Enhanced activation of peroxysulfate by strontium modified BiFeO$_3$ perovskite for ciprofloxacin degradation

Caicai Wang$^{1,2,3}$, Shengwang Gao$^{1,2}$, Jianchao Zhu$^{1,2}$, Xunfeng Xia$^{1,2,*}$, Mingxin Wang$^{3,*}$, Yanna Xiong$^4$

$^1$ State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
$^2$ State Environmental Protection Key Laboratory of Simulation and Control of Groundwater Pollution, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
$^3$ School of Environmental and Safety Engineering, Changzhou University, Changzhou 213164, China
$^4$ Solid Waste and Chemicals Management Center, Ministry of Ecology and Environment, Beijing 100029, China

Abstract

A series of Sr-doped BiFeO$_3$ perovskites (Bi$_{1-x}$Sr$_x$FeO$_3$, BSFO) fabricated via sol-gel method was applied as peroxysulfate (PDS) activator for ciprofloxacin (CIP) degradation. Various technologies were used to characterize the morphology and physicochemical features of prepared BSFO samples and the results indicated that Sr was successfully inserted into the perovskites lattice. The catalytic performance of BiFeO$_3$ was significantly boosted by strontium doping. Specifically, Bi$_{0.8}$Sr$_{0.2}$FeO$_3$ (0.1BSFO) exhibited the highest catalytic performance for PDS activation to remove CIP, where 95% of CIP (10 mg/L) could be degraded with the addition of 1 g/L 0.1BSFO and 1 mmol/L PDS within 60 min. Moreover, 0.1BSFO displayed high reusability and stability with lower metal leaching. Weak acidic condition was preferred to neutral and alkaline conditions in 0.1BSFO/PDS system. The boosted catalytic performance can be interpreted as the lower oxidation state of Fe and the existence of affluent oxygen vacancies generated by Sr doping, that induced the formation of solute oxygen ($^\cdot$O$_2$) which was confirmed as the dominant reactive species by radical scavenging studies and electron spin resonance (ESR) tests. The catalytic oxidation mechanism related to major $^\cdot$O$_2$ and minor free radicals was proposed. Current study opens a new avenue to develop effective A-site modified perovskite and expands their application for PDS activation in wastewater remediation.

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Ciprofloxacin (CIP), a typical broad spectrum antibiotic belonging to fluoroquinolones (FQs), has been extensively utilized to treat human and veterinary diseases (Zhang et al., 2015). As a result, huge amount of CIP is discharged into aquatic environment since it is hard to be completely metabolized by physiological activities (Balakrishna et al., 2016; Porras et al., 2016). Sadly, the conventional treatment technologies for CIP removal relied mainly on the adsorption of activated sludge instead of biodegradation (Yao et al., 2017). Non-destructively removal of it from wastewater may lead potential harm to human beings.
and ecosystems by the means of promoting the bacterial tolerance to antibiotics (Oberle et al., 2012). Thus, there is an urgent need for the development of efficient treatment techniques to solve the severe matter.

Recently, advanced oxidation processes (AOPs) based on sulfate radical (SO₄⁻) and hydroxyl radical (HO•) have been recognized as a feasible strategy for contaminants remediation (Anipsitakis and Dionysiou, 2003). In particular, sulfate radical-based AOPs (SR-AOPs) have gained widely attention thanks to the strong oxidation potential (2.5–3.1 V) (Chauh and Tuqan, 2012), higher selectivity and efficiency to oxidize organic contaminants, longer half-life (30–40 μs) and wider operating pH range in comparison with HO•-based methods (Ahmed et al., 2012). Generally, SO₄⁻ can be generated through hemolytic cleavage of the peroxide bond in peroxysulfate (PDS, S₂O₅²⁻) or peroxymonosulfate (PMS, HSO₅⁻) (Bu et al., 2018). Hitherto, studies for PDS or PMS activation have focused on ultrasound (Liu et al., 2017), UV light (Fu et al., 2019), heat (Ji et al., 2015), transition metals (Anipsitakis and Dionysiou, 2004) and metal free catalysts like carbon materials (Lee et al., 2015). Among them, transition metals, especially iron ion, initiated catalysis is one of the most viable approaches due to its high activation performance, natural abundance and relatively low operational costs (Golshan et al., 2018; Guo et al., 2020). However, the difficulties of recovery and the secondary contamination associated with iron sludge limit the application of iron ion in homogeneous form (Wang and Wang, 2018). Therefore, heterogeneous catalysts containing iron with high reusability and low iron leaching are expected to overcome drawbacks of homogeneous iron ion.

