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**Mechanism and performance of singlet oxygen dominated
peroxymonosulfate activation on CoOOH nanoparticles for 2,4-
dichlorophenol degradation in water**

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Graphic abstract

Highlights:

- CoOOH is an efficient peroxymonosulfate activator.
- CoOOH has good stability, efficient electron transfer and strong hydrophilicity.
- CoOOH/PMS system showed effective catalysis oxidation activity over broad pH range.
- $^1\text{O}_2$ was identified as dominant reactive oxygen species in the CoOOH/PMS system.

Abstract

Peroxymonosulfate (PMS) has gained attention as oxidant for SR-AOPs. It is essential to develop a stable heterogeneous catalyst with strong hydrophilicity and high electron transfer capability for PMS activating. In this study, cobalt oxyhydroxide (CoOOH) was synthesized and activated PMS for degradation of 2,4-dichlorophenol (2,4-DCP) aiming to assess the feasibility of CoOOH/PMS system. 50 mg/L of 2,4-DCP could be 100% degraded within 120 min with 0.20 g/L CoOOH and 6 mM PMS. CoOOH/PMS system possessed a high degradation efficiency (0.0462 min^{-1}), which was about 10 and 4 times higher than $\text{Co}_3\text{O}_4/\text{PMS}$ and $\text{CoFe}_2\text{O}_4/\text{PMS}$ system, respectively. Furthermore, it was found that

CoOOH/PMS system displayed effective catalytic performance over broad pH range (e.g. 3-9). Importantly, the quenching tests revealed that $^1\text{O}_2$ was identified as dominant reactive oxygen species (ROS). Co (III) was rapidly reduced to Co (II) owing to the efficient electron transfer rate performance of CoOOH in the catalytic reaction. Then, the regeneration of Co (II) facilitated CoOH⁺ owing to the surface of CoOOH with sufficient hydroxyl group, which is crucial for PMS activation and reactive oxygen species-ROS generation. This study proposed an alternative technology based on peroxymonosulfate catalyzed by cobalt-based hydroxide for waste water treatment.

Keywords: CoOOH, sulfate radical, singlet oxygen, surface hydroxyl density, electron transfer

1. Introduction

2,4-dichlorophenol (2,4-DCP) has attracted a lot of attention due to its wide application in fungicides and pharmaceuticals[1]. Its high toxicity and biorefractory resulting in harm for human and living creatures [2, 3] , discharge of water containing 2,4-DCP poses a great threaten to the environment and human beings. However, conventional treatment methods have some drawbacks such as slow reaction rate and requirement of proper pH/temperature, etc.[4]. Therefore, developing an efficiency chemical oxidation technology is desired.

As reported, advanced oxidation processes (AOPs) is an alternative and effective technology for toxic and recalcitrant organic pollutants removal [5-9]. Recently,

compared with hydroxyl radical-based AOPs ($\bullet\text{OH}$, $E_0 = 1.8\text{-}2.7\text{ V}$), sulfate radical-based AOPs (SR-AOPs) ($\text{SO}_4\bullet^-$, $E_0 = 2.5\text{-}3.1\text{ V}$) attracted more attention owing to its higher oxidized ability, independence for pH, and superior selective oxidation [10-12]. $\text{SO}_4\bullet^-$ is formatted via persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) activation or peroxymonosulfate (PMS, HSO_5^-). The activated approaches included heat, transition metals or UV irradiation, etc. Among them, transition metal activation cost less energy and less complex in reactor/system configuration [5].

As reported, Co^{2+} exhibited highest catalytic activity as PMS activator. Besides, Co^{2+} /PMS system displayed superior performance and lower reagent dosages than Fenton reaction at neutral pH [8, 11, 13]. In the Co^{2+} /PMS system, the generation of CoOH^+ , which is considered as the active species for sulfate radical generation as well as the rate-limiting step [14, 15]. Besides, Co^{2+} as PMS activator has also disadvantages of low recycle utilization, potential environmental risks of Co^{2+} discharge and dependence of pH [8]. According to the reports, cobalt containing materials as heterogeneous catalysts attract attentions. Up to date, cobalt-based oxides as heterogeneous catalysts, such as Co_3O_4 , spinel cobalt-ferrite (CoFe_2O_4) have been investigated. Though promising, the electronic transmission rate, catalytic activity, the hydrophilic capability and pH flexibility of the above catalysts are required to be enhanced. Hence, developing a new cobalt-based heterogeneous catalyst for PMS activation is essential.

