



Catalytic oxidation of aqueous organic contaminants by persulfate activated with sulfur-doped hierarchically porous carbon derived from thiophene



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ABSTRACT

Sulfate radicals ($\text{SO}_4^{\cdot-}$) generated from persulfate (PS) activated by carbocatalysis is expected to provide an environmentally friendly and highly efficient catalytic oxidation process for aqueous organics degradation. Herein, a novel sulfur-doped hierarchically porous carbon with both structural and compositional modification was proposed for PS activation by using thiophene as sulfur/carbon precursor and KOH as activator. The effect of annealing temperature on its textural properties and surface chemistry was characterized by Elemental analysis, N_2 sorption isotherms, X-ray photoelectron spectroscopy, Fourier transform infrared spectra, Raman spectra and X-ray diffraction. The as-prepared sample treated at 800 °C (SDAC-800) demonstrated outstanding catalytic activity for activation of PS to degrade 4-chlorophenol (4CP). Studies on the role of sulfur in the catalytic activity enhancement were carried out by comparing with a sulfur-free activated carbon and a carbon model (reduced graphene oxide (rGO)). The effects of catalyst dosage, initial 4CP concentration, and reaction temperature on 4CP degradation were comprehensively investigated. In addition, contrast tests with other conventional PS activation methods, SDAC-800 reusability and its general applicability tests were also carried out. The mechanism of PS activation and 4CP oxidation was elucidated by using quenching tests with chloridion, L-histidine and ethanol as radical scavengers. It revealed that the conventional radical pathway was not a critical role in 4CP degradation. In contrast, the process was controlled by both particle-surface interaction and non-radical pathway, and the latter played a dominant role.

1. Introduction

With the rapid development of industry, industrial wastewater inevitably contains a large number of hazardous substances, such as particles, toxic refractory organics, and heavy metals [1], which has been far beyond the natural degradation ability by the ecosystem [2]. Owing to the challenges from environmental pollution, green technologies for environmental remediation have been extensively investigated [3]. In terms of organic contaminants in wastewater, advanced oxidation processes (AOPs) based on highly reactive radicals were widely acknowledged to be one of the most excellent and powerful technologies since they can provide an almost total degradation [4].

Recently, AOPs based on sulfate radical ($\text{SO}_4^{\cdot-}$) generated from persulfate (PS) or peroxymonosulfate (PMS) have attracted much attention for aqueous organics oxidation. $\text{SO}_4^{\cdot-}$ possesses a high oxidative potential ($E_0 = +2.5$ to $+3.1$ V vs. NHE), a longer lifetime ($t_{1/2} = 30\text{--}40$ μs of $\text{SO}_4^{\cdot-}$ versus $t_{1/2} = < 1$ μs of HO^{\cdot} [5]), and a wide operative pH range as well as avoiding the flocculation [6–8], which

can be a promising alternative to the classic hydroxyl radical (HO^{\cdot})-based Fenton reaction. Therefore, more studies were focused on the development of PS/PMS activation technologies for $\text{SO}_4^{\cdot-}$ generation. The conventional approaches such as thermal treatment and UV irradiation [9–11] have been found to be efficient for PS/PMS activation but they were at the expense of high energy inputs. Transition metals (Fe(II) , Co(II) , Ag(I) , Fe^0) catalysis [12–15] was demonstrated the most simple and efficient method, attributing to the variable valency of transition metals. The empty orbitals of the outer shell could easily bond with PS/PMS molecules and then facilitate the electron transfer process involving reduced/oxidized metal ions [16,17]. In addition, it was reported that the peroxides could also be activated by metal oxides or metal oxides-based heterogeneous catalysts such as Fe_3O_4 , $\alpha\text{-MnO}_2$, Co_3O_4 , and LaCoO_3 [18–23]. Nevertheless, the possible secondary pollution and toxic metal leaching would impede their practical applications.

Based on these considerations, more research groups have focused their attention on the preparation of carbonaceous materials for $\text{SO}_4^{\cdot-}$

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generation due to their non-toxicity, excellent regulation performance, porous structure, and good thermal stability [8,24,25]. Studies on carbocatalysis demonstrated that carbon materials, such as activated carbon (AC), reduced graphene oxide (rGO), carbon nanotubes (CNTs), and nanodiamond (ND) can be also employed as activator for PS/PMS oxidation of organic contaminants [17,26–28]. While the catalytic oxidation process on carbocatalysis was much different from the metal-based catalysis. It was widely accepted that the generated reactive radicals contributed to the rapid degradation of organics. But in some carbocatalysis systems, it was proposed that the processes were dominated by the surface-bound radicals or the non-radical mechanism [16,17,29].

It was expected that structural modification and chemical compositional modification would bring about intrinsic changes to the catalytic activity of carbon materials. Therefore, the addition of activating reagent and the doping of heteroatom were widely investigated [6,30–35]. Sun et al. [1,6,32] demonstrated that GO, rGO and CNTs with nitrogen doping showed enhanced performance in PMS activation for organics oxidation. Also, sulfur could act as a promising co-dopant to further improve the performance of nitrogen doped graphene toward PMS activation [36]. Although these modified carbon materials show high performance to activate PMS or PS, the preparation of the samples is relatively complex, expensive and even involves harsh treatment. Therefore, simple, cheap and available synthesis would be more favorable. In addition, post-treatment of carbonaceous materials with heteroatom precursors fails to incorporate heteroatom into sp² carbon networks [32]. Thus the surface functionalization may lead to the decrease of surface area, and the loss of heteroatom-based functional groups due to the weak anchoring between heteroatom groups and the basal surface of carbon [37]. In this regard, in-situ process could make sulfur groups homogeneously distributed throughout the matrix and permanently fused into the backbone of the carbon framework [37]. In the previous study, we first discovered that unitary sulfur doped porous carbon with 2-thiophenemethanol as S/C precursor and KOH as activator exhibited outstanding catalytic activity for PS oxidation of 4-chlorophenol (4CP) [38]. As 2-thiophenemethanol is very expensive (¥980/100 g), search for low-cost S/C precursors would be much economic and favorable for wastewater remediation. In addition, the mechanism of PS activation on this emerging carbocatalysis is still not fully understood.

