



Extremely enhanced generation of reactive oxygen species for oxidation of pollutants from peroxymonosulfate induced by a supported copper oxide catalyst

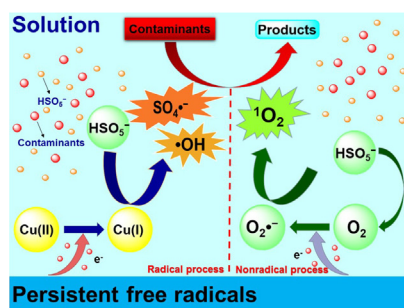
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HIGHLIGHTS

- CFs (PFRs) was coupled with CuO to construct an efficient catalytic oxidation system.
- The introduction of PFRs endowed the constructed catalyst with strong catalytic activity.
- Radicals process and non-radicals process were involved in CuO-CFs/PMS system and CuO-CFs/PMS/HCO₃⁻ system.
- The enhanced activity was attributed to more reactive oxygen species generation including ·OH, SO₄^{·-} and ¹O₂.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, carbon fibers (CFs), were innovatively integrated with copper oxide (CuO) to construct a distinctive catalyst with strong catalytic activity, CuO-CFs, which can effectively activate peroxymonosulfate (PMS) to generate reactive oxygen species (ROS) for the decomposition of contaminants. The introduction of CFs significantly improved the catalytic performance of CuO, leading to a higher removal efficiency with AR1 as model compounds, which was attributed to the increased generation of ROS (·OH, SO₄^{·-} and ¹O₂). Furthermore, the TOC removal rate indicated that CuO-CFs/PMS system could mineralize contaminant. Also, other contaminants such as benzoic acid (BA), phenol, sulfamethoxazole (SMX) and 8-hydroxyquinoline (8-HQ) could be also removed to some extent in the system. An investigation into the reaction mechanism suggested that the persistent free radicals (PFRs) in CFs serve as an electron sink to offer electrons to CuO and O₂, accelerating the key reaction step of Cu(II) to Cu(I) and O₂ to O₂^{·-}, thus enhancing the generation of ROS, which has been reported herein, for the first time, and offers a new and deeper insight into the positive effect of PFRs in CFs. Moreover, the addition of bicarbonate ion (HCO₃⁻) further enhanced the oxidation performance of the CuO-CFs/PMS system, this observation contradicted previous reports stating the negative role of HCO₃⁻. This discovery has major significance for recognizing the role of PFRs contained-carbonaceous materials, which not only provide a novel and simple strategy for PMS activation, but also initiated the latest study field of PFRs-enhanced catalysis.

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1. Introduction

Over the past few years, it has been discovered that some radicals, such as semiquinones and phenoxy radicals, have half-lives in the order of hours and days under atmospheric conditions,

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which are referred to as persistent free radicals (PFRs) [1,2]. Recently, due to their persistence and radical reactivity, PFRs has received an increasing amount of attention in biological and environmental fields [3]. In the previous reports, PFRs are mainly considered as hazardous substances, which have the potential to induce oxidative stress and a variety of illnesses. In addition, they also could damage the structure of the human body in exposed populations, such as DNA damage and pneumonia [4–6]. Recently, some researchers have reported that PFRs could directly activate H_2O_2 to oxidize organic contaminants [1], however, studies exploring the positive roles of PFRs are still scarce.

It is worth noting that PFRs contains an abundance of unpaired electrons, which can serve as an electron sink and enable some electron-acceptors such as higher valent metals, to accept electrons from PFRs, accelerating the reduction of higher valent metals [7,8]. Our previous research showed that the catalytic performance of metal catalyst mainly depend on the electron transfer and accepting behavior found between the central metal ion and reagent [9], therefore, the characteristic of PFRs have great potential to accelerate important metal catalytic redox processes such as the reaction rate-determining step of higher valent metal to lower valent metal (e.g., the Fe(III)/Fe(II) cycle in the Fenton reaction) [3]. Hence, PFRs may play a positive role in enhancing the catalytic oxidation performance for the treatment of contaminants.

Lately, CuO has been frequently reported as a catalyst to activate oxidant such as persulfate (PS), PMS for the treatment of contaminants. Zhang et al. showed that the copper oxide particles can directly activate PS for the degradation of 2,4-dichlorophenol and they concluded that a non-radical process was involved in this reaction [10]. Ji et al. also reported that a well-crystallized CuO can activate PMS for the removal of phenol [11]. Although CuO activate some oxidants for the removal of pollutant has been widely investigated, CuO directly used as a catalyst in an aqueous solution is still challenging, because (1) the separation of catalysts from the reaction system is difficult [12], and (2) CuO can only work efficiently in a narrow pH range [11]. The development of supports for CuO is a simple and effective strategy to overcome the above drawbacks of the powdered CuO catalyst, which could enable the reuse of CuO catalyst and expand its effective pH range. Recently, many attempts towards the immobilization of CuO have been made to construct a novel copper-based catalysts [13,14] and many kinds of supports such as zeolites [15], hydrotalcite [16] and montmorillonite [17] have been used to prepare the heterogeneous catalysts. Though many efforts have been made to develop efficient heterogeneous catalysts, it is still a meaningful and challenging task to further enhance the catalytic activity of copper-base heterogeneous catalysts when the CuO particles have improved dispersion on the support

