



Rapid removal of dyes under visible irradiation over activated carbon fibers supported Fe(III)–citrate at neutral pH



Lie Wang, Yuyuan Yao*, Lijie Sun, Yajun Mao, Wangyang Lu, Sanqing Huang, Wenxing Chen*

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China

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ABSTRACT

Activated carbon fibers supported ferric citrate (FeCit@ACFs) as a heterogeneous catalyst for the rapid removal of dyes under visible light irradiation is reported. The FeCit@ACFs/H₂O₂ system exhibited remarkable catalytic activity across a wide pH range (2–10). Moreover, the catalyst presented excellent sustained catalytic ability in these experiments. The effects of catalyst dosage, and H₂O₂ concentration were also evaluated. Electron paramagnetic resonance (EPR) spectroscopy confirmed the hydroxyl radicals ([•]OH) involved as the active species in the catalytic system. Moreover, the superoxide radical (O₂^{•-}) was not detected by EPR, suggesting better use of H₂O₂ for removal of dyes. According to the observed effects of the scavengers *n*-butanol and KI, hydroxyl radicals, especially the surface-bounded [•]OH, had a dominant role in the oxidation of dyes. More importantly, the high adsorption capacity of ACFs could efficiently enhance the removal rate of dyes by the surface-bounded [•]OH. This paper discusses a possible catalytic oxidation mechanism in the FeCit@ACFs/H₂O₂ system, which provides a feasible approach for the elimination of widely existing pollutants.

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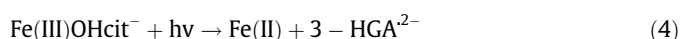
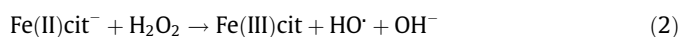
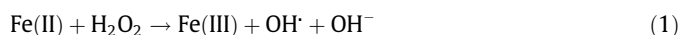
1. Introduction

In recent decades, advanced oxidation processes (AOPs) as efficient methods for eliminating dyes from wastewaters have attracted increasing attention [1–4]. The Fenton reaction (H₂O₂ + Fe²⁺/Fe³⁺) is one of the most efficient AOPs for the treatment of dye effluents because of its low toxicity, fast reaction rate, and simplicity of control. It can rapidly convert hydrogen peroxide into the oxidizing hydroxyl radical ([•]OH), which can degrade organic pollutants quickly and non-selectively [5,6]. However, the widespread application of the Fenton process is limited by some drawbacks. First, the high concentration of iron ions can result in the formation of sludges, and the removal of the sludges at the end of treatment is an expensive process [7]. Second, the Fenton reaction has to be carried out in a narrow pH range (2–4), so the strong acids and bases must be added into the reaction system, resulting in an additional cost [8].

Fe(III) is capable of being present as the Fe(III)–carboxylate species at pH > 4 in the presence of carboxylate ligand, which outcompetes the complexation of hydroxide ions with Fe(III) in aqueous solution. Among these Fe(III)–carboxylate species, Fe(III)–citrate has a higher cumulative stabilization constant (log β = 14.29) compared with Fe(III)–oxalate (log β = 5.52) [9],

enabling it to outcompete hydroxide ions for Fe(III)/Fe(II) at high pH. Moreover, citric acid is a naturally occurring hydroxyl carboxylic acid and is ubiquitous in natural waters, which provided the possibility for its wider application.

Over the past years, visible light-assisted catalysis has been generally regarded as a cleaner and greener technology for the treatment of organic pollutants in wastewater. In particular, due to their low toxicity and remarkable photoactivity, the photoreduction ability and photoreactivity of Fe(III)–citrate complexes have recently been intensively investigated (reactions 1–4) [10–13]. However, most of the reported catalytic reactions involving Fe(III)–citrate have been usually carried out in homogeneous media, in which the recycling of Fe(III)–citrate is difficult. At the same time, Fe(III)–citrate in homogeneous systems can easily enter the environment, thereby causing secondary pollution.



The development of heterogeneous catalysts is an interesting alternative that avoids these drawbacks and enables the reuse of the catalysts in consecutive batch cycles. In recent decades, various supports such as nafion [14], zeolite [15], resin [16], clay [17] and

* Corresponding authors. Tel.: +86 571 86843810; fax: +86 571 86843255 (Y.Y. Yao). Tel./fax: +86 571 86843251 (W.X. Chen).

E-mail addresses: yyy0571@126.com (Y. Yao), wxchen@zstu.edu.cn (W. Chen).

activated carbon [18] have been used to prepare novel heterogeneous catalysts. Compared with these supports, activated carbon fibers (ACFs) may be an ideal candidate to construct excellent heterogeneous catalysts. Activated carbon fibers (ACFs) is one kind of highly microporous carbon material with an extremely high adsorption capacity, a uniform micropore size distribution, and a large surface area. In addition, ACFs may be formed into felts or fabrics of various shapes, and is therefore amenable to handling compared with granular supports. However, few researchers have studied its catalytic activity as a solid support in the presence of H_2O_2 and visible light.

In the present study, we used ferric citrate as an appropriate and efficient catalytic active site that was supported onto ACFs (denoted as FeCit@ACFs). The catalytic properties of FeCit@ACFs were evaluated in terms of the removal rates of dyes in the presence of H_2O_2 under visible light irradiation. The effects of the main variables (e.g., pH, H_2O_2 concentration, and amount of catalyst), and reaction mechanism were investigated. Electron paramagnetic resonance (EPR) spectroscopy was performed to detect active hydroxyl radicals in the catalytic system. This investigation provides a new practical approach for using the heterogeneous Fe(III)–citrate system in the efficient treatment of dye effluent.

