Catalytic ozonation of pharmaceuticals – From experiments to modelling

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Significance and Relevance

A new kinetic model based on molecular mechanisms was developed for the destruction of pharmaceuticals by combined ozonation and heterogeneous catalysis. The model describes the concentration courses of ibuprofen and its partially oxidized products and can be applied to other pharmaceuticals. Valuable insights into the design and optimization of catalytic ozonation processes were obtained, thus enabling an improved treatment efficiency and minimized environmental impact.

Preferred and 2nd choice for the topic: Water treatment; Multiscale modelling
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral

Introduction and Motivations

Hundreds of pharmaceuticals enter aquatic systems via several pathways: incomplete metabolism and subsequent excretion of medications through human excreta, agricultural runoff containing antibiotics and other veterinary drugs used in animal husbandry, and industrial discharges. The surface and ground waters get polluted by these contaminants. Existing commercial technologies are unable to eliminate all the pharmaceuticals from wastewaters and in the worst case, only partial oxidation of the pharmaceuticals takes place leading to harmful or even poisonous intermediates[1,2]. Ozonation is an appropriate water cleaning technology but ozonation alone is not always sufficient to achieve efficient total oxidation of the organic species. Combination of ozonation with heterogeneous catalysis is an efficient method for the degradation of pharmaceuticals and it was studied in detail in this work.

Materials and Methods

Experimental kinetic data were obtained with a laboratory-scale semi-batch reactor by varying the key operational parameters: temperature, gas flow rate and stirring arrangement. The catalyst (Cu-H-Beta-150DP) was placed in a rotating bed. An ozone generator was connected to the reactor vessel via a dispenser. Liquid-phase samples were withdrawn and analyzed with GC, LC-MC and NMR[1].

Results and Discussion

This study presents a new and comprehensive mathematical model describing the degradation of ibuprofen (IBU) and its transformation by-products in aqueous environment utilizing both ozonation and heterogeneously catalyzed ozonation as a semi-batch process. The model incorporates the formation and subsequent degradation of four partially oxidized by-products: 2-OH-IBU, 1-OH-IBU, 1-OXO-IBU, and APMP. The reaction paths are displayed in Figure 1.

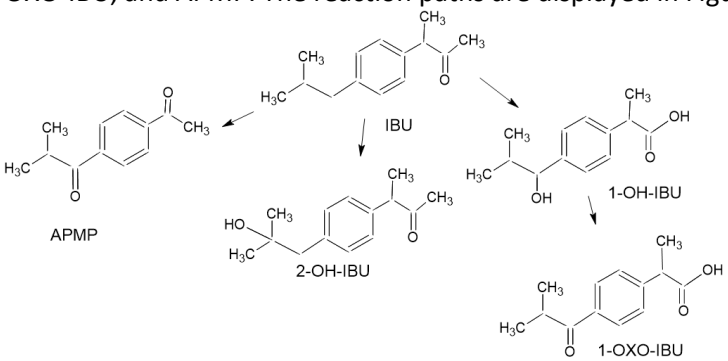

Figure 1. Partially oxidized intermediates of IBU. The intermediates were confirmed by NMR and MS[1].

The reaction mechanism is very complex since it comprises both non-catalytic and catalytic steps. Elementary reaction steps for the degradation of IBU as well as formation and disappearance of the by-products were assumed and rate equations were derived based on the elementary steps and quasi-steady state hypothesis for the radical intermediates. The reaction steps are summarized below.

$$O_3 + H_2O \xrightarrow{k_i} 2HO^\circ + O_2 \quad O_3 + HO^\circ \xrightarrow{k_1} O_2 + HO_2^\circ \quad O_3 + HO_2^\circ \xrightarrow{k_2} 2O_2 + HO^\circ \quad 2HO_2^\circ \xrightarrow{k_T} 2O_2 + H_2O_2$$

$$IBU + OH^\circ \xrightarrow{K_{c1}} 2-OH-IBU + H^\circ \qquad IBU + OH^\circ \xrightarrow{K_{c2}} 1-OH-IBU + H^\circ$$

$$1-OH-IBU \xrightarrow{K_{c3}} 1-OX-IBU + H_2 \qquad IBU \xrightarrow{K_{c4}} APMP \qquad H^\circ + OH^\circ \rightarrow H_2O$$

Besides the kinetics, the gas-liquid mass transfer parameters and experimentally measured gas solubilities were included in the mathematical model. The mass balances, the ordinary differential equations were solved using MATLAB. The kinetic parameters were estimated with non-linear regression analysis. The model predicts accurately the concentrations of IBU and the by-products over time; an example of the model fit to experimental data is shown in Figure 2. This model offers valuable insights into the design and optimization of ozonation processes for the IBU removal from wastewaters, thus enabling an improved treatment efficiency and minimized environmental impact. The concept applied in this work can be expanded to other pharmaceutical molecules.

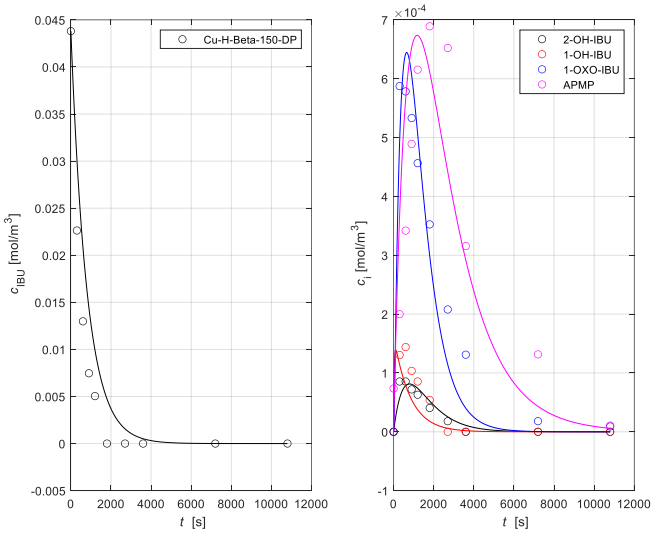

Figure 2. Catalytic ozonation of IBU in the presence of Cu-H-Beta-150-DP and concentrations of by-products formed during the IBU decomposition. Experimental data: symbols, model predictions: continuous lines.

References

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Acknowledgements

The work is a part of the activities of Johan Gadolin Process Chemistry Centre (PCC) at Åbo Akademi. Financial support from Åbo Akademi is gratefully acknowledged (Soudabeh Saeid).