Removal of pharmaceuticals from drinking water matrix in a flow-through AOPs reactor

Macsek T.[1,2,*], Švestková T.[1,3], Úterský M.[1,2], Landová P.[1,3], Hlavínek P.[1,2] And Vávrová M.[1,3]

[1]AdMas centre, Faculty of Civil Engineering, Brno University of Technology, Purkyňova 651/139, Brno, Czech Republic

[2]Institute of Municipal Water Management, Faculty of Civil Engineering, Brno University of Technology, Veveří 331/95, Brno, Czech Republic

[3]Institute of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, Brno, Czech Republic

*corresponding author:

e-mail:macsek.t@fce.vutbr.cz

Abstract

The paper deals with the first stage of research project aimed at macrolide antibiotics (azithromycin, clarithromycin, erythromycin, roxithromycin), sulfonamides antibiotics (sulfamethazine, sulfamethoxazole, sulfathiazole) and non-steroidal anti-inflammatory drugs (diclofenac, ibuprofen, ketoprofen, naproxen) removal from wastewaters by advanced oxidation processes (AOPs) in flow-through AOPs pilot unit. The study focuses on removal efficiencies of various combinations of advanced oxidation processes (O_3, H_2O_2, UV, O_3/UV, H_2O_2/UV, O_3/H_2O_2) from artificially contaminated drinking water matrix. The study investigates the dependence of removal efficiency on added amount of oxidizing agent(s) in each combination. Combinations that reach the best removal efficiencies will be tested in the second stage of the research project as the tertiary step of treatment at municipal wastewater treatment plant.

Keywords: Advanced oxidation processes, Macrolide and sulfonamides antibiotics, Non-steroidal anti-inflammatory drugs, water matrix

1. Introduction

The appearance of pharmaceuticals in all types of water environment is a current world-wide emerging problem, which causes a potential threat of irreversible changes in the environment. The source of these pollutants is in anthropogenic activities connected with human and veterinary medicine. Un-metabolized or metabolized substances are excreted from human and animal bodies via urine and feces, which enter the environment in wastewaters or via agricultural use – usage of manure and sludge on fields (Santos *et al*., 2009; Kim and Aga, 2007). Conventional wastewater treatment plants are effective at removing organic compounds and nutrients, but insufficient at removing low bio-degradable pharmaceuticals (Klavarioti *et al*., 2009).

In general, pharmaceuticals in wastewater are usually presented in low concentrations from ng/l to µg/l (Aymerich *et al*., 2016). Despite minute amounts in water, these micropollutants are toxic on living organisms (Klavarioti *et al*., 2009; Santos *et al*., 2009), interfere with endogenous hormonal signaling system (Bredhult *et al*., 2007) or cause changes in bacterial DNA (Kim and Aga, 2007).

This study is aimed at removal of sulfonamide and macrolide antibiotics as well as non-steroidal anti-inflammatory drugs by the advanced oxidation processes, which is a promising technology capable of degrading these substances to carbon dioxide and water or at least degrading them to more biodegradable or non-toxic substances (A.R. Ribeiro *et al*., 2015; Klavarioti *et al*., 2009).

1.1. Antibiotics

Antibiotics are one of the most watched micropollutants in a water environment. They present acute and chronic toxicity to aquatic organisms (Santos *et al*., 2009), but the main risk resides in the development of antibiotic-resistant bacteria (ECDC, 2016) that cause death from illnesses, which were previously treated with antibiotics. The study (Everage, 2014) that investigated antibiotic-resistant bacteria E.coli, S. aureus, E. feacalis and E. cloacae, were found in every step of wastewater treatment plant. The study shows that antibiotic resistant bacteria already occur in the sewerage system, WWTP cannot remove the bacteria from wastewaters and antibiotic resistant bacteria are entering the environment via effluent of WWTP.

Our study was focused on removal of wide-spread and wide-used sulfonamide antibiotics - sulfamethazine (SMZ), sulfamethoxazole (SMX), sulfathiazole (STZ) and macrolide antibiotics – azithromycin (AZI), clarithromycin (CLA), erythromycin (ERY), roxithromycin (ROX), which are included in the decision 2015/495/EU as substances potentially posing a significant risk.

