New combined technology for degradation of pharmaceutical mixtures: ozonation, heterogeneous catalysis and UV-irradiation

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Highlights

- Comparative study of ozonation and UV-driven oxidation for pharmaceutical mixtures.
- Degradation kinetics of degradation in single and multi-component systems.
- Catalyst-assisted ozonation for enhancement of degradation efficiency.
- Preliminary analysis of transformation product formation.

1. Introduction

The presence of pharmaceutical residues in aquatic environment has become a major environmental concern. Many pharmaceutical ingredients (APIs), including anti-inflammatory drugs, antibiotics and antiepileptics, are frequently detected in surface waters and wastewater effluents. Conventional biological wastewater treatment processes are inefficient in removing these persistent micropollutants, resulting in their continuous release as multi-component mixtures into natural waters.

Advanced oxidation processes (AOPs) have received increasing attention as promising technologies for the degradation of recalcitrant organic contaminants. Among these methods, ozonation is widely applied due to its high oxidation potential and its ability to oxidize a broad range of organic compounds. However, ozonation alone may lead to incomplete mineralization and the formation of transformation products (TPs) that can persist in the ecosystem. In combined systems, heterogeneous catalysts can enhance ozone decomposition, promote the formation of reactive oxygen species, and facilitate a more complete removal of both parent compounds and their transformation products. Recent studies from our group have demonstrated that catalytic ozonation using metal-modified zeolite catalysts significantly enhances the degradation kinetics and mineralization efficiency compared with non-catalytic ozonation, both for single pharmaceuticals [1] and for multi-component mixtures of pharmaceuticals [2].

An alternative approach involves UV-driven oxidation processes, including direct photolysis and photocatalysis, which generate reactive oxygen species capable of degrading complex organic molecules [3]. Combining different AOP strategies may therefore improve the degradation efficiency while limiting the accumulation of intermediate compounds.

In this work, the comparative degradation of selected pharmaceutical mixtures containing ibuprofen, diclofenac, carbamazepine, sulfadiazine and sulfamethoxazole was investigated using ozonation and UV-driven oxidation. Particular attention has been paid to mixture kinetics, catalyst effects and transformation product formation in multi-component systems, supported by reference experiments with single compounds.

2. Methods

Ozonation experiments were performed in laboratory-scale semibatch reactor with continuous ozone bubbling into the liquid phase, both in the absence of catalyst and in the presence of Fe-H-Beta-25, while UV experiments involved external lamp irradiation of a glass reactor. Kinetic data were obtained by HPLC analysis of the samples, with LC–MS identification of transformation products and TOC analysis to assess the overall degree of mineralization.

3. Results and discussion

Preliminary experiments quantified the degradation kinetics of the pharmaceuticals under ozonation and UV-driven oxidation in single systems and multi-component mixtures. Several compounds degraded rapidly during ozonation, although reaction rates varied with molecular structure and operating conditions (Figure 1). The apparent degradation kinetics remained relatively similar in catalytic and non-catalytic ozonation, whereas the presence of catalyst promoted further the oxidation of intermediates, resulting in lower concentrations of transformation products and higher degree of mineralization. In mixtures, interactions between pharmaceuticals influenced degradation kinetics and oxidation pathways, which is why single-compound experiments were used as references. The normalized concentration profiles (C/C_0) were fitted with pseudo-first-order models to obtain apparent rate constants (k_{app}) for comparison of mixtures and catalysts. In parallel, UV-based processes introduced additional pathways through direct photolysis or photocatalytic radical generation. Comparing ozonation and UV-driven oxidation clarified the relative efficiency of these oxidation strategies for pharmaceutical mixtures. Preliminary results showed compound-dependent kinetics and mixture effects, highlighting that molecular structure and catalyst interactions govern the oxidation pathways. Further experiments are underway to quantify transformation products and assess the roles of the catalysts in formation and degradation of intermediates.

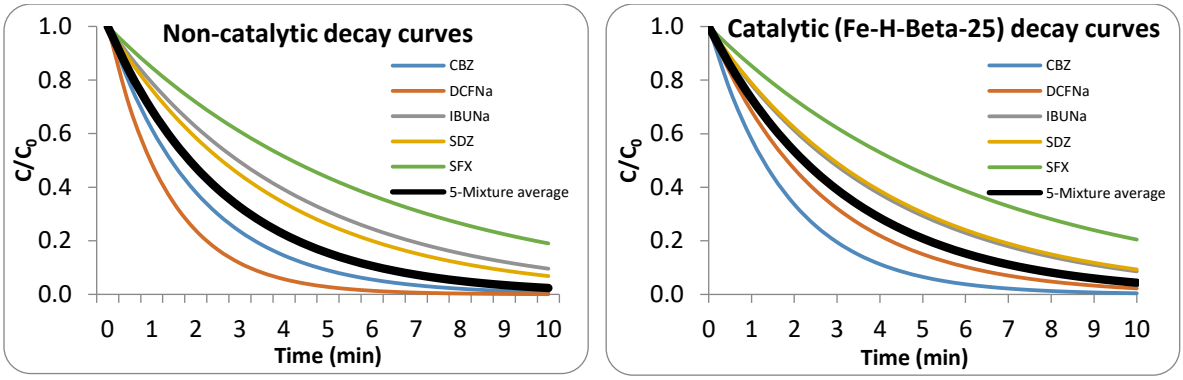

Figure 1. Normalized concentration (C/C_0) of five pharmaceuticals (IBU, DCF, CBZ, SDZ, SMX) during ozonation. Left: non-catalytic; right: catalytic ozonation over Fe-H-Beta-25. The continuous lines represent the pseudo-first-order decay profiles, with the thick lines indicate the average mixture behaviour.

4. Conclusions and future perspectives

The present work was devoted to degradation of multi-component pharmaceutical mixtures using ozonation and UV-driven advanced oxidation processes. The results provided a comparative understanding of mixture-specific efficiency, kinetics and selectivity for the removal of pharmaceuticals from water. Preliminary experiments suggested that catalytic ozonation and UV-driven processes both offer promising pathways for degrading complex mixtures of pharmaceuticals, although apparent reaction rates and mechanisms vary with the compound identity, mixture composition and operating conditions. The ongoing work focuses on detailed kinetic evaluation and LC–MS-based identification of transformation products, which are essential for assessing the environmental safety and treatment efficiency in realistic wastewater matrices and supporting the future implementation in large-scale wastewater treatment.

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Keywords Advanced oxidation processes; catalytic ozonation; pharmaceutical mixtures; transformation products