMC was prepared by triconstituent co-assembly of resols, oligomer silicates from TEOS, and triblock copolymer F127 template, followed by carbonization and silica removal according to the literature (Liu et al., 2006). Typically, 1.0 g of F127 and 1.0 g of 0.2 mol/L HCl were dissolved in 10.0 g of ethanol and stirred for 1 hr at 40°C. Then 2.08 g of TEOS and 2.5 g of 20 wt% resols' ethanolic solution were added in sequence. After being stirred for 2 hr at 40°C, the solution was transferred into dishes. It

took 5–10 hr at room temperature to evaporate ethanol and 24 hr at 100°C in an oven for the thermopolymerization. The product was scraped from the dishes and ground into powders. Calcination was carried out in a tubular furnace at 600°C for 3 hr with a ramping rate of 1°C/min under N<sub>2</sub> flow. The obtained silica-carbon nanocomposite was immersed in 10 wt.% HF solution for 24 hr at room temperature to remove silica and finally OMC was obtained.

The Fe/OMC catalysts were prepared by the incipient wetness impregnation of OMC with iron nitrate solution. The iron content in the Fe/OMC catalysts was 4.1 wt%. After impregnation, the catalyst was left at room temperature for 24 hr. Then it was dried at 110°C for 12 hr, followed by calcination at 300°C, 500°C, or 700°C for 3 hr under N<sub>2</sub> flow. The catalysts were denoted as Fe/OMC-T, where T represents the calcination temperature.

### 1.3 Catalyst characterization

The morphology of the samples was observed by transmission electron microscope (TEM, JEM-2100(UHR), JEOL, Japan). The phase identification of the catalysts was carried out by X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, the Netherlands) with the Cu K $\alpha$  radiation at 40 kV and 40 mA. Nitrogen sorption isotherms were measured at 77 K with an automated gas sorption analyzer (autosorb iQ, Quantachrome, USA). Before measurements, the samples were degassed under vacuum at 200°C for 8 hr. The specific surface area ( $S_{\text{BET}}$ ) was determined by Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) curve was derived based on the quenched solid density functional theory (QSDFT). The main pore size represents the pore diameter corresponding to the peak positions in PSD curve. The micropore volume ( $V_{\text{mi}}$ ) and micropore surface area ( $S_{\text{mi}}$ ) were calculated by the QSDFT method. The total pore volume ( $V_{\text{t}}$ ) was estimated from the amount adsorbed at a relative pressure of about 0.990.

### 1.4 Catalytic evaluation

The Fenton oxidation experiments were conducted in a 250 mL brown glass jar with a magnetic stirrer and a thermostatic water bath. The stirring velocity was around 950 r/min. A volume of 200 mL 100 mg/L 4CP aqueous solution and a weight of 40 mg catalyst were always used. The initial pH value was adjusted by HNO<sub>3</sub> solution. As the adsorption equilibrium was reached during 10 min (**Fig. 4**), a certain amount of H<sub>2</sub>O<sub>2</sub> was added to start the Fenton reaction after adsorption for 30 min. The specified volume of sample was withdrawn at given time intervals, filtered by 0.22  $\mu\text{m}$  membrane and analyzed immediately. The H<sub>2</sub>O<sub>2</sub> concentration was determined by spectrophotometric analysis with potassium titanium (IV) oxalate reagent at 397 nm (Sellers, 1980). 4CP and intermediates were analyzed by high performance liquid chromatography (HPLC, 1200 infinity series, Agilent,

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