



Promoting effect of ammonia modification on activated carbon catalyzed peroxymonosulfate oxidation



Shiyang Yang^{a,b,c,*}, Lei Li^{a,c}, Tuo Xiao^{c,d}, Yitao Zhang^{a,c}, Di Zheng^{a,c}

^a Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China

^b Shandong Provincial Key Laboratory of Marine Environment and Geological Engineering (MEGE), Qingdao 266100, China

^c College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

^d China City Environment Protection Engineering Limited Company, Wuhan 430071, China

ARTICLE INFO

Article history:

Received 24 November 2015

Received in revised form 7 January 2016

Accepted 14 January 2016

Available online 16 January 2016

Keywords:

Ammonia modification

Activated carbon

Catalyzed peroxymonosulfate oxidation

XPS spectra deconvolution

Nitrogen-containing functional groups

ABSTRACT

Ammonia modified cotton-based activated carbon (AC-NH₃) was prepared and utilized to investigate the effect of ammonia modification on the chemical properties of activated carbon in catalyzed peroxymonosulfate (PMS) oxidation of aqueous organic pollutant. Activated carbons with and without modification were characterized by N₂ adsorption/desorption, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Boehm titration, Fourier Transform Infrared Reflection (FTIR) and X-ray photoelectron spectroscopy (XPS), respectively. Results indicated that ammonia modification has a promoting effect on the catalytic ability of AC in our system. And as small amount as 0.04 g/L AC-NH₃ can efficiently activate PMS and subsequently degrade a model contaminant, Reactive Black 5 (RB5). Considering RB5 was barely removed by sole-AC-NH₃ or sole-PMS, adsorption and catalytic oxidation have a significant synergistic effect in the combined AC-NH₃/PMS system. With the XPS spectra deconvolution, we inferred that the π-π and pyrrolic functional groups resulted in the promoting catalytic ability of AC-NH₃. However, the pyridine seems to play a nonsignificant role in our process. In addition, the parameters in the AC-NH₃/PMS system, including the mole ratio of PMS to RB5, the dosage of AC-NH₃, the initial concentration of RB5, initial pH, and the feeding method of PMS, were also discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs), which are effective to eliminate the nonbiodegradable organic pollutants in water or wastewater, have been paid more and more attention in the last decades [1–4]. Due to the free radicals generated in AOPs, a majority of contaminants could be degraded fast and efficiently, and even be mineralized to CO₂ and H₂O. Compared with conventional AOPs, based on the hydroxyl radical (OH[•]) with a redox potential of +1.8 to +2.7 V vs. NHE, in recent years, the sulfate radical (SO₄^{•-})-based AOPs have attracted many scholars' attention because SO₄^{•-} has the same or even higher redox potential of +2.5 to +3.1 V vs. NHE than OH[•] [5–9]. Peroxymonosulfate (PMS) is the most commonly used oxidant to produce SO₄^{•-} with the activation of UV [10] and transition metals [11–13].

Lately, activated carbon (AC), which has been utilized as an excellent adsorbent or catalyst supporter for a long time in gas

and water treatment, was applied as a kind of catalyst in AOPs [14,15]. In our previous work, we have found that AC can directly catalyze PMS to generate SO₄^{•-} to oxidize organic contaminants in aqueous solution on account of the functional groups on the AC [16–18].

In carbon structure, the main functionalities, such as carboxyl, carbonyl, phenols, lactones and quinones, make a contribution to the uptake of pollutants and can significantly influence the adsorption and catalytic properties [19,20]. Therefore, many researchers devote to seeking various modification methods to enhance the potential of AC, including oxidation treatment [21], sulfuration treatment [22], nitrogenation treatment [23] and coordinated ligand functionalization treatment [24]. Among these, nitrogenation modification of AC was applied extensively because nitrogen treatment can increase the polarity of AC surface so that the AC surface is in favor of the interaction with polar adsorbates. In addition, nitrogenation treatment of AC can also affect its porous structure, which depended on the starting AC, the chemical agent and the experimental method. Both the increase and decrease in S_{BET} were reported [25,26]. Moreover, nitrogenation can increase the basicity of AC, which is required in adsorption and catalysis pro-

* Corresponding author at: College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China.

E-mail address: ysy@ouc.edu.cn (S. Yang).

cesses [23,27]. In many pioneering researches, it was accepted that surface basic groups are beneficial to the adsorption and catalytic property of AC. Basic surface is obtained mainly by the removal of surface acidic complexes or by the increase of basic oxygen- and nitrogen-containing groups. Among the various modification methods, it has been confirmed that ammonia treatment can reduce oxygen-containing groups and introduce nitrogen-containing functional groups which contribute to the distinct enhancement in adsorption of pollutants including CO₂ [28], SO₂ [29], phenol [30] and dissolved natural organic matter (DOM) [31]. In addition, investigations demonstrated that ammonia treatment of AC can increase catalytic performance for oxygen reduction in neutral media and enhance the biodegradability of coking wastewater in the catalytic wet oxidation [32]. Although the catalytic ability of AC for the activation of peroxymonosulfate (PMS) oxidation has been testified [16–18], the influence of different surface functional groups of AC in the catalyzed PMS oxidation system, especially the effect of nitrogenation modification of AC, has not been identified yet.

