



# Catalytic ozonation of benzotriazole over alumina supported transition metal oxide catalysts in water



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## ABSTRACT

Mineralization of benzotriazole (BTZ) by heterogeneous catalytic ozonation was studied in aqueous phase. Performance of three catalysts (Mn/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and Mn–Cu/Al<sub>2</sub>O<sub>3</sub>) were compared at various pH levels and operating conditions. Compared to noncatalytic ozonation, a higher level of mineralization of BTZ was achieved over a wide range of pH values. Adsorption of BTZ on alumina support and catalysts was negligible. At neutral pH, Cu/Al<sub>2</sub>O<sub>3</sub> was the most effective catalyst with close to 90% mineralization in 15 min reaction time. At pH 2, Mn/Al<sub>2</sub>O<sub>3</sub> had the fastest ozone decomposition and the fastest reaction with 75% mineralization of BTZ in 10 min. Under an alkaline pH environment, the mineralization of BTZ by using Cu/Al<sub>2</sub>O<sub>3</sub> showed a weak catalytic activity (22%) whereas mineralization with Mn–Cu/Al<sub>2</sub>O<sub>3</sub> was 77% complete in 30 min of reaction. It was observed that the presence of molecular ozone is essential for catalytic oxidation of organic compounds and ozone decomposition has a direct relationship with catalyst activity. The results indicate that not only the pH of solution but also the type of buffer used can influence the catalytic activity. The chloride and sulfate ions in aqueous solutions act as hydroxyl radical scavengers. All the catalysts showed high stability and reusability.

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## 1. Introduction

The presence of emerging contaminants in surface waters and sources of drinking water across the world is a growing concern [1–3]. This indicates that conventional water and wastewater treatment processes cannot remove these low concentration pollutants [4–7]. Benzotriazole (BTZ) is an important chemical which is used in various industrial processes and household chemicals such as aircraft de-icing fluids, antifreeze, cutting fluids, hydraulic brake fluids, dishwasher detergents for silver protection, and industrial cooling systems [8,9]. Due to its extensive use and recalcitrant nature, BTZ has been found in a number of rivers in Switzerland [8] and effluent of wastewater treatment plants in Germany in the µg/L range [9]. A number of methods have been studied in order to degrade BTZ in aqueous solution [10–14]. The kinetic rate constant of reaction of BTZ with molecular ozone is reported as  $20 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$ , indicating a slow reaction [10]. Application of advanced oxidation processes based on ozonation is an attractive option for the removal of BTZ. Although the benefits of ozone are well documented, its limited ability in oxidation of recalcitrant contaminants and formation of nonreactive byproducts remain a

challenge. The reactions of ozone with organic compounds generally result in the formation of aldehydes and carboxylic acids, none of which react with molecular ozone [15]. This is an important limitation of ozonation as total mineralization of organic compounds cannot be attained in reaction with ozone. Furthermore, oxidative reactions with ozone are relatively slow and selective. In an effort to overcome the limitations of ozonation process, application of different heterogeneous catalysts such as metal oxides (e.g. MnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and FeOOH) and metals (Ru and Pt) on supports (e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, and activated carbon) in enhancing the reaction rate of ozone has been studied [16–27]. Several studies have reported that removal efficiencies of organic pollutants by catalytic ozonation are significantly higher compared to ozonation alone [19,22,28].

The results obtained from a number of studies suggested different mechanisms for catalytic ozonation process. Adsorption of ozone and its further decomposition lead to production of surface bound O-radicals and ·OH radicals, which are active oxidative species. Transfer of electrons from the supported metals to ozone molecules with the production of O<sub>3</sub><sup>·-</sup> and/or final OH<sup>·</sup> generation and further reaction with organic compounds are among the proposed mechanisms for different reactions [15,16,29]. There are different views about the role of adsorption of organic molecules on the surface of catalyst, requiring further investigation [23,28]. Among the

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catalysts which have been studied, the transition metal manganese (Mn) supported on alumina has been used more than other metals to degrade various organic compounds in water [20–23]. The efficiency of catalytic ozonation of oxalic acid solution by copper (homogenous Cu (II) and heterogeneous CuO/Al<sub>2</sub>O<sub>3</sub> catalyst) was investigated by Pi et al. [30]. The results showed that at low pH, the effectiveness of ozone improved in the presence of CuO/Al<sub>2</sub>O<sub>3</sub>. However, the addition of a phosphate buffer strongly reduced the reaction rate because phosphate ions reacted as scavenger for hydroxyl radicals. Phosphate ions might also coordinate with the catalyst activate sites, reducing the catalyst activity. In another study, CuO/Al<sub>2</sub>O<sub>3</sub> catalyst was used for oxidation of aqueous solutions of substituted phenols, concluding that CuO/Al<sub>2</sub>O<sub>3</sub> can increase the reaction rate and decrease the ozone consumption [30]. Martins and Quinta-Ferreira examined different bimetallic catalysts for the ozonation of simulated phenolic wastewater [21]. Since the reaction rate of molecular ozone with BTZ is low, application of catalytic ozonation increases the rate of degradation of BTZ. The role of catalysts in increasing the reaction rate of ozone with BTZ needs to be studied. In addition, the effectiveness of catalysts in enhancing the mineralization process of BTZ needs to be clarified.

Although manganese-based catalysts were found to have high activity in degrading organic compounds, effectiveness of a bimetallic catalyst has not been explored adequately [21]. The aim of the present experimental research was to study the mineralization of BTZ by catalytic ozonation using single metal and bimetallic supported catalysts of Cu and Mn (Mn/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, and Mn–Cu/Al<sub>2</sub>O<sub>3</sub>) and to investigate the effect of operating parameters on performance of the catalysts.