Perovskite-type oxides with the general formula ABO₃ are considered as favorable heterogeneous catalysts by virtue of their flexible chemical composition and high structural stability (Peña A and Fierro, 2001). The cation A and /or B sites can be partially or completely substituted by foreign elements without damaging the matrix structure and simultaneously producing some oxygen vacancies and controlling the change of the cation oxidation states (Zhang et al., 2012). Specifically, BiFeO₃ (BFO), a common kind of perovskite, has been systematically studied to catalyze different oxidants involving H₂O₂, PDS and PMS for organic elimination, and exhibited superior stability and reactivity (Han et al., 2020; Hussain et al., 2018; Rusevova et al., 2014). Even though the excellent Fenton catalytic performance BFO has, there are several limitations of BFO owing to its intrinsic properties, such as impurity phases, defect states and low magnetization (Irani et al., 2017), resulting in the decrease of catalytic activity and restriction for its application. Introduction of suitable elements for A and or B site is a convenient and feasible method to enhance ferromagnetism and the catalytic performance of BFO (Das and Mandal, 2012; Yang et al., 2012). For instance, it was reported that substitution of Ba for Bi site could enhance the magnetic and catalytic activities of BFO (Soltani and Lee, 2016). Soltani and Lee revealed that Cu and Ba/Cu co-doped BFO could efficiently mineralize 2-chlorophenol with only 70 min of reaction by catalyzing H₂O₂ or PDS under visible light irradiation (Soltani and Lee, 2017). However, the requirement of simulated visible light led to more energy inputs. Therefore, the modification of BFO by metal doping as heterogeneous Fenton-like catalyst should be further investigated.

It has been reported that Bi site doping by Ca and Sr can result in the generation of mixed Fe valences and some anion defects like oxygen vacancies in BFO (Arya and Negi, 2013; Li et al., 2011). Intriguingly, the presence of oxygen vacancies may contribute to the formation of non-racial reactive species such as singlet oxygen (O₁₂). For example, Yu et al. reported that the doping of Cu in zinc ferrite resulted in the formation of oxygen vacancies, which were participated in the production of O₁₂ in PMS activation process (Yu et al., 2019). Hao et al. found the reaction between oxygen vacancies and chemisorbed oxygen could also generate O₁₂ (Hao et al., 2017). Unlike SO₄⁻ and HO•, the non-radical species O₁₂ has a great resistance to some anions and is widely used for selective degradation contaminants owing to the electrophilic nature (Zhang et al., 2014). It was reported that O₁₂ could be generated through the activation of PMS by Fe, Bi-based oxides such as Fe₃O₄/β-FeOOH (Li et al., 2019) and Bi₂FeO₉ (Liu et al., 2018). Furthermore, Wang et al. found that O₁₂ could also be produced in BFO/PMS system, where the oxygen vacancies and lattice oxygen on porous BiFeO₃ were responsible for the generation of O₁₂ (Wang et al., 2020). However, the non-radical processes are mostly observed in Bi, Fe-oxides/PMS system, whereas the studies concerning PDS activation are sparse. Several researches have shown that the non-radical reactive species like O₁₂ could be generated from PDS catalyzed by MnO₂ (Zhu et al., 2019b) and carbon materials such as carbon nanotubes (Cheng et al., 2019; Cheng et al., 2017). However, to the best of our knowledge, no previous reports have explored the generation of O₁₂ when PDS was activated by Bi, Fe-based oxides for environmental remediation.

Herein, in present study, a series of Sr-substituted BFO perovskites Biₓ−₃SrₓFeO₃ (x = 0.05, 0.08, 0.1, 0.2, 0.5 named as 0.5BSFO, 0.08BSFO, 0.1BSFO and 0.2BSFO, respectively) were synthetized by a sol-gel method. The properties of the obtained catalysts were characterized from various aspects involving crystalline structure, morphology and textural property. The degradation performance of CIP by BSOF catalyzing PDS was examined and the effects of operational parameters (catalyst dosage and PDS concentration) and environmental factors (initial pH, NO₃⁻, Cl⁻ and HCO₃⁻) on CIP elimination were investigated. On the basis of electron spin resonance (ESR) tests and the selectively radical scavenger experiments, the reactive oxygen species (ROS) for CIP degradation were determined and the PDS activation mechanism was further explored.

1. Materials and methods

1.1. Reagents

Ciprofloxacin (CIP, ≥ 99.9%), PDS (Na₂S₂O₈), 2,2,6,6-tetramethyl-4-piperidinol (TEMP, 97%) and 5,5-dimethyl-1-pyrroldine N-oxide (DMPO, 97%) were provided from Sigma-Aldrich (Saint Louis, USA). Ferric(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), strontium nitrate (Sr(NO₃)₂) and Ethylene glycol (EG) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethanol (EtOH), furfuryl alcohol (FFA) and tert-butyl-alcohol (TBA) were obtained by Tianjin Chemical Reagent Co., Ltd (Tianjin, China). Milli-Q® water (Sartorius 611, Germany) was used throughout the study.

