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Heterogeneous activation of peroxymonosulfate by sillenite $Bi_{25}FeO_{40}$: Singlet oxygen generation and degradation for aquatic levofloxacin

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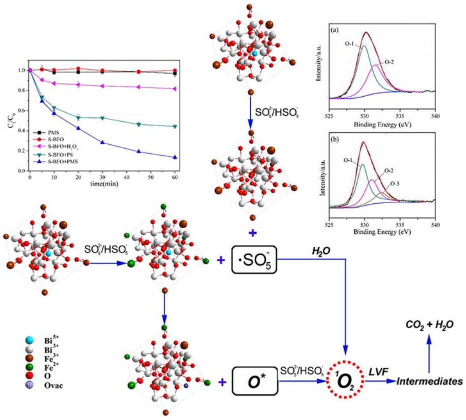
HIGHLIGHTS

- Sillenite $Bi_{25}FeO_{40}$ catalyst was synthesized and characterized.
- Activation of PMS using S-BFO showed a superior effect on degradation of LVF.
- Singlet oxygen was identified as the main reactive oxygen species using EPR, HPLC–MS and DO monitoring experiments.
- Parallel generations of $^1O_2$ including the PMS activation and the oxygen vacancy/O^* production were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Sillenite bismuth ferrite (S-BFO) $Bi_{25}FeO_{40}$ was synthesized by a hydrothermal process and firstly adopted for the activation of peroxymonosulfate (PMS). Multiple characterization was conducted for the morphology and physicochemical features of S-BFO. Degradation of aquatic levofloxacin (LVF) was thoroughly evaluated by using a coupled process for the decontamination of the typical emerging organics. Some crucial parameters for the activation kinetics as well as economic recyclability were examined with the detailed mechanism proposed. For the first time, singlet oxygen ($^1O_2$) was identified as the main reactive oxygen species through radical scavenging experiments, electron paramagnetic resonance spectroscopy (EPR) and HPLC-MS determination. Based on the XPS and EPR results, a catalytic mechanism is proposed concerning the parallel generations of $^1O_2$: (i) Bi^{5+} is replaced by Bi^{3+}, resulting in the formation of an oxygen vacancy in the lattice and an active oxygen (O^*), which could produce $^1O_2$ through the reactions with PMS; (ii) direct formation of $^1O_2$ from radSO-5 generated by the interaction between Bi^{5+} and PMS. This study demonstrates a novel catalyst for heterogeneous activation of PMS via a non-radical mechanism, which could be alternatively adopted in the decontamination in surface/ground water.

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1. Introduction

$BiFeO_3$ (2.0–2.7 eV) with a perovskite structure showed great potential on organic pollutant degradation and water splitting, because of its high chemical stability, ferroelectricity and ferromagnetic properties [1]. Differing from TiO_2, the traditional catalyst in UV-activated photocatalysis, many studies have been reported on the visible light photodegradation performance of $BiFeO_3$, including water decontamination for surface/ground water [2,3]. However, due to the synthesizing difficulty of single-phase perovskite-type bismuth ferrite, many impurity phases are derived in the preparation process [4]. Sillenite bismuth ferrite ($Bi_{25}FeO_{40}$, S-BFO) a typical byproduct in the synthesis of $BiFeO_3$, shows great photocatalytic activity for the narrower energy gap (1.68 eV) and high superparamagnetic behavior, providing advantages for feasible separation and recovery [5]. Previous study has revealed that the formation of sillenite-type and perovskite-type bismuth ferrites mainly depend on the reaction-time [6].

During the past few years, the advanced oxidation processes (AOPs) based on sulfate radicals ($\cdot SO_4^-$, 2.5–3.1 V) have been extensively utilized in decontaminations due to the high nonselective reactivity towards most organic pollutants [7]. Thermolysis [8], transition metals [9], ultrasound [10], bases [11], UV [12] and other oxidants (i.e. hydrogen peroxide, ozone) [13,14] are commonly used to active peroxymonosulfate (PMS) or persulfate (PS) to generate $\cdot SO_4^-$. Due to its higher energy efficiency and being more economical, the transition metal activation technology has been reported in previous studies. Generally, the transition metal activation of PMS or PS can be achieved in homogeneous and heterogeneous systems. However, the heterogeneous catalysis system is advantageous over the homogeneous catalysis system due to its easily separation and reuse, requiring no secondary treatment and having a broader pH range [15]. Many studies have demonstrated superb degradation efficiency because of the variable chemical states and unoccupied orbitals of these metal-based catalysts and nonmetal catalysts for the activation of PMS by heterogeneous catalyst, such as Co- [16], Mn- [17], Fe- [18], Cu- [19] and C-based [20]. Among these catalysts, ferrite and ferrite composites are relatively low cost, nontoxic, and have high potential to be engineered as effective PMS activator. Previous studies have demonstrated that Fe_2O_3 [21], Fe_3O_4 [22], FeS_2 [23], MFe_2O_4 (M = Cu, Mn, Zn and Co) [24,25] and $Bi_2Fe_4O_9$ [26] were frequently used for PMS activation. In addition, $BiFeO_3$ and $BiFeO_3$-based composites have been applied to catalytic activation of H_2O_2, PS or PMS due to the excellent stability and effective recoverability. For instance, Luo et al. reported about the using of $BiFeO_3$ as a Fenton-like catalyst for degrading organic pollutants [27]. An et al. prepared $BiFeO_3$ and graphene-$BiFeO_3$ composite for photo-Fenton like degradation of tetrabromobisphenol A [28,29]. However, most of the incentives for the activation of PMS by ferrite or ferrite composites are extremely related with sulfate radicals, and the contribution of different types of active sites to the ferrite or ferrite catalyst is still not clear and conclusive. Moreover, to the best of our knowledge, there is no research reported on the interactions between PMS and S-BFO for the treatment of organic wastewater.

