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Metal-free activation of persulfate by cubic mesoporous carbons for catalytic oxidation via radical and nonradical processes

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ABSTRACT

Carbon materials have been demonstrated as effective and metal-free carbocatalysts for substituting the toxic and/or expensive transition and noble metals/oxides for various green chemical processes. In this study, three-dimensional cubic mesoporous carbon (CMK) materials were employed for adsorptive and oxidative removal (via heterogeneous persulfate activation) of toxic phenolic compounds. CMK-3 and CMK-8 are constructed with porous structures and larger specific areas of 1129 and 1072 m^2/g, respectively. They achieved 39.2% and 31.3% of phenol adsorption in aqueous solutions. CMK-3 and CMK-8 also demonstrated as superb persulfate (PS) activators, providing 100% phenol oxidation in 20 and 45 min accordingly with high rate constants of 0.209 and 0.104 min^{-1}, respectively. The metal-free systems are more efficient than Fe^{2+} or Ag^{+} based homogeneous systems. Moreover, CMK-3/PS can be comparable to the classical zero-valent iron (ZVI)/PS system without inducing any metal ions to the waterbody. The mechanistic study indicated that persulfate activation on CMKs was different from the Fe^{2+}/PS, Ag^{+}/PS, and ZVI/PS systems. A nonradical pathway was unveiled in the metal-free persulfate activation for catalytic oxidation in which persulfate was activated on the carbon lattice and oxidized the adsorbed phenol molecules via a rapid electron transfer. The edging sites and kenotic groups of carbon materials would mediate persulfate to produce sulfate radicals. Both the radical pathway and nonradical process contributed to the complete phenol removal, and the great adsorption capability of CMKs further promoted the adsorption of the organic and oxidant for enhanced catalytic processes. The study dedicates to a metal-free oxidative system with cheap carbon materials for wastewater treatment and environmental remediation.

1. Introduction

Potassium persulfate (PS, also known as peroxydisulfate or PDS) has been widely utilized to provide oxidative sulfate radicals ($SO_4\cdot^-$, E^0 ($SO_4\cdot^-/SO_4^{2-}$) = + 2.5–3.1 V_{NHE}) for in situ chemical oxidation (ISCO) in remediation of contaminated soil and water. Persulfate possesses a high solubility in water, a great stability in subsurface applications at a low cost, and a wider operative pH range, making it a more environmentally-benign product than permanganate (MnO_4^-) and ozone (O_3)[1–3]. Physical approaches such as UV irradiation [4,5], heat [6,7], and ultrasonic/microwaves [8,9] can promote the cleavage of persulfate to generate $SO_4\cdot^-$. However, the physical processes usually involve continuously intensive energy inputs and exhibit a moderate efficiency for oxidation. Chemical activators such as a base, phenol, and quinone were reported to be able to activate PS to produce superoxide ($O_2\cdot^-$), hydroxyl ($\cdot OH$), and sulfate radicals ($SO_4\cdot^-$) for degradation of organic compounds [10–12]. The processes require a high dosage of the chemicals (base) and harsh reaction conditions or will induce toxic substances into the water matrix.

Anipsitakis et al. compared several transition metals interacting with common oxidants (persulfate, peroxymonosulfate (PMS), and hydrogen peroxide) and demonstrated that silver (Ag^+) is most effective for homogeneous persulfate activation [13]. Besides, studies also applied minerals (such as amorphous ferrihydrite, pyrolusite, cobaltite, and siderite), magnetite nanoparticles (Fe_3O_4) to promote the persulfate decomposition to generate reactive oxygen species for organic degradation [14–17]. Zero-valent iron (ZVI, Fe^0) was most widely studied in persulfate-based advanced oxidation processes (AOPs). ZVI, a reductive agent, can directly transfer electrons to persulfate to generate $SO_4\cdot^-$, meanwhile releasing Fe^{2+} to aqueous solution [18–20]. Fe^{2+} would then donate an electron to persulfate or sulfate radical to form Fe^{3+}. Nevertheless, the metal-based catalysts are highly effective, the metal catalysts would inevitably induce toxic metal-leaching to the water, which is undesirable for the sustainable

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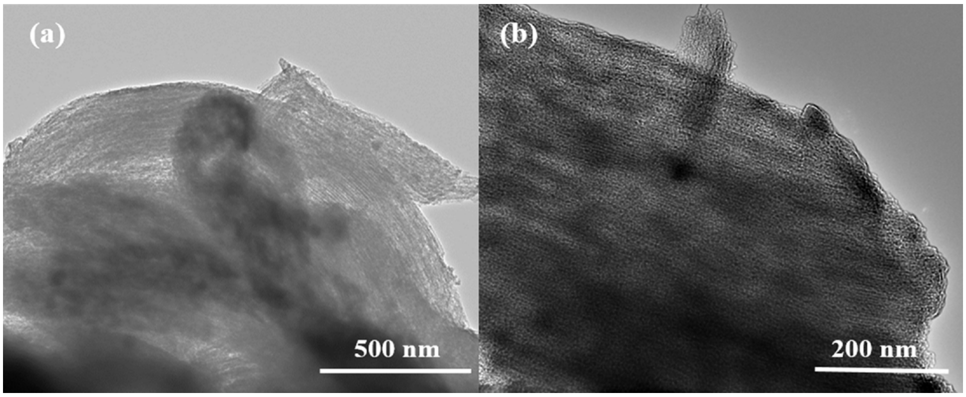

Fig. 1. TEM images of (a) CMK-3, and (b) CMK-8.

development of the environment, economy, and human society. Developing efficient and non-toxic catalysts as persulfate activators are imperative in green remediation of emerging contaminants with metal-free AOPs.