1.2. Non-steroidal anti-inflammatory drugs (NSAID)

As representatives of this wide-used group of drugs that are mostly available without prescription, diclofenac (DIC), ibuprofen (IBU), ketoprofen (KET) and naproxen (NAP) were chosen. Studies of toxic effects of these drugs

are briefly summarized in Santos *et al*., 2009. Diclofenac is also classified in the decision 2015/495/EU.

1.3. AOPs

Advanced oxidation processes are based on generating highly reactive and non-selective hydroxyl radical OH• (redox potential 2.8V versus standard hydrogen electrode) to further oxidize contaminants. There are many processes that lead to formation of OH• in an aqueous matrix, of which the most common are: hydrogen peroxide based processes (H_2O_2, H_2O_2+UV, Fenton process, photo-Fenton process), ozone-based processes (O_3, O_3+UV, O_3+H_2O_2), heterogeneous photocatalysis, electrochemical processes and sonolysis (Ghatak, 2014). Despite every process reaching a generation of hydroxyl radical, it is important to evaluate them on treated matrices, due to differences in requirements of usage under various conditions, in order to get the best treatment and economic efficiency (Hernandez, 2002).

This study is aimed at pharmaceutical removal by hydrogen peroxide (H_2O_2, H_2O_2+UV) and ozone based processes (O_3, O_3+UV, O_3+H_2O_2) excluding Fenton and photo-Fenton processes, due to its drawbacks, especially the necessity of low pH (2-4) in matrices (Oturan and Aaron, 2014), which the authors of this study consider as the impenetrable economical barrier in treating of communal wastewaters. The OH• generation mechanisms of selected processes are well described in Ghatak, 2014; Hernandez, 2002; Oturan and Aaron, 2014; Peyton, 1988.

2. Materials and methods

2.1. Chemicals and materials

Regarding optimization method for determination of our target compounds, high purity grade pharmaceuticals standards were used. The solvents, HPLC grade methanol, acetonitrile (both J. T. Baker), Milli-Q water (Millipore QGARD, Academic, Germany), nitrogen for drying (4.7, SIAD Czech spol. s r.o.), helium (6.0, Linde, gas a. s.), formic acid (≥ 98 %, Sigma-Aldrich). The cartridges used for solid phase extraction were Supelco HLB (200 mg, 6mL).

All experiments were conducted with artificially contaminated water. This water was prepared by dissolution of commercially used drug pills which contained target compounds (ibuprofen, naproxen, azithromycin) or analytical standards (diclofenac, ketoprofen, sulfamethazine, sulfamethoxazole, sulfathiazole, clarithromycin, erythromycin and roxithromycin) in drinking water in concentrations ranging from ng/L to ug/L similar to real wastewaters.

2.2 AOPs pilot unit

A flow-through prototype unit for advanced oxidation processes studies, illustrated in Fig.1, was used for all conducted experiments during this study. The unit contains ozone generator (WEDECO EFFIZONE GSO 10) generating max. 30g O_3/h with ozone analyzer (WEDECO MC 400plus), hydrogen peroxide dosing pump (GrundfosAlldos DDA 7.5-16) and a pair of UV reactors with single LP UV-C lamp (WEDECO AQUADA Proxima 7, 80W). In addition, the prototype is equipped with flow measuring (Sika VVX 25) at the inlet, ozone injector, static mixing after ozone and hydrogen peroxide dosage.