1.2. Synthesis and characterization of BSFO

BiFeO₃ (BFO) and Biₓ₁−₃SrₓFeO₃ (BSFO, x = 0.05, 0.08, 0.1, 0.2) were fabricated via a sol-gel method using EG as complex agent. Typically, a certain amount of Bi(NO₃)₃·5H₂O was dissolved in EG with constant stirring for 30 min to form a clear solution. By retaining the same conditions, stoichiometric ratio of Sr(NO₃)₂ and Fe(NO₃)₃·9H₂O were added to the previous solution with continuous magnetic stirring for another 20 min to form a brownish red sol. A dried gel was then formed after being incubated at 70 °C, which was finally calcined at 300 °C for 1 hr and subsequently at 550 °C for 1 hr. The as-synthesized catalysts were ground into a fine powder and the Sr-doped BFO samples were obtained. For the preparation of pure BFO, same
The crystal structures of the catalysts were carried out by X-ray diffractometer (XRD) (D8 ADVANCE, Bruker, Germany) using Cu-Kα1 radiation. The morphologies of the materials were investigated using the scanning electron microscope (SEM) (SU8000, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS) for the analysis of the surface elements composition. The microstructures of samples were also observed by high resolution transmission electron microscope (HR-TEM) (JEM-2100, JEOL, Japan). The average pore size and surface area of BFO and 0.1BSFO were obtained from a sorption analyzer (TRISTAR 3020i, Micromeritics, USA). The valence state and surface chemical information were analyzed based on X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo, USA) with a monochromatic Al-Kα X-ray gun. All binding energy was calibrated by C 1 s peak at 284.80 eV. The point of zero change (PZC) of catalysts catalyst detected by Zeta potential analyzer (Zetasizer Nano ZS, Malvern, British).

### 1.3. Experiment procedures and analysis

Batch CIP removal tests were performed in the dark using cylindrical glass reactors containing 50 mL CIP solution with initial concentration of 10 mg/L at room temperature. In a typical reaction, the desirable amount of catalyst was dispersed into the CIP solution with magnetic stirrer for 30 min to establish the adsorption-desorption equilibrium. After that, the degradation reaction was initiated by adding PDS solution with the final concentration of 1 mmol/L. The initial pH of CIP solution was 6.05 and was adjusted with H2SO4 or NaOH solution (0.1 mol/L) if necessary. At pre-determined intervals, the mixture was collected and filtered through 0.22 μm polytetrafluorethylene membrane, following adding immediately with 0.5 mL methanol to terminate the reaction. The concentration of CIP was measured using a ShimadzuUV2800 spectrophotometer at 277 nm. Meanwhile, the values of solution pH were measured by an Orion 2-Star benchtop pH meter. The amount of leached Fe in system was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8000, Perkin-Elmer, USA). The mineralization of CIP was measured using a TOC analyzer (MutiN/C2100, Analytikjena, Germany). Moreover, the ROS during the reaction was determined by the electron spin resonance (ESR) (JES-FA200, JEOL, Japan). Besides, the ROS trapping experiments were also carried out using ETOH, TBA, and FFA as the quenching agents.

### 2. Results and discussion

#### 2.1. Characterization

The XRD patterns of the synthesized samples were shown in Fig. 1a. All the characteristic peaks of BFO were matched well with the structure of BiFeO3 (JCPDS Card No. 86–1518) with a rhombohedral structure, suggesting the successful preparation of pure BFO by the present sol-gel process. The crystallinity of BFO was decreased with Sr doping, which possibly owing to the separation from the spiral spin structure and the reduction of the leaky behavior of BSFO system (Makhdoom et al., 2012). Besides, it was worth to note that the doublet Bragg peaks of (104) and (110) at around 32° for BSFO was overlapped to a single (110) peak due to the Sr2+ substitution in the host BFO (Fig. 1b), which suggested that the rhombohedral structure of BFO tended to be distorted with the increase of Sr content. Similar results have been also reported (Soltani and Lee, 2016). In addition, a small fraction of impurity phase (Bi2FeO4) was observed in both BFO and BSFO samples, which had been commonly reported (Zheng et al., 2011). As a metastable structure, the synthesis of BFO was always accompanied by some secondary phases such as Bi2O3, Bi2FeO4 and Bi2Fe2O9 due to the kinetics of phase formation (Chen et al., 2006).

The typical morphologies of the BSFO perovskites were presented in Fig. 2a-b and Appendix A Fig. S1. Both BFO and Sr-doped BFO exhibited the similar shapes with spherical agglomerates. The energy dispersive spectroscopy (EDS) (Appendix A Fig. S2a) and SEM elemental mapping analysis (Appendix A Fig. S2b) of 0.1BSFO evidenced that the obtained sample was composed of Bi, Fe, O and Sr elements and they were uniformly distributed on the surface of catalyst. The sphere-like agglomeration morphology was also obtained from the TEM images of 0.1BSFO (Fig. 2c-d). Besides, the high-resolution TEM (HR-TEM) images (Fig. 2e) revealed that the interplanar spacing for the 0.1BSFO sample was 0.139 Å referring to the (220) crystal plane of BFO, indicating the 0.1BSFO was prepared.

The surface area and pore size distributions of the as-synthesized samples were analyzed by N2 adsorption-desorption isotherms. The two samples exhibited IV isotherm with H4 hysteresis loop (Appendix A Fig. S3), suggesting that both BFO and 0.1BSFO were mesoporous structure. Besides, the specific surface area (SSA), Barret-Joyner-Halenda diameters and volumes of BFO and 0.1BSFO were presented in Table 1. All these parameters of 0.1BSFO were lower than pure BFO, which indicated that the excellent catalytic activity of 0.1BSFO was ascribed to its inherent activity instead of extrinsic surface contact.

