



A comparative study of iron-based PAN fibrous catalysts for peroxymonosulfate activation in decomposing organic contaminants

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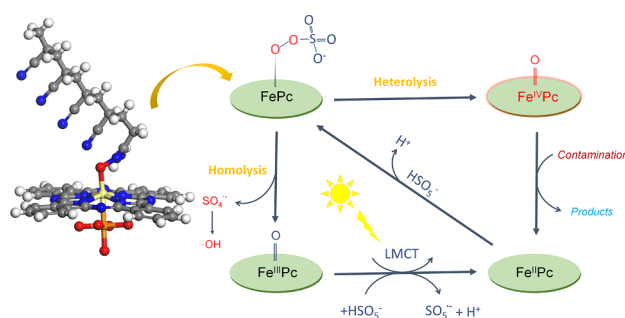
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HIGHLIGHTS

- A series of iron-based PAN fibrous catalysts were used for PMS activation.
- The reaction mechanism of these PMS activated systems was compared.
- The FePc supported PAN fiber exhibits the highest catalytic activity.
- High activity originates from rich electrons and axial coordinate sites of FePc.
- Optimization and reusability of the FePc supported catalyst was studied.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic and comparative investigation of a series of iron-based polyacrylonitrile (PAN) fibrous catalysts, synthesized by supporting Fe(III), Cu(II)/Fe(III), iron(II) 2,2'-bipyridine (FePy) and iron(II) phthalocyanine (FePc) onto amidoximated PAN fiber respectively, for peroxymonosulfate (PMS) activation towards the oxidative degradation of organic contaminations was conducted. We found that there are significant differences in the catalytic activity of iron with various chemical environments. Taking the oxidation of reactive red 195 as model reaction, the FePc supported fibrous catalyst achieved the highest catalytic activity, which mainly originated from the enhanced regeneration of Fe(II) from Fe(III) by the electron-rich characteristic of FePc, as well as the rapid PMS adsorption through abundant axial coordinate sites of FePc. In addition, visible light could significantly accelerate the dye degradation by PMS activation over these catalysts, with the catalytic activities shown in order as follows: FePc > FePy > Cu(II)/Fe(III) > Fe(III). ESR and designed experiments revealed that sulfate and hydroxyl radicals were produced during PMS activation over these catalysts, and high-valent iron-oxo species was also involved in the FePc supported PAN fibrous catalytic system. Furthermore, the excellent pH tolerance and recycling capability, as well as the high activity for dye mineralization enabled FePc supported PAN fibrous catalyst to hold great promise for environmental remediation via PMS activation. Our findings provide further insight into the catalytic mechanism of PMS activation over iron-based catalyst and also allow the design of more efficiency iron-mediated PMS-based advanced oxidation process.

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1. Introduction

The increasing environmental pollution caused by organic contaminations calls for the development of purification technology toward high decomposing efficiency, which can chemically transform them into non-hazardous compounds [1]. Advanced oxidation technologies (AOTs), which can generate highly oxidizing transient species through the activation of oxidants [2,3], hold great promise to substantially realize the environmental remediation. In AOTs, hydroxyl radical ($\cdot\text{OH}$) is the most common active species, which could be generated from hydrogen peroxide (H_2O_2) activation by Fenton or Fenton-like reactions [4–6]. Because of the high standard redox potential (1.9–2.7 V), $\cdot\text{OH}$ shows high oxidation efficiency toward nearly all organic pollutants. On the other hand, sulfate radical ($\text{SO}_4^{\cdot-}$) has been recognized as another effective active species and gained increasing attention in the field of wastewater purification, probably due to its comparable redox potential (2.5–3.1 V) to $\cdot\text{OH}$ [7]. In recent years, sulfate radical-based AOTs have proven most effective in rapid degradation and complete mineralization of many recalcitrant organic pollutants, including dyes [8,9], pharmaceuticals [10–12], brominated flame retardant [13] and polychlorinated biphenyls [14]. As a powerful oxidant for $\text{SO}_4^{\cdot-}$ production, peroxymonosulfate (PMS) has been developed as a promising alternative to H_2O_2 in AOTs process, because of its persistent nature and wide operating pH range, as well as the ability to generate both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals [15,16].

Numerous methods have been proposed for activating PMS to generate active radicals, such as transition metals [17–19], ultraviolet (UV) [20], heat [15] and ultrasound [21]. Compared with other processes, using transition metals is generally more easily operated and handled for PMS activation. Over the past few years, various metals have been tested to activate PMS, with Co(II)/PMS system gives the best activity for $\text{SO}_4^{\cdot-}$ generation. However, the Co(II) catalytic process has limitations in practical applications owing to its high toxicity and potential carcinogenic effects [22]. Even if the heterogeneous cobalt catalysts could reduce the amount of Co(II) in water, there might be still secondary pollution caused by leaching of Co ions [23,24]. Driven by the need of overcoming the limitations of Co based catalysts and seeking for green process that conducted in an environmentally friendly manner, iron has been used for developing catalysts to activate PMS due to its non-toxicity, low cost and effectiveness [14,25]. The homogenous PMS/Fe(II) system has been reported to effectively produce highly reactive radicals, however, its application was limited by the harsh acid pH conditions and difficult catalyst recovery [26,27]. Direct and effective approach to avoid these disadvantages is to construct heterogeneous catalysts by anchoring iron ions onto certain supports. Various materials, such as carbon [28], activated carbon fibers [27] and polyvinylidene fluoride membrane [29], have been applied to prepare heterogeneous iron-based catalysts. Unfortunately, most of these catalysts exhibited relatively lower efficiency in PMS activation compared to Co based catalysts, which specifically originated from two bottlenecks: (i) the immobilization of iron ions depressed its contact and reaction with the oxidants, leading to the generation of active radicals not as fast as in a homogeneous system [30]; (ii) the slow regeneration of Fe(II) from Fe(III) greatly suppressed the transformation of Fe(II)/Fe(III) cycle, which is mainly responsible for PMS activation and active radicals production [31,32]. Therefore, the construction of heterogeneous iron-based catalyst with high efficiency for PMS activation remains a priority.

