Science of the Total Environment 575 (2017) 50–57

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Removal of aqueous oxalic acid by heterogeneous catalytic ozonation with MnO_x/sewage sludge-derived activated carbon as catalysts

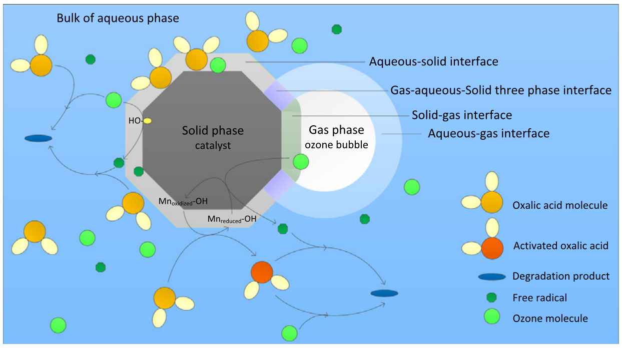
Yuanxing Huang [a], Yaru Sun [a], Zhihua Xu [a], Mengyu Luo [a], Chunlei Zhu [b], Liang Li [a],*

[a] School of Environment and Architecture, University of Shanghai for Science and Technology, No. 516, Jungong Road, Shanghai 200093, China
[b] Qinhuangdao Qinre Power Generation Co., Ltd., Qinhuangdao, Hebei 066003, China

HIGHLIGHTS

- Sewage sludge was converted into catalyst (MnO_x/SAC) in ozonation and characterized.
- The effectiveness of mineralization of oxalic acid by catalytic ozonation with MnO_x/SAC was proved under various conditions.
- The enhancement of catalytic activity was attributed to surface reactions and hydroxyl radical generation.
- The removal rate of oxalic acid had a positive relationship with the surface hydroxyl group in the catalyst.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 August 2016
Received in revised form 1 October 2016
Accepted 3 October 2016
Available online xxxx

Editor: Jay Gan

Keywords:
Heterogeneous catalytic ozonation
Oxalic acid
Sewage sludge
MnO_x/sewage sludge-derived activated carbon

ABSTRACT

MnO_x/sewage sludge-derived activated carbon (MnO_x/SAC) was prepared as catalysts to improve the performance of aqueous oxalic acid degradation by ozonation. The results indicated that MnO_x/SAC had excellent catalytic activity in mineralization of oxalic acid during heterogeneous catalytic ozonation process. MnO_x/SAC with a manganese load of 30% exhibited the strongest catalytic activity under the condition of solution pH 3.5, which enhanced the oxalic acid removal from 10.3% to 92.2% in 60 min compared with that treated by ozone alone. Increase of catalyst dosage and aqueous ozone concentration was advantageous for oxalic acid removal from water. On the basis of catalyst characterization analysis and the observation of inhibitory effect induced by higher pH, less catalyst dosage as well as the presence of hydroxyl radical scavenger, it was deduced that the reaction mechanism involved both hydroxyl radicals attack and surface reactions.

1. Introduction

Heterogeneous catalytic ozonation could provide fast degradation and more effective mineralization of many organic pollutants, thus is becoming the focus point in the field of ozone utilization as a promising advanced oxidation process (AOP) (Nawrocki and Kasprzyk-Hordern, 2010). The catalysts that had been frequently studied mainly include activated carbon (AC), metals supported AC (Athalathil et al., 2015), metallic oxides, natural minerals (Shahidi et al., 2014) and some novel materials (Ding et al., 2016; Gharbani and Mehrizad, 2014; Huang et al., 2015; Polat et al., 2015; Wang et al., 2016). Among these, AC was one of the most frequently used catalysts not only for its stability and reasonable cost, but also for its high adsorption capacity and its usage

---

* Corresponding author.
E-mail address: liliang@usst.edu.cn (L. Li).

http://dx.doi.org/10.1016/j.scitotenv.2016.10.026
0048-9697/

as support for other catalysts (Zhuang et al., 2014). The metals have been utilized to modify AC include Mn, Fe, Cu, Ce, Sn, etc., as well as their oxides (Abdedayem et al., 2015; Hao et al., 2012; Rai et al., 2015; Wang et al., 2014; Wu et al., 2015). The combined catalysts usually achieve higher organic contaminants removal in the process of catalytic ozonation.

