

# Catalytic ozonation of dye in a microbubble system: Hydroxyl radical contribution and effect of salt



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## ABSTRACT

Catalytic ozonation using metal ions is a promising method to enhance the hydroxyl radical generation from ozone. In this study, four common metal ions i.e., Fe(II), Fe(III), Mn(II) and Cu(II) were used as the catalyst in a microbubble reactor. The metal ions increased the decolorization efficiency of the azo dye, Congo Red (CR). The combined use of metal ion and microbubble increased the effective factor to a good extent. Based on the pseudo-first-order reaction rate constant  $k$  ( $\text{min}^{-1}$ ),  $\text{O}_3 + \text{Cu(III)}$  showed higher value for both with and without microbubbles at acidic pH. The performance of the metal catalyst on the decolorization of CR followed an order  $\text{Fe(III)} < \text{Fe(II)} < \text{Mn(II)} < \text{Cu(II)}$ . The effect of pH, metal ion concentration on the dye oxidation, and the presence of NaCl and  $\text{CaCO}_3$  were also studied. The pCBA was used as the radical probe to calculate the hydroxyl radical concentration by using an indirect method. From the depletion rate of pCBA it was observed that the generation of hydroxyl radical was more by the use of Cu(II) and the trend was  $\text{Fe(III)} < \text{Fe(II)} < \text{Mn(II)} < \text{Cu(II)}$ . The removal of TOC followed the same order too.

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## 1. Introduction

Azo dyes are the widely used in the textile, paper and ink industries [1]. These dyes contain  $\text{N}=\text{N}$  bond which makes them stable and difficult to remove. Therefore many advanced methods have been developed in past decades to remove these compounds partially or completely [2–7]. Amongst all the oxidants used so far, ozone is one of the powerful and favorable oxidant used in the water treatment processes for disinfection, and oxidation of many organic and inorganic materials [8]. However, some organics show slow reactivity towards ozone such as inactivated aromatics. To overcome this, the catalytic ozonation methods are being preferred. The catalysts are used with ozone to generate hydroxyl radicals, which has more oxidation potential than ozone and readily reacts with the organic compounds. Many types of catalytic ozonation processes are used such as  $\text{O}_3 + \text{H}_2\text{O}_2$ ,  $\text{O}_3 + \text{UV}$ ,  $\text{O}_3 + \text{UV} + \text{H}_2\text{O}_2$  etc. [9–12]. The use of these catalytic ozonation and their effects on various water quality parameters such as BOD, COD, DO, pH, TDS were reported in the literature [13]. Along with that, the cytotoxicity and mutagenicity evaluation were also performed

[14–16]. Besides these, many transition metal catalysts are also used and categorized as the homogenous catalysts, such as Fe, Co, Ni, Cu, Cd, Mn, Cr, Zn and Ag. The use of metal ion catalysts such as Fe(II), Fe(III), Mn(II), Zn(II), Co(II), Ni(II), Cu(II), Ag(II) and Ti(II) are also used for decolorization of various dyes [17,18]. These metal catalysts increase the hydroxyl radical generation and the oxidation of the compound occurs via both directly and indirectly [19–23]. The addition of these metals also increases the TOC removal efficiency [24].

The catalytic ozonation is more efficient than the ozonation alone by decreasing the ozone loss. However, another method of increasing the ozonation efficiency is to enhance the dissolution of ozone in water. The lower solubility of ozone is one of the major limitations of this process. Most of the ozonation processes are performed in the batch or semi-batch bubble columns [25–28]. It is believed that, decreasing the bubble size increases the mass transfer coefficient of the gas. Therefore, the use of microbubbles (MB) is a good substitute over normal bubbling method [29]. Many other advantages of microbubbles help in increasing the oxidation of the pollutants and removal of TOC [30].

In this work, a comparative study of the oxidation performance of Congo Red dye (CR) using normal ozonation and microbubbles have been evaluated. In real effluents, the presence of various metal ions and salts play a major role in the effectiveness of the process. These ions might act as the catalyst or the scavengers of

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the oxidants. It is reported that, the metal ions such as Mn(II), Fe(II), Fe(III), Zn(II), Co(II), Ni(II) and Cu(II) have higher catalytic ozonation efficiency than that in ozone alone [17,31,32]. In past few years, the rapid dissolution of ozone and the generation of a small amount of hydroxyl radicals were observed in the microbubble ozonation system [33–35]. The behavior of these metal ions on the degradation of the pollutants might be of interest to study in a microbubble ozonation system. Therefore, four commonly found metal ions [i.e., Fe(II), Fe(III), Mn(II) and Cu(II)] were used for the catalytic ozonation using normal dissolution ozone and ozone microbubbles. The radicals generated from the catalytic ozonation was measured by the indirect method given by Elovitz and von Gunten [36] using pCBA as the radical probe. The effect of some common ions on the dye decolorization was examined. In addition, the TOC removal efficiency was also studied. So far, no work has been done on the CR ozonation and calculation of radicals using microbubbles. Therefore, this work might be of interest for the comparative study of the above four catalysts in the ozonation process using the normal ozone dissolution method and the ozone microbubbles.