Herein, we proposed an efficient and low-cost route towards sulfur-doped hierarchically porous carbon (SDAC). The carbons were constructed by using thiophene as precursor and KOH as activator under different annealing temperatures. The resultant samples were employed as catalysts for activation of PS to degrade aqueous organic contaminants. The effects of annealing temperature on their textural properties and surface chemistry were characterized in detail. The role of sulfur in catalytic activity enhancement was illustrated by comparing with a sulfur-free activated carbon and a carbon model (reduced graphene oxide (rGO)). Classic quenching tests were employed to uncover the mechanism of PS activation on SDAC. It is expected that the SDAC/PS system would be an environmentally friendly and efficient technology for wastewater remediation.

2. Experimental

2.1. Reagents

Thiophene (C₄H₄S, 97%), ferric trichloride (FeCl₃), and potassium persulfate (K₂S₂O₈) were purchased from Aladdin. Acetonitrile (C₂H₃N) was purchased from walk world chemical reagent co., Ltd. (Shanghai, China). 4-chlorophenol (C₆H₅ClO, ≥99.0%), 2,4-dichlorophenol (C₆H₄Cl₂O), 4-acetamidophenol (C₈H₉NO₂), sodium methylparaben (C₈H₇NaO₃) and salicylic acid (C₇H₆O₃) were obtained from Sigma-Aldrich. Other reagents used in this study were provided by Taiyuan Chemicals Co. (Taiyuan, China). All chemicals were of analytical grade

or higher and used as received without further purification. Milli-Q water was employed throughout the experiments.

2.2. Preparation of sulfur-doped hierarchically porous carbon (SDACs)

In-situ S-doped activated carbons (SDACs) were synthesized by chemical activation of polythiophene (PTh) with KOH as activator under different annealing temperatures (Scheme S1). Firstly, polythiophene (PTh) was prepared using thiophene as starting material and FeCl₃ as initiator. Typically, 32 g of FeCl₃ was dissolved into 100 mL of CH₃CN, then 200 mL of CH₃CN dissolving 3.4 g of thiophene was slowly added with magnetically stirring. After stirring for 24 h at room temperature, the polymers were collected and washed with acetone and acetonitrile several times to remove the residue, then dried at 65 °C in vacuum for 24 h to obtain PTh.

Thereafter, SDACs were prepared by chemical activation of PTh with KOH as activator. In a typical synthesis, PTh and KOH with a weight ratio of 1:2 was dispersed into 50 mL of water, dried in an oven at 105 °C for 12 h, and finally subjected to annealing in a tubular furnace under nitrogen atmosphere (3 °C min⁻¹) at 600, 700, 800 °C for 1 h to obtain SDAC-600, -700, and -800, respectively. In the annealing process, the textural properties, sulfur doping levels and the loading of functional groups can be tuned by controlling the annealing temperature. After cooling to room temperature in nitrogen atmosphere, the activated samples were washed with 10 wt.% HCl solution twice and ultrapure water several times to remove any impurities, following by drying in an oven at 110 °C overnight. Finally, all the yielded sulfur-doped hierarchically porous carbons were stored in a desiccator prior to use. For a comparison, a sulfur-free porous carbon was prepared similarly but with annealing of polyphenylether (PPO) at 800 °C instead of PTh. The resultant sample was denoted as AC-800.

2.3. Cost analysis of the SDAC-800 sample

According to the price and the consumption of raw material in the catalyst preparation processes (Table S1), cost analysis of the SDAC-800 sample was conducted and compared with our previous prepared sulfur doped porous carbon (ACS) with 2-thiophenemethanol as S/C precursor [38]. Results show that compared with ACS, the cost of the SDAC-800 sample was greatly reduced (Supporting information).

2.4. Characterization of materials

Elemental analysis (EA) was performed by using a Vario EL CUBE elemental analyzer with the oxygen content calculated by mass difference. Thermogravimetric analysis (TGA) was conducted in a Netzsch thermal analyzer in an air atmosphere with a heating rate of 5 °C min⁻¹ from 25 °C to 800 °C. The textural properties of the materials were determined by nitrogen sorption isotherms at 77 K using a TriStar II 3020. All samples were degassed at 80 °C for 8 h under vacuum before measurement. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation. The total pore volume was calculated from the volume adsorbed at a relative pressure of 0.99. The Dubinin-Astakhov equation adapted for micro-pore carbon was applied to detect the micropore surface area and micropore volume of the as-prepared samples, and Original Density Functional Theory (ODFT) were applied to determine the pore size distribution (PSD). Scanning electron microscope (SEM, JSM-7001F, JEOL, Japan) was used to observe the morphologies of the samples. X-ray photoelectron spectroscopy (XPS) was performed on a specs spectrometer (AXIS ULTRA DLD) using Al Kα X-ray source (1486.6 eV). Fourier transform infrared spectra (FTIR) were recorded on a Bruker Tensor 27 FTIR spectrometer fitted with a transmission attachment. Raman spectra were acquired on a Horiba (LabRAM HR800) dispersive Raman spectrometer using argon ion laser source with λ at 514 nm. X-ray diffraction (XRD) patterns were obtained on a Bruker D8-Advanced diffractometer system using Cu-Kα

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