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Strong promoted catalytic ozonation of atrazine at low temperature using tourmaline as catalyst: Influencing factors, reaction mechanisms and pathways

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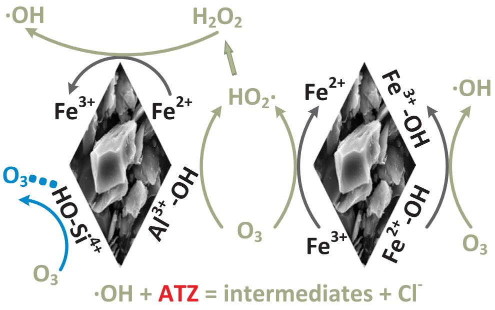
HIGHLIGHTS

- Catalytic ozonation of atrazine on tourmaline was studied.
- Tourmaline exhibited superior catalytic performance even in low temperature (278 K).
- Surface properties of tourmaline was characterized in detail.
- 31 kinds of intermediates were identified and the degradation pathways of atrazine were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Tourmaline, an economical and eco-friendly natural mineral, has been widely used during the water treatment processes. In this investigation, the raw tourmaline has been found to be effective as a catalyst for ozonation in the degradation of atrazine (ATZ) under low temperature (278 K). Within typical experimental conditions (tourmaline dosage = $1\,g\,L^{-1}$, $[ATZ]_0 = 5\,\mu M$, $[O_3]_0 = 3\,mg\,L^{-1}$, at pH 7.0 and 278 K), the removal efficiency of ATZ in catalytic ozonation was 98% after 10 min, compared with only 27% ATZ removal in the absence of catalyst. Surface properties and components of tourmaline were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FTIR), pyridine-FTIR and energy dispersive X-ray (EDX). The characterization studies showed that metal attached hydroxyl groups (M—OH, M = Fe, Al and Si) were the main active sites for ozone adsorption and decomposition. The formation of hydroxyl radicals (·OH) as well as hydrogen peroxide (H_2O_2) led to fast ATZ degradation and 31 kinds of intermediates; meanwhile, possible degradation pathways of ATZ were detected and proposed. The mechanisms of reaction were proposed for tourmaline-catalyzed ozonation based on all the experimental results and material characterizations.

1. Introduction

Refractory organic compounds, often existing in treated municipal and surface waters which are self-indecomposable and poorly-biodegradable, have aroused concerns on the global scale [1]. Atrazine (ATZ) is such a kind of persistent triazine herbicide which is widely applied in

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agriculture. Approximately 32 million kg of ATZ were applied in 2013 for agricultural use in US [2]. Although atrazine was banned in European Union (EU) and some other countries, it could still be easily detected in waters and was listed as a priority pollutant in the EU Water Framework Directive [3].

Using ozone as an oxidant to degrade pollutants has attracted increasing interest in drinking water and wastewater treatment for many years because ozone not only reacts with organic compounds containing unsaturated bonds and amino groups quickly, but also reveals strong disinfection capacity [4]. However, refractory organic compounds such as ATZ scarcely react with molecular ozone ($k_{O3, ATZ} = 6.0\,M^{-1}\,s^{-1}$) [5]. In order to improve the degradation efficiencies of these refractory organic compounds, ozone based advanced oxidation processes (AOPs) such as O_3/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$, Ozone with peroxymonosulfate (O_3/PMS), sonolytic ozonation, catalytic ozonation, and electrocatalytic ozonation have been rapidly developed and investigated as emerging technologies [6,7]. Among these AOPs, catalytic ozonation is a promising way to improve the degradation efficiency of organic pollutants. The introduction of certain catalysts can enhance the decomposition of ozone and promote the generation of free radicals such as hydroxyl radicals ($\cdot OH$) and superoxide radicals ($O_2\cdot^-$), while other catalysts may induce non radicals mechanisms [8]. It has been reported that the $\cdot OH$ generated during the catalytic ozonation process can significantly enhance the degradation efficiency of ATZ ($k_{\cdot OH, ATZ} = 3.0 \times 10^9\,M^{-1}\,s^{-1}$, at neutral form) [9].

Some countries and regions (mainly the northern parts of Asia, America and Europe) may stay cold over half of the year and the low temperature is one of the major factors affecting drinking water treatment since there is a suitable temperature range for all biochemical systems. Compared with AOPs operated at ambient temperature, several kinds of AOPs such as O_3/H_2O_2 and heat activated persulfate tend to be weak or even ineffective at low temperature because temperature has a drastic effect on ozone decomposition and mass transfer [6,10]. Catalytic ozonation usually achieves satisfactory results since $\cdot OH$ is induced by surface active sites mainly on the catalyst–solution interface, which would be less effected by the change of temperature. Our previous work reported that the introduction of Mn-ceramic honeycomb catalysts increased the nitrobenzene degradation for 3.1–fold at 283 K while only 1.05–fold at 293 K, indicating that the contribution of catalyst is more obvious under low temperature condition [11]. Fe-MCM-41 and Fe/SBA-15 prepared by Li achieved high TOC removal abilities during the catalytic ozonation processes [12,13]. The TOC removal efficiency of Fe-MCM-41 at 298 K was almost 11–fold enhanced compared with the efficiency at 278 K while for Fe/SBA-15, only 0.8–fold enhancement was achieved. These results imply that the type of catalysts is quite essential during the catalytic ozonation applied at low temperature. Finding a novel catalyst is still a key mission for refractory pollutants removal under low temperature in catalytic ozonation process.