In the preliminary studies, we employed some nanocarbons as promising candidates for persulfate activation and catalytic oxidation. The reduced graphene oxide (rGO), multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), and annealed nanodiamonds can effectively promote persulfate to generate reactive species for the rapid degradation of organic pollutants into harmless carbon dioxide, water, and mineralized by-products [21–23]. However, as the nanocarbon materials are expensive for large-scale production at the present stage, the commercial access of nanocarbons for industrial applications is still problematic. Cheap and available carbon materials with outstanding adsorptive capability and catalytic activity would be much favorable for environmental remediation technologies. Therefore, activated carbons, biochars, and other porous carbon materials, derived from the green and available carbon-rich precursors with ultrahigh specific surface areas and manipulated porous construction and surface chemistry, stand out as excellent candidates for environmental applications in adsorption and catalysis in terms of economic efficiency, compared with nanocarbons and popular transition metals/oxides. In this study, we utilized three-dimensional cubic mesoporous carbons as carbocatalysts for adsorptive and oxidative removal of phenolic compounds in aqueous solutions. The mesoporous carbons presented better performances than the homogeneous Ag^+/PS and Fe^{2+}/PS for phenol removal. A CMK-3/PS presented a comparable performance to the most popular ZVI/PS system. Besides, we discovered that carbocatalysis exhibited a greater tolerance to the radical scavengers, suggesting that a nonradical pathway may accompany the radical generations during PS activation. This study utilizes cheap and efficient mesoporous carbon materials for environmental remediation and the mechanistic findings also facilitate new insights into carbocatalysis for persulfate activation.

2. Experimental

2.1. Chemicals and materials

Three-dimensional, cubic mesoporous carbons of CMK-3 (No. XFP03) and CMK-8 (No. XFP02) were purchased from Nanjing XFNano Material Tech Co. Ltd, China. The CMK-3 and CMK-8 were synthesized using cubic mesoporous SBA-15 and KIT-6 silicas as the hard templates, respectively. The other chemicals in this study, such as phenol, methanol (MeOH), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), iron powder (fine), potassium peroxymonosulfate (OXONE®, PMS, $KHSO_5{\cdot}0.5KHSO_4{\cdot}0.5K_2SO_4$), potassium persulfate (PS, $K_2S_2O_8$), and hydrogen peroxide (H_2O_2, 30 wt.% in H_2O), were all obtained from Sigma-Aldrich, Australia.

2.2. Characterization of nanocarbons

Transmission electron microscopy (TEM) was utilized to analyze the morphology and crystal structure of carbon materials on a JEOL equipment. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD system under an ultrahigh vacuum atmosphere (1×10^{-9} mBar). All elements were calibrated by setting the dominant C1s peak at 284.5 eV. The peaks were fitted with the Shirley background and quantified by the CasaXPS software. The BET surface areas and porous information of the carbocatalysts were acquired from a Micrometrics-Tristar instrument at the temperature of liquid nitrogen (−196 °C). The thermal gravimetric-differential scanning calorimetry (TG-DSC) was obtained on a Mettler-Toledo-Star system under the air atmosphere with a flowing rate of 10 mL/min, and a heating rate of 10 °C/min from 35 to 900 °C.

2.3. Catalytic oxidation of phenolic contaminants

The oxidation reaction was carried out in a conical flask with a mixture of catalyst, phenol solution, and oxidant (PMS, PS, or H_2O_2). The temperature was controlled by a water bath and the solution was kept homogeneous by constant stirring. After a certain interval, the aqueous mixture was withdrawn and filtered to remove the solid catalyst. Then 1 mL of the filtrate solution was injected into a HPLC (high-performance liquid chromatography) vial and mixed with 0.5 mL ethanol to consume the remaining radicals and terminate the oxidation. The sample was then analyzed on a Thermal UltiMate™ 3000 RSLCnano System through a C18 column using an UV detector ($\lambda = 270$ nm). The mobile phase consists of 30% acetonitrile and 70% deionized water with a flow rate of 1 mL/min.

3. Results and discussion

3.1. Characterization of the carbon materials

The crystal structure and morphology of the carbon materials were revealed by TEM as shown in Fig. 1. The well-ordered layers and tunnels can be discovered for the cubic mesoporous carbons (CMK-3 (Fig. 1a) and CMK-8 (Fig. 1b)). The porous structures were derived from chemical removal of templates. Fig. 2a indicates that CMK-3 possesses an ultrahigh specific surface area of 1129 m^2/g estimated by the Brunauer–Emmett–Teller (BET) equation. CMK-3 contains a pore volume of 1.38 cm^3/g and an average pore size of 3.2 nm (Table 1), measured by the Barrett–Joyner–Halenda (BJH) equation. Fig. 2b indicates that CMK-3 is constructed by both micropores (0–2 nm) and mesopores (2–20 nm). The mesoporous CMK-8 possesses a surface area of 1072 m^2/g with a larger pore volume of 1.64 cm^3/g and an average pore size of 5.2 nm.

X-ray photoelectron spectroscopy was utilized to probe the surface