Previous studies have demonstrated that various heterogeneous catalysts (such as CuO, carbons and nitrogen doped reduced graphene oxide) can effectively activate persulfate via a non-radical oxidation process for the removal of organics [30–32]. Recently, it was reported that the non-radical oxidation process could be observed on the activation of PMS via benzoquinone [33]. These studies revealed that other non-radical reactive oxygen species (ROS) do exist in the activation of PMS or PS, nevertheless, the crucial role still seems unclear in most of the studies. In our recent study, singlet oxygen ($^1O_2$), instead of $\cdot OH$ or $\cdot SO_4^-$, was found as a vital species on the degradation of 2,4-dichlorophenol in the coupled carbon nanotube/persulfate system [34]. As a non-radical reactive oxygen species (ROS), singlet oxygen has been widely used for selective oxidation of organic substrates. Nevertheless, studies on the heterogeneous oxidation for Fe-based heterogeneous activators have not been demonstrated via non-radical reactions concerning PMS.

Fluoroquinolone antibiotics (FQs) is a kind of important and broad-spectrum pharmaceuticals for human and veterinary purpose, with limited biodegradable ability [35]. Levofloxacin (LVF) is a typical fluoroquinolone used to treat severe bacteria and nosocomial infections, which has been recently encountered in the surface or ground water in many countries [36,37]. LVF is known to be resistant to conventional biological oxidation, and causing long-term concerns in the environment, since it has substantial activity against a broad array of gram-positive and gram-negative bacteria [38]. The continuous introduction of LVF into the environment can affect natural waters quality and potentially impact drinking water supplies, and induce proliferation of bacterial drug resistance in ecosystem system [39].

In this study, sillenite bismuth ferrite (S-BFO) was prepared by a hydrothermal synthesis technique, and adopted to activate PMS as a heterogeneous activator for the first time. The crystalline structure, morphology and textural property of the prepared S-BFO were thoroughly characterized by various characterizations. The catalytic performance of S-BFO was evaluated by activation of PMS for the removal of levofloxacin (LVF). In the heterogeneous activation, the critical impacting factors (including PMS concentration, catalyst dosage, pH and temperature) on the degradation of LVF were investigated. The interaction mechanism between bismuth ferrite and PMS was proposed by performing experiments using different radical scavengers and electron spin resonance (ESR) measurement. The results demonstrated new findings concerning the non-radical mechanism for PMS activation by S-BFO, and the great potential in the water decontamination for reluctant compounds.

2. Material and methods

2.1. Chemicals

Peroxymonosulfate ($2KHSO_5.KHSO_4.K_2SO_4$, AR) and acetonitrile (HPLC grade) were acquired from Sigma-Aldrich (Shanghai, China). Levofloxacin (LVF, 98%), 2,2,6,6-Tetramethyl-4-piperidinol (TEMP, 98%) and 9,10-diphenylanthracene (DPA, 99%) were purchased from TCI Scientific Ltd. (Shanghai, China). 5,5-dimethyl-1-pyrrpline-N-oxide (DMPO) and furfuryl alcohol (FFA, 98%) were purchased from Aladdin Scientific Ltd. (Shanghai, China). Ferric (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), tert-butanol (TBA), ethanol, isopropanol (IPA) and other reagents of analytical grade quality were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). All chemical reagents were used without further purification.

2.2. Synthesis of S-BFO

Similar with perovskite-type bismuth ferrites, S-BFO could be synthesized via sol–gel [40], hydrothermal [41], and combustion [42]. In this work, S-BFO was synthesized by a hydrothermal synthesis technique at low temperature. In a typical synthesis procedure, 10 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 10 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in dilute 100 mL nitric acid solution (1 mol/L), and then, a 20 mL KOH (10.0 mol/L) solution was slowly added into the mixed solution under magnetical stirring. The final pH of mixture was about 13–14. Subsequently, the suspension was kept under stirring for 15 min, followed by centrifugation and repeated washing with deionized water more than 5 times until neutral pH. The obtained precipitant was dried in a vacuum drying oven at 80 °C for 12 h, and the pressure was remained at $-0.09 \sim -0.10$ MPa. The product was then added into a 70.0 mL KOH (4.0 mol/L) solution, which was regarded as an alkali mineralizer, made with both ethanol and water (V:V = 4:3), and the mixture was vigorously stirred for 30 min to obtain a uniform suspension. The above mixture was transferred into a 100 mL stainless-steel autoclave