



Efficient enhancement of ozonation performance via ZVZ immobilized g-C₃N₄ towards superior oxidation of micropollutants

Xiangjuan Yuan^{a, b}, Wenlei Qin^a, Xiaoman Lei^a, Lei Sun^{a, c}, Qiang Li^a, Dongya Li^a, Haiming Xu^a, Dongsheng Xia^{a, b, *}

^a School of Environmental Engineering, Wuhan Textile University, Wuhan 430073, China

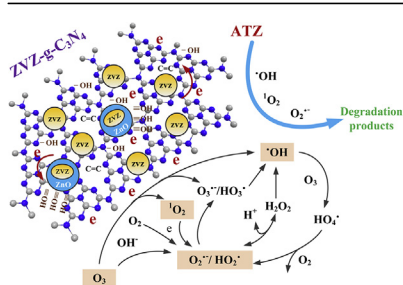
^b Engineering Research Center for Clean Production of Textile Dyeing and Printing, Ministry of Education, Wuhan 430073, China

^c Shishi Zhanyao Textile Technology Limited Co. LTD, Dabao Industrial Zone, Shishi 362712, China

HIGHLIGHTS

- First report about g-C₃N₄ as an excellent catalyst support for ZVZ immobilization.
- ZVZ-g-C₃N₄ was successfully prepared by a fast and facile synthetic approach.
- ZVZ-g-C₃N₄ exhibits superior catalytic performance towards ozonation.
- O₂⁻, •OH, and ¹O₂ are demonstrated as main reactive species.

GRAPHICAL ABSTRACT



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ABSTRACT

A functional organic-metal composite material zero-valent zinc immobilized graphitic carbon nitride (ZVZ-g-C₃N₄) was prepared by a fast and facile two-step synthetic approach with an optimal ZVZ content of 5.4 wt%. The structure, surface morphology and chemical composition of the as-synthesized ZVZ-g-C₃N₄ were characterized by BET surface area, XRD, FT-IR, SEM, TEM, and XPS, respectively. ZVZ-g-C₃N₄ composite exhibited superior catalytic ozonation activity with an improvement of 61.2% on atrazine (ATZ) degradation efficiency in 1.5 min reaction, more than 12 times of the pseudo-first-order rate constant, and almost 16-fold of the R_{ct} value obtained in O₃/ZVZ-g-C₃N₄ process compared to O₃ alone. Meanwhile, the ATZ degradation efficiency was gradually enhanced with increasing ZVZ-g-C₃N₄ dosage and initial solution pH in the range from 3.0 to 9.0, and a higher amount of ATZ was degraded when the initial concentration of ATZ rose from 1 to 10 mg L⁻¹. The enhanced catalytic ozonation activity of ZVZ-g-C₃N₄ is attributed to the synergistic effects among ZVZ, ZnO and g-C₃N₄, as well as the improved dispersibility, increased surface area, and intensive electron-transfer ascribed to the electronic and surface properties modification. The radical scavengers experiments demonstrated that O₂⁻, •OH, and ¹O₂ were the dominant reactive radical species in the multifunctional processes. Moreover, an empirical kinetic model was proposed to predict ATZ degradation. The results indicated that the ZVZ-g-C₃N₄ composite was a highly efficient, recoverable, and durable catalyst, which would provide a promising alternative in catalytic ozonation.

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* Corresponding author. School of Environmental Engineering, Wuhan Textile University, Wuhan 430073, China.

E-mail address: dongsheng_xia@wtu.edu.cn (D. Xia).

1. Introduction

The presence of micropollutants, such as pharmaceuticals, pesticides, personal care products, and endocrine disrupting chemicals, has attracted increasing concerns in recent years because of their potential undesirable effects on human health and aquatic ecosystems (Schwarzenbach et al., 2006). Ozonation is one of the most effective wastewater treatment technologies and has been widely adopted for micropollutants oxidation (Oller et al., 2011; Gomes et al., 2017a, 2017b). In particular, heterogeneous catalytic ozonation as an alternative technique of advanced oxidation processes (AOPs) for wastewater treatment has recently gained significant attention due to its better ozone (O_3) utilization, shorter operation time, higher mineralization rates, efficient contaminant removal, and easy separation of catalysts (Kasprzyk-Hordern et al., 2003). Up to now, metal or metal oxides on supports have been widely applied in heterogeneous catalytic ozonation for pollutants decontamination, which could improve the treatability and degradation of recalcitrant organic compounds through radical reactions (Nawrocki and Kasprzyk-Hordern, 2010).

Zinc is a moderate reactive metal and strong reducing agent. Zinc and zinc oxide are well-known heterogeneous catalyst materials used in a large number of industrial processes, owing to their advantages of high catalytic activity, nontoxicity, and low costs (Lee et al., 2016). It has been found that zero-valent zinc (ZVZ) is an efficient reduction reagent for dechlorination of chlorinated organic pollutants (Wang et al., 2008; Choi and Kim, 2009), also it can reduce pollutants directly or indirectly by the formation of superoxide radical (O_2^-) in the presence of oxygen (Noradoun and Cheng, 2005). Previous studies pointed out that the combination of O_3 and ZVZ showed an obvious synergetic effect on the degradation of di-*n*-butyl phthalate, *p*-chloronitrobenzene and aniline (Wen et al., 2014; Zhang et al., 2015a, 2015b), and ZVZ played a key role. Nevertheless, the corrosive dissolution of ZVZ and the release of extensive zinc ion (Zn^{2+}) have severely limited the direct application of ZVZ into water treatment. Therefore, in order to improve the catalyst stability and explore the potential applicability, it is essential to investigate the innovative immobilization technology and seek for appropriate catalyst supports to pave the way for practical application of ZVZ in water treatment.