CoOOH nanoparticles gain our attention as an alternative catalyst attributed to its following properties [16]: it is a hydrophilic compound with sufficient active sites

and hydroxyl groups. Moreover, CoOOH has been used as CO sensor [17], supercapacitor [18-20] and precursor for electrode materials [21, 22] in industry. It turns out that CoOOH has good electronic transmission rate. To date, there is little report on the catalysis oxidation system of peroxymonosulfate activated via CoOOH nanoparticles for 2,4-dichlorophenol degradation in water. Herein, the objectives of this study are: (i) to employ CoOOH/PMS system for pollutant degradation in water; (ii) to evaluate degradation efficiency for organic pollutant via system of peroxymonosulfate activation on CoOOH nanoparticles; (iii) to investigate mechanism of singlet oxygen dominated peroxymonosulfate activation on CoOOH nanoparticles via quenching experiments, ESR, FT-IR and XPS analysis.

2. Materials and Methods

2.1 Chemicals

The chemicals and reagents in this study are all commercially available and analytical grade. 2,4-dichlorophenol, methanol, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_2O_2 (30%) and oxone ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$) were provided by Aladdin Chemistry Co., Ltd (Shanghai, China). Quencher agents included furfuryl alcohol (FFA), sodium azide (NaN_3), tert-butyl alcohol (TBA), ethanol (EtOH) and *p*-benzoquinone (*p*-BQ) were provided by Tianjin Kermel Chemical Reagents Company, China. Spin-trapping reagent for ESR experiments including 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMP) were purchased from Sigma.

Solutions in this study were deionized water.

2.2 Synthesis of CoOOH

The CoOOH was prepared by the modified method of chemical precipitation [22]. 100 mL of NaOH solution (2.5 mol/L) was added dropwise into 100 mL of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5 mol/L) solution to get $\text{Co}(\text{OH})_2$ precursor. After holding in 60 °C water lasting 2 hours, H_2O_2 was added to the beaker. Then, the formation $\text{Co}(\text{OH})_3 \cdot \text{CoOOH}$ was obtained from $\text{Co}(\text{OH})_3$ by holding in 60 °C water bath. Afterwards, the final precipitate was filtered and washed many times, then dried at 60 °C, and collected as CoOOH.

2.3 Experimental operation

To evaluate the catalytic activity of CoOOH, Co_3O_4 and CoFe_2O_4 which have been well reported as most popular and efficient PMS activator was selected as a reference. A series of batch experiments under different conditions were implemented to assess the stability and catalytic performance activity of CoOOH nanoparticles for PMS activation. Each sample contained 50 mg/L 2,4-DCP with an amount of PMS and catalyst. Except for investigating effect of the initial pH on 2,4-DCP degradation, the other experiments were under the initial condition of neutral pH (pH = 7). And the initial condition of acidic pH and alkaline pH were achieved by adding 0.1 M H_2SO_4 and 0.1 M NaOH solution into the reaction system, respectively. Moreover, each sample was at a rotation speed of 180 rpm, 23 ± 2 °C. Then, samples were collected at different time intervals and quenched by methanol. Afterwards, the samples were filtered through a 0.22 μm membrane for further analysis by liquid chromatography instrument. Besides, all experiments were in duplicated.

2.4 Characterization and analysis

X-Ray Diffraction Analysis (XRD) was measured for probing the structure of catalyst (XD-3, Shimadzu Corporation, Japan). Energy dispersive spectrometer (EDS) was the method for detecting component elements (X-Max 50, Oxford Instrument, U.K.). Fourier transform infrared spectrometer (FTIR) was the method for further determining functional groups (8400S, Shimadzu Corporation, Japan). Additionally, scanning electron microscope (SEM) (JSM-6700 F, JEOL Ltd., Japan) was used for investigating the morphology of synthesized material. The X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo Corporation, USA) was used for valance variation on different elements during the reaction. Electrochemical characteristics (CV and EIS) of CoOOH was tested by electrochemical workstation (CHI630E, Shanghai chenghua instrument co. LTD.).

