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A novel heterogeneous system for sulfate radical generation through sulfite activation on a $CoFe_2O_4$ nanocatalyst surface

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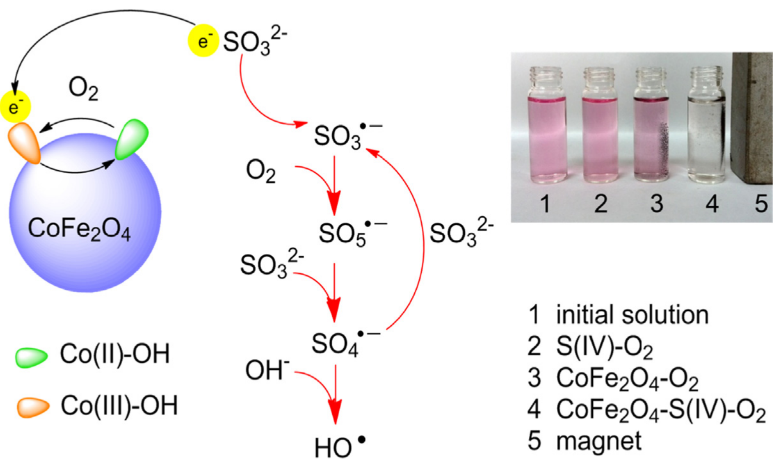
HIGHLIGHTS

- $CoFe_2O_4$—S(IV)—O_2 system is proposed as a new system of sulfate radical based AOPs.
- Alkaline pH favors the activation of sulfite on $CoFe_2O_4$ surface to produce oxysulfur radicals.
- Generation of Co—OH complexes on the surface of $CoFe_2O_4$ is the main factor for sulfite activation.
- Degradation of organic contaminants by $CoFe_2O_4$—S(IV)—O_2 system were achieved.
- Main intermediates and pathways for the degradation of metoprolol were identified.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous catalytic activation is important for potential application of new sulfate-radical-based advanced oxidation process using sulfite as source of sulfate radical. We report herein a heterogeneous system for sulfite activation by $CoFe_2O_4$ nanocatalyst for metoprolol removal. Factors that influence metoprolol removal were investigated, including pH and initial concentrations of components. The $CoFe_2O_4$ nanocatalyst was characterized by X-ray diffractometry (XRD) and transmission electron microscopy (TEM), and the catalytic stability was tested by consecutive runs. Radicals generated in the $CoFe_2O_4$—S(IV)—O_2 system were identified through radical quenching experiments and by electron spin resonance (ESR). The catalytic mechanism was elucidated further by X-ray photoelectron spectroscopy (XPS). The catalytic process was dependent on initial pH, and more than 80% of the metoprolol can be removed at pH 10.0 following the Langmubir-Hinshelwood equation. The generation of Co-OH complexes on the $CoFe_2O_4$ surface was crucial for sulfite activation. $SO_4^{\bullet-}$ was verified to be the main oxidative species responsible for metoprolol

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degradation. Other organic pollutants, such as sulfanilamide, sulfasalazine, 2-nitroaniline, sulfapyridine, aniline, azo dye X-3B and 4-chloroaniline, could also be removed in this $CoFe_2O_4$—S(IV)—O_2 system. The results suggest that the $CoFe_2O_4$—S(IV)—O_2 system has good application prospects in alkaline organic wastewater treatment.

1. Introduction

An efficient method for chemical oxidation based on the sulfate radical ($SO_4^{\bullet-}$) has gained widespread attention [1,2]. $SO_4^{\bullet-}$ has a high standard reduction potential (2.5–3.1 V [3]), which can be used to selectively oxidize organics [4]. In recent decades, studies have focused on the application of $SO_4^{\bullet-}$ in the removal of organic contaminants, such as dyes, pesticides, and antibiotics that are recalcitrant in conventional wastewater treatment [5–8]. $SO_4^{\bullet-}$ can be produced from potassium persulfate (PS) or peroxymonosulfate salts (PMS) by a variety of approaches such as photolysis, radiation, and thermal activation [9–13]. In these approaches, the addition of transition metals is recognized to be a viable way to achieve PS/PMS homogeneous activation [2,14]. Co(II) and Fe(II)/Fe(III) are the most commonly used metal activators because of their natural existence in environmental media [1,15,16].