As a kind of synthetic polymer material, polyacrylonitrile (PAN) fiber is widely used in modern textile process due to its low cost and good resistance to oxidizing agents and sunlight. Recently, there have been a number of works devoted to the modification of PAN fiber for metal ions sorption, as its nitrile groups could be easily transformed into functional groups [33–35]. The unique chemical structure endows PAN fiber with great potential for supporting Fe ions, and thus, a series of efficient iron-based heterogeneous catalytic systems have been

constructed via PAN fibrous materials [36–43]. The PAN fiber modified with a mixture of hydrazine and hydroxylamine has been successfully employed as a Fe(III) support, and the obtained catalyst showed obvious efficiency for H_2O_2 activation to degrade organic pollutants in industrial effluent [36,37]. Our previous study has used amidoximated PAN fiber as Fe(III) support to prepare effective heterogeneous Fenton catalyst for degradation of organic dyes, since the amidoxime groups in fiber have great capability to anchor Fe ions through coordination bonds [38]. More importantly, this fibrous catalyst could utilize visible light to accelerate the conversion of Fe(III) to Fe(II) through ligand-to-metal charge transfer (LMCT) effect, and in turn led to a higher activity for H_2O_2 decomposition. To further enhance its catalytic performance, we have explored a series of iron-based PAN fibrous catalysts during the past few years [39–42]. We found that adding certain metals (Cu(II), Co(II), Ce(II), etc) into the iron-based PAN fibrous catalyst could successfully improve its catalytic activity [39,40], probably due to the synergetic effect caused by the assisted metals in the bimetallic catalysts. Furthermore, using iron complex with organic ligands (pyridine, phthalocyanine) to replace Fe ions could construct bioinspired catalyst, which also significantly enhanced the catalytic performance of PAN fibrous catalyst [41,42]. As a solid catalyst, the PAN fibrous material was a feasible candidate for practical application in water treatment because of its specific advantages [36,44,45], such as low cost, mild preparation conditions, suitable chemical stability, easy catalyst recovery and capability of utilizing solar light, as well as excellent flexibility to meet the demands of different reactor geometries. However, these studies have been focused on the H_2O_2 activation based on Fenton or Fenton-like reaction [36–43]. To the best of our knowledge, it has not been reported about PMS activation by using modified PAN fibrous catalysts, which have shown particular promise to constructed PMS-based heterogeneous catalytic systems with high efficiency for environmental remediation.

Within this background, the main objective of this work was to systematically investigate the catalytic performance of iron-based PAN fibrous catalysts for PMS activation. Herein, a series of catalysts with amidoximated PAN fiber as iron support were prepared and employed in PMS activation, and several organic pollutants were selected as probe contaminations to evaluate their catalytic activity. The effect of Cu(II) as the assisted metal was studied by preparing Cu(II)/Fe(III) supported bimetallic catalysts, since Cu ions has proven effective to enhance the catalytic activity of other iron catalysts for PMS activation. In addition, the role of organic ligands was investigated in particular by using iron(II) 2,2'-bipyridine (FePy) and iron(II) phthalocyanine (FePc) as the substitutes of Fe ions, respectively, since the electron-rich ligands exhibited obvious ability to accelerate the transformation of Fe(III)/Fe(II) cycle [46,47]. The reaction mechanism for PMS activation over different catalysts was proposed and compared based on the results of Electron spin resonance (ESR) and several desired experiments, and the possible pathway for dye degradation was analyzed using gas chromatography/mass spectrometry. This study may provide a useful enlightenment for the design of more efficiency and practical iron-mediated catalyst for PMS activation.

2. Experimental

2.1. Materials and reagents

The commercial PAN knitting bulky yarns that consisted of twisted PAN fibers (the content of acrylonitrile monomer: 86.96%) were obtained from Shanghai Shilin Spinning Co. Ltd. Hydroxylamine hydrochloride, ferric chloride, cupric sulfate, ferrous perchlorate, 2,2'-bipyridine, FePc, PMS ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$), H_2O_2 (30% w/w), methanol (MA), tert-butylalcohol (TBA), Rhodamine B (RhB), 4-chlorophenol (4-CP), 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) and dimethyl sulfoxide (DMSO) were of laboratory grade. C.I. Reactive Red 195 (RR195), C.I. Basic Red 29 (BR29) and C.I. Acid Black 234 (AB234)

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