Chemical Engineering Journal 328 (2017) 397–405

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Heterogeneous Fenton-like degradation of ofloxacin over a wide pH range of 3.6–10.0 over modified mesoporous iron oxide

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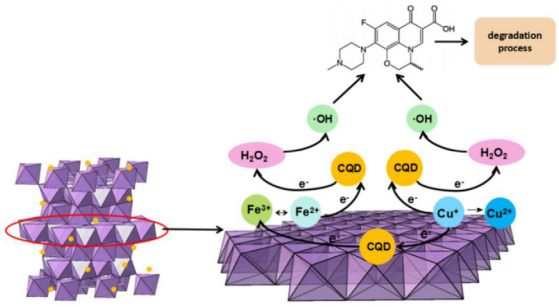
HIGHLIGHTS

- Carbon quantum dots supported on mesoporous Cu doped iron oxide was prepared.
- It was proven to be an excellent heterogeneous Fenton catalyst with good stability.
- Ofloxacin was efficiently degraded over a wide pH range of 3.6–10.0.
- Key role of CQDs in enhancement of the Fenton activity was detailed investigated.
- Heterogeneous Fenton-like reaction mechanism towards OFX degradation was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 April 2017
Received in revised form 16 June 2017
Accepted 9 July 2017
Available online 10 July 2017

Keywords:
Fenton
Mesoporous iron oxide
Cu doping
CQDs
Activity enhancement

ABSTRACT

To develop an efficient heterogeneous Fenton catalyst over a wide pH range without any external energy input is still a challenging work. In this study, the Fenton activity of mesoporous iron oxide was firstly extended to pH of 3.6–10.0 by the carbon quantum dots (CQDs) and Cu modification (CQDs/Cu-MIO). The characterization studies indicated that CQDs/Cu-MIO had a typical mesoporous structure and CQDs was highly dispersed on the surface of catalyst. While Cu element with Cu (I) and Cu (II) was introduced in the framework of iron oxide by chemical binding of Fe—O—Cu. Without the aids of UV, CQDs/Cu-MIO exhibited an excellent efficiency and the ofloxacin (OFX) degradation followed the pseudo-first order kinetic model with a reaction constant of 0.1109 min^{-1}. Moreover, the catalyst can be reused for 6 times with good stability, in which the maximum concentration of leaching Fe and Cu ions were 0.085 and 0.015 mmol/L. The optimum reaction condition was evaluated and the degradation process of OFX was further investigated by FT-IR spectrum. The reactive oxygen species involved in OFX degradation, the effects of mesoporous structure, Cu/Fe multivalent state and the excellent capability of electron transformation/energy exchange of CQDs on the enhancement of CQDs/Cu-MIO Fenton activity were also discussed. Finally, the heterogeneous Fenton reaction mechanism was proposed based on the experimental results.

1. Introduction

Nowadays, the frequent use of antibiotics results in serious environment issues [1]. Ofloxacin (OFX), one of the 2nd-generation of fluoroquinolone drugs, along with human's life for

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http://dx.doi.org/10.1016/j.cej.2017.07.049
1385-8947/

its activity in against bacteria [2,3]. Moreover, OFX is also toxic to mammalian cells for it can induce oxidative stress, lipid peroxidation and DNA oxidative damage to chondrocytes [4]. In addition, it is characterized by its very poor biodegradability and thus, they commonly reach the environment due the ineffectiveness of the urban wastewater treatment plants (WWTPs) for their removal. Its average concentration in WWTPs discharge and surface water in China are 780 ± 132 ng/L and 74 ± 15 ng/L, respectively [5,6]. Of course, high concentration of OFX will pose a potential threat to the underground water due to the effect of infiltration or runoff, which has caused increasing diseases such as cancer and becomes one of the main organic pollutants worldwide [7].

Advanced oxidation process as a green technology will eliminate organic pollution in underground water efficiently and environmentally friendly [8]. Fenton process, a kind of typical advanced oxidation reaction, should also be competent in the treatment of environmental contaminant [9,10]. However, there are three main disadvantages of the Fenton process. Firstly, extra energy such as UV is necessarily introduced into the reaction system to extend the working pH range. Secondly, the consumption of the reagent (Fe^{2+} and H_2O_2) is huge in conventional homogeneous Fenton and production of Fe containing sludge after the reaction. Thirdly, the conventional Fenton process requires strong acidic conditions (pH ≈ 3), which makes the Fenton reaction efficiency decrease since the acidity of aquatic environment is usually at near neutral pH [11,12]. Some solutions were then put forward to solve these problems. To save extra energy, visible light and natural light were used to replace UV irradiation in the latest researches [13,14]. To avoid the waste of reagent and enhance the efficiency of catalyst, Fe_2O_3 nanoparticles mixed with Mg were synthesized and exhibited enhanced catalytic activity for the degradation of methylene blue [15]. Seyed Ghorban Hosseini et al. also fabricated mesoporous Fe_2O_3 nanocomposite by SBA-15 silica as template to increase active sites of the catalyst [16]. Moreover, many researches are devoted to extend the applied pH range, such as doped S [11,17], combined with amino acid [18,19] or bonded with phenols [12]. Nevertheless, most of the researches can only extend the working pH to neutral but not alkaline conditions. Therefore, it is still a challenging work to solve all the three drawbacks of classic Fenton process.