The XPS analysis was used to examine the elemental composition and surface valence states of BFO and 0.1BSFO. As illustrated in Appendix A Fig. S4a, the peak signal of Sr 3d appeared in survey spectra of 0.1BSFO except for the Bi 4f, Fe 2p and O 1 s, indicating that Sr was introduced into the perovskite lattice successfully. Two peaks located at 158.6 and 163.9 eV in Bi 4f core level spectrum of two samples were the signal of Bi 4f7/2 and Bi 4f5/2, respectively (Appendix A Fig. S4b), which were all corresponding to Bi3+ (Jia et al., 2018; Wang et al., 2020). The Fe 2p spectrum of BFO and 0.1BSFO exhibited three peaks with binding energies at 723.8, 717.8 and 710.3 eV, which could be assigned to Fe 2p3/2, shake-up satellite and Fe 2p1/2, respectively (Appendix A Fig. S4c). The shake-up satellite is a spin-exchange splitting of the two 2p levels. The Fe 2p3/2 could be deconvoluted into four contributions at 709.3, 710.5, 711.9 and 713.8 eV, where the peak at 709.3 eV was related to Fe(II) and the other three belonged to Fe(III) (Ding et al., 2015; Huang et al., 2018; Wang et al., 2019a), suggesting that both Fe(II) and Fe(III) were present in the structure of BFO. The characteristic spectra of O 1s could be resolved into four peaks (Appendix A Fig. S4d). The peak at around 528.9 eV was identified as the lattice oxygen ions (O2−) within the perovskite oxides. The other three peaks centered approximately at 529.4, 530.3 and 531.4 eV corresponded to less electron rich-oxygen species (O2−/O3−), surface-adsorbed oxygen or the hydroxyl groups (O2−/OH−) and adsorbed molecular water and carbonates (H2O/CO32−), respectively (Duan et al., 2018; Miao et al., 2017). Compared with BFO, the Fe 2p and O 1s peaks of 0.1BSFO shifted obviously, especially O 1 s, indicating the ratio of Fe and O species changed after Sr substitution. To reveal the variation of oxidation states after Sr doping, the relative concentration ratios of elements in two samples were calculated based on the areas of fitting peaks and 

---

**Table 1 – Textural properties of BFO and 0.1BSFO.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFO</td>
<td>9.4919</td>
<td>0.0377</td>
<td>19.3357</td>
</tr>
<tr>
<td>0.1BSFO</td>
<td>5.4493</td>
<td>0.0190</td>
<td>15.6743</td>
</tr>
</tbody>
</table>

---

**References:**

- Chen et al., 2006
- Duan et al., 2018
- Miao et al., 2017
- Jia et al., 2018
- Ding et al., 2015
- Huang et al., 2018
- Wang et al., 2019a
- Soltani and Lee, 2016
- Makhdoom et al., 2012
- Zheng et al., 2011
the results were listed in Table 2. For 0.1BSFO, the content of Fe(II) raised from 26.7% to 31.1%, suggesting that part of Fe(III) on the surface of 0.1BSFO was changed to reductive valence state by Sr doping. Based on the principle of electrical neutrality, it is generally believed that replacing the cation at A site (Bi3+) by a foreign cation (Sr2+) with lower oxidation state can induce B site (Fe) to form a higher valence state. Nevertheless, the valence of Fe in 0.1BSFO was reduced. Therefore, to keep the electrical neutrality of material, it was considered that more oxygen vacancies were formed (Cheng et al., 2020; Jauhar and Singhal, 2014). With the introduction of Sr in BFO, the proportion of O2−, O22−/O−, O2/OH− and H2O/CO32− were changed from 31.8%, 33.3%, 23.3% and 11.5% to 18.9%, 18.0%, 23.3% and 28.3%, respectively. The O22−/O− generated on the surface of materials are closely related to the surficial oxygen vacancies (Lim et al., 2019; Zhu et al., 2014; Zhu et al., 2016). The significant reduction of O22−/O− percentage meant that part lattice oxygen lost, implying rich oxygen vacancies were formed by Sr doping (Cheng et al., 2020). Therefore, Sr doped BFO possessed not only large amount of oxygen vacancies but also lower average oxidation state of iron, which were both responsible for the improvement of catalytic properties (Su et al., 2016).
2.2. Catalytic activity and stability

The catalytic capability of these obtained samples were evaluated by activating PDS for CIP degradation. As shown in Fig. 3a, it was found that the elimination of CIP was less than 10% when PDS or 0.1BSFO was added alone, implying that the sole PDS oxidation for CIP degradation was feeble and the removal of CIP by adsorption could be ignored. Besides, only less than 20% of CIP was degraded by PDS catalyzed with BFO within 60 min. While the degradation rate of CIP raised significantly with the substitution of Sr. Among the BSFO catalysts, 0.1BSFO exhibited the highest catalytic performance and CIP removal rate over 30 min was 95.1%, followed by 0.08BSFO (80.1%), 0.05BSFO (69.8%) and 0.2BSFO (61.6%). The pseudo-first-order rate constants ($k_{obs}$) of CIP removal in 0.1BSFO/PDS system was calculated to be 0.0935 min$^{-1}$ (Appendix A Fig. S5), which was much higher than other correlative catalysts. The results confirmed the catalytic role of Sr in BSFO catalysts for PDS activation and suggested the superior performance of 0.1BSFO. Thus the 0.1BSFO was selected as the following PDS activator. Besides, the leached concentration of Fe in 0.1BSFO/PDS system was measured to be 0.12 mg/L after 60 min reaction. In order to elucidate the role of leached ions in 0.1BSFO/PDS system, the leached metal filtrate was used for homogeneous activation of PDS. The experimental detail was shown in Appendix A Text S1. Results (Appendix A Fig. S6) showed that less than 10% of CIP was degraded in filtrate/PDS system, implying that the homogeneous reaction played very little part in PDS activation and the CIP elimination was dominantly ascribed to the heterogeneous activation of PDS by 0.1BSFO. In addition to the catalytic degradation performance, total organic carbon (TOC) reduction was further investigated in 0.1BSFO/PDS system. During the 420 min reaction, the mineralization ratio was 52% (Appendix A Fig. S7), indicating that part of CIP and its intermediates could be mineralized.

