



# Novel green activation processes and mechanism of peroxymonosulfate based on supported cobalt phthalocyanine catalyst



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## ABSTRACT

Catalytic activation of peroxymonosulfate (PMS) to generate radicals has received considerable and increasing attention in environmental catalysis field. The development of highly efficient and environmentally friendly oxidation processes has been one of the most important and greatly challenging goals in PMS activation field. Herein, an effective and stable catalyst (ACFs-CoPc) was proposed for PMS activation by supporting cobalt phthalocyanine (CoPc) onto activated carbon fibers (ACFs) covalently. With the dye of Acid Red 1 (AR1) as probe compound, ACFs-CoPc could effectively activate PMS to eliminate AR1, and the catalytic activity of ACFs-CoPc was almost not impaired during ten successive runs without detectable cobalt leaching, indicating that ACFs-CoPc/PMS system was a pro-environmental and efficient oxidation system. A hybrid method that combines electron paramagnetic resonance (EPR) technology with different radical scavengers effect on PMS activation was employed for the investigation of active species during the catalytic reaction. It was found that both hydroxyl and sulfate radical ( $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ ) were generated; importantly,  $\text{SO}_4^{\cdot-}$  was speculated to serve as the dominant active species in the catalytic oxidation of AR1. Based on these results, a possible mechanism was proposed.

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## 1. Introduction

The generation of active species, such as reactive oxygen species (ROS), is an important process in nature, occurring from human body to natural world [1]. Such active species have been widely investigated in various chemical areas, especially in catalysis field due to their high oxidative activity [2–4]. Sulfate radical ( $\text{SO}_4^{\cdot-}$ ) has been known as one of the most powerful reactive oxygen species for its high standard redox potential (2.5–3.1 V) [5], which is comparable to that of hydroxyl radical ( $\cdot\text{OH}$ , 1.8–2.7 V) [6], and has attracted increasing attention for their high efficiency of oxidation of organic pollutants [7–9]. As one of the most efficient sources of  $\text{SO}_4^{\cdot-}$ , the activation of peroxymonosulfate (PMS) has been widely studied [10–12]. Recently, the most common catalysts for PMS activation are transition metals, with  $\text{Co}^{2+}$ /PMS system gives the best results of  $\text{SO}_4^{\cdot-}$  generation [13,14]. However, employing  $\text{Co}^{2+}$  to active PMS under a homogeneous system will result in loss of Co, and since Co is recognized as a prior aqueous pollutant which can cause

several health problems such as asthma, pneumonia and other lung problems [15,16], the development of  $\text{Co}^{2+}$ /PMS homogeneous system has been restricted.

Therefore, the development of green processes to generate  $\text{SO}_4^{\cdot-}$  is highly desired on the basis of environmental consideration. On the one hand, developing heterogeneous Co catalysts for PMS activation is an efficient strategy to restrict the discharge of Co ion. Many efforts have been made on studies of heterogeneous Co catalysts, such as Co oxides [17,18], Co exchanged zeolites [19], Co-SBA-15 [20], or other supported Co catalysts [21,22]. However, Co ion leaching is still observed in different scales for many of them, which is regarded as a secondary pollution and loss of the catalyst. On the other hand, PMS activation by other transition metals with less environmental hazards, such as Fe catalysts, is considered as a relatively environmentally friendly technology [23,24]. However, most of these catalysts are generally not as efficient as Co catalysts in PMS activation. Thus, it is still a great challenge to balance the requirements of environmental friendliness and efficiency for PMS activation process.

Cobalt phthalocyanine (CoPc), which has a tetra N-donor macrocyclic structural similarity to the naturally occurring metalloporphyrin, has attracted a considerable interest as an oxidation catalyst because of its remarkable chemical and thermal stability

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[25]. Compared with Co ion alone, the coordination of CoPc possesses attractive characteristics: (i) as CoPc has functional groups, such as amino, sulfo, and carboxyl in the peripheral benzene rings of the phthalocyanine structure, stable chemical bonds such as covalent bonds can be formed between CoPc and support to effectively restrict the loss of catalyst [26]; (ii) the catalytic properties of CoPc are facile to be tuned by the change of the substituent groups on the phthalocyanine ring [27]. However, CoPc as a homogeneous catalyst in aqueous solution is usually prone to aggregate at a relatively low concentration, negatively resulting in catalytically inactive dimers [28]. Moreover, the oxidative self-destruction of CoPc may occur in the catalytic oxidation, causing the loss of the catalyst. An efficient way to solve these problems is to immobilize it onto various supports, such as graphene [29], carbon nanotube [30], MCM-41 [31], chitosan [32] for improved catalytic ability and stability. Unfortunately, some of these catalysts such as CoPc-graphene, CoPc-carbon nanotube are inconvenient to separate from the reaction solution, which is likely to produce secondary pollution. Moreover, CoPc-MCM-41 exhibits unsatisfactory stability in recycling experiments, while CoPc-chitosan shows low effective catalytic activity. It is well known that excellent supports will bring excellent catalytic activity. Therefore, the selection of supports for CoPc is very significant to construct remarkable heterogeneous catalyst.

