



Synergistic effects of persistent free radicals and visible radiation on peroxydisulfate activation by ferric citrate for the decomposition of organic contaminants



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ABSTRACT

In this work, persistent free radicals (PFRs) of activated carbon fibers (ACFs) were innovatively coupled with Fe(III)-photocatalysts to construct a distinctive catalytic oxidation system, FeCit@ACFs/PMS/visible light. Herein, PFRs acted as an electron sink by donating electrons to ferric citrate (Cit-Fe), thereby accelerating the ligand-to-metal charge transfer (LMCT) processes that govern the rate-determining step of the reaction transforming Cit-Fe^{III} to Cit-Fe^{II}. Moreover, visible radiation can serve as another powerful assistant to further enhance the LMCT processes because Cit-Fe exhibits highly intrinsic photosensitivity. The synergistic enhancement effect of PFRs and visible light endowed the constructed FeCit@ACFs catalyst with strong catalytic activity, which could effectively activate peroxydisulfate (PMS) to generate reactive oxygen species (ROS) for contaminants decomposition. To investigate the ROS generated in this experiment, we adopted a hybrid method that combines electron paramagnetic resonance technology with different radical scavengers, and the results indicated that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were generated and played a major role in the catalytic oxidation process. This work provided a new insight into the positive role of PFRs and presented an up-to-date research domain of PFRs-enhanced catalysis. It also paved an avenue for developing high-efficiency processes for the generation of ROS, which can be subsequently used in environmental catalysis.

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1. Introduction

Persistent free radicals (PFRs) have half-lives on the order of hours to days under various atmospheric conditions. They have been widely detected in combustion-generated particulate matters [1,2], sediments [3], and even in soils [4]. Owing to their persistence and radical reactivity, PFRs are attracting a lot of attention of researchers in biological and environmental fields. In previous research studies, it has been reported that PFRs are pernicious species, because they have the potential to induce oxidative stress that causes a variety of illnesses in exposed populations [5–7]. For example, Balakrishna et al. reported that neonates exposed to PFRs-containing combustion generated ultrafine particles developed significant pulmonary inflammation, and airway hyperreactivity; these ultrafine particles contain a significant number of PFRs [7]. Although reports have described how PFRs directly activate ox-

dants to oxidize organic compounds [8,9], very few studies have investigated the positive role of PFRs in various reactions.

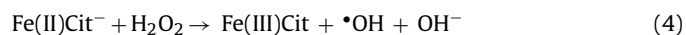
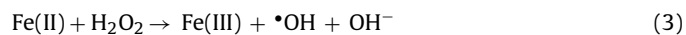
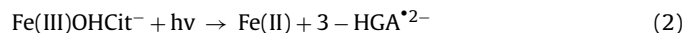
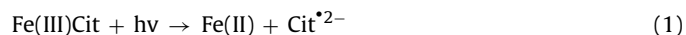
It is worthwhile to mention that PFRs are also known as resonance-stabilized radicals, with an abundance of unpaired electrons. Therefore, PFRs can act as electron donors and bring about a sustainable electron transfer to other electron-acceptors, such as higher valent metals. In other words, PFRs reduce these metals by donating electrons [10,11]. Therefore, PFRs can accelerate some important catalytic redox processes, such as the iron-mediated catalytic cycle that activates oxidants used in the treatment of environmental contaminants; this cycle has an intrinsic drawback of slow reduction rate of iron. Thus, PFRs might play an important role in enhancing the catalytic oxidation performance of ROS (reactive oxygen species), which are used in the decomposition of contaminants. However, only a handful of research studies have reported about this positive effect of PFRs.

Over the past years, visible light-assisted catalysis has been recognized as an extremely promising technology for the treatment of organic pollutants [12–14]. In particular, ferric citrate (Cit-Fe) complexes have been thoroughly investigated (Reactions

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(1)–(4)) as they have low toxicity and high photoreactivity; it has been found that Cit-Fe complexes serve as outstanding photocatalysts [15,16]. However, previous research studies involving Cit-Fe catalysis mainly focused on the homogeneous media in which the reduction of Fe(III) ions underwent reduction through ligand-to-metal charge transfer (LMCT) processes (Reactions (1) and (2)): this is the key step to improving catalysis efficiency; these processes are sensitive to reaction conditions (especially pH) and it is easy to strictly control them [17]. In homogeneous media, Cit-Fe complexes have high mobility, so they may adversely affect the ecosystem. One of the most effective yet simple strategies is to develop the heterogeneous catalysts that can alleviate these limitations and enable the reuse of Cit-Fe catalyst. Recently, various supports, such as Nafion, zeolite, resin, and clay, have been used to develop the heterogeneous catalysts [18–21]. Compared to these supports, activated carbon fibers (ACFs) may be a more satisfactory candidate as it has remarkable characteristics. Firstly, ACFs is a kind of carbon material with highly microporous structure and remarkably high adsorption ability. Moreover, ACFs have a uniform micropore size distribution and a large surface area [22]. ACFs can be used to synthesize felts or fabrics of various types, while granular or powder supports cannot be used for the same. Thus, ACFs have more applications as compared to conventional supports that exist in either granular or powdered form. Most importantly, ACFs was the ideal representative of PFRs, and PFRs in ACFs are capable of providing electrons to Cit-Fe, which might contribute to further accelerating the LMCT processes and bring about the reduction of Fe(III) to Fe(II) state. And our previous reports have demonstrated that PFRs in ACFs initiate electron transfer and improve the catalytic activity of iron porphyrin (hemin), which is used to activate H₂O₂ and bring about the degradation of contaminants [23]. Since the inherent PFRs in ACFs initiate electron transfer in oxidative catalysis, they might be collaborated with the visible light-assisted photocatalysis to dramatically enhance the catalytic activity of Cit-Fe. Based on the above considerations, ACF was selected as the support to improve the catalytic activity of Cit-Fe in this study; peroxymonosulfate (PMS) were selected as the oxidant due to its outstanding characteristic. Compared to H₂O₂, PMS was easier to handle as it existed in the solid form. Furthermore, PMS could be activated to generate sulfate radicals (SO₄^{•-}, 2.5–3.1 V vs NHE), which possess higher oxidizing capacity than •OH (1.9–2.7 V, pH dependent), especially at higher pH levels [24–26]. Thus, we constructed a simple and practical catalytic oxidation system: FeCit@ACFs/PMS/visible light. It was used to bring about the decomposition of contaminants.