Many researchers have indicated that PFRs are widely found in carbonaceous materials, which has attracted increasing interest in the catalysis field [18,19]. Hence, the electrons transfer behavior of the CuO catalytic system may be enhanced with the introduction of carbonaceous materials in view of the distinct properties of PFRs. Among all carbonaceous materials, carbon fibers possess excellent electrochemical properties, mechanical strength and high temperature resistance [20–22]. Herein, CFs were selected as the support to prepare a novel and efficient catalyst (CuO-CFs). To the best of our knowledge, the research on the catalytic performance of CuO-CFs and the key role of PFRs in CFs has not been reported to date.

In this work, we have prepared a novel catalyst, CuO-CFs, which was coupled with PMS to build an efficient catalytic oxidation system. The catalytic activity of CuO-CFs was investigated with multiple contaminants including phenol, antibiotic and dyes as model compounds. Electron paramagnetic resonance (EPR) technology and kinds of capture agents were employed to reveal the key role

of PFRs in CFs. The results of the research not only offer a novel perspective into the positive effect of PFRs, but also initiated a promising research field of PFRs-enhanced catalysis. Furthermore, we also reveal the mechanism of PMS activation using carbonaceous materials, providing guidance for the development of robust processes to generate reactive species (e.g., $SO_4^{\cdot-}$, $\cdot OH$ and 1O_2) for the removal of pollutant in environmental catalysis.

2. Experimental

2.1. Materials and reagents

Carbon fiber was obtained from Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Science. Copper nitrate hydrate ($Cu(NO_3)_2 \cdot xH_2O$) was purchased from Shanghai Macklin Biochemical Co., Ltd. Potassium peroxymonosulfate (PMS: oxone, Aladdin Industrial Corporation) were used as analytical reagents. The spin trapping reagent 5,5-dimethyl-pyrroline-oxide (DMPO) was supplied from Tokyo Chemical Industry Co., Ltd. All contaminants, including Acid Red 1 (AR1), Reactive Red 3BF (3BF), Acid Orange 7 (AO7), Methylene Blue (MB), Rhodamine B (RhB) and Reactive Red X-3B (X-3B) are commercial compounds without further purification. All other chemical reagents used in this study were provided by Hangzhou Mike Chemical Instrument Co., Ltd. (Hangzhou, China). Doubly distilled water was used throughout this study.

2.2. Catalyst preparation

Carbon fibers were impregnated into a nitric acid solution (15 M) for 2 h at 100 °C. Afterwards, the treated CFs were taken out and rinsed repeatedly with distilled water to neutrality, and then dried to obtain oxidated CFs. The dried oxidated CFs (2 g) was immersed in copper nitrate aqueous solution with 0.06 M; the reaction was carried out at 50 °C for 24 h, the resulting product was dried at 60 °C for 24 h. Finally, the dried product was calcined at 400 °C in a muffle furnace for 4 h, and then the catalyst was dried at 60 °C for 12 h. The atomic absorption spectrum (AAS) indicated that the CuO loading was about 2.5 wt%. (Hitachi 170–70 atomic absorption spectrometer)

2.3. Experimental procedures and analysis

The removal of contaminants was carried out in a 40 mL glass beaker, with the temperature set at 50 °C or other temperatures as required using a constant temperature shaker water bath (DSHZ-300A, Taicang, Jiangsu). A reaction volume of 20 mL was used in all experiments. A typical reaction mixture contained the following initial concentrations: the contaminants (50 μM), CuO-CFs (2 g/L), CFs (2 g/L), CuO (0.05 g/L), PMS (0.5 mM). At predetermined intervals (1 min), samples were passed through 0.22 μm pore size cellulose filters and analyzed immediately with a UV-vis spectrometer (Hitachi U-3010) by measuring the degradation efficiency of contaminants at the maximal wavelength. The TOC removal was measured by a TOC instrument (The Elementar Liqui TOC II type TOC/TN analyzer, Germany). The initial solution pH was adjusted with NaOH or $HClO_4$ prior to the addition of catalyst and oxidant for all of the experiments. The settings for the EPR spectrometer were: center field, 3520 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 20.00 mW. The total number of electrons released during the oxidation in the system was detected by the ABTS method.

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