Graphitic carbon nitride ($g-C_3N_4$), a polymeric, metal-free semiconductor with a mild band gap (2.7 eV) has become a hot-spot in various scientific exploits (Mamba and Mishra, 2016). It is highly stable with respect to chemical, thermal, and light irradiation due to the strong covalent bonds between the carbon and nitrogen atoms, which is expected to serve as an effective catalyst or catalyst support (Wang et al., 2016; Liu et al., 2017). As an analogue of graphite, $g-C_3N_4$ possesses a stacked two-dimensional structure. Therefore, it could be engineered by charge-transfer complexation via doping selected heteroatoms into the framework to form a composite, which results in rearranging electron density and/or modifying the surface properties to implement the multifunctional processes in catalytic oxidation (Zheng et al., 2012; Wen et al., 2016). However, reports on its use as the catalyst or catalyst support in ozonation are few. Recently, $g-C_3N_4$ was reported to trigger a potent synergy between visible light photocatalysis and ozonation towards enhanced degradation of water pollutants (Liao et al., 2014; Xiao et al., 2015, 2016a). In fact, with its graphene-like structure and high chemical stability, $g-C_3N_4$ may be more suitable as a support for facilitating the uniform dispersion of active components and for providing more active sites in catalytic reaction. In addition, $g-C_3N_4$ is inexpensive, non-toxic, can easily be fabricated from readily available precursors and its polymeric structure allows for easy modification to improve its surface and electronic properties (Zheng et al., 2012).

Furthermore, with the assistant of catalysts, catalytic ozonation is a very complex and efficient process involving lots of possible reaction pathways responsible for the eventual decomposition of the pollutants. Therefore, in order to improve the stability of ZVZ and further implement the multifunctional processes during catalytic ozonation, ZVZ modified $g-C_3N_4$ (ZVZ- $g-C_3N_4$) was prepared and applied in this work. To the best of our knowledge, the present study is the first report on the enhanced catalytic ozonation activity via ZVZ- $g-C_3N_4$ composite. This study is mainly focused on five aspects: 1) preparation and characterization of ZVZ- $g-C_3N_4$; 2) comparisons of O_3 alone and catalytic ozonation with ZVZ- $g-C_3N_4$; 3) effects of key operational factors in O_3 /ZVZ- $g-C_3N_4$ process, including ZVZ- $g-C_3N_4$ dosage, initial ATZ concentration, solution pH, natural organic matter (NOM) and inorganic anions; 4) investigation of the catalytic mechanism of ZVZ- $g-C_3N_4$; 5) kinetic study in O_3 /ZVZ- $g-C_3N_4$ process. In this study, atrazine (ATZ) is selected as a model micropollutant to estimate the catalytic ozonation performance of ZVZ- $g-C_3N_4$.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and solvents used were at least in analytical grade without further purification, and as received from various commercial suppliers. Melamine, *Tert*-butanol (TBA), *p*-benzoquinone (BQ), sodium azide (NaN_3), indigo carmine, sodium thiosulfate ($Na_2S_2O_3$) were supplied by Sinopharm Chemical Reagent Company (Shanghai, China). The ZVZ (size: 600 meshes, purity: 99.99%) was purchased from Aladdin Industrial Corporation (Shanghai, China). ATZ with the highest purity available (>97%) was provided by TCI Chemicals (Tokyo, Japan). HPLC-grade acetonitrile was purchased from Fisher Scientific (Geel, Belgium) and humic acid sodium salt was obtained from Sigma–Aldrich (St. Louis, MO, USA). Ultrapure water (>18.2 M Ω cm) obtained from a Millipore Milli-Q system (A10, Millipore, Billerica, MA, USA), was used for all the synthesis and treatment.

2.2. Preparation of catalysts

The $g-C_3N_4$ was synthesized by direct polycondensation of melamine. Briefly, 7 g of melamine was put in a capped alumina crucible, which was then transferred into a muffle furnace and heated to 550 °C for 4 h with a heating rate of 3 °C min^{-1} . ZVZ- $g-C_3N_4$ was prepared by mixing 6 g of $g-C_3N_4$ with a certain amount of ZVZ in 45 mL ultrapure water with ultrasonic and stir at 80 °C to remove all the water. The resultant solids were calcined at 350 °C for 2 h with a ramp rate of 3 °C min^{-1} to obtain the final samples. A series of ZVZ- $g-C_3N_4$ composites with different mass ratios were prepared by changing the amounts of ZVZ. The optimal ZVZ content in the composite is 5.4 wt% based on the catalytic activity experiments (Fig. S1). Hence, all the characterization and catalytic ozonation experiments were proceeded with the 5.4 wt% ZVZ- $g-C_3N_4$ in the following contents.

2.3. Characterization of catalysts

The Brunauer–Emmett–Teller (BET) surface area of the samples was determined by a Micromeritics ASAP 2010 porosimeter (Norcross, GA, USA). The X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro MPD X-ray diffractometer (Almelo, Netherlands) with Cu K α radiation ($\lambda = 0.154178$ nm). A Thermo Scientific Nicolet iS5 spectrometer (Waltham, MA, USA) was employed to collect the Fourier transform infrared (FT-IR) spectra. Morphological studies were carried out using a field emission

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