

# Combining electro-catalytic ozonation with zeolite-supported iron catalyst for pharmaceutical degradation

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## Highlights

- In situ electrochemical ozone production integrated with a heterogeneous catalyst provides an effective method for removing pharmaceutical contaminants from water.
- Catalytic oxidation of metoprolol is used as a model pharmaceutical contaminant that resists conventional water treatment.
- Electro-catalytic ozone evolution reaction (OZER) is performed using a heterojunction Ni–Sb–SnO<sub>2</sub> (NSS); and the oxidation of metoprolol by the reactive oxygen species is enhanced significantly using an iron functionalized zeolite catalyst.

## 1. Introduction

Pharmaceuticals present ecological risk due to their design for both bioactivity and chemical stability. Consequently, pharmaceuticals that reach the environment may alter organisms (e.g., gender and reproduction) and may not effectively be removed by water treatment processes. The extreme chemical diversity of pharmaceuticals requires robust chemical degradation process for water treatment to avoid discharging pharmaceuticals to the environment. Advanced oxidation processes (AOPs) are acknowledged as modern, highly effective techniques employed as a mechanism to eliminate residues of pharmaceuticals (e.g. ozonation, Fenton reaction, photocatalysis, electrochemical oxidation) [1][2][3]. Ozonation is an AOP that provides direct advantages in disinfection, sterilization, and wastewater treatment. Given its high reactivity and low stability, ozone must be generated in situ. Electrochemical ozone production (EOP) entails the electrolysis of water, providing a gaseous ozone-oxygen blend within an aqueous environment. Unlike corona discharge methods, aqueous EOP has the potential to enhance energy efficiency, while reducing the risk of fire or explosion commonly associated with ozone generation in air [4]. From our previous studies we noticed, ozonation alone is not sufficient for removal of pharmaceuticals, as it leaves substantial amounts of partially oxidized intermediates, the toxicities of which are in most case unknown [5]. Catalytic ozonation employs catalysts to accelerate the breakdown of ozone into highly reactive free radicals. These reactive radicals enable catalytic ozonation to drive the rapid and efficient degradation of various organic pollutants, addressing the limitations of ozone alone [6]. To completely oxidize byproducts of the ozonation process, we identified a Fe modified zeolite solid heterogeneous catalysts [5]. Here, we combine the Fe-modified zeolite catalyst with EOP with the goal of complete degradation of pharmaceuticals.

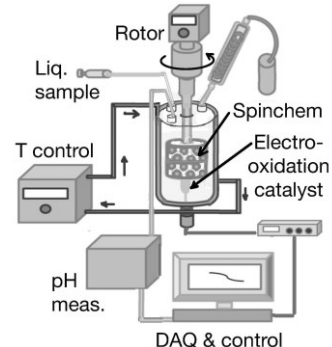
Metoprolol, a widely prescribed beta-blocker for cardiovascular conditions, is increasingly detected in surface waters [7]. In a study by the US Geological Survey (USGS) in 2013, the levels of metoprolol in surface waters across the United States ranged from 0.2 to 11.4 nanograms per liter (ng/L), with the highest being found in a stream in Los Angeles County, CA; and a 2017 study by the University of Minnesota reported metoprolol concentrations in surface waters ranging from 0.1 to 6.2 ng/L, with the highest being found in a river in Minneapolis, MN [8]. While these levels are currently low compared with toxic thresholds (>1 µg/L) [9], the results show that metoprolol is not being completely degraded by urban water treatment systems at a time when metoprolol use is increasing. In this investigation, the degradation of metoprolol was examined in the context of an EOP system, comparing its efficacy with and without a heterogeneous catalyst.