The concentration of target pollutant, 2,4-DCP, was analyzed by a high-performance liquid chromatograph (HPLC, Agilent 1260 Infinity, Germany) with an Atlantis C18 column (4.6 mm $\times$ 150 mm). Electron spin resonance (ESR) experiments were conducted on a JES FA200 spectrometer with DMPO and TEMP as a spin-trapping agent. Free metal ions in solution were determined via atomic absorption spectrophotometer (Shimadzu AA-6000CF, Japan). The chloride ion was conducted by an ion chromatograph (Diane ICS-2100, USA). Jena TOC analyzer was used to determine total organic carbon (TOC) of pollutant.

3. Results and discussion

3.1 Phrase and morphology

The synthesized material was consistent with the JCPDS Card No. 73-1213

according to the XRD spectrum in Fig.1a, which was CoOOH. On the basis of the result from EDS spectrum (Fig.1b), the ratio between atomic percent of cobalt and oxygen was about 0.5. According to the characteristic peak at 3429 cm^{-1} , 1639 cm^{-1} and 581.5 cm^{-1} ($< 1000\text{ cm}^{-1}$) in Fig.1c, it turned out that groups of H-bonded hydroxyl ($-\text{OH}$), $\text{Co}-\text{O}$ and $\text{Co}-\text{OH}$ were existed in the synthesized material [23, 24]. Thus, integrated with the SEM image in Fig.1d, the synthesized material can be confirmed as CoOOH nanoparticles with ring structure.

3.2 Catalytic performance evaluation

The catalytic performance evaluation of CoOOH on peroxymonosulfate activation for 2,4-DCP degradation was evaluated. The results were compared with that obtained from Co_3O_4 and CoFe_2O_4 which as a reference have been well reported as most popular and efficient PMS activator. And the structure properties of Co_3O_4 and CoFe_2O_4 were displayed in Fig.S1. As illustrated in Fig.2a, in 120 min reaction, 2,4-DCP was completely degraded in CoOOH/PMS system, whereas only 33% and 73% degradation was achieved in PMS/ Co_3O_4 and PMS/ CoFe_2O_4 system, respectively. Moreover, based on the first-order dynamics, the reaction rate constant of processes including PMS activation by CoOOH nanoparticle (0.0462 min^{-1}) was about 10 and 4 times higher than that by Co_3O_4 and CoFe_2O_4 , respectively. Besides, the contribution of physical adsorption by Co_3O_4 , CoFe_2O_4 and CoOOH to the organic degradation was negligible according to the results (Fig.2b). It may be explained by the structure properties of these three cobalt-based catalyst and the discussion was displayed in Text.S1. These findings clearly demonstrated that CoOOH displayed the

higher catalytic performance for PMS activation than other reported cobalt-based oxides.

3.2.1 Effect of CoOOH, PMS and 2,4-DCP dosage on system performance

It was found that with increasing of CoOOH dosage, 2,4-DCP degradation rate increased significantly (Fig.S2a). Interestingly, the activation efficiency will be strongly inhibited when the dosage of CoOOH over 0.20 g/L. As Wahiba Najjar reported, it can be explained by the diffusion limitation in heterogeneous reactions. When the catalyst dosage over the optimum value, the invalid oxidant on the surface will be dominantly consumed before ROS attacking pollutant, resulting in low degradation efficiency [25, 26]. Thus, 0.20 g/L was the selected proper dosage for catalyst.

Fig. S2b showed the relationship between target pollutant efficiency of degradation and ratio between PMS and target pollutant. Apparently, the more PMS concentration resulting in the higher efficiency for pollutant degradation, however, when ratio of PMS and pollutant over 20:1, the degradation efficiency enhanced slightly. The ineffective PMS consumption can be explained as the limitation of the quantity of active sites for PMS activation [27]. Generally, 20:1 was selected as the optimal ratio of PMS and 2,4-DCP.

3.2.2 Effect of pH

The SR-AOPs can be performed over a wider range of pH by contrast with Fenton reaction [8, 28]. As Fig.S2c showed, when the initial pH range of 3.0-9.0, the 2,4-DCP degradation efficiency varied little, but significantly decreased at pH of 11.

