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Catalytic degradation of 2-phenylbenzimidazole-5-sulfonic acid by peroxymonosulfate activated with nitrogen and sulfur co-doped CNTs-COOH loaded $CuFe_2O_4$

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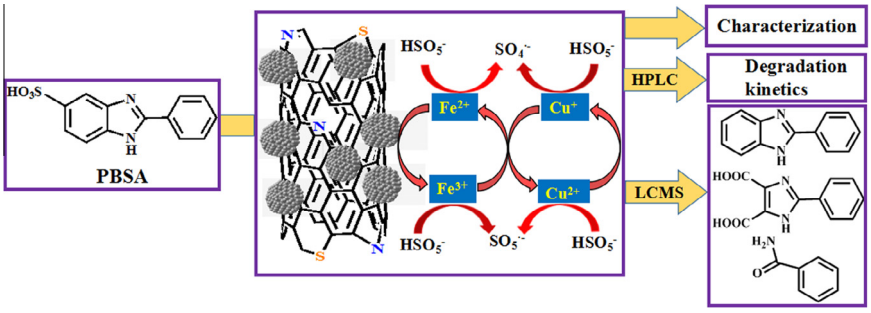
HIGHLIGHTS

- NS-CNTs/$CuFe_2O_4$ catalyst was successfully synthesized and characterized.
- The activation mechanisms by NS-CNTs/$CuFe_2O_4$ were studied.
- The degradation pathways of PBSA in PMS system were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Recently, the toxicity of sunscreen has received extensive attention due to their potential endocrine disrupting effect. In the present study, nitrogen and sulfur co-doped multi-walled carbon nanotubes loaded $CuFe_2O_4$ (NS-CNTs/$CuFe_2O_4$) catalyst was rationally designed and synthesized by co-precipitation method for the degradation of 2-phenylbenzimidazole-5-sulfonic acid (PBSA, a typical sunscreen addition). The catalyst was fully characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction, Fourier transform infrared spectroscopy, nitrogen gas uptake, and X-ray photoelectron spectroscopy. Then the kinetics, pathways and mechanisms of catalytic degradation of PBSA were studied in NS-CNTs/$CuFe_2O_4$ activated peroxymonosulfate (PMS) solution. The catalyst showed high catalytic activity, stability and reusability in PBSA removal. The results of electron paramagnetic resonance (EPR) and quenching experiments suggested that sulfate radicals ($SO_4^{\cdot-}$) predominated in the activation of PMS by NS-CNTs/$CuFe_2O_4$. The synergistic effect between $CuFe_2O_4$ and NS-CNTs was proposed in PMS activation. In addition, eight degradation intermediates of PBSA were identified by liquid chromatography mass spectrometry (LC–MS), and degradation pathways were further proposed. Overall, this study provides insights of PBSA removal by NS-CNTs/$CuFe_2O_4$ activated PMS at ambient temperature.

1. Introduction

In the past a few decades, sunscreens are widely used in personal care products (PCPs) to prevent the burns and skin cancer caused by sunlight radiation [1]. 2-Phenylbenzimidazole-5-sulfonic acid (PBSA), exhibiting high absorption capacity in the UV-B region (290–320 nm), has become one of the most effective and typical additives in sunscreens. However, PBSA was reported to possess ecological toxicity such as estrogenic activity [2,3] and phytotoxic effect [4]. Therefore, PBSA is regarded as environmental emerging contaminants by the U.S. Environmental Protection

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Agency [5] and has been classified as one of the endocrine disrupting chemicals (EDCs) in the environment [6,7]. Nowadays, relative high concentration of PBSA (109–2679 ng L^{-1} [8]) has been detected in natural environment, resulting from its easily releasing into waters from the wide application of PCPs and incomplete elimination in wastewater purification. The photochemical degradation of PBSA has been discovered as an effective method and has attracted extensive attention [9–12]. However, to our best knowledge, ultraviolet irradiation cannot be avoided in previously reported photochemical processes, which leads to increasing cost in water treatment and potential of radiation-induced cancer. Unfortunately, very limited strategies are known for degradation of PBSA. It is of urgency to develop alternative processes for destructing PBSA in aqueous solutions.

In recent years, sulfate free radicals ($SO_4^{\cdot-}$) based advanced oxidation technologies (AOTs) have received considerable studies, which were used to eliminate organic pollutants in water treatment [13–17]. $SO_4^{\cdot-}$ had stronger oxidizing capacity of 2.5–3.1 V at different pH in solution compared with hydroxyl radicals (·OH, oxidizing potential 1.9–2.7 V) [18,19]. Thus, $SO_4^{\cdot-}$ has been applied to degrade numerous recalcitrant organic substances, such as perfluorinated compounds, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and volatile organic compounds [14,16,20]. $SO_4^{\cdot-}$ can be generated efficiently and conveniently from peroxymonosulfate (PMS) by various activation methods (such as heat, UV, transition metals cations or metal oxides) [21–24], which is very promising for large scale water treatment. Interestingly, although the photodegradation of PBSA has been studying for years and the advantage of usage of $SO_4^{\cdot-}$ is obvious, PMS based AOTs in destructing PBSA in aqueous solution is rarely reported.