In the past, the raw materials that have been used to produce AC were mineral or biomass such as wood, coal, shell, bamboo, coconut shell, corn stalk and soybean (Fu et al., 2016; Zhou et al., 2016). Recently more researches were carried out to prepare AC from solid wastes like petroleum coke, lignin from papermaking black liquid and sewage sludge from biological wastewater treatment plants (Gao et al., 2016; Tu et al., 2014).

As the major byproduct of wastewater treatment plants, the disposal of huge amount of sewage sludge is becoming a growing problem (Boualem et al., 2014). Its traditional handling and utilization include agriculture application, incineration, landfill, and sea dumping, however each of these routs was hampered by their limitations. The decline of the conventional disposal ways for sewage sludge promoted the demand for more environmentally benign alternatives (Smith et al., 2009). To convert the sewage sludge rich in carbonaceous content into AC is one of the emerging attempts. The sewage sludge based AC (SAC) could be applied as adsorbent to eliminate heavy metals and organic pollutants from water, or as efficient catalyst in catalytic ozonation and photocatalytic degradation of pollutants (Kacan, 2016; Zhang et al., 2004). As a carbon material, SAC could also serve as catalyst support, just as the commercial AC. According to Wen et al. (2012), the combination of sludge based catalyst with ozone showed a strong synergistic effect, and the dose of 0.2 g L^{-1} catalyst increased the removal of 0.1 mM oxalic acid by approximately 75% during 40 min of treatment. The study of Pan et al. (2011) found that the meso-macropore adsorbent prepared from hybrid sludge of biological and chemical sludge exhibited comparable adsorption capacities for UV_{254} with the commercial AC. Gupta and Garg reported that sewage sludge based adsorbents showed reasonable performance for the removal of lignin and amoxicillin from synthetic wastewater (Gupta and Garg, 2015).

In this work, activated carbon was prepared from municipal sewage sludge by means of pyrolysis with $ZnCl_2$ and H_2SO_4 as activation agents, and the prepared SAC was further loaded with the transition metal of manganese to make MnO_x/SAC. The catalytic activity of the prepared MnO_x/SAC was evaluated in heterogeneous catalytic ozonation. Here oxalic acid was selected as the target organic component to be treated by the process, for oxalic acid has been identified as a common final oxidation product from organic compounds degradation during ozonation. It is resistant to molecule ozone with low reaction rate constant of $k < 0.04\ M^{-1}\ s^{-1}$ at $pH > 5$ (Hoigné and Bader, 1983b), and has high reactivity ($k \approx 10^6\ M^{-1}\ s^{-1}$) towards hydroxyl radicals (•OH) generated from the decomposition of ozone in aqueous solution (Faria et al., 2008; Wen et al., 2012). Extensive research proved that heterogeneous catalytic ozonation involved the generation of hydroxyl radicals (•OH), while there were also some exceptions observed (Nawrocki, 2013; Zhang and Croué, 2014; Zhang et al., 2012), for instance, surface reaction was referred as another important mechanism (Nawrocki and Kasprzyk-Hordern, 2010). Andreozzi et al. and Orge et al. proposed that the catalytic ozonation of oxalic acid occurred through the direct reactions between surface metal-oxalic complex and ozone (Andreozzi et al., 1996; Legube and Leitner, 1999; Orge et al., 2012). Using oxalic acid as the model compound would be helpful to clarify the mechanisms of heterogeneous catalytic ozonation process in this study.

2. Materials and methods

2.1. Materials and reagents

All reagents such as $ZnCl_2$, $KMnO_4$ were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Potassium indigo trisulfonate were purchased from Supelco (Bellefonte, PA, USA). Deionized water was used to prepare all solutions. pH of the solution was controlled by adding sodium hydroxide or sulphuric acid. The secondary municipal sewage sludge (water content: 82.3%) was collected from Shanghai Eastern wastewater treatment plant (Shanghai, China) equipped with conventional secondary biological treatment.

