Enhanced activation of periodate by iodine-doped granular activated carbon for organic contaminant degradation

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HIGHLIGHTS

- I-GAC was fabricated and utilized in heterogeneous IO_4^- oxidation process.
- I-GAC exhibited excellent catalytic activity toward IO_4^- for AO7 degradation.
- Dominant radical and potential mechanism in I-GAC/IO_4^- system were investigated.
- Possible degradation pathway of AO7 in the I-GAC/IO_4^- system was proposed.

GRAPHICAL ABSTRACT
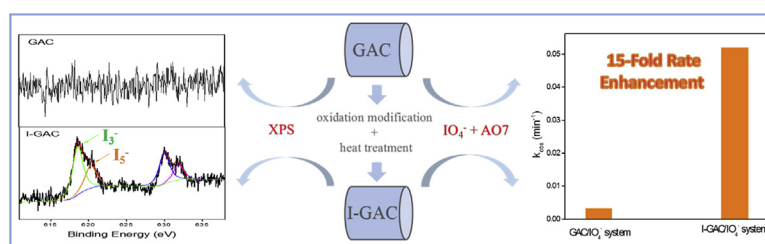
ABSTRACT

In this study, iodine-doped granular activated carbon (I-GAC) was prepared and subsequently applied to activate periodate (IO_4^-) to degrade organic contaminants at ambient temperature. The physicochemical properties of GAC and I-GAC were examined using scanning electron microscopy, N_2 adsorption/desorption, Raman spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. No significant difference was observed between the two except for the existence of triiodide (I_3^-) and pentaiodide (I_5^-) on I-GAC. The catalytic activity of I-GAC towards IO_4^- was evaluated by the degradation of acid orange 7 (AO7), and superior catalytic performance was achieved compared with GAC. The effects of some influential parameters (preparation conditions, initial solution pH, and coexisting anions) on the catalytic ability were also investigated. Based on radical scavenging experiments, it appeared that $IO_3^\bullet$ was the predominant reactive species in the I-GAC/IO_4^- system. The mechanism underlying the enhanced catalytic performance of I-GAC could be explained by the introduction of negatively charged I_3^- and I_5^- into I-GAC, which induced positive charge density on the surface of I-GAC. This accelerated the interaction between I-GAC and IO_4^-, and subsequently mediated the increasing generation of iodyl radicals ($IO_3^\bullet$). Furthermore, a possible degradation pathway of AO7 was proposed according to the intermediate products identified by gas chromatography-mass spectrometry.

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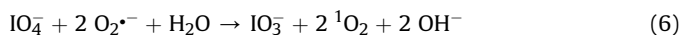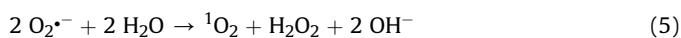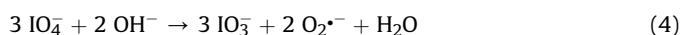
1. Introduction

Periodate (IO_4^-, E^0 = 1.6 V (Lee and Yoon, 2004)), a well-known oxidant, can be reductively converted into reactive radical intermediates through various catalyst-mediated activation pathways that have the demonstrated capability of effectively degrading organic contaminants. Chia et al. applied photo-activated periodate (UV/IO_4^-) to degrade 4-chlorophenol (4-CP), during which $O(^3P)$ and $IO_3^\bullet$ were generated through intramolecular electron-transfer reactions (Eq. (1)) (Chia et al., 2004). These were suspected of being the predominant reactive species. In addition to

UV, ultrasound (US) was also employed to activate IO_4^-, and efficient degradation of perfluoro-octanoic acid (PFOA) was achieved (Lee et al., 2016). The enhanced PFOA degradation in the US/IO_4^- system was likely associated with the generation of $IO_3^\bullet$ and thermal decomposition. Researchers also attempted the use of a bimetallic nFe^0/IO_4^- system for the degradation of several contaminants and found that the system was substrate-dependent due to the selective nature of $IO_3^\bullet$. The generation of $IO_3^\bullet$ was attributed to the one-electron reduction of periodate by nFe^0-Ni or nFe^0-Cu (Eqs. (2)–(3)) (Lee et al., 2014). Recently, alkali-mediated activation of IO_4^- (pH > 8) was investigated for the selective degradation of contaminants, and singlet oxygen ($^1O_2$) rather than $IO_3^\bullet$ was identified as the dominant radical in the OH^-/IO_4^- system. According to Eqs. (4)–(6), $^1O_2$ was initiated by spontaneous reaction between OH^- and IO_4^-, and the superoxide radical ($O_2^{\bullet-}$) played an irreplaceable bridging role in generating $^1O_2$ (Bokare and Choi, 2015).

