Fate of acetyl salicylic acid, diclofenac, gabapentin and trimethoprim during wet air oxidation

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1. Introduction

To date, advanced oxidation processes (AOPs) are one of the most successful approaches to eliminate contaminants of emerging concern from wastewaters. Among the multiple AOPs developed for such applications thus far, non-catalytic wet air oxidation (WAO) is of interest to remove pharmaceuticals from hospital effluents, one of the major contributors to the presence of pharmaceuticals in the environment. WAO does not need toxic or expensive catalysts and it uses air as oxidant and water in subcritical conditions. A study by Boucher, et al. [1] demonstrated that WAO is able to remove after 15 min of residence time between 95% and 99.1% of several pharmaceuticals in hospital wastewater spiked at 10 μg L^{-1}, even at relatively low chemical oxygen demand (COD) conditions (1400 mg O_2 per L). The potential of WAO for on-site hospital effluent treatment was studied by a techno-economic analysis presented by the same authors. Their analysis showed that operational expenditures of an industrial-scale WAO unit were about $ 27 per m^3 of hospital effluent, and such cost could be further reduced by performing modifications on the unit. However, as other AOPs, WAO also generated transformation products that increased the toxicity of hospital effluents towards two model species *Daphnia magna* (crustacean) and *Aliivibrio fischeri* (bacterium). Therefore, in order to find the toxic transformation products responsible for such increase of toxicity, detailed studies on the fate of pharmaceuticals during WAO treatment are necessary.

The objective of the present study was to perform a comparative survey on targeted and non-targeted transformation products generated by four pharmaceuticals (salicylic acid, diclofenac, gabapentin, and trimethoprim) treated by WAO.

2. Materials and Methods

The Cellule 2646 11000 horizontal batch reactor designed by TOP Industrie, (Vaux-le-Pénil, France) with an internal vessel volume of 150 mL was used. Each pharmaceutical was studied individually by dissolving it in a volume of deionized water inside the WAO reactor to attain a COD of about 600 mg O_2 L^{-1} (acetylsalicylic acid: 375 mg L^{-1}, diclofenac: 376 mg L^{-1}, gabapentin: 279 mg L^{-1}, and trimethoprim 389 mg L^{-1}). After 30 min of mixing inside the reactor (without heating) dissolved oxygen was purged from the solution using nitrogen. Next, the solution was heated to 60 °C and then to 290°C using a 6 °C min^{-1} linear heating ramp which took about 45 min. After this, the temperature was kept at 290°C until the end of the experiment. Previous experiments showed that 290°C was the optimal temperature for pharmaceutical removal [1].

Samples were collected via a sampling valve in the reactor at several stages of the treatment: before heating, at 200°C and at 290°C before addition of air (oxidant) and then at 290°C and 7.5, 15, 30 and 60 min after addition of the oxidant. Quantification of diclofenac, gabapentin and trimethoprim was done by laser diode thermal desorption-triple quadrupole mass spectrometry (LDTD-QqQMS) and for acetylsalicylic acid, gas chromatography-quadrupole mass spectrometry (GC-QMS) was used. Targeted transformation products (small organic acids and other volatile or semi-volatile compounds) were quantified by GC-QMS. Non-targeted transformation products were identified by GC-QMS and liquid chromatography-quadrupole-time-of-flight mass spectrometry (LC-QqTOFMS).

3. Results and discussion

Results showed that all model compounds except trimethoprim were removed chiefly (> 90%) by the initial heating period of the WAO treatment. Addition of oxidant was necessary to remove > 95 % of trimethoprim. For all model compounds, the formation of acetic acid and succinic acid was detected, which is commonly observed during WAO treatment of organic compounds[2]. It should be noted that these same acids were also observed during the treatment of hospital effluents in a previous study[3]. Depending on the molecular structure of the target compound, acetic acid was mostly formed from the first minutes of oxidation at concentrations around 20 to 29 mg L^{-1}, except for acetylsalicylic acid, where acetic acid was formed during heating at a concentration of approximately 200 mg L^{-1} due to deacetylation of the molecule. Acetic acid reached high concentrations and a plateau during oxidation because it is difficult to further oxidize and it is the main transformation product generated by WAO [4, 5]. Succinic acid was the second major transformation product formed, reaching concentrations between 5 and 11 mg L^{-1} after 7.5 min of residence time and then decreasing, except for trimethoprim. The stability of succinic acid concentration and the steady increase of acetic acid in the case of trimethoprim suggest that further transformations still take place, even after 60 minutes, unlike other model compounds. For all compounds except for acetylsalicylic acid, the formation of low concentrations (< 2.5 mg L^{-1}) of glycolic acid was observed but it was rapidly eliminated depending on the treatment time.

For trimethoprim, its elimination took place gradually and ended during oxidation, which may also explain the gradual and slower formation of transformation products. Lactic acid, glycerol and oxalic acid were also observed, during its degradation by WAO unlike other molecules treated. Multiple non-targeted transformation products were also observed for each compound in both GC-QMS and LC-QqTOFMS. In most cases, these transformation products were eliminated after 15 to 30 min of residence time. However, analysis of the theoretical versus experimental COD showed that even after 60 min of residence time, a significant fraction of the residual COD was not identified: 15% (diclofenac), 30% (gabapentin), and 74% (trimethoprim). For acetylsalicylic acid 100% of the residual COD was identified and it was due mostly to the presence of acetic acid.

4. Conclusions

The formation and elimination trends of two major transformation products (acetic acid and succinic acid) appears to be the same for the three compounds that are rapidly eliminated, i.e., gabapentin, diclofenac and acetylsalicylic acid. However, in the case of trimethoprim, which is the compound eliminated the slowest, a shift in the trend was observed in these transformation products, i.e., acids formed later and were eliminated more slowly. Multiple non-targeted transformation products were also formed and were detected in both GC-QMS and LC-QqTOMS except for acetylsalicylic acid for which only small organic acids (≤ 138 Da) were detected by GC-QMS. The more refractory and unidentified compounds (still present after 60 min of residence time) could have an impact on the toxicity of samples treated by WAO as demonstrated in previous studies.

References

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