$CuFe_2O_4$ exhibited superior catalytic activity for PMS based $SO_4^{\cdot-}$ generation [21,22]. Moreover, the magnetic nature of $CuFe_2O_4$ makes it easy to be separated from aqueous systems. Nevertheless, it should be noted that the conductivity and the number of active sites in bulk $CuFe_2O_4$ are limited, which potentially hinders its electron transfer rate and catalytic efficiency, respectively. Loading $CuFe_2O_4$ on CNTs not only confines the size of particles to nanoscale to expose more active sites but also facilitates electron transfer in the catalyst. Meanwhile, as previous studies have reported, CNTs as catalyst can improve the ozonation reaction [25,26]. On the other hand, CNTs and graphene can be co-doped by elements with different electronegativity (such as N, S, P) to introduce extra active sites with preserved conductivity [27–30]. Considering the promising properties mentioned above, coupling doped CNTs-COOH with $CuFe_2O_4$ is expected to show high catalytic activity and efficiency for PMS based degradation of PBSA.

In this study, NS-CNTs/$CuFe_2O_4$ as the highly active and environment-friendly catalyst was prepared and characterized. The catalytic degradation kinetics, mechanisms and pathways of PBSA in PMS system were systematically investigated. Moreover, quenching tests and electron paramagnetic resonance (EPR) studies were employed to elucidate the types of active free radicals. Liquid chromatography mass spectrometry (LC–MS) analysis was applied to identify the major degradation products of PBSA, from which the possible degradation pathways of PBSA in PMS system were proposed.

2. Materials and methods

2.1. Chemicals and materials

PBSA (CAS NO. 27503-81-7, purity >95%) was purchased from J&K company (Shanghai, China). Peroxymonosulfate (PMS, $KHSO_5$·$0.5KHSO_4$·$0.5K_2SO_4$, purity ⩾47% $KHSO_5$) and 5,5-dimethyl-1-

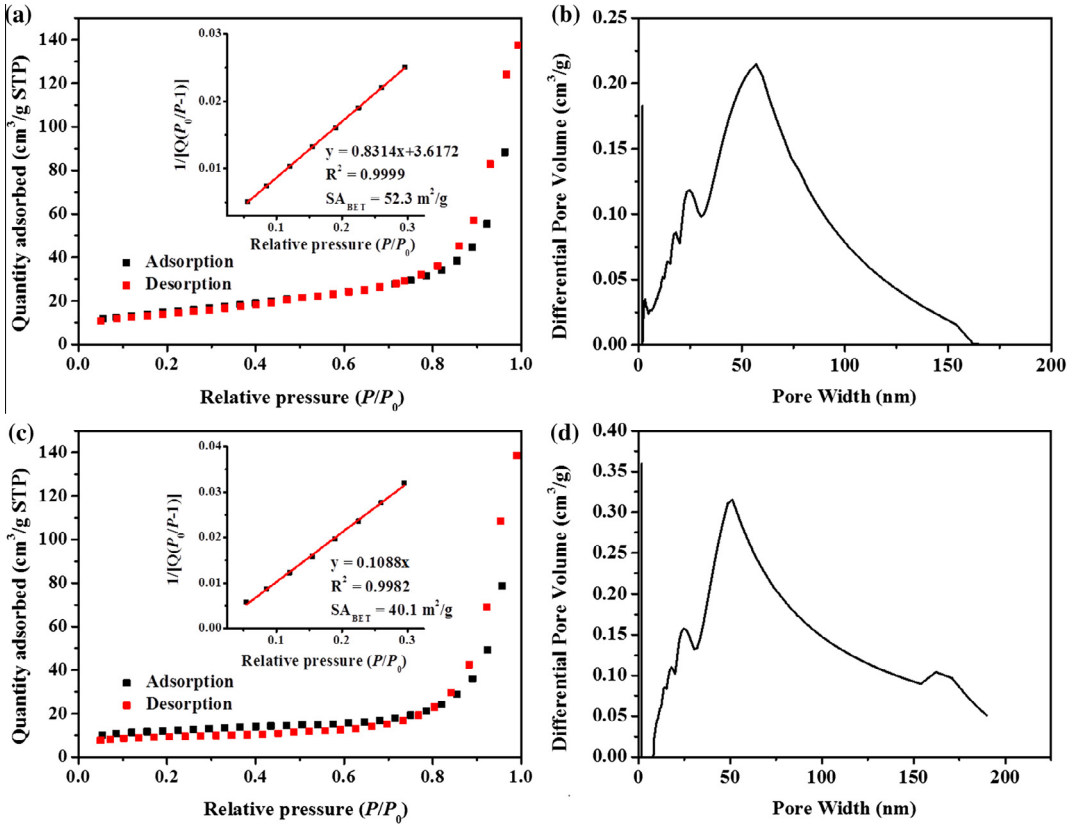

Fig. 1. Nitrogen adsorption-desorption isotherms of (a) NS-CNTs/$CuFe_2O_4$ and (c) the reused NS-CNTs/$CuFe_2O_4$ (the insets of the graphs are BET surface area plots), pore size distributions of (b) NS-CNTs/$CuFe_2O_4$ and (d) the reused NS-CNTs/$CuFe_2O_4$.