Herein, ammonia-treated cotton based AC was utilized as a heterogeneous catalyst to activate PMS for the decolorization of a model azo dye Reactive Black 5 (RB5). The textural morphology, chemistry property and activities of AC before and after modification were compared through N₂ adsorption/desorption, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Boehm titration and Fourier transform Infrared Reflection (FTIR). Besides, the relationship between surface functional groups and catalytic ability of AC were distinguished through X-ray photoelectron spectroscopy (XPS). And the effects of parameters on the performance of AC-NH₃/PMS system were discussed.

2. Experimental

2.1. Preparation and modification of catalysts

In this study, cotton, utilized as the precursor of AC, was purchased from Weixian Garment Factory. A set amount of cotton (5 g) was immersed into 100 mL H₃PO₄ solution and stirred for 5 min. After 1 h, cotton was taken out and washed for several times. Then steeped the cotton into 7.5% (NH₄)₂HPO₄ for 3 h and dried for 24 h at 80 °C. The carbonization and activation of samples were carried out according to a previously reported method [33]. The obtained samples were labeled AC-0.

Ammonia modification of AC-0 was carried out in a tube furnace (SLG1200-60) by the previous method [30]. AC-0 was placed in two ceramic boats and then put into quartz tube of the furnace. At the initial step, N₂ gas (500 mL/min) was flowing through the tube at the increasing temperature of 5 °C/min. After the temperature reached the scheduled value (900 °C), the atmosphere was switched to NH₃ (50 mL/min). Then samples were maintained with the flow of NH₃ gas for 40 min. Finally the furnace was cooled to room temperature under N₂ gas. Samples obtained by the procedures above were described as AC-NH₃ and put into a desiccator for subsequent use.

2.2. Characterization of catalysts

2.2.1. Texture

The textural properties of samples were calculated by nitrogen adsorption/desorption test with a physical instrument (Autosorb-iQ3). T-plot and Brunauer–Emmett–Teller (BET) equation were applied to estimate the micropore volumes and the specific surface area (S_{BET}), respectively. Scanning electron microscopy-energy dispersive spectrometer (SEM-EDS) was performed by Hitachi S-4800.

2.2.2. Surface chemistry characterization

Boehm titration [34] was used to quantitatively and qualitatively determine the surface functional groups on the AC. Accurate amount of AC (0.200 g) was placed in a series of 100 mL flasks containing 50 mL of 0.05 mol/L: NaOH, Na₂CO₃, NaHCO₃, NaOC₂H₅, and HCl solutions. After stirred at room temperature for 24 h, samples were filtrated and washed. The filtrates were diluted to 100 mL and then titrated with a 0.05 mol/L HCl or NaOH solution. The number of acidic groups was calculated based on the following assumptions: NaHCO₃ merely neutralizes carboxyls; Na₂CO₃ can neutralize carboxyls and lactones; NaOH can neutralize carboxyls, lactones and phenolic groups; And NaOC₂H₅ can neutralize carboxyls, lactones, phenols and carbonyls/quinones. The number of basic sites was determined from the amount of HCl that reacts with AC.

Fourier Transform Infrared Reflection (FTIR) [35] was utilized to complement the results of Boehm titration. FTIR spectra were obtained by a spectrometer (BRUKER TENSOR 27). KBr was added into a small amount of dried AC samples with the mass ratio of 200/1. The mixture was pressed to a wafer for analysis.

XPS analysis was performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K α radiation ($h\nu = 1253.6$ eV) or Al K α radiation ($h\nu = 1486.6$ eV). Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). The data analysis was carried out by using XPS Peak4.1 provided by Raymond W.M. Kwok (The Chinese University of Hongkong, China).

2.3. Adsorption and catalytic oxidation of RB5

The adsorption and catalytic oxidation of RB5 was utilized to probe the effect of ammonia modification on the adsorption and catalytic ability of AC. A 500 mL flask containing 250 mL of 0.25 mmol/L RB5 was immersed in a water bath and stirred constantly at 25 ± 1 °C. The initial pH was adjusted to 5 with 1 mol/L NaOH or 1 H₂SO₄. Without specific instrument, the dosage of AC was 0.04 g/L, and the mole ratio of PMS to RB5 was 25/1. At a fixed interval, samples were withdrawn and filtered by 0.45 μm Millipore film before analyzed. The decolorization of RB5 was monitored by measuring the absorbance of samples at 598 nm (UNICO 2100 spectrophotometer, UNICO (Shanghai) Instruments Co., Ltd., China).

In the special experiments involving the experiments of the feeding method, the total dosage of PMS and ACF-NH were as the above. PMS was added according to adding times at the appointed time: (1) All the PMS added at 0 min; (2) All the PMS added at 60 min; (3) One half of PMS added at 0 min and the other added at 90 min; (4) One fifth of PMS added at 0 min, 30 min, 60 min, 90 min and 120 min.

3. Results and discussion

3.1. Characterization of AC

3.1.1. Texture

The N₂ adsorption/desorption isotherms of AC samples before and after ammonia modification were shown in Fig. 1. Accordingly, Table 1 displayed the parameters including the total and external surface area, the micropore and mesopore volumes. The prepared AC sample has huge specific surface area. After ammonia modification, the S_{BET} of AC decreased from 1529.3 m²/g to 1102.5 m²/g, which consisted with Przepiński [30] and Xie et al. [36]. They modified AC with dry NH₃ at 473–1073 K and demonstrated an obvious decrease in S_{BET} . The reason may be that NH₃ would react with the carbon surface to form functional groups which may block the narrowed pore entrance. In addition, the high temperature

Download English Version:

<https://daneshyari.com/en/article/640024>

Download Persian Version:

<https://daneshyari.com/article/640024>

[Daneshyari.com](https://daneshyari.com)