The recyclability and stability of 0.1BSFO were also tested in three cycles. As depicted in Fig. 4a, the degradation of CIP achieved 95% within 60 min for the first run, while it was descended to 91% for the second recycle and 87% for the third run. The results were mainly attributed to the corrosion on the surface of 0.1BSFO (Lai et al., 2018). Besides, the adsorbed substance could also cause the poisoning of catalyst during the reaction (Gong et al., 2017). Therefore, XRD analysis of the used 0.1BSFO was detected. As shown in Fig. 4b, there was no obvious difference between the fresh and used 0.1BSFO besides the slight decline of the peak intensity. Even so, 0.1BSFO still showed satisfactory reusability and stability for CIP degradation.

2.3. Effect of pivotal factors on CIP degradation

2.3.1. Effect of catalyst dosage and PDS concentration

In order to optimize the catalytic degradation parameter of CIP, the effect of 0.1BSFO loading and PDS concentration on CIP elimination was studied. As illustrated in Fig. 3b, CIP removal efficiency was significantly boosted from 14% to 95% within 60 min with elevation level of 0.1BSFO from 0.25 to 1.0 g/L, and the corresponding $k_{obs}$ were 0.0073 and 0.0935 min$^{-1}$, respectively (Fig. 3c). However, when the catalyst loading elevated from 1.0 to 2.0 g/L, no noticeable enhancement in degradation performance was observed during the reaction. The degradation efficiency of CIP reached a maximum and then kept invariable with continuously increasing the 0.1BSFO dosage, which might due to the radicals self-quenching or invalid PDS decomposition caused by excessive catalyst (Feng et al., 2016; Zhu et al., 2019a). Hence, the optimum dosage of 0.1BSFO was 1 g/L.
As depicted in Fig. 3d, PDS dosage had a propitious effect on CIP removal when its concentration raised from 0.25 to 1 mmol/L. However, the enhancement of CIP removal was limited with further increasing PDS dosage (1 to 2 mmol/L). Notably, the degradation rate was obviously declined when PDS dose was increased to 5 mmol/L, where the \( k_{\text{obs}} \) was reduced to 0.0299 min\(^{-1}\) (inset of Fig. 3d), which might due to the quenching effect on the \( S_2O_8^{2-} \) caused by excess PDS (Eq. (1)) (Hisao et al., 2005; Salari et al., 2009). Hence the optimum dosage of PDS was selected to be 1 mmol/L.

\[
S_2O_8^{2-} + S_8 \rightarrow S_2O_6^{2-} + SO_4^{2-}
\]

(1)

2.3.2. Effect of initial pH

The influence of different initial pH (pH\(_i\)) for CIP degradation was examined with pH ranging from 3 to 11. As illustrated in Fig. 5a-b, the degradation rate was restrained both when pH\(_i\) was reduced from 6.05 to 3 and elevated to 9. Almost no CIP was removed at pH\(_i\) = 11. This result suggested that weak acidic condition (pH\(_i\) = 6.05) was more beneficial for CIP degradation. In general, the initial pH could influence the surface charge of catalyst and the speciation of target organics and oxidants, consequently affecting the catalytic activity of heterogeneous system (Fan et al., 2017). PDS is generally stable in the solution at different pH (Wang and Wang, 2018). However, the pKa1 of CIP is 6.09 and its pKa2 is 8.62 (Wang et al., 2010), indicating that CIP exists as anion ion specie at pH > 8.62, while it exists as cation ion at pH < 6.09 and as neutral at 6.09 < pH < 8.62. The pH of point zero charge (pH\(_{\text{pzc}}\)) for 0.1BSFO was detected at around 6.6 (Appendix A Fig. S8), suggesting that when pH > 6.6 the surface charge of 0.1BSFO was negative and when pH < 6.6 it was positive. Therefore, at 3 < pH < 6.6, 0.1BSFO with positive charge would appeal more negatively charged \( S_2O_8^{2-} \) by electrostatic attraction and consequently achieved higher CIP removal rate. Nevertheless, the removal efficiency significantly declined at pH\(_i\) > 3, which was probably due to the scavenging effect for \( S_2O_8^{2-} \) and \( OH^- \) by H\(^+\) (Eqs. (2) and (3)) (Huang and Huang, 2009). At 6.6 < pH < 11, the electrostatic repulsion between the negatively charged \( S_2O_8^{2-} \) and 0.1BSFO would inhibit the interaction between them, resulting in the limited CIP removal efficiency. In addition, the CIP molecules presented as anionic species in alkaline circumstance could also cause electrostatic repulsion of the catalyst, which was another reason for the inhibited CIP degradation efficiency at high pH.

\[
\text{HO} + \text{H}^+ \rightarrow \text{H}_2\text{O}
\]

(2)

\[
\text{SO}_4^{2-} + \text{H}^+ + e^- \rightarrow \text{HSO}_4^-
\]

(3)

2.3.3. Effect of inorganic anions

Inorganic anions involving nitrate (NO\(_3^-\)), chloride (Cl\(^-\)) and bicarbonate (HCO\(_3^-\)) are common constituents of natural water and some of them are considered to be detrimental to AOPs. Thus, it is essential to investigate the inorganic ions with different concentration on CIP removal. As illustrated in Fig. 6, the presence of anions usually had contrasting impacts on the CIP degradation with various concentration.

