



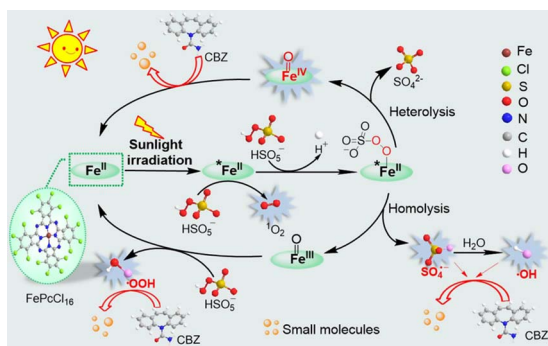
# Solar-initiated photocatalytic degradation of carbamazepine on excited-state hexadecachlorophthalocyanine in the presence of peroxymonosulfate



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## GRAPHICAL ABSTRACT



## ARTICLE INFO

**Keywords:**  
Photocatalytic  
Iron hexadecachlorophthalocyanine  
Peroxymonosulfate  
Mechanism

## ABSTRACT

In the field of environmental catalysis, the construction of highly efficient and stable catalytic oxidation processes has raised considerable attention. In this study, a novel solar-initiated photocatalytic oxidation system, FePcCl<sub>16</sub>/PMS/Sunlight, was established by iron hexadecachlorophthalocyanine (FePcCl<sub>16</sub>) with peroxymonosulfate (PMS) in the presence of sunlight excitation. Under sunlight irradiation, the phthalocyanine ring of the FePcCl<sub>16</sub> is motivated to FePcCl<sub>16</sub>\* in the excited state, which activates PMS to generate free radicals or high-valent iron(IV)-oxo intermediates (Fe(IV) = O) to oxidize carbamazepine (CBZ). The system could degrade CBZ effectively and total-organic-carbon removal from solution reached nearly 80% within 90 min. FePcCl<sub>16</sub> catalytic activity was almost without loss and without iron leaching after twenty recycles, indicating that the FePcCl<sub>16</sub>/PMS/Sunlight was a stable and efficient photocatalytic oxidation system. Electron paramagnetic resonance, gas chromatography-mass spectrometry and photocatalytic-activity-experiment analysis shows that Fe(IV) = O species, singlet oxygen (<sup>1</sup>O<sub>2</sub>), hydroxyl and sulfate radicals (<sup>•</sup>OH, SO<sub>4</sub><sup>•-</sup>) are the main active species in the catalytic oxidation of CBZ. Density functional theory (DFT) calculations exhibits that the electronic cloud for excited state FePcCl<sub>16</sub>\* is transferred from the porphyrine ring and peripheral substituents to the central Fe atom and its axial position. The main degradation intermediates and possible degradation pathway of CBZ were proposed by ultra-performance liquid chromatography and high-resolution mass spectrometry (UPLC Synapt G2-S HDMS). This study provides efficient catalytic oxidation support for wastewater treatment.

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## 1. Introduction

The growing consumption of pharmaceutical products has raised concerns ascribe to their high persistence which cannot be decreased by traditional wastewater-treatment processes [1,2]. Amongst the psychotropic drugs, carbamazepine (CBZ) is one of the most commonly detected drugs in the city's damaged surface water and it has been presented as a marker of anthropogenic contamination [3]. CBZ is an anticonvulsant and mood-stabilizing drug that is used extensively in the clinical treatment of epilepsy, trigeminal neuralgia, and other psychiatric disorders [4,5]. As a human pharmaceutical, CBZ is almost completely absorbed by the gastrointestinal tract, and 72% of the dose being recovered to the urine [6]. Hence, CBZ is excreted in pharmaceutical residues and their metabolites remain in aquatic biota [7,8]. A microcosm experiment indicated that horizontal subsurface-flow-constructed wetlands had no significant effect on CBZ removal efficiencies [9]. Due to their frequent use and incomplete removal by a variety of traditional processing methods, CBZ is considered to be an emerging pollutant that can damage environments and human health [10,11]. Therefore, an efficient technology for the removal of CBZ is in need.

A series of studies have focused on CBZ degradation to reduce damage [12–14]. Possible solutions of the problem have been provided from research. For instance, oxidation depolymerization of carbamazepine was performed using persulfate anions under given conditions (heat energy, UV-C light,  $\text{Fe}^{2+}$  ions, and hydrogen peroxide) [15]. Moreover, some authors suggest that photochemical degradation and oxidative treatment (the photo-Fenton reaction,  $\text{UV}/\text{H}_2\text{O}_2$ , el) are feasible methods for the treatment of CBZ [16–18]. Although CBZ can be degraded by these catalysts under certain conditions, its removal efficiency is poor and it is difficult to degrade the CBZ completely. Sometimes, because of the relatively high treatment costs and secondary pollution, large-scale applications are limited; some improvements in treatment methods are required.