Moreover, it turned out that the degradation of target pollutant followed the dynamics of first-order reaction. And it suggested that k decreased with 2,4-DCP concentration increasing. The relationship between the k and the initial pollutant concentration was dependent on the fitting equation.

$$k = 790.95C^{-1.462}$$

(1)

Where C is the initial concentration of target pollutant, 2,4-DCP, and k is the first-order reaction rate constant.

3.2.3 Effect of HCO_3^- and natural organic matter (NOM) addition

Fig.S3a and Fig.S3b showed the effect of HCO_3^- and NOM on the 2,4-DCP degradation efficiency, respectively. It turned out that the 2,4-DCP degradation efficiency was significantly inhibited with increasing HCO_3^- concentration adding in the reaction solution. It can be explained that HCO_3^- can react with both $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$ (Eq. (2)–(3))[29].

NOM is a compound in natural waters and soils and would either enhance or inhibit the pollutant degradation with increasing NOM concentration [30]. In this study, NOM displayed inhibition effect on target pollutant degradation (Fig.S3b). According to Yao's study [31], NOM usually acts as a quencher of $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$. Moreover, the phenolic hydroxyl and carboxyl groups of NOM could be adsorbed onto the surface of catalysts leading to prohibiting the contact of active sites and PMS

[32]. Thus, NOM would be one of the inevitable factors when the heterogeneous CoOOH/PMS system put into application for waste water treatment.

3.2.4 TOC removal and chloride ion detectable rate

To explore the potential mineralization of 2,4-DCP in CoOOH/PMS system, the TOC and degradation product-chloride ion was determined in this study, shown in Fig.S4. Compared with Yang's study [33], TOC removal efficiency in this study was much higher than that in Yang's study. The TOC removal rate increased up to 50% after 1.5 h reaction. Moreover, the results of dechlorination further confirmed that the catalysis oxidation system of PMS activated by CoOOH had contributions to 2,4-DCP mineralization. After 24 h reaction, TOC removal and Cl^- detected rate were both increased up to 55.37% and 56.38%, respectively, indicating that more intermediate products of 2,4-DCP was further completely degraded.

3.3 Stability of CoOOH

The leaching of cobalt ion in CoOOH/PMS system under acid conditions (initial pH of 3) was investigated (Fig.3a). It was can be seen that the leaching of cobalt ion was about 0.3 mg/L. Meanwhile, the recycle experiments and ion leaching concentrations at different cycles were carried out for catalyst stability evaluation (Fig.3b). It was found that little decline of pollutant degradation efficiency after 4 times cycles. Besides, cobalt ion leaching concentrations at different runs remained the same as the first run. Firstly, it is inevitable for cobalt leaching under the condition of acid, leading to relatively less reaction active sites on the surface of catalyst.

Secondly, the active sites may be decreased owing to the intermediates of 2,4-DCP

covering the surface of catalyst. Thirdly, the surface properties on the catalyst may be varied under the condition of highly oxidative [34]. Integrated with XRD spectrums shown in Fig.S6, it turned out that CoOOH possessed a good stability after the PMS activation reaction.

3.4 CV and EIS analysis

Aiming to further investigate the superior properties of CoOOH than other cobalt oxides (Co_3O_4 , CoFe_2O_4), the characterization of CV and EIS were implemented (Fig.S7). And the multi-cycle cyclic voltammograms (CVs) of the CoOOH in 0.1 M Na_2SO_4 solution were conducted in Fig. 4a and the EIS spectrum of CoOOH displayed in Fig.4b. Apparently, the CV spectra showed obvious REDOX peak shape, demonstrating that CoOOH underwent rapid faradic redox reactions (Co (III) to Co (II)). Thus, CoOOH displayed a good stability and recyclability owing to the little variant of measured CV curves during 3 cycles. Additionally, the EIS spectrum of CoOOH displayed as a semi-circle, demonstrating CoOOH possessed good conductivity.