As shown in Fig. 6a, the removal rate of CIP was slightly decreased with the addition of NO\(_3^-\) (2–20 mmol/L). The \( k_{\text{obs}} \) of CIP removal descended gradually from 0.0935 to 0.0463 min\(^{-1}\) with NO\(_3^-\) increasing to 20 mmol/L. The results could be explicated that the added NO\(_3^-\) could behave as a scavenger to
consume free radicals (SO₄²⁻ and HO·) and generate some active species with lower potential, such as NO₃⁻ (2.30 V) and NO₂⁻ (1.03 V) Eqs. (4)–(6) (Wang et al., 2016), leading to the inhibited CIP degradation efficiency.

\[
\text{HO}^- + \text{NO}_3^- \rightarrow \text{OH}^- + \text{NO}_3^- \quad (4)
\]

\[
\text{SO}_4^{2-} + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{SO}_4^{2-} \quad (5)
\]

\[
\text{NO}_3^- + \text{H}_2\text{O} + e_{aq} \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (6)
\]

As for Cl⁻: Fig. 6b), the removal of CIP descended from 95% to 75% as Cl⁻ concentrations raised from 0 to 20 mmol/L, and the corresponding \(k_{obs}\) declined notably from 0.0935 to 0.0284 min⁻¹, indicating Cl⁻ presented a negative effect on CIP degradation. Cl⁻ could act as a scavenger to react with SO₄²⁻ and generate Cl⁻ and Cl₂⁻ (Eqs. (7) and (8)) with low oxidation-reduction potential (ORP) values, which may interpret the suppression of catalytic oxidation by Cl⁻ (Zhou et al., 2016).

\[
\text{Cl}^- + \text{SO}_4^{2-} \leftrightarrow \text{Cl}^- + \text{SO}_4^{2-} \quad (7)
\]

\[
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^- \quad (8)
\]

As for HCO₃⁻: Fig. 6c-d), a significant reduction of CIP removal (from 95% to 8%) was shown after adding HCO₃⁻ (increased from 0 to 20 mmol/L) to the 0.1BSFO/PDS system and the corresponding \(k_{obs}\) dramatically declined from 0.0935 to 0.0041 min⁻¹. The inhibitory impact of HCO₃⁻ could be attributed to its competition with CIP for SO₄²⁻ and HO· (Eqs. (9) and (10)) (Deng et al., 2013). Besides, addition of HCO₃⁻ would dramatically effect solution pH (Deng et al., 2017). As shown in Appendix A Fig. S9, the reaction system maintained alkaline in presence of HCO₃⁻ with different concentration from 2 to 20 mmol/L, which had adverse effect on CIP degradation.

\[
\text{HO}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^- \quad (9)
\]

\[
\text{SO}_4^{2-} + \text{HCO}_3^- \rightarrow \text{HCO}_3^- + \text{SO}_4^{2-} \quad (10)
\]

### 2.4. Reactive species and possible mechanism

#### 2.4.1. Identification of reactive species

It is generally believed that SO₄²⁻ and HO· could be generated in heterogeneous PMS or PDS activation by transition metal catalysts. To probe the principle ROS on CIP degradation in 0.1BSFO/PDS system, several quenching tests were conducted. TBA was used as scavenger for HO· (\(k_{obs} = (3.8-7.6) \times 10^6 \text{L/(mol·sec)}\), \(k_{obs} = (4.0-9.1) \times 10^6 \text{L/(mol·sec)}\)) while EtOH as radical scavenger for both SO₄²⁻ and HO· (\(k_{obs} = (1.2-2.8) \times 10^6 \text{L/(mol·sec)}\), \(k_{obs} = (1.6-7.7) \times 10^6 \text{L/(mol·sec)}\)) (Bao et al., 2018; Peng et al., 2016). As displayed in Fig. 7a, 71% and 80% of CIP degradation efficiency were achieved by the addition of 1 mol/L EtOH and TBA separately, where the corresponding \(k_{obs}\) declined from 0.0935 to 0.0257 and 0.0194 min⁻¹ (Fig. 7b), indicating that SO₄²⁻ and HO· were formed and contributed to the CIP degradation. However, the incomplete inhibition of EtOH and TBA implied that other ROS might be involved in 0.1BSFO/PDS system. Previous studies have reported that \(^1\text{O}_2\) could also be generated and play an important role in the reactions associated with PMS or PDS (Cheng et al., 2017; Liu et al., 2018; Wang et al., 2020). Thus, FFA was selected as scavenger for \(^1\text{O}_2\) (\(k_{obs} = 1.2 \times 10^7 \text{L/(mol·sec)}\)). As shown in Fig. 7b, when FFA was doped to the reaction system, the CIP degradation was obviously restrained with the reaction rate descended substantially from 0.0935 to 0.0054 min⁻¹, suggesting that \(^1\text{O}_2\) was also generated and played a dominant role in 0.1BSFO/PDS system.