At present, the heterogeneous Fenton process provides an effective alternative to the classical homogeneous Fenton reaction. Generally, the principal factor determining catalytic efficiency in heterogeneous catalysis is the sufficiently large surface area, which can be achieved by the use of either nanoparticles or granular particles with porous character. Iron oxides (γ-Fe_2O_3, α-FeOOH, Fe^0/Fe_3O_4) have been widely used in activation of H_2O_2 towards the removal of organic pollutants in water. Unfortunately, the process is relatively slow and inefficient at circumneutral pH values due to the limited surface reaction sites [20,21]. The porous materials with unique nanostructure had a large surface area by providing high dispersion of active component and enhancing the mass transportation [22–24]. But up to now, few studies were conducted to synthesize porous iron oxide assembled quantum dots and use it as heterogeneous Fenton catalyst. Moreover, carbon quantum dots (CQDs) is a new class of nanomaterial that possess excellent physicochemical characteristics, fluorescence emissions, and optical properties [25,26]. It can be used as photocatalyst in organic pollutant degradation owe to the capability of electron transformation and energy exchange with supporting species, for instance, TiO_2/CQDs composite stimulated by visible-light catalysis and the hydroxyapatite supported N-doped CQDs towards methylene blue degradation were developed and exhibited excellent performance [26]. TiO_2/CQD nanocomposites are able to completely degrade methylene blue (50 mg/mL) within 25 min under visible light irradiation, where only 5% of MB is degraded when pure TiO_2 is used as the photocatalyst. The modification with CQDs can obtain the rapidly electron transformation in the reaction system and improve the catalytic activity even in alkaline conditions [27]. Hence, we draw CQDs into our research to devise a kind of catalyst which can be used to catalyze Fenton process in a wide pH range without the aid of UV/ultrasonic.

In this study, the Fenton like activity of mesoporous iron oxide was enhanced by tailoring the surface electron transfer process via CQDs and Cu modification. Without UV or ultrasonic irradiation, the as-prepared CQDs/Cu-MIO exhibited an excellent performance in the ofloxacin degradation at a pH range of 3.6–10.0. The reaction mechanism and the effects of mesoporous structure, Cu and CQDs modification on the enhancement of Fenton catalytic activity was further discussed.

2. Experimental

2.1. Catalyst preparation

Mesoporous Cu doped iron oxide (Cu-MIO) was synthesized by a hard template method, in which the template of SBA-15 was prepared according to the procedure described by Chen et al. [28]. In a typical experiment, 0.4 g SBA-15 was added in 5 mL deionized water and stirred for several minutes. Different amounts of $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ ([Cu]/[Cu+Fe] = 5–25% in molar ratio) were then added into the above suspension and kept stirring for 4 h. After filtered and drying overnight, the obtained powder was calcined at 600 °C for 6 h. Finally, SBA-15 was removed by 20 mL 1 M NaOH solution under boiled condition and Cu-MIO was then obtained by washing with deionized water and anhydrous ethanol. CQDs were synthesized via a hydrothermal method [29] and were used to modify Cu-MIO as followed: a given amount of Cu-MIO was added into a CQDs containing solution, which was followed by ultra-sonication for one hour. The brown powder of CQDs/Cu-MIO was finally obtained after drying at 80 °C under stirring.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAXRC X-ray diffractrometer using Cu Kα radiation (γ = 0.154 nm) as the X-ray source. Transmission electron microscopy (TEM) images were collected on a transmission electron microscope with field emission gun at 200 kV (JEOL 2000EX, JEOL, Japan). N_2 adsorption-desorption isotherms were measured at a Micromeritics TriStar II sorptometer, the specific surface area and pore size distribution curves were obtained using the Brunauer-Emmett-Teller (BET) method from the adsorption data. X-ray photoelectron spectroscopy (XPS) was recorded on a MULT1LAB2000 photoelectron spectroscopy. Fourier transform infrared (FT-IR) spectroscopy was performed to assess different functional groups of the OFX degradation procedure using KBr pressed disks with a FTIR 650 spectrometer transmission analyzer. ICP-MS analysis was carried out on a ICAPQ01890.

2.3. Fenton activity evaluation

The Fenton catalytic activity of as-prepared catalyst was evaluated at ambient conditions, which meant that there was no requirement of the extra energy input such UV or ultrasonic irradiation. In a typical experiment, 25 mg catalyst were dispersed in 100 mL 12 mg/L of OFX solution, which was magnetically stirred for about 50 min to establish the adsorption/desorption equilibrium [30]. Then, the desired amount of 30 wt% H_2O_2 (the molar concentration of 30 wt% H_2O_2 was 9.7 mol/L) was added to the above suspension under continuous magnetic stirring. At given