## 2. Material and methods

### 2.1. Solutions and chemicals

High purity benzotriazole, tert-butyl alcohol (t-BuOH), Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, and potassium indigo trisulfonate were purchased from Sigma–Aldrich. The high surface area (220 m<sup>2</sup> g<sup>-1</sup>)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was supplied by Alfa Aesar. All other chemicals were purchased from Alfa Aesar and used as received. All stock solutions were prepared using ultrapure water with a resistivity of at least 18 M $\Omega$  cm at 25 °C obtained from a Millipore system.

### 2.2. Ozonation and catalytic ozonation protocol

Ozone was produced from pure oxygen by a laboratory ozone generator (OZV-8, Ozone Solutions). Ozonation and catalytic ozonation were carried out in a 1 L semi-batch reactor with continuous supply of ozone. The unreacted ozone leaving the reactor was destroyed by an ozone destruction unit (ODS-2, Ozone Solutions). The experiments were carried out using Milli-Q ultra-pure water at 25 °C with constant pH values of 2, 7.4 and 10, in order to determine the effectiveness of the different catalysts. The fixed pH values were achieved by: adding sulfuric acid for pH 2; buffering (KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>, 0.05 M ionic strength) for pH 7.4; and adding NaOH for pH 10. In the ozonation experiments, ozone was introduced into the reactor containing 995 ml of ultra-pure water at the desired pH level. The reactor was mixed using a magnetic stirrer (700 rpm). Ozone concentration was allowed to stabilize in the reactor and then 5 ml of BTZ solution (BTZ 10 mg L<sup>-1</sup>  $\approx$  TOC 6 mg L<sup>-1</sup>) was added to the reactor. Samples from the reactor were withdrawn by a glass syringe at different time intervals and were transferred into vials (25 ml) containing 200  $\mu$ L of sodium thiosulfate (32 mM) to quench the residual ozone and to stop the oxidation reaction. For catalytic

ozonation, the same protocol was applied except that a given amount of catalyst was added together with BTZ solution into the reactor. The samples were filtered through a 0.45  $\mu$ m membrane filter. The time zero was taken at the point when BTZ and catalyst were introduced into the reactor. To study the  $\cdot$ OH scavenging effect on BTZ degradation, ozonation experiments were carried out in the presence of 60 mM tert-butyl alcohol (TBA). In all experimental series, the flow of gaseous ozone was fixed at 2.6 g h<sup>-1</sup> while oxygen flow rate was controlled at 3 L min<sup>-1</sup>. The adsorption experiments on the alumina support and catalysts were carried out using the same experimental setup but in the absence of ozone.

### 2.3. Catalyst preparation and characterization

Activated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{BET}}$  = 220 m<sup>2</sup> g<sup>-1</sup>, pore volume = 0.6 cm<sup>3</sup> g<sup>-1</sup>, particle size = 0.2–0.4 mm) was used as the support. This support has shown stable performance in previous catalytic ozonation studies [26,27,31]. The active metals used in this study were manganese, copper, and a combination of both. Three catalysts were prepared by dry impregnation and co-impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Aqueous solutions of Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, were used to obtain catalyst loadings of Mn (10 wt.%), Cu (10 wt.%), and Mn–Cu (5–5 wt.%). The impregnated  $\gamma$ -alumina support was dried overnight at 110 °C and then calcined in a furnace at 500 °C for 4 h. After calcination, the catalyst particles were crushed and sieved. The particles in the range of 0.2–0.4 mm were chosen for the experiment. Powder X-ray diffraction (XRD) of the catalysts was recorded using an XRD system (Bruker D8-Advance, Germany) with copper K $\alpha$  radiation. The surface area and pore volume of the catalysts were measured using a Micromeritics ASAP 2020 instrument (model V3.01 H). Before the BET analysis, the samples were degassed under a vacuum of 1  $\times$  10<sup>-3</sup> mm Hg at 200 °C for 4 h. The point of zero charge (PZC) of the catalysts was determined using the mass titration method described elsewhere [32].

### 2.4. Analytical method

Concentration of benzotriazole was determined by HPLC (Agilent 1100, Agilent Technologies Inc.) using a Luna 5u C8 (2) 100 A (250  $\times$  4.60 mm, 5  $\mu$ m) column from Phenomenex and a diode array detector set at 275 nm. A methanol/water mixture (30:70, v/v) was used as the mobile phase at a constant flow rate of 1 mL min<sup>-1</sup> and the injection volume was 100  $\mu$ L. Total organic carbon (TOC) was determined with a Shimadzu TOC-VCSH total carbon analyzer equipped with ASI-V auto sampler. ICP-MS (Perkin-Elmer optima 5300DV) was used to determine the metals concentration in the fresh catalyst and in the reaction solution during catalytic ozonation. ICP-MS works under the principle of ionizing the sample by inductively coupled plasma (ICP) followed by the identification and quantification of the atoms by mass spectrometer (MS). The concentration of dissolved ozone in the reactor was measured by an amperometric ozone microsensor (MS-08, AMT Analysenmesstechnik, GmbH). Solution pH was measured using a single junction pH combination electrode (R-27012-06, Cole-Parmer Inc.). During reaction, a data acquisition system (cDAQ-9172, National Instruments Corp.) recorded the solution ozone concentration, pH, and temperature every 30 s.

## 3. Results and discussion

### 3.1. Characterization of catalysts

Results of catalyst characterization are summarized in Table 1. It is observed that the surface area of the alumina support

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