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Photodegradation of Orange II using waste paper sludge-derived heterogeneous catalyst in the presence of oxalate under ultraviolet light emitting diode irradiation

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ABSTRACT

A waste paper sludge-derived heterogeneous catalyst (WPS-Fe-350) was synthesized via a facile method and successfully applied for the degradation of Orange II in the presence of oxalic acid under the illumination of ultraviolet light emitting diode (UV-LED) Powder X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electronic microscopy and N_2 sorption isotherm analysis indicated the formation of α-Fe_2O_3 in the mesoporous nanocomposite. The degradation test showed that WPS-Fe-350 exhibited rapid Orange II (OII) degradation and mineralization in the presence of oxalic acid under the illumination of UV-LED. The effects of pH, oxalic acid concentration and dosage of the catalyst on the degradation of OII were evaluated, respectively. Under the optimal conditions (1 g/L catalyst dosage, 2 mmol/L oxalic acid and pH 3.0), the degradation percentage for a solution containing 30 mg/L OII reached 83.4% under illumination by UV-LED for 80 min. Moreover, five cyclic tests for OII degradation suggested that WPS-Fe-350 exhibited excellent stability of catalytic activity. Hence, this study provides an alternative environmentally friendly way to reuse waste paper sludge and an effective and economically viable method for degradation of azo dyes and other refractory organic pollutants in water.

Introduction

The photo-Fenton process, as one of the most popular advanced oxidation processes (AOPs), is extensively applied in the treatment of industrial wastewaters (Oller et al., 2011). The photo-Fenton system mainly involves the formation of strongly oxidizing hydroxyl radicals (•OH), which can completely mineralize most organic compounds due to their high oxidation potential (E^0 = +2.8 V *versus* normal hydrogen electrode) (Haag and David Yao, 1992). Recently, photo-Fenton and photo-Fenton-like reactions have been widely employed as effective methods to degrade azo dyes (Chen et al., 2013; Guo et al., 2014, 2015; Liu et al., 2012). In these reactions, H_2O_2 is necessary to initiate the process, because H_2O_2 is the only source of •OH (Kremer, 1999; Pera-Titus et al., 2004). However, H_2O_2 is a very reactive chemical reagent with high oxidizing power and does not survive for long under normal conditions. Thus, the direct use of reactive H_2O_2 is inconvenient for practical industrial applications.

Polycarboxylic acids and iron oxides are capable of forming a photochemical system to initiate a photo-Fenton-like reaction generating •OH without the addition of H_2O_2 (Lei et al., 2006). It is notable that Fe(III)-carboxylate complex photochemical systems can achieve higher quantum efficiency than that of

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the photo-Fenton process or photocatalytic reaction with Fe(III) alone (Faust and Zepp, 1993; Li et al., 2007; Siffert and Sulzberger, 1991; Zuo and Deng, 1997). The photoexcitation of Fe(III)-carboxylate complexes can form Fe(II) and carboxylate radicals via a ligand-to-metal charge transfer (LMCT) mechanism, which has been previously elucidated in detail (Balmer and Sulzberger, 1999; Zuo and Deng, 1997).

It is well known that the usage of ultraviolet (UV) light sources is one of the major drawbacks limiting the commercialization of photocatalytic technologies. Low-pressure mercury vapor lights are typically employed as the UV source in conventional photocatalytic reactions, and have some drawbacks, such as containing highly toxic mercury, being relatively energy intensive and having short life spans. However, ultraviolet light emitting diode (UV-LED) can substitute for mercury lamps in photocatalytic process. UV-LED does not contain toxic mercury and have the advantages of longer life spans and lower energy consumption, allowing flexibility in engineering application (Hossaini et al., 2014). UV-LED has been successfully applied in photocatalysis processes for the degradation of several xenobiotics, including formaldehyde (Shie et al., 2008), bisphenol (Wang and Lim, 2010), and chlorophenol (Yu et al., 2013) in contaminated wastewater. However, little has been reported about the application of UV-LED as UV light-sources in Fe(III)-carboxylate complexes involved in photo-Fenton-like processes so far.