ESR experiments were employed to further confirm the types of ROS generated in 0.1BSFO/PDS process using TEMP as the spin-trapping agent for \(^1\text{O}_2\) and DMPO for SO₄²⁻ and HO·. As noticed from Fig. 7c, no obvious characteristic signals were identified in the ESR spectra of experiments conducted in both BFO/PDS and PDS alone system. However, the signal peaks of DMPO-OH and DMPO-SO₄⁻ were observed in 0.1BSFO/PDS system on the basis of hyperfine splitting constants (DMPO-OH: \(a_{HH} = a_{HL} = 1.49 \text{ mT}\), DMPO-SO₄⁻: \(a_{NN} = 1.39 \text{ mT}\), \(a_{NH} = 0.96 \text{ mT}\), \(a_{LH} = 0.14 \text{ mT}\), \(a_{LL} = 0.06 \text{ mT}\)), revealing that both SO₄²⁻ and HO· were generated in 0.1BSFO activating PDS system. As shown in Fig. 7d, a relatively weak 1:1:1 triplet signal characteristic of
TEMP-O₂ (ϕ₁₉ = 1.72 mT) appeared in single PDS system with the presence of TEMP, which could be attributed to the self-decomposition of PDS (Cheng et al., 2017). In contrast, a strong three-line signal with equal intensities appeared when TEMP was dosed to the 0.1BSFO/PDS system, demonstrating that O₂ was existed in 0.1BSFO/PDS system.

To summarize, based on the combined results of competitive radical tests and ESR spectrum, both free radical (SO₄⁻ and HO') and non-radical (O₂) were formed in PDS activation process, in which O₂ was confirmed as the major reactive species.

2.4.2. Possible active sites and activation mechanism of PDS

Generally, catalytic activity was mainly relied on the amount of active sites over the surface of catalyst. Thus, the variation in chemical states was further examined by using XPS analysis to recognize the major catalytic active sites. As depicted in Fig. 8a, no significant change of Bi 4f spectrum was observed after the reaction in comparison with fresh 0.1BSFO, indicating that Bi^{3+} was not involved in PDS activation (Wang et al., 2017). The Sr 3d spectrum before and after reaction was shown in Fig. 8b. The deconvoluted Sr 3d spectrum exhibited four peaks located at 135.1, 133.8, 133.2 and 132.5 eV, where the peaks at higher binding energy (BE) ranges belonged to Sr 3d₂/₂ components while the peaks at relatively lower BE ranges referred to Sr 3d₃/₂ (Heide, 2002; Wang et al., 2015). Sr 3d₂/₂ peak at 132.5 and 133.2 eV represented Sr in the perovskite phase, while Sr 3d peak at around 133.8 eV was likely related to the strontium carbonate on the surface (Kuhn and Ozkan, 2008; Liu et al., 2011). As shown in Fig. 8c, the percentage of Fe (II) descended from 31.1% to 19.6% after the catalytic reaction (Table 2), which indicated that the surface Fe(II) species was partial oxidized through electronic transfer in the PDS activation process. The above results confirmed that the Fe(II)/Fe(III) redox pairs was involved in the PDS activation by 0.1BSFO.

In addition, the change of O 1 s spectrum was also analyzed by comparing fresh and used 0.1BSFO. As shown in Fig. 8d, comparing to the fresh 0.1BSFO sample, the proportion of O_2− slightly descended from 62.6% to 61.8% while the O_3−/O− increased from 18.0% to 24.0% (Table 2). The increased O_3−/O− content indicated that the concentration of oxygen vacancies was descended after the reaction, implying that oxygen vacancies were involved in the catalytic reaction. Such oxygen vacancies behaved as active sites and not only facilitate the redox cycle of Fe(III)/Fe(II) (Gao et al., 2018; Yu et al., 2019), but also receive rapid oxygen exchange to promote the formation of O₂⁻ (Miao et al., 2015; Wang et al., 2019b; Wu et al., 2019), thereby resulting in the enhanced catalytic performance.

According to previous studies, the types of interfacial reaction in heterogeneous system involved two mechanisms: the inner-sphere and the outer-sphere, which could be differentiated by investigating the influence of ionic strength (Feng et al., 2017). Electrostatic interactions occurred via outer-sphere mechanism could be affected by increasing ionic strength to compress the thickness of electrical double layers. However, the inner-sphere complexation existed as covalent bonds or a combination of covalent and ionic bonds was not affect (Feng et al., 2016; Zhang et al., 2013). Thus, NaClO₄ (represented as ionic strength) was used to investigated the outer-sphere interactions in 0.1BSFO/PDS system (Fig. 9). The degradation of CIP was nearly not influenced with the addition of NaClO₄, suggesting the inner-sphere interaction probably occurred between 0.1BSFO and PDS. Actually, the inner-sphere mechanism generally carried out through the complexation between active metals and hydroxyl groups (–OH) on the surface of catalyst (Xu et al., 2016), which was characterized by XPS (Appendix A Fig. S4). It has been found that phosphate ions could substitute the hydroxyl groups on the catalyst surface owing to its high affinity for the active sites (Zhang et al., 2008). Therefore, H₃PO₄⁻ was applied to investigated the role of –OH in 0.1BSFO/PDS system. As shown in Fig. 9, almost no CIP degradation was observed in the presence of H₃PO₄⁻. The strong inhibition implied that the replacement of –OH affected the catalytic capacity of 0.1BSFO, revealing that –OH of 0.1BSFO might play an important role for the PDS activation.