Integrated with the CV and EIS characterization of Co_3O_4 and CoFe_2O_4 , the results were shown as follows. Firstly, it has been reported that the electric potential for redox peaks (ΔE_p) calculated by CV curves could suggest the electron transmission capability of catalysts [35]. Besides, the diameter of semi-circle represented the polarization resistance (R_p) and the smaller of diameter implying lower pure charge-transfer resistance and higher electrode potential [36]. Notably, compared with the calculated electric potential for redox peaks (ΔE_p) of CoOOH

(0.50 eV), it turned out that Co₃O₄ (0.82 eV) displayed higher ΔE_p while CoFe₂O₄ (0.32 eV) showed lower ΔE_p . It indicated that CoOOH possessed higher electronic transmission rate than CoFe₂O₄. Moreover, compared with the diameter of semi-circle of CoOOH, apparently, Co₃O₄ possessed much larger diameter while CoFe₂O₄ showed slightly smaller diameter. It indicated that CoOOH displayed much lower higher polarization resistance than Co₃O₄. Thus, neither Co₃O₄ nor CoFe₂O₄ exhibited higher electrochemical properties than CoOOH as PMS activator. It was concluded that Co₃O₄ and CoFe₂O₄ possessed lower catalysis activity than CoOOH in the PMS activation system for pollutant degradation.

3.5 Mechanisms of CoOOH activated PMS system.

3.5.1 XPS analysis

In the survey spectra of CoOOH (Fig.S8), the characteristic spectrum of Co and O was clearly observed, further confirming the composition of CoOOH [37]. Fig.5a showed the varied valence of cobalt element before and after the reaction. The Co 2p peak at 780.0 eV presented Co (III). The generated peak after the reaction presented the generated Co (II). About 21.8% Co (III) transferred into Co (II) indicating the cycle of Co (III)/Co (II) generated in the system, which may be occurred as following equations (4-5) [6].

Fig. 5b illustrates the O 1s spectra of CoOOH before the reaction, which was assigned to three peaks at 532.9, 531.3 and 529.9 eV. The three peaks following the order from high to low binding energy were represented as surface adsorbed oxygen (O_{abs}), metal hydroxide (Co-OH) and metal oxide (Co-O), respectively. The peak at 532.9 eV representing O_{abs} disappeared after the reaction, indicating that O_{abs} was involved in the reaction. Integrated with the content of species before and after the reaction, it turned out that the increased content of Co-OH after (23.8%) about as twice as that of Co-O (11.3%). And the ratio of Co-OH/Co-O was raised from 1.56 to 1.70 by contrast with the fresh and used catalyst (Tab.S2). Thus, the content of CoOH^+ generated most, which played key role for PMS activation.

3.5.2 FTIR analysis

The vibration band of catalyst at 3429 cm^{-1} , 1639 cm^{-1} and 581.5 cm^{-1} (Fig.5c) indicated the existence of the H-bonded hydroxyl group (-OH), Co-O and Co-OH, respectively [23, 24]. It can be seen that the responses of peak at 3429 cm^{-1} and 581.5 cm^{-1} after oxidation reaction were stronger than that before oxidation reaction. The result indicated that more -OH and Co-OH groups were formed on the surface of CoOOH during the catalytic oxidation process. As CoOH^+ species is acknowledged as the key step for PMS activation, which limited the reaction rate [38, 39], the formation of -OH and Co-OH groups on the surface of CoOOH would play a significant role in facilitating PMS activation. Integrated with the result from XPS, the regeneration Co (II) on the surface of CoOOH with sufficient hydroxyl groups accelerated generation of CoOH^+ , leading to higher catalytic oxidation rate.

Subsequently, CoOOH displayed good catalytic activity of PMS activation for target pollutant degradation. All these above findings had a good explanation for why CoOOH exhibited high efficient catalytic for PMS activation.

