Catalytic ozonation of pharmaceutical mixtures: A comprehensive analysis of catalyst efficacy, degradation pathways and recyclability

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Significance and Relevance

This study explores catalytic ozonation as a promising approach for the degradation of pharmaceutical contaminants in wastewaters. Leveraging our previous work on single pharmaceuticals, such as ibuprofen, diclofenac, carbamazepine, and sulfadiazine, this work is focused on the effectiveness of various heterogeneous catalysts in degrading complex pharmaceutical mixtures. The findings include degradation efficiencies, key degradation products, and the structural stability of catalysts, potentially advancing catalytic ozonation as a viable solution for environmentally sustainable water treatment.

Preferred choice for topic: Water treatment; Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Pharmaceutical residues in wastewaters present a persistent environmental threat, since they accumulate in aquatic environments, especially in sensitive regions such as the Baltic Sea where concentrations can persist for decades[1]. In our previous studies we have demonstrated that combined ozonation and heterogeneous catalysis can successfully degrade individual pharmaceuticals, such as ibuprofen, diclofenac, carbamazepine, and sulfadiazine[2-5]. In Figure 1, these pharmaceuticals along with their main transformation products are depicted. In general, the decomposition proceeds in two stages: ozone creates radicals which initiate the decomposition, and the primary decomposition products are degraded by heterogeneous catalysts[2-5]. However, in real wastewaters, pharmaceuticals appear as complex mixtures. Therefore, our current research is focused on the investigation of mixtures of pharmaceuticals. Important synergistic and antagonistic effects will be carefully monitored when these multiple compounds as well as their break-down components interact, to ensure that the treated mixture becomes less toxic than before the treatment. Effective and inexpensive catalysts are explored, focusing on iron- and copper-based materials, with the aim of scalability and economic feasibility for industrial applications.

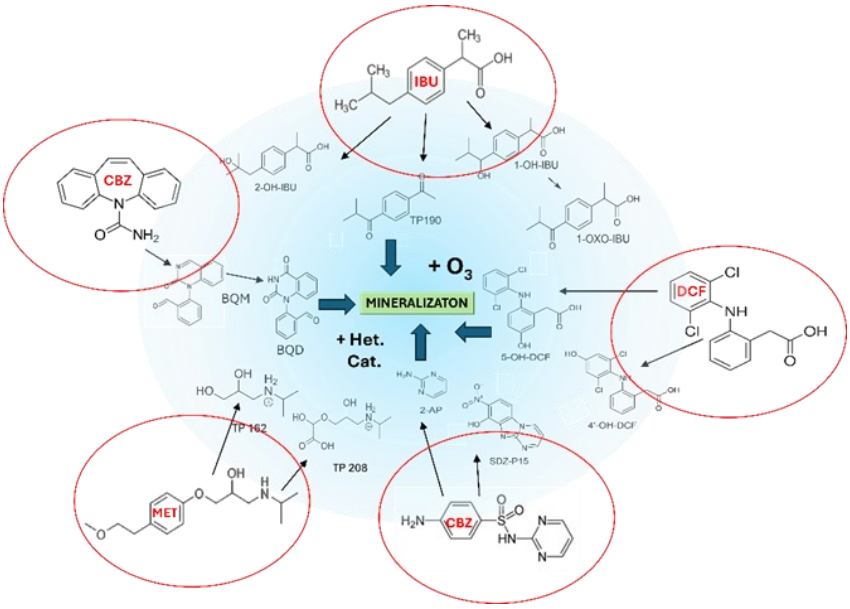

Figure 1. Primary transformation products identified from the ozonation of the five pharmaceuticals studied. These compounds feature a variety of reactive functional groups, including amines and quinones, which can facilitate further breakdown through additional reactions, ultimately aiding in the progression toward complete mineralization.

Materials and Methods

The study employs batch and continuous ozonation reactors to screen a range of heterogeneous catalysts, including transition metal oxides and modified carbon materials. Characterization techniques, such as nitrogen physisorption, SEM, and XRD, were used to monitor the changes of the material properties before and after the catalytic ozonation experiments. Pharmaceutical mixtures representative of five common highly detected contaminants in wastewater are prepared, and HPLC and MS are utilized to track the degradation intermediates and identify degradation pathways. Key degradation products, including potentially toxic intermediates such as quinones, are identified to provide insights into the reaction mechanisms and minimize the amounts of harmful by-products.

Results and Discussion

Initial findings from catalytic ozonation experiments on single pharmaceuticals reveal significant differences in the degradation efficiency depending on the catalyst. For instance, previous research has shown that Pt-modified catalysts enhance ozonation efficiency for diclofenac, yielding higher degradation rates and reducing the amount of toxic by-products[2]. On the other hand, the toxic intermediates BQD and BQM arising from ozonation of carbamapezine were closely monitored, since they are known for their persistency. The best catalyst for eliminating these compounds have found to be Pd-H-Y-12-EIM, but Pd is an expensive metal. Therefore, Fe and Cu based catalysts are screened here, due to their cost-effectiveness and high activity in generating reactive oxygen species (ROS), which drive the degradation process. Preliminary hypotheses suggest that catalysts promoting ozone decomposition enhance the production of hydroxyl radicals, accelerating the degradation process. Attention is also given to the formation of harmful by-products and the catalyst durability studies. Therefore, the spent catalysts are analyzed to provide insights into catalyst life time.

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