Based on the above analysis, two possible heterogeneous activation mechanisms of PDS by 0.1BSFO was proposed and as illustrated in Fig. 10. The first was the minor free radical oxidation process. On the one side, the surface Fe(II) as active site could active the adsorbed S₂O₅²⁻ to produce SO₄²⁻...
Eq. (11)). Meanwhile, part of $S_2O_8^{2-}$ would react with $H_2O$ to form $HSO_5^-$ (Eq. (12)). On the other side, the inner-sphere complexation between $-OH$ and $HSO_5^-$ could form a surface complex $Fe(II)-(H)OSO_5^-$, which subsequently decomposed into $SO_4^{2-}$ (Eqs. (13) and (14)) Wang et al. 2019a). In addition, $SO_4^{2-}$ could be transformed to $HO^-$ by further reaction with $H_2O$ (Eq. (15)). The second was non-radical oxidation process involving the formation of $^1O_2$. The charge transfer between $HSO_5^-$ and active metal could be promoted by rich oxygen vacancies on the surface of 0.1BSFO and consequently enhancing the redox cycle of $Fe(II)/Fe(III)$ (Eqs. (16) and (17)). Meanwhile, the oxygen vacancies ($V_o^-$) of 0.1BSFO could be converted to active oxygen ($O_o^-$) by electron transfer (Liu et al., 2018). Then $^1O_2$ was produced from the reaction between $O_o^-$ and $HSO_5^-$ (Eq. (18)) (Miao et al., 2019). $^1O_2$ might also be produced from the self-reaction of peroxyxymonosulfate radical ($SO_5^{2-}$) in the solution (Eq. (19)) (Liu et al., 2018). Thus, low oxidation state of Fe and the abundant of oxygen vacancies by Sr doping synergistically boosted the catalytic capacity of 0.1BSFO for PDS activation, consequently promoting the degradation of CIP.

\[
\begin{align*}
\equiv Fe(II) + S_2O_8^{2-} &\rightarrow \equiv Fe(III) + SO_4^{2-} + SO_2^{2-} & (11) \\
S_2O_8^{2-} + H_2O &\rightarrow HSO_5^- + HSO_4^- & (12) \\
\equiv Fe(II) - OH^- + HSO_5^- &\rightarrow \equiv Fe(II) - (H)OSO_5^- + OH^- & (13)
\end{align*}
\]
3. Conclusion

In summary, Sr-doped BiFeO₃ perovskites BiₓSrₓFeO₃ synthesized via sol-gel method were first tested to effectively activate PDS for CIP elimination. 0.1BSFO exhibited excellent catalytic activity and high stability with lower metal leaching in the activation of PDS. More than 90% of CIP (10 mg/L) degradation was achieved with the addition of 1 g/L 0.1BSFO and 1 mmol/L PDS within 60 min. And the removal efficiency maintained 87% after three consecutive cycle reaction. The weak acidity condition was more favorable to CIP decomposition than neutral condition and the alkaline circumstance exerted significant inhibition on CIP degradation. The existence of NO₃⁻ and Cl⁻ shown a slight impact on CIP removal whereas HCO₃⁻ markedly inhibited the removal of CIP. Chemical quenching and EPR spectra implied that SO₄²⁻, HO· and O₂ were all generated and among them O₂ was determined as the predominant reactive species for CIP decomposition. The activation process was promoted by lower oxidation state of Fe. The surface hydroxyl groups as active sites also participated in the PDS activation. Oxygen vacancies produced by Sr doping induced the generation of O₂ and enhanced the redox cycle of Fe(II)/Fe(III). This study demonstrates that A-sites modified BiFeO₃ perovskite has a great potential for PDS activation via O₂-based mechanism towards wastewater remediation.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (Nos. 2018YFD1100505, 2019YFD1100201).

Appendix A Supplementary data

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jes.2020.04.026

REFERENCES


Golshan, M., Kakkavandi, B., Ahmad, M., Anizi, M., 2018. Photocatalytic activation of peroxymonosulfate by TiO₂ anchored on copper ferrite (TiO₂@CuFeOₓ) into 2,4-D degradation: process feasibility, mechanism and pathway. J. Hazard. Mater. 359, 325–337.


Huang, Y.F., Huang, Y.H., 2019. Identification of produced powerful radicals


Jauhar, S., Singhal, S. 2014. Substituted cobalt nano-ferrites, Co3Fe2-xCoxO4 (M=Co, Ni); Cu2+, Zn2+; 0.2≤x≤1.0 as heterogeneous catalysts for modified Fenton reaction. Ceram. Int. 40, 11845–11855.