3.5.3 Identification of reactive oxidizing species by specific quenchers

A series of selective radical quenching tests were implemented in order to determine the predominant reactive species in the CoOOH/PMS system and the quenching agents included EtOH, TBA, *p*-BQ, FFA and NaN₃ (Fig. 6a) [40]. As reported [41], *p*-BQ can selectively react with O₂•⁻. EtOH can easily react with SO₄•⁻ ($k = 10^7 \text{ M}^{-1}\text{s}^{-1}$) and OH• ($k = 10^9 \text{ M}^{-1}\text{s}^{-1}$) while TBA has much higher reaction rate with OH• ($4\text{-}9.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) than that with SO₄•⁻ ($3.8\text{-}7.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), thus, the TBA can be considered as the mainly OH• quencher. Besides, FFA exhibited high reactivity with OH• ($k(\text{FFA}, \text{OH}\bullet) = 1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) and ¹O₂ ($k(\text{FFA}, ^1\text{O}_2) = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). Additionally, NaN₃ can react with OH• ($k(\text{NaN}_3, \text{OH}\bullet) = 2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), SO₄•⁻ ($k(\text{NaN}_3, \text{SO}_4\bullet^-) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) and ¹O₂ ($k(\text{NaN}_3, ^1\text{O}_2) = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Firstly, as Fig.S9 displayed, though the concentration ratio of TBA and PMS increased up to 100:1, TBA addition hardly impede degradation of pollutant ($k_{[\text{TBA}]=100[\text{PMS}]} = 0.0369 \text{ min}^{-1} < k_{[\text{TBA}]=500[\text{PMS}]} = 0.0396 \text{ min}^{-1} < k_{\text{No quencher}} = 0.0404 \text{ min}^{-1}$), indicating little OH• existed in the oxidation reaction.

Secondly, in order to further evaluate the role of ¹O₂ in the system, quenching experiments with different concentrations of FFA addition were carried out. It turned out that with the increasing concentrations of FFA, the 2,4-DCP degradation efficiency inhibited more. Especially, when the concentrations of FFA achieved 80

mM, the 2,4-DCP degradation showed the most significantly inhibition effect

$$(k_{[\text{FFA}]=80\text{ mM}} = 0.0038\text{ min}^{-1} < k_{[\text{FFA}]=50\text{ mM}} = 0.0081\text{ min}^{-1} < k_{\text{No quencher}} = 0.0404\text{ min}^{-1}).$$

Integrated with the results of FFA and TBA, it was found that the inhibition effect of FFA was attributed to quenching $^1\text{O}_2$ rather than $\text{OH}\cdot$, owing to little $\text{OH}\cdot$ existence in the system.

Thirdly, the 2,4-DCP degradation efficiency was inhibited with *p*-BQ addition, indicating the existence of $\text{O}_2\cdot^-$ in the CoOOH/PMS system. Moreover, the result of EtOH addition displayed that the initial reaction rate constant with EtOH addition was 0.0151 min^{-1} , which was over 2 times less than that with no quencher addition (0.0396 min^{-1}). Moreover, the increasing concentration of EtOH lead to the more significant inhibition effect on 2,4-DCP degradation ($k_{[\text{EtOH}]=500[\text{PMS}]} = 0.0043\text{ min}^{-1} < k_{[\text{EtOH}]=100[\text{PMS}]} = 0.0151\text{ min}^{-1} < k_{\text{No quencher}} = 0.0404\text{ min}^{-1}$). It indicated that amount of $\text{SO}_4\cdot^-$ existed in the system. And integrated with the results from the experiments with 50mM NaN_3 addition, it turned out that the 2,4-DCP degradation was significantly inhibited. And the 2,4-DCP degradation inhibited more with increasing concentration of NaN_3 . It was owing to the capability NaN_3 for quenching $\text{SO}_4\cdot^-$ and $^1\text{O}_2$ in the reaction system. Thus, it existed little $\text{OH}\cdot$ in the CoOOH/PMS system. Notably, integrated with the reaction rate of different quenchers, it was concluded that $^1\text{O}_2$ played a more crucial role than $\text{SO}_4\cdot^-$ and $\text{O}_2\cdot^-$ in the 2,4-DCP degradation. The reaction system of peroxymonosulfate activation on CoOOH was the singlet oxygen dominated oxidation system for 2,4-DCP degradation.

3.5.4 ESR analysis

The ROS which have contributions to the CoOOH/PMS system was further verified by ESR analysis. As shown in ESR spectrums (Fig. 6b and 6c), the generation of DMPO-SO₄ adduct, DMPO-OH adduct and DMPO-O₂ adduct under the conditions of secondary oxidation-reduction process between substances with high oxidized capability and DMPO [42]. Thus, it can be confirmed that OH•, SO₄•⁻, O₂•⁻ had contributions to the reaction system. Moreover, TEMP could capture ¹O₂ accompanying formatting TEMPO, which was a substance with stable structure and displayed as three-equal-intensity-line in ESR pattern [43]. Thus, it indicated that non-radical oxidation occurred in PMS activation on CoOOH. As reported [44, 45], ¹O₂ could be slowly formatted with 0.2 M⁻¹s⁻¹ rate constant (equation (6)).