2. Materials and methods

2.1. Materials and reagents

ACFs was purchased from Jiangsu Sutong Carbon Fiber Co., Ltd. Ferric chloride hexahydrate, trisodium citrate dihydrate, and hydrogen peroxide (9.7 M, Sinopharm Chemical Reagent Co., Ltd.) were used as analytical reagents. The spin-trapping reagent, 5,5-dimethyl-pyrroline-oxide (DMPO) was obtained from Tokyo Chemical Industry Co., Ltd. All dyes, namely, Reactive Brilliant Red X-3B (X-3B), Reactive Brilliant Yellow M-3RE (M-3RE), Acid Red 1 (AR 1), and Methylene Blue (MB) (Fig. 1) are commercial compounds. They were used without further purification. Doubly distilled water was used throughout the dye decomposition process.

2.2. Preparation of FeCit@ACFs

A 3 M nitric acid solution was impregnated with 50 g of ACFs, and the resulting suspension was maintained at 25 °C for 24 h. Afterward, it was washed with deionized water until washings reached neutrality, and then dried to obtain acidified ACFs. The

acidified ACFs (10 g) was immersed in ferric citrate solution (0.01 M, Fe (III): Cit = 1:1) at 25 °C for 24 h. The treated ACFs was removed from the solution, rinsed with distilled water many times to remove free ferric citrate and other residues, and then dried in vacuo at room temperature to obtain the heterogeneous catalyst, FeCit@ACFs. The ferric citrate content of FeCit@ACFs was found to be $52.4 \mu\text{mol g}^{-1}$ on the basis of atomic absorption spectroscopy measurements of the iron content of FeCit@ACFs (Hitachi 170–70 atomic absorption spectrometer).

2.3. Catalytic experiments and analysis

The catalytic oxidation reaction was carried out in a magnetically stirred Pyrex reactor. The light source was a 100 W xenon–mercury lamp. A 400 nm glass cut-off filter was used to exclude ultraviolet light. The distance between the reaction vessel and light source was adjusted to about 10 cm. The temperature was maintained at 25 °C during the entire reaction. A reaction volume of 20 mL was used in all experiments. The reaction mixture was composed of 50 μM dye, 5 g L^{-1} FeCit@ACFs, and 20 mM H_2O_2 . Its pH was adjusted using a dilute aqueous solution of NaOH or $HClO_4$.

At given time intervals, the decoloration efficiency of the dyes was determined using an ultraviolet–visible (UV–vis) spectrometer (Hitachi U-3010). The kinetics of decoloration of the dyes may be described by a pseudo-first-order equation (Eqs. (5) and (6)):

$$dC/dt = -kC \quad (5)$$

$$C_t = C_0 \exp(-kt) \quad (6)$$

where C_t is the actual concentration of the target dye after exposure to visible irradiation for a period of time t ; C_0 is the initial concentration of dyes, and k is the pseudo-first-order rate constant (min^{-1}). The k values were obtained from the slopes of the regression lines fitted with the plot of $-\ln(C_t/C_0)$ versus t .

The Brunauer–Emmet–Teller specific surface area (S_{BET}), the micropore volume (W_0), and the mean micropore size (L_0) of the samples were determined using a high-speed automated area and pore size analyzer. EPR signals of radicals trapped by DMPO were recorded at ambient temperature on a Bruker A300 spectrometer equipped with a Quanta-Ray Nd: YAG laser (532 nm). The settings for the EPR spectrometer were as follows: center field, 3520 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 12.72 mW. The leaching of iron ion was measured by atomic absorption spectroscopy (Hitachi 170–70 atomic absorption spectrometer). The concentration

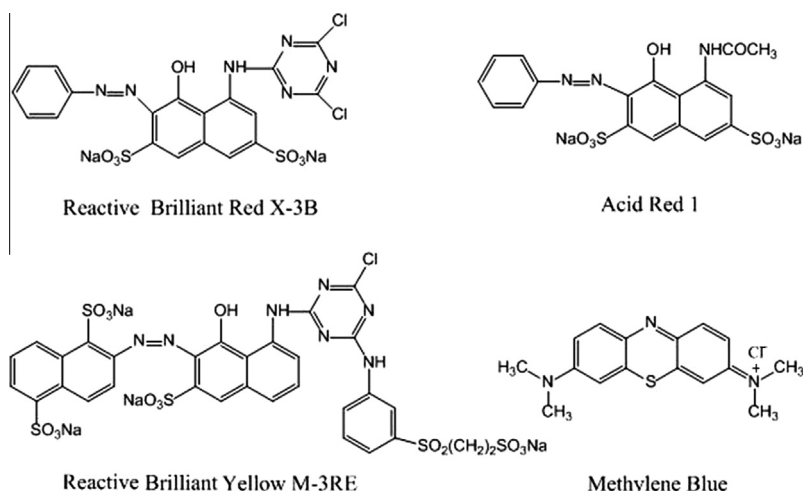


Fig. 1. The molecular structures of Reactive Brilliant Red X-3B, Acid Red 1, Reaction Brilliant Yellow M-3RE, and Methylene Blue.

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