In this study, our aim is to investigate the catalytic activity of FeCit@ACFs and to comprehend the role of PFRs and visible light in a catalytic oxidation process. The decolorization of Reactive Red M-3BE (RR M-3BE) dye was selected as the model reaction to evaluate the catalytic oxidation performance of FeCit@ACFs/PMS/visible light system. Electron paramagnetic resonance (EPR) coupled with different scavengers (e.g., electron capture agents and radical scavengers) were used to investigate the mechanism through which PFRs exerted a positive effect on oxidative catalysis, and we also deciphered the synergistic effect of PFRs and visible light. In this study, we elucidated how PFRs could assist visible light-assisted photocatalytic degradation, offering a new insight into the positive role of PFRs. Thus, we presented a novel approach through which PFRs enhance the process of oxidative catalysis. Furthermore, we

also paved the way towards developing robust processes that could be used for efficiently generating reactive oxidation species ROS (SO₄^{•-} and •OH⁻): they are generally employed in environmental catalysis.

2. Experimental

2.1. Materials and reagents

Activated carbon fibers (ACFs) were bought from Jiangsu Sutong Carbon Fiber Co., Ltd. (Jiangsu, China). Ferric chloride hexahydrate (FeCl₃·6H₂O), trisodium citrate dehydrate (Na₃C₆H₅O₇·H₂O), PMS and hydrogen peroxide (30 wt%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were the analytical grade reagents used in this study. The spin trapping agent 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was supplied by Tokyo Chemical Industry Co. Ltd., Tokyo, Japan. Reactive Red M-3BE (RR M-3BE), Acid Red 1 (AR1), Rhodamine B (RHB), Acid Orange 7 (AO7), Methylene Blue (MB) and Basic Green 1 (BG1) were used as the model contaminants without further purification. The other chemical reagents used in this study were provided by Hangzhou Mike Chemical Instrument Co., Ltd. (Hangzhou, China). We used doubly distilled water throughout the experiment.

2.2. Catalyst preparation

Thirty grams of ACFs was impregnated with nitric acid solution (3 M), and the resulting suspension was maintained at 25 °C for 12 h. Then, the treated ACFs was taken out and rinsed repeatedly with distilled water. Finally, it was dried to obtain acidified ACFs. Ten grams of acidified ACFs was immersed in ferric citrate solution (2 mM, Fe(III): Cit = 1:1); the suspension was stored at 25 °C for 12 h. The treated ACFs was taken out from the solution and repeatedly rinsed with distilled water to remove free ferric citrate and other residues. Finally, it was dried at 60 °C to obtain the heterogeneous catalyst: FeCit@ACFs. On the heterogeneous catalyst FeCit@ACFs, we performed atomic absorption spectroscopy (Hitachi 170–70 atomic absorption spectrometer) and determined the iron content of FeCit@ACFs. From these measurements, we found that the ferric citrate content of FeCit@ACFs was 48.6 μmol g⁻¹.

2.3. Experimental procedures and analysis

In a magnetically stirred Pyrex reactor we carried out batch experiments to bring about the catalytic oxidation of the dyes. We used a 500 W mercury lamp as the source of light, while a 400 nm glass cut-off filter was used to exclude ultraviolet light. A 10-cm distance was maintained between the light source and reaction vessel. A constant temperature of 25 °C was maintained throughout the reaction. A reaction volume of 20 mL was used in all the experiments, and it contained the following initial concentrations: (a) dyes (50 μM, 20 mL); (b) supported catalyst FeCit@ACFs (2 g/L) or Cit-Fe (97.2 μM); and (c) oxidant PMS or H₂O₂. The values of apparent rate constant *k*_{obs} for the catalytic reaction can be obtained by determining the slope of the following plot: ln(*C*_{*t*}/*C*₀) versus time (see the Supporting information for details). At predetermined time intervals (3 min), samples were withdrawn from the flask and placed in an ultraviolet/visible (UV-vis) spectrophotometer (Hitachi U-3010) to determine the absorbance. Before adding the catalyst and oxidant, the pH of the initial solution was adjusted with NaOH or HClO₄.

Electron paramagnetic resonance (EPR) signals of ROS were trapped by DMPO and recorded at an ambient temperature in a Bruker A300 spectrometer (Bruker, Germany). The settings of EPR spectrometer were as follows: center field, 3520 G; sweep

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