However, it may be explained that the main pathway for ¹O₂ generation may owing to the direct oxidation or recombination of O₂•⁻ [46] (equation (11)). Integrated with the results from experiments with *p*-BQ addition, it was found that amount of O₂•⁻ was existence in the system. Thus, it indicated that O₂•⁻ had main contributions for ¹O₂ generation in CoOOH/PMS system. In summary, the generation of the reactive oxygen species including •OH, O₂•⁻ and ¹O₂ can be illustrated according to the following equations (7-11). It turned out that O₂•⁻ and ¹O₂ had contributions to the 2,4-DCP degradation over pH ranges.

Furthermore, aiming for confirming whether bound radicals occurred during the CoOOH/PMS system, the experiment with potassium iodide (KI) addition implemented (Fig.S10), owing to the capability of KI for quenching the bound radicals on composite surface [48]. It turned out that the reaction rate of 2,4-DCP degradation was decreased from 0.0404 min^{-1} to 0.0018 min^{-1} after adding KI into the CoOOH/PMS system. Thus, the results demonstrated that the surface-bound radicals occurred on the surface of CoOOH. Therefore, non-radical and radical oxidation were involved during peroxymonosulfate activation on the surface of CoOOH. Besides, among the ROS identified in this system, ${}^1\text{O}_2$ played the key role in the oxidation reaction. The generation of CoOH^+ as well as the cycles of Co (III)/Co (II) and $\text{O}_2^{\bullet-}/\text{O}_2$ are critical for the high PMS activation.

4. Conclusions

This work outlined the performance and mechanism of CoOOH/PMS system for degradation of target pollutant, 2,4-DCP. The CoOOH/PMS system integrated the strengths of heterogeneous catalysts and technology of AOP. 50 mg/L 2,4-DCP could be 100% degraded within 120 min by adding 0.20 g/L CoOOH and 6 mM PMS. Moreover, CoOOH exhibited much higher heterogeneous catalytic activity than

Co₃O₄ and CoFe₂O₄ over a broader pH value (e.g. 3-9). Interestingly, the results suggested that ¹O₂ was the dominated ROS in the CoOOH/PMS system for 2,4-DCP degradation. Due to the efficient electron transfer rate performance of CoOOH, Co (III) was rapidly turned to Co (II) due to redox oxidation, then, the regeneration of Co (II) on the surface of catalyst with high hydroxyl groups greatly facilitated the generation of CoOH⁺, which plays key role for PMS activation and reactive oxygen species generation. Generally, this study provides a promising alternative to cobalt-based heterogeneous catalysts for activating PMS, suggesting a potential technology in waste water treatment.

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Figure 1 XRD spectrum (a), EDS spectrum (b), FT-IR spectrum (c) and SEM image (d) of CoOOH.

Figure 2 Degradation kinetics (a) and reaction rate constants (b) of 2,4-DCP in three different catalytic PMS system. Conditions: [2,4-DCP] = 50 mg/L, [PMS] = 6.0 mM and [catalysts] = 0.2 g/L.

Figure 3 Cobalt leaching (a) and recycle experiments (b) for 2,4-DCP degradation in CoOOH/PMS system. Conditions: [2,4-DCP] = 50 mg/L, [PMS] = 6.0 mM and [CoOOH] = 0.2 g/L.

Figure 4 Cyclic voltammetry curves (a) and EIS Nyquist plots (b) of CoOOH.

Figure 5 XPS spectra of CoOOH catalyst before and after reaction: Co 2p (a) and O 1s (b). FT-IR spectra of CoOOH before and after reaction (c).

Figure 6 Competitive radical tests using EtOH, TBA, p -BQ, FFA and NaN_3 as quenchers. ESR spectra using DMPO (b, c) and TEMP (d) as spin-trapping reagent. Conditions: [2,4-DCP] = 50 mg/L, [PMS] = 6.0 mM, [CoOOH] = 0.2 g/L, [EtOH] = [TBA] = 3 M, [p -BQ] = 60 mM, [NaN_3] = [FFA] = 50-80 mM.