Recently, various kinds of supports such as mesoporous activated carbon (Karthikeyan et al., 2011), nanoporous activated carbon, activated carbon fibers (Karthikeyan et al., 2014), zeolites (Fukuchi et al., 2014), resins (Shu et al., 2010), and hydrogel (Wang et al., 2014) have been used to prepare heterogeneous photo-Fenton or photo-Fenton-like catalysts. However, these efficient catalysts have challenges in terms of high cost of production and technical complexity, to some extent, which limit their full-scale practical application. Thus, a major issue researchers confront is the development of a novel and highly active catalyst with a facile and low-cost synthesis process, which is suitable for extensive engineering application. On the other hand, an increasing amount of sludge is generated as a byproduct of the paper wastewater treatment process, which contains 20% or more solids, with 45%–55% moisture, which would cause serious environmental problems in the event of inappropriate management and disposal (Hamzeh et al., 2011). More recently, waste paper sludge has been used by converting it into mesoporous adsorbents to remove organic pollutants from water or reclaimed as an industrial raw material (Calisto et al., 2014; Devi and Saroha, 2014; Hamzeh et al., 2011). These methods are among the most feasible and environmentally friendly ways to make use of waste paper sludge. It is anticipated that waste paper sludge can be converted into a heterogeneous photo-Fenton-like catalyst of high catalytic activity.

The present study aimed to evaluate the potential of an as-synthesized catalyst (WPS-Fe-350) to degrade Orange II (OII) (as a model pollutant) in the presence of oxalic acid by using UV-LEDs as the activation source. Several significant factors such as the catalyst dosage, oxalic acid concentration and pH were investigated to optimize the reaction conditions and gain a clear understanding of this photochemical reaction. To the best of our knowledge, this is the first attempt to use a waste paper sludge-derived catalyst for effective degradation of OII in the presence of oxalic acid under illumination of UV-LEDs.

1. Experimental

1.1. Materials

The hydrous waste paper sludge used as raw material for the synthesis of catalyst in this study was sampled from a paper mill effluent treatment plant located in Zhejiang, China, with a designed capacity of 20,000 m^3/day. The moisture content of the wet sludge was 89.7% ± 0.3%. The sludge was stored at 4°C before use. Ferrous sulfate ($FeSO_4{\cdot}4H_2O$) and oxalic acid ($H_2C_2O_4$) were purchased from Aldrich Co. Orange II ($C_{16}H_{11}N_2NaO_4S$, 99.9%) was acquired from Fluka Co. All reagents were analytical grade unless otherwise stated. All of the solutions were prepared with water from a water purification system (Merck Millipore Co., Shanghai, China). Diluted solutions of sodium hydroxide or hydrochloric acid were employed for pH adjustment.

1.2. Preparation of catalyst

The dewatered waste paper sludge sample was dried at 105°C for 24 hr, and ground and sieved to a uniform size of <0.1 mm. Then the sample was heated to 350°C in a muffle furnace in air for 2 hr to obtain the material designated as WPS-350. The waste paper sludge-derived catalyst was prepared following the procedure below: a 10 g ground and sieved sample was impregnated in a 100 mL of 1 mol/L $FeSO_4$ solution for 24 hr at room temperature. After the supernatant liquid was completely removed, the sample was dried at 105°C for another 24 hr. Subsequently, the sample was heated to 350°C in a muffle furnace in air for 2 hr to obtain the material designated as WPS-Fe-350. Finally, the catalyst was washed three times with 95% alcohol and another three times with distilled water to remove anions and organic impurities. The waste paper sludge-derived Fe-loaded nanocomposite was designated as WPS-Fe-350 and used for characterization and degradation experiments.

1.3. Characterization of catalyst

The crystal phase was determined by X-ray diffraction (XRD, Ultima IV, Rigaku Co., Japan) with monochromatic Cu Kα radiation (45 kV, 50 mA). The functional groups were detected by Fourier transform infrared (FT-IR) spectroscopy (Nexus, Thermo Nicolet Lt., USA) using the potassium bromide (KBr) pellet method. The surface morphology was analyzed by scanning electron microscopy (SEM, FEI Co., The Netherlands). The specific surface area (S_{BET}), micropore surface and total pore volume were measured by the Brunauer–Emmett–Teller (BET) method (ASIC-2, PE Co., USA). The bulk chemical composition was analyzed via an energy dispersive X-ray detector (EDX) attached to the SEM.

1.4. Experimental procedures

The degradation experiments were conducted in a glass photoreactor, which has an internal diameter of 12 cm and a