$$IO_4^- + h\nu \rightarrow IO_3^\bullet + O(^3P) \tag{1}$$

$$nFe^0\text{-Ni (or } nFe^0\text{-Cu)} \rightarrow Fe^{2+} + 2\ e^- \tag{2}$$

$$IO_4^- + 2\ H^+ + e^- \rightarrow IO_3^\bullet + H_2O \tag{3}$$

$$3\ IO_4^- + 2\ OH^- \rightarrow 3\ IO_3^- + 2\ O_2^{\bullet-} + H_2O \tag{4}$$

$$2\ O_2^{\bullet-} + 2\ H_2O \rightarrow {}^1O_2 + H_2O_2 + 2\ OH^- \tag{5}$$

$$IO_4^- + 2\ O_2^{\bullet-} + H_2O \rightarrow IO_3^- + 2\ {}^1O_2 + 2\ OH^- \tag{6}$$
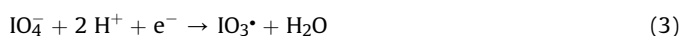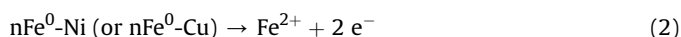
Granular activated carbon (GAC) is widely recognized as a promising catalyst with the advantages of a large surface area, well-developed internal micro porosity, and abundant surface functional groups (Rivera-Utrilla et al., 2011; Zhang et al., 2013). It has also been exploited to activate IO_4^- for contaminant degradation, but only mediocre catalytic performance of GAC for IO_4^- activation was achieved (Li et al., 2016). To improve its catalytic ability, substantial efforts have been dedicated to mediating the physicochemical properties of GAC. Based on previous studies, iodine doping is an effective way to modify carbon materials chemically, including activated carbon (Barpanda et al., 2007a; Lota et al., 2016), graphene (Yao et al., 2012), and carbon nanotubes (Fan and Xu, 2015); and to tailor their intrinsic characteristics. Generally, these iodated carbon materials underwent marked physical and electrochemical modification and hence exhibited excellent electrochemical performance. Researchers believed that the incorporation of iodine into carbon materials could potentially prompt charge transfer reactions with carbon, trigger the formation of negatively charged polyiodide species (i.e., I_3^- and I_5^-), and induce positive charge density on the surface of carbon materials. This would lead to the improvement of certain properties, especially their electrochemical characteristics (Barpanda et al., 2010; Zhan et al., 2015).

At present, intensive investigations concerning the superior electrochemical activity of I-doped carbon materials have been reported, whereas related research on their catalytic ability is rare. In addition, I-doped carbon materials were commonly modified by vapor iodine, while those modified with IO_4^- have been hardly done. Moreover, due to the moderate catalytic performance of GAC, iodine doping is highly desired to improve the catalytic ability of GAC toward IO_4^- for pollutant degradation.

Therefore, I-GAC, prepared via IO_4^- modification followed by heat treatment, was applied in this study to explore the feasibility of enhancing the activation of IO_4^- for degradation of acid orange 7 (AO7). Comprehensive characterization techniques were employed to establish a well-founded relationship between the physicochemical properties and catalytic activity of I-GAC. In addition, the dominant reactive species and possible mechanism involved in the $I\text{-}GAC/IO_4^-$ system were explored and discussed. A plausible degradation pathway of AO7 was also proposed based on the GC-MS analysis.

2. Materials and methods

2.1. Materials

Granular activated carbon (GAC), was supplied by Tangshan Chemical Corporation, and was used as a starting material. Prior to use, GAC was washed with distilled water, heated in boiling water for 2 h to remove fine particles and impurities, dried at 105 °C for 24 h, and stored in a desiccator.

Sodium periodate ($NaIO_4$) was purchased from the Xilong Huagong Co., Ltd. (Guangdong, China). AO7, sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium sulfite (Na_2SO_3), ascorbic acid (AA), and sodium azide (NaN_3) were purchased from Sinopharm (Shanghai, China). Phenol, 4-CP, ibuprofen (IBP), and sulfamethoxazole (SMX) were obtained from Sigma-Aldrich (St. Louis, USA). Acetonitrile, dichloromethane, methanol (MeOH), and p-benzoquinone (BQ) were supplied by J&K Scientific (Beijing, China). All chemicals were of at least analytical grade and were used as received without further purification. All solutions were prepared using ultrapure water with resistance of 18.2 MΩ cm from a Milli-Q Integral 5 system (EMD Millipore, Billerica, MA, USA).

2.2. Preparation of I-GAC

I-GAC was prepared via IO_4^- modification followed by thermal treatment. The typical steps for preparation of I-GAC were carried out as follows. GAC (0.2 g) was added to a glass conical flask containing 50 mL of 6 mM IO_4^- solution and mixed for 60 min under magnetic stirring at ambient temperature. Afterwards, the immersed GAC was separated from the solution, washed sufficiently with distilled water, placed in a 2 mL brown vial and its lid sealed with tin foil. Then it was heated at 105 °C for 24 h, and labeled as I-GAC.

2.3. Characterization of GAC samples

The physiochemical properties of GAC and I-GAC were characterized by various techniques. Their morphological characteristics were investigated via scanning electron microscopy (SEM). The SEM images were obtained using a Hitachi X650. A nitrogen adsorption/desorption test was performed with a physical instrument (Autosorb-iQ3). A Raman spectrometer (LabRAM Aramis, Horiba Jobin Yvon, France) was used with a scan range from 200 to 2000 cm^{-1}. Fourier transform infrared spectroscopy (FTIR) was conducted on a Nicolet 6700 (NEXUS 670, East Branch Instrument, USA) with the KBr disk method in the range of 400–4000 cm^{-1}. X-ray photoelectron spectrometry (XPS) was performed using a scanning X-ray microprobe (ESCSLAB 250Xi, Thermo Fisher, USA). The determination method of pH_{zpc} was elaborated in Text S1.

2.4. Catalytic degradation experiment

The catalytic activity of I-GAC was evaluated by the degradation of AO7 in magnetically stirred 250 mL conical flasks containing 200 mL of AO7 solution. In a typical experiment, coexisting anions or scavengers (if necessary) were first added to a 50 μM AO7 solution, and the catalytic reaction was then initiated by the quick sequential addition of IO_4^- and I-GAC. Unless otherwise mentioned, the pH of the initial solution was not adjusted and was 5.27 under