## 2. Experimental

### 2.1. Material

All the chemicals were used as procured from the manufacturers. *p*-chlorobenzoic acid (pCBA, 98% assay), was purchased from Alfa Aesar (India). HPLC reagent grade methanol (99.7% assay),  $\text{H}_3\text{PO}_4$  (42.5% assay), sodium hydroxide (>98% assay), sodium carbonate (99.9% assay), sodium dihydrogen phosphate (99% assay), and hydrochloric acid (35% assay) were purchased from Merck (India). Potassium indigo trisulfonate (99% assay) was purchased from Sigma Aldrich (India). Malonic acid (99% assay) and phosphoric acid (85% assay) were purchased from Spectrochem (India). Congo red dye (95% assay) was purchased from Loba Chemie, India.  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were purchased from Merck, India as the source of Mn(II), Fe(II), Fe(III) and Cu(II) respectively.

### 2.2. The experimental setup

Ozone was generated by a corona discharge ozonator (Oz-Air, ISM 10 Oxy EC, India), from oxygen concentrator (Oz-Air, HG 03, India). The oxygen concentrator employs the pressure swing adsorption technique to generate high-purity oxygen (>98% by volume) from air. The ozonator produce ozone in the range of 0–3 mg/s. The flow rate of the gas mixture (i.e., oxygen and ozone) coming out of the ozonator was measured by a rotameter, which had a range of 8–80 ml/s. The percentage of ozone in the gas mixture was varied in the range of 0.7–2%. Tap water was filtered through an iron filter (Eureka Forbes, Iron-Nil, India). The dye solution was prepared using this water. The gas containing ozone and oxygen was passed into the microbubble generator (MBG) (Riverforest Corporation, AS MK-III, USA). The gas was dissolved in water (inside the MBG) by applying a high pressure. After dissolution, the microbubbles were generated by the release of pressure. The mean diameter of the microbubbles was 25  $\mu\text{m}$ . The gas intake capacity of the MBG was 1.7 ml/s. The MBG operated in a continuous recirculation mode. The aqueous phase reaction mixture, contained in a polycarbonate reactor of 20 L capacity, was recirculated through the MBG, as shown in Fig. 1. The excess gas, coming out of the reactor and the MBG, was passed through an ozone destructor (Oz-Air, Dest-50, India), which catalytically converts the ozone to oxygen and released it to atmosphere. The temperature of the reaction medium was controlled by a water bath controlled by an external circulator (JeioTech, RW-2025G,

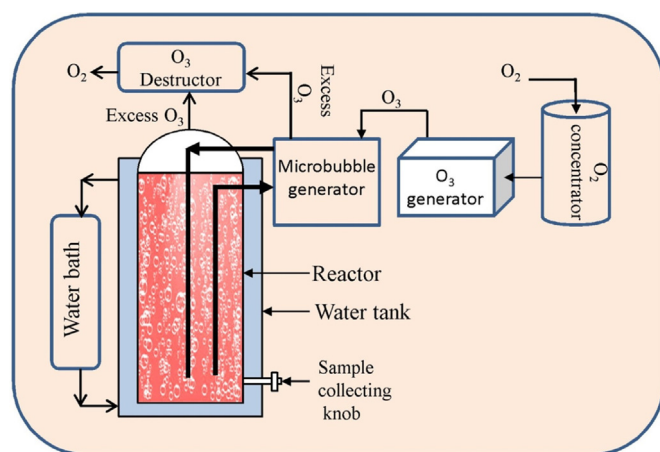


Fig. 1. Schematic of the experimental setup.

Korea). The temperature of the aqueous phase within the reactor was controlled at  $298 \pm 1 \text{ K}$  by this method.

### 2.3. Methods

The ozonation reactions were carried out for 1 h 15 mL samples were withdrawn from the reactor at 5 min intervals. 2 g of sodium thiosulfate pentahydrate was added to the sample under continuous stirring to quench the reaction. The absorbance of the dye was measured at the maximum absorption wavelength of 497 nm using a UV-visible spectrophotometer (PerkinElmer, Lambda 35, Switzerland).

The pH of the medium was maintained by using 0.1 M HCl and 0.1 M NaOH solutions. The pH was checked by using a pH meter (Eutech, pH 2700, electrode: 93  $\times$  218819, Singapore). The ozone concentration was measured by using the Indigo Colorimetric Method using potassium indigo trisulfonate and UV-vis spectrophotometer at 600 nm [37]. The concentration of pCBA (0.05 mg/L in the solution) was detected using a Shimadzu LC-20AD HPLC (Tokyo, Japan) equipped with a ternary pump delivery system and UV detector. 300  $\mu\text{L}$  sample was injected into the C18 column (Hypersil ODS, 250 mm length, 4.6 mm ID, 5  $\mu\text{m}$  particle size). The mobile phase consists of 55%:45% methanol:H<sub>2</sub>O (adjusted to pH  $\sim$  2 by adding 10 mg/L  $\text{H}_3\text{PO}_4$ ) was used for pCBA detection at UV absorbance 234 nm. With a 300  $\mu\text{L}$  injection, the detection limit was 0.05  $\mu\text{M}$ .

The dye decolorization was performed in semi-batch process. For without-microbubble system, the water was circulated by the MBG continuously, without pressurizing the pump. In the microbubble system, the dye and the metal ion were dissolved in the required concentration and ozone was allowed to dissolve using microbubbles continuously. The measurement of the radical concentration using the pCBA was done in a batch process. The ozone was spiked for 20–30 min for saturation ozone concentration. After that, pCBA was added and the sample was collected at required time intervals for both with and without microbubble system. TOC was measured by using a TOC analyzer (O.I. Analytical, Aurora 1030, USA). 15 mL samples were withdrawn from the reactor at different time intervals and the TOC was measured.

## 3. Results and discussion

### 3.1. Catalytic ozonation in presence of metal ions

The ozonation of CR was studied in presence of four metal ions in absence and presence of microbubbles. The decolorization of CR

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