2.2. Preparation and characterization of catalyst

The preparation of SAC followed the methods previously developed (Gupta and Garg, 2015; Pan et al., 2011; Wen et al., 2012). The oven-dried sludges were grounded and sieved to obtain the powder with the diameter of about 0.15 mm, then activated chemically with three different activation agents, respectively: (1). 3.0 $mol \cdot L^{-1}$ $ZnCl_2$, (2). 3.0 $mol \cdot L^{-1}$ H_2SO_4, (3). The mixture of 3.0 $mol \cdot L^{-1}$ H_2SO_4 and 3.0 $mol \cdot L^{-1}$$ZnCl_2$ (H_2SO_4: $ZnCl_2$ v/v ratio = 1:2). Briefly, impregnated 10 g dry sludge powder into 10 mL activation agent for 24 h at room temperature, and then dried at 105 °C. After activation the samples were pyrolyzed in a muffle furnace. The furnace temperature was increased to 550 °C at 10 °C min^{-1} and maintained at 550 °C for 1 h under the protection of N_2 gas before cooled to room temperature. After pyrolysis the products were washed with HCl 10% (w/w) to remove the acid-soluble inorganic impurities, rinsed with deionized water until the pH of elution >6, and dried at 105 °C. The $ZnCl_2$, H_2SO_4, $ZnCl_2 + H_2SO_4$ activated SACs were designated as zSAC, sSAC and szSAC, respectively.

The szSAC were further loaded with manganese by wet impregnation. 5 g szSAC particles were dipped into 40 mL $KMnO_4$ solution and mixed with ultrasonic for 2 h under room temperature, and the $KMnO_4$ solution concentrations varied to get 5, 15, 30 and 45 wt.% manganese loaded szSAC, followed by drying at 105 °C, and finally calcinated at 550 °C for 1 h under the protection of N_2 gas to obtain the desired catalysts, which were marked as szSAC/Mn5%, szSAC/Mn15%, szSAC/Mn30% and szSAC/Mn45%, respectively. Before use, the catalysts were grounded and sieved by screen of 100 mesh (correspond to the average size of 150 μm).

The specific surface area, average pore diameter and pore volume of the SACs were measured by nitrogen adsorption/desorption isotherms at 77 K by Physisorption Analyzer (ASAP 2020, Micromeritics, USA). The specific surface area was obtained by Brunauer-Emmett-Teller (BET) method. The pore diameter and pore volume were calculated by Density Functional Theory (DFT) method. The percentage contents of major elements on SACs surface were determined by X-ray fluorescence (XRF) with X-ray spectrometer (ZSX Primus II, Japan). To observe the surface morphology, the SACs were visualized by a scanning electron microscopy (SEM, S 4800, Hitachi, Japan). The pH at the point of zero charge (pH_{pzc}) of the catalyst was measured with a mass titration method (Newcombe et al., 1993). X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surface composition of the prepared SACs with an instrument (Amicus, Shimadzu, Japan). The infrared spectra of the SACs were observed by a Fourier transform infrared red (FT-IR) spectroscope (Tensor27, BRUKER, Germany).

2.3. Catalytic ozonation procedure

The catalytic ozonation experiments were carried out in a glass reactor at room temperature (15–20 °C). Ozone gas produced in situ with dry air as feeding gas by an ozone generator (3S-A3, Tonglin Technology, Beijing, China) was continuously bubbled into 2 L oxalic acid water solutions through a sintered-glass diffuser after the addition of fixed amount of catalysts. Water samples were taken at regular intervals to analyze the total organic carbon (TOC) concentrations by a TOC/TN analyzer (multi N/C 3100, Jena, Germany). The oxalic acid concentration in the sample was measured by a high performance liquid chromatography (HPLC), (Waters, e2695, USA) equipped with a column (Atlantis, T3, Waters, USA) and a UV–Visible detector (Waters, 2489, USA) at 254 nm, the mobile phase was 10 mM H_3PO_4. The aqueous ozone