Several types of catalysts were developed such as metal oxides (TiO_2), natural and artificial minerals (honeycomb and zeolites), carbonaceous matters (activated carbon and carbon nanotubes) and metal supported compounds (metal supported metal oxides or minerals) for catalytic ozonation application as reported [12,14,15]. In our previous work [16–18], we reported that manganese was able to catalyze the decomposition of ozone and the degradation of ATZ via intermediate manganese species and the effect of pH and humic substances were also investigated. However, continuously adding homogeneous catalysts was still an inconvenient way. Other investigations reported the positive effect of transition metal oxides (MnO_x/Al_2O_3, MnO_x/SBA-15 and TiO_2) [19,20] on the decomposition of aqueous ozone to hydroxyl radicals in the liquid bulk which could further accelerate ATZ degradation. Also, it has been reported that carbonaceous matters such as activated carbon [21] and multiwalled carbon nanotubes (MWCNTs) [22] could activate ozone decomposition and promote ATZ oxidation. However, using artificial materials as catalysts still has cost issues. Since the catalysts used during catalytic ozonation processes should be inexpensive, easily accessible, innocuous, eco-friendly and highly active for water treatment plant application, natural minerals may be good choices to satisfy these conditions. Tourmaline (also named as schorl), a common natural mineral, is widely and abundantly distributed in the earth's crust. It has gained significant attention with its capability of producing spontaneous electric field, permanently releasing negative ions and radiating far infrared energy [23]. Tourmaline has been used as photocatalyst, Fenton-like oxidation catalyst and heavy metal adsorbent in the water treatment filed and achieved favorable effects [23–25]. However, no previous studies have reported the application of tourmaline in the field of catalytic ozonation.

In the present study, tourmaline was characterized in detail and ATZ was chosen as the model refractory micropollutant to evaluate the catalytic ability and properties of the catalyst at low temperature. In order to better illustrate the catalytic performance, several factors such as pH, catalyst dosage, water matrix, H_2O_2 generation as well as the stability of tourmaline during catalytic process were investigated. Furthermore, the catalytic mechanism, degradation intermediates and possible degradation pathways for ATZ were also discussed.

2. Experimental section

2.1. Reagents and materials

tert-butanol (TBA), potassium indigotrisulfonate, ATZ and the standards of its degradation intermediates CAIT, CEAT, OAIT, OAAT, OEIT and CAAT (the detailed compounds name could be found in Table S1) were purchased from Sigma-Aldrich, USA. Methanol and acetic acid of HPLC grade were purchased from Tedia, USA. All other chemicals used in this study were of analytical grade without further purification which were purchased from Aladdin Chemical Reagent Co., Ltd., China. Commercial tourmaline powder was purchased from Shifeng Mining, Co., Ltd., China and the detail parameters will be shown in next section. Fe_2O_3, α-Al_2O_3 and Fe_3O_4 powders were purchased from Aladdin Chemical Reagent Co., Ltd., China and were used without further treatment. It was washed with deionized (DI) water and dried at 353 K in oven overnight, and then stored in a glass desiccator prior to use. All solutions were prepared using DI water (18.2 MΩ cm) produced from Milli-Q purification system (Millipore, USA).

2.2. Characterization

The X-ray diffraction (XRD) pattern was obtained using a diffractometer (D/max-TTR-III, Rigaku D, Japan) and a Cu-Kα radiation source at 45 kV and 40 mA over the 2θ range 10–70°. Morphological information and elemental analyses of the samples were evaluated by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Japan) equipped with an energy dispersive X-ray (EDX) detector system (Genesis 4000, Ametek, Germany). Morphology and crystal structures were further analyzed using high-resolution transmission electron microscopy (HR-TEM) (JEM-2100, JEOL, Japan) with a 200 kV accelerating voltage. X-ray photoelectron spectra (XPS) were recorded using a photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific, USA) equipped with a dual X-ray source using Al-Kα. Catalyst surface groups were determined using Fourier transform infrared (FTIR) spectrometer (Spectrum 100, PerkinElmer, USA) and the spectra were recorded over 400–4000 cm^{-1} by the KBr pellet method. Pyridine-FTIR was carried out by the same FTIR spectrometer. Self-supporting water (30 mg, 18 mm diameter) was first evacuated at 673 K for 60 min and then exposed to pyridine at 423 and 623 K for 10 min. The spectra obtained were presented by subtracting the spectra recorded before and after pyridine adsorption. Zeta potential measurement of catalyst was carried out by dynamic light scattering (Zetasizer Nano-ZS90, Malvern, USA). Brunauer–Emmett–Teller (BET) surface area of the catalyst was analyzed by nitrogen adsorption–desorption isotherm measurements at