Compared with the above mentioned supports, activated carbon fibers (ACFs) have the potential of being an excellent support for the construction of heterogeneous CoPc catalysts because of its attractive features: (i) with a high surface area and microporous structure, ACFs have an extremely high adsorption capacity; (ii) as ACFs have plenty of active groups on the surface, they can provide a frame to anchor active sites for their stable immobilization and excellent dispersion on the support; (iii) the unusual chemical stability and inert structure can protect ACFs from the damage and improve the stability of the active sites under the attack of radicals in the oxidation reactions; (iv) ACFs can be confined in different textile structure, such as fiber tows, fabric and felts, aiding their handling. Based on afore considerations, we reported an efficient and stable heterogeneous catalyst, ACFs-CoPc, which was constructed by supporting CoPc onto ACFs via a covalent bond. This catalyst exhibited excellent catalytic activity for H<sub>2</sub>O<sub>2</sub> activation for elimination of phenols, such as 4-nitrophenol [33]. However, the ACFs-CoPc/H<sub>2</sub>O<sub>2</sub> system was almost ineffective for the degradation of dyes. In this work, we innovatively introduced PMS as the oxidant and used ACFs-CoPc as the activator of PMS to generate active species for the dyes elimination. To our best knowledge, it is the first report that supported CoPc catalyst is applied in PMS activation so far.

The primary concerns of this study were to verify the following questions: (i) can ACFs-CoPc effectively activate PMS to generate active species to catalytically oxidate dyes; (ii) can ACFs-CoPc be stable and reach the environmental friendly requirement during the activation process; (iii) what is the mechanism of PMS activation by ACFs-CoPc. Herein, Acid Red 1 (AR1) was selected as a probe compound to evaluate the catalytic activity of ACFs-CoPc for PMS activation. Electron paramagnetic resonance (EPR) technology combined with various radical scavengers has been employed to investigate the mechanism of PMS activation by ACFs-CoPc. It is expected that ACFs-CoPc/PMS system will open up a new area of potential research in the development of green oxidation processes.

## 2. Experimental

### 2.1. Materials and reagents

ACFs were purchased from Jiangsu Sutong Carbon Fiber Co., Ltd. (Jiangsu, China). Cobalt chloride hexahydrate, urea, ammonium molybdate, cyanuric chloride, and potassium peroxydisulfate

(PMS: oxone, Aladdin Industrial Corporation) were used as analytical reagents. The spin trapping reagent 5,5-dimethylpyrroline-oxide (DMPO) was supplied from Tokyo Chemical Industry Co., Ltd. All dyes, including Acid Red 1 (AR1) and Reactive Brilliant Red M-3BE (RR M-3BE) are commercial compounds without further purification. Doubly distilled water was used throughout the dyes degradation process.

### 2.2. Preparation of ACFs-CoPc

CoPc with active groups was synthesized from cobalt teraaminophthalocyanine and cyanuric chloride according to the method described by Chen et al. [34]. ACFs were treated with acid for 12 h, washed with water to neutrality, and dried to obtain oxidated ACFs (o-ACFs). ACFs-CoPc was prepared by supporting CoPc to o-ACFs by covalent bond (see Supplementary Information for details of the process). The bonding site between CoPc and o-ACFs was investigated using X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD, UK) and the results were shown in Fig. S1 (see Supplementary Information for details of the process).

### 2.3. Experimental procedures and analysis

The removal of dyes was carried out in a 40 mL glass beaker, with the temperature set at 50 °C using a constant temperature shaker water bath (DSHZ-300A, Taicang, Jiangsu). In all reactions, a reaction volume of 30 mL was used. A typical reaction mixture contained the following initial concentrations and amounts: the dyes (50 μM, except for MB (25 μM)), ACFs-CoPc (1 g/L), o-ACFs (1 g/L), PMS (0.6 mM). At given time intervals, the degradation efficiency of the dyes was determined by a UV-vis spectrometer (Hitachi U-3010) (see Supplementary Information for details of the process).

The cobalt ion content in the solution after the reaction was detected by an atomic adsorption spectrometer (Hitachi 170-70 atomic absorption spectrometer). EPR signals of radicals trapped by DMPO were recorded at ambient temperature on a Bruker A300 spectrometer. The settings for the EPR spectrometer were the following: center field, 3480 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 12.72 mW.

## 3. Results and discussion

### 3.1. The catalytic activity of ACFs-CoPc

#### 3.1.1. Oxidation removal of AR1

Control experiments were conducted to compare the eliminated efficiencies of AR1 by various processes with reaction temperature 50 °C, as presented in Fig. 1. With ACFs-CoPc only, a slight removal of AR1 was observed, and about 3% of AR1 was removed in 50 min (curve a), due to the adsorption of ACFs-CoPc. In the presence of PMS alone, about 14% of AR1 was degraded in 50 min (curve b). With addition of o-ACFs and PMS, AR1 elimination rate increased to 35%, while in the presence of ACFs-CoPc and PMS, fast and efficient degradation of AR1 was achieved, and nearly 100% of AR1 was degraded in 50 min, indicating that the introduction of CoPc to ACFs greatly enhanced the PMS activation and catalytic degradation of AR1. Besides, GC-MS analysis was performed to investigate the catalytic oxidation products of AR1. The possible structure of the intermediates and the methyl ester derivatives of the intermediates were given in Table S1. The residual products were identified including some small molecular biodegradable aliphatic carboxylic compounds such as oxalic acid, fumaric acid, adipic acid. The results show that ACFs-CoPc is an efficient catalyst for oxidation elimination of AR1 in the presence of PMS. Furthermore, compared with the efficiency of AR1 degradation by ACFs-CoPc/H<sub>2</sub>O<sub>2</sub> system

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