Recently, combinations of some oxidants (hydrogen peroxide, ozone, permanganate, and persulfate) have been explored [19–21]. To the best of our knowledge, because of its aqueous solubility, relatively high stability and low cost, peroxymonosulfate (PMS) with transition metals can be used as a source of sulfate radicals, which are the major oxidizing species [22]. Previously, our team found that CFs-CoPc/PMS and pyridyl-functionalized graphitic carbon nitride coordinated with iron phthalocyanine, as novel oxidation systems, exhibited catalytic activity for PMS activation to degrade contaminants [23,24]. In the PMS activation processes, ACF has an abundance of nonbonding free electrons playing a key role in improving catalytic activity. In this study, we have used solar irradiation to obtain excited-state hexadecachlorophthalocyanine ( $\text{FePcCl}_{16}^*$ ), which activates PMS for efficient degradation of contaminant, such as CBZ, phenol, and dye. On account of its easy preparation, high activity and stability, and low cost,  $\text{FePcCl}_{16}$  is very deal product. As we all know, solar is virtually inexhaustible, and compared with other metals, iron compounds are environmentally friendly. Recently, photocatalysis has been a most active research areas, for example, in light-energy transformation to chemical energy. The  $\text{FePcCl}_{16}$ /PMS system could use sunlight in which the phthalocyanine ring is motivated to  $\text{FePcCl}_{16}^*$  and finally activates PMS with the generation of anchored  $\text{Fe(IV)}=\text{O}$ ,  $^1\text{O}_2$  and radicals ( $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ ) to eliminate CBZ.

The aim of the study was to investigate: (i) the catalytic activity and reusability of excited-state  $\text{FePcCl}_{16}$  with PMS under solar irradiation for pollutant decomposition, (ii) the degradation of pollutant CBZ, and (iii) the mechanism of PMS activation during the reaction process. Apart from contents mentioned above, this study may inspire others to improve the utilization of solar energy and the application of PMS activation in environmental governance.

## 2. Material and methods

### 2.1. Materials and reagents

Carbamazepine (CBZ  $\geq 98.0\%$ ) and potassium peroxymonosulfate (PMS) were from Aladdin Chemical Inc. (Shanghai, China). The spin-trapping reagent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). High-performance-liquid-chromatography-grade acetonitrile, methanol, and formic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA), Merck (Darmstadt, Germany), and J & K Chemical Inc. (Beijing, China), respectively. Iron(II) chloride tetrahydrate, urea, ammonium molybdate, and 1,2,4-trichlorobenzene were of analytical grade. Milli-Q UltraPure water was used in all experiments.

### 2.2. Preparation and characterization of $\text{FePcCl}_{16}$

The  $\text{FePcCl}_{16}$  catalyst was synthesized according to previously reported methods [25]. Briefly, 70 g of urea, 8.5 g of  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ , 48 g of tetrachlorophthalic anhydride, and 0.2 g of ammonium molybdate were added into 150 ml of 1,2,4-trichlorobenzene, and stirred for 5 h at  $190^\circ\text{C}$ . After cooling, the obtain suspension was diluted with ethanol, boiled for 10 min, and filtered hot. The crude products were washed with boiling 1% HCl solution and then 1% NaOH solution. Then, the solution was extracted with acetone and methylene chloride, and finally freeze-dried for 18 h to collect the  $\text{FePcCl}_{16}$  catalyst. UV-visible and attenuated total reflection Fourier-transform infrared spectroscopy analysis were used to investigate the structure of the as-prepared  $\text{FePcCl}_{16}$  with the results as shown in Figs. S1 and S2 (see Supplementary Information for details).

### 2.3. Photocatalytic experiments

Photocatalytic experiments were performed in a SUN-Q-Light test chamber (Xe-1-BC, Q-Lab, Cleveland, OH, USA). The spectra power distribution of Q-SUN Xe-1 with daylight is shown in Fig. S3. During the experiment, 20 mL CBZ (0.025 mM) aqueous solution was placed in a 40-mL glass sample beaker. The initial pH was adjusted by the addition of a moderate amount of  $\text{H}_2\text{SO}_4$  or NaOH. Prior to light irradiation,  $\text{FePcCl}_{16}$  was added into the CBZ aqueous solution, followed by PMS stock solution to initiate the reaction. At given time intervals, sample was withdrawn with a syringe and filtered with  $0.22\ \mu\text{m}$  PTFE filters for further analysis.

### 2.4. Electron paramagnetic resonance (EPR) studies

Electron paramagnetic resonance (EPR) spectra of free radicals that were trapped by DMPO and TEMP were measured on a Bruker A300 spectrometer (Bruker, Karlsruhe, Germany). The EPR parameters were as follows: microwave frequency, 9.85 GHz; microwave power, 12.72 mW; modulation frequency, 100 kHz; center field, 3507 G; sweep width, 80 G; and static field, 3467 G. EPR signals of the  $\text{FePcCl}_{16}$  suspension that contained 100 mM DMPO were obtained in the presence of PMS after 2 min reaction.

### 2.5. Analytical methods

The CBZ concentration was determined by ultra-performance liquid chromatography (UPLC, Waters, Milford, MA, USA), which equipped with an Acquity BEH C18 column ( $1.7\ \mu\text{m}$ ,  $2.1\ \text{mm} \times 50\ \text{mm}$ ). An acetonitrile and water eluent with a ratio of 15:85 (V/V) was used as the mobile phase at a flow rate of 0.4 mL/min. The total organic carbon (TOC) concentration was detected by a GE Sievers innovOx TOC analyzer (GE Analytical Instruments, Boulder, CO, USA).

To analyze the photocatalytic degradation of CBZ, we used a Waters ACQUITY UPLC I-Class coupled with a Waters SYNAPT G2-S HDMS

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