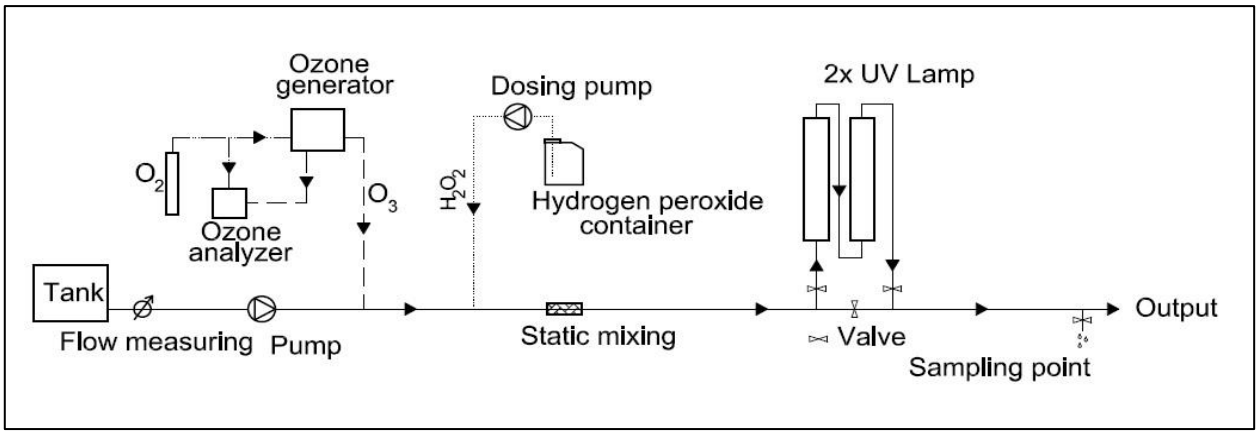

Figure 1. Scheme of pilot unit for advanced oxidation processes studies

2.3 Experimental procedure

Raw water (a mixture of drinking water and added chemicals; pH=7) was pumped from accumulation tank to the system in constant flow 3.024 m^3/h troughs pipes with inner diameter 25 mm. This created turbulent flow (Reynolds number approx. 36 000) and the mixture was permanently mixed not only in static mixer, but also in the pipes. In this study, following AOPs combinations were tested: O_3, H_2O_2, O_3 + UV, H_2O_2 + UV, O_3 + H_2O_2. Every combination was also tested with different concentration of oxidants (O_3, H_2O_2) to determine the dosage required for satisfactory micropollutant removal. Samples were taken at the outlet from the unit.

2.4 Analytical methods

Raw water was sampled as grab samples to 1 L dark, glass bottles. Once prepared, the collected samples were kept at

4 °C until arrival to the laboratory and processed within 24 h.

Target compounds were extracted from raw water samples by solid-phase extraction (SPE) (Supel^{TM}-Select HLB, 200 mg, 6 mL, Supelco, Sigma-Aldrich) using a Baker vacuum system (J.T. Baker, Deventer, The Netherlands).

Final analysis, identification and quantification, was done by high-performance liquid chromatography with DAD detector and mass spectrometry detector with ion trap analyzer and electrospray ionization (HPLC-DAD-MS; HPLC Agilent 1100 Series; Mass spectrometer Agilent 6320 Series, Ion Trap LC/MS).

3. Results and discussion

Experiments showed that ozone based processes were more effective for degradation of studied micropollutants than hydrogen peroxide processes. A simple ozonation (Fig. 2) was able to remove all ERY, AZI, CLA, ROX, STZ, SMX, NAP at very low concentration of ozone (0.024 mmol/L). On the other side, IBU and KET removal is just slightly increasing with O_3 dosage and the removal is approximately 83% at 0.116 mmol O_3/L. The addition of hydrogen peroxide in ratio H_2O_2/O_3 = 0.5 (Fig. 3) increased removal of SMZ, IBU by 9% in average, KET 12% in average. Experiment with ozonation combined with UV did not show any significant improvement in removal compared to the simple ozonation (except KET due to UV-C absorption).

On the other hand, hydrogen peroxide processes showed unsatisfactory removal effect. Almost no removal of studied micropollutants was observed, when only H_2O_2 was dosed in the range of 0.5 – 3.03 mmol/L. The significant removal effect occurred, when combination H_2O_2/UV-C (Fig. 4) was used. Removal of sulfonamides antibiotics was observed above 70%, KET and DIC above 80%, besides macrolide antibiotics removal rate was only 50% at H_2O_2concentration 3.03 mmol/L.

In addition, similar removal trends were observed across each pharmaceutical group. It was noticed that all studied macrolide antibiotics have similar removal trend and rate in each combination of AOPs. On the other side, in both sulfonamides antibiotic and NSAID group, there is a representative drug whose removal efficiencies are always the lowest in their pharmaceutical group i.e. SMZ in sulfonamides antibiotics group and IBU in NSAID group. This fact is worthy of further study due to the possibility of using these substances as markers of removal efficiencies to reduce the number of analyzed substances to reduce costs during long-term experiments.