Although Co/PMS homogeneous catalysis is very efficient for removing organic contaminants in water, the potential health hazards caused by dissolved cobalt in water limit its practical application [17–19]. Heterogeneous catalysis using cobalt oxides was used to overcome drawbacks of homogeneous Co/PMS catalysis. Anipsitakis and Dionysiou [20] first demonstrated the potential of Co_3O_4 for PMS activation and discovered that the Co_3O_4/PMS system achieved good performance in the degradation of 2,4-dichlorophenol. More recently, nano-Co_3O_4 and modified Co_3O_4 catalysts that use Al_2O_3, TiO_2, MgO, and graphene oxide were used to activate PMS and these exhibited a high efficiency for organic contaminant removal [18,21–24]. Although these catalysts have a good long-term stability and yielded a low concentration of dissolved cobalt ions, they are difficult to be separated from water and may cause secondary environmental problems. Therefore, the development of a catalyst that can be readily recovered after its application is desirable. Dionysiou's group has reported on the performance of the cobalt–iron catalyst, $CoFe_2O_4$, which is environmentally friendly and can be recovered easily using magnetic-based separation because of its ferromagnetic properties [18]. Subsequently, several groups focused on the Co-Fe mixed oxide/PMS heterogeneous system. Su et al. [25] investigated the performance of $Co_xFe_{3\text{-}x}O_4$ nanocatalysts to activate PMS for rhodamine B degradation, and found that the special structure of $Co_xFe_{3\text{-}x}O_4$ and the Fe—Co interaction are key reaction mechanisms. Ren et al. [26] and Li et al. [27] demonstrated the existence of Co^{2+}—Co^{3+}—Co^{2+} redox processes during the reaction, and $SO_4^{\bullet-}$ and $HO^\bullet$ played an important role during PMS activation. Wei et al. [28] compared the role of different transition metals in the $Fe_{3-x}M_xO_4$/PMS system for Acid Orange II degradation at neutral pH, and discovered that Co, Mn, and Ni improved the catalytic activity of magnetite, whereas Cr showed an inert effect.

In our previous work, we reported on novel systems that utilize Fe(II)-sulfite, Fe(III)-sulfite, and photo-Fe(II)-sulfite for the $SO_4^{\bullet-}$-mediated decolorization of Orange II between 2012 and 2015 [29–32]. In homogeneous Fe—S(IV)—O_2 systems, sulfite oxidation by dissolved oxygen occurs through a series of chain reactions that generate several oxysulfur radicals ($SO_x^{\bullet-}$), including the sulfite radical ($SO_3^{\bullet-}$), the sulfate radical ($SO_4^{\bullet-}$), and the PMS radical ($SO_5^{\bullet-}$). The formation of HSO_5^- and $HO^\bullet$ has been also reported [33,34]. Similarly, Kuo et al. [35] reviewed the state-of-the-art of chemistry in the aqueous Fe—S(IV)—O_2 system, and explained the basic chain oxidation mechanisms of sulfur–oxygen radical generation. To date, an investigation of the industrial or environmental application of S(IV) systems has been more limited than the PS/PMS systems. Na_2SO_3 is much more stable than $K_2S_2O_8$, and is more environmentally friendly than systems that contain $K_2S_2O_8$ [29,36]. However, to the best of our knowledge, limited work has been reported on heterogeneous systems that use sulfite to replace PS or PMS.

In this work, the heterogeneous catalytic performance of $CoFe_2O_4$ for sulfite activation has been evaluated. Metoprolol (MET), which is a model cardiovascular active pharmaceutical ingredient that has been detected extensively in surface waters, was chosen as a target contaminant. The aim of this study was to examine the effect of different process parameters and to explain the catalysis mechanism on MET degradation. The effects of sulfite concentration, $CoFe_2O_4$ concentration, initial pH on the MET degradation process, and catalyst reusability were investigated. MET products were determined by LC-ESI-MS, and a possible degradation pathway was proposed. The involved $SO_4^{\bullet-}$ and $HO^\bullet$ were identified, and the mechanism of sulfite activated by $CoFe_2O_4$ was explored by XPS technique.

2. Materials and methods

2.1. Materials

MET (CAS No. 56392-17-7) was obtained from Sigma-Aldrich Co. (3050 Spruce Street. St. Louis, MO 63103 USA). Sulfanilamide, sulfasalazine, 2-nitroaniline, sulfapyridine, aniline, X-3B and 4-chloroaniline were from Sinopharm Chemical Reagent Co., Ltd (52 Ningbo RD, Shanghai, China). The substance structures are provided in the Supporting information (SI) Table S1. Sodium sulfite (Na_2SO_3), potassium persulfate ($K_2S_2O_8$, ≥99.5%), PMS ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$), hydrogen peroxide ($H_2O_2$), cobalt iron oxide ($CoFe_2O_4$), cobaltous oxide (CoO), cobaltosic oxide (Co_3O_4), cobaltic oxide (Co_2O_3), and ferric oxide (Fe_2O_3) were from Aladdin Co. (1008 Qigang RD, Nanqiao Town, Fengxian Shanghai, China). NaOH and H_2SO_4 were from Sinopharm Chemical Reagent Co., Ltd., and were used to adjust the solution pH. *tert*-Butyl alcohol (TBA) and ethanol (EtOH) were obtained from Sinopharm Chemical Reagent Co., Ltd., and were used as scavengers of the relevant radicals. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was from Sigma-Aldrich Co., China. All chemicals were of analytical reagent grade or of higher purity and were used without further purification. Doubly-distilled deionized water (Milli-Q) was used to prepare all solutions.

2.2. Characterization

X-ray diffractometry was performed on a PANalytical X'Pert Pro X-ray diffractometer. The sample was scanned at 2θ from 10° to 80°. The sample morphologies and structures were characterized by transmission electron microscopy (TEM, HITACHI H-7000FA). XPS analysis was performed on a Thermo Scientific, Escalab 250Xi spectrometer. DMPO was used as the spin-trapping agent in the

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