## 2. Methods

A batch reactor with a capacity of 250 ml was assembled for experimental analysis. Ozone generation was facilitated through a catalytic electrode strategically positioned at the reactor's base. The aqueous phase comprised a mixture of metoprolol and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). The oxidation process was initiated at the anode catalyst's surface, propelled by the application of direct electric current, which resulted in the generation of reactive oxygen species (ROS, including ozone and hydroxyl radicals) at the anode's surface. The catalytic anodes used in this study were developed by Kim *et al.* [10] using a heterojunction approach incorporating metal oxide overlayers to enhance the electrocatalytic ozone

evolution reaction (OZER) on Ni–Sb–SnO<sub>2</sub> (NSS) anodes. Their study reported a significant enhancement in OZER current efficiency by 2.7-fold and a decrease in oxygen evolution for the NSS/SiO<sub>x</sub> composite when assessed in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a current density of 10 mA cm<sup>-2</sup> compared to the pristine NSS anode [10].

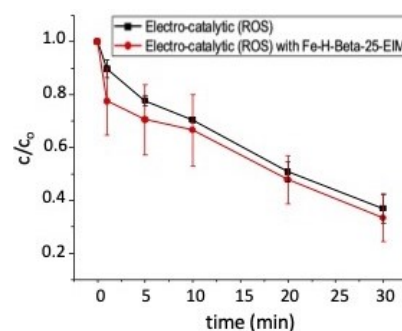
A heterogeneous catalyst was employed in a rotating bed apparatus (SpinChem), using the rotation to drive flow of solution of pharmaceutical and reactive oxygen species into the bottom center and radially outward through the catalyst bed to enhance reactant-catalyst interaction. The Fe-functionalization of Beta zeolite was achieved using an evaporation-impregnation technique [11]. The catalyst's specific surface area (953 m<sup>2</sup>/g), as determined from nitrogen adsorption-desorption isotherms using Dubinin's method. The catalyst's structural features were measured via X-ray diffraction (XRD), while its morphological properties such as shape, size and distributions of crystals were determined using scanning electron microscopy (regular spherical, 72 to 468 nm diameter zeolite particles, which were fused into aggregates, sieved to approximately 120-150µm size). Energy dispersive X-ray microanalysis (EDX) was conducted for the chemical analysis of the catalyst (on the outer surface of the zeolite particles, iron particles were observed, on average 21.2 nm across). The reactor is used with equipment to control its temperature, measure pH, and withdraw samples from the liquid and headspace (**Figure 1**). Liquid samples from the reactor were analyzed using liquid chromatography-mass spectrometry (LC-MS) to quantify metoprolol and identify its degradation by-products.



**Figure 1.** Reactor schematic (batch reactor for metoprolol degradation).

### 3. Results and Discussion

The decrease in metoprolol concentration is used to compare the effect of reactive oxygen species (ROS) alone to that with the heterogeneous oxidation catalyst: both modes degrade metoprolol, with the combined NSS/SiO<sub>x</sub> EOP and Fe-H-Beta-25-EIM zeolite catalyst system significantly increasing the rate of degradation (**Figure 2**). The standalone EOP system was used to examine effects of convection and temperature. Increasing the SpinChem rotation rate from 60 to 400 rpm more than doubled the degradation rate at 20°C. Decreasing reactor temperature from 20 to 5°C slowed the reaction by more than a factor of two.



**Figure 2.** Decomposition of metoprolol through electro-catalytic production of Reactive Oxygen Species (ROS): with (red) and without (black) Fe-H-Beta-25-EIM catalyst. T = 20°C. Spinchem 60rpm. Applied current of 100 mA.

### 4. Conclusions

The findings indicated that metoprolol underwent substantial decomposition via electro-catalytic ozone generation in the absence of the Fe-H-Beta-25-EIM catalyst, achieving significant degradation within 30 minutes (T=20°C, SpinChem 60 rpm, EOP applied current 100mA). Incorporation of Fe-H-Beta-25 catalyst notably augmented the degradation efficiency (**Figure 2**), underscoring the effectiveness of the combined catalytic system.

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### Keywords

Ozone; Electrocatalyst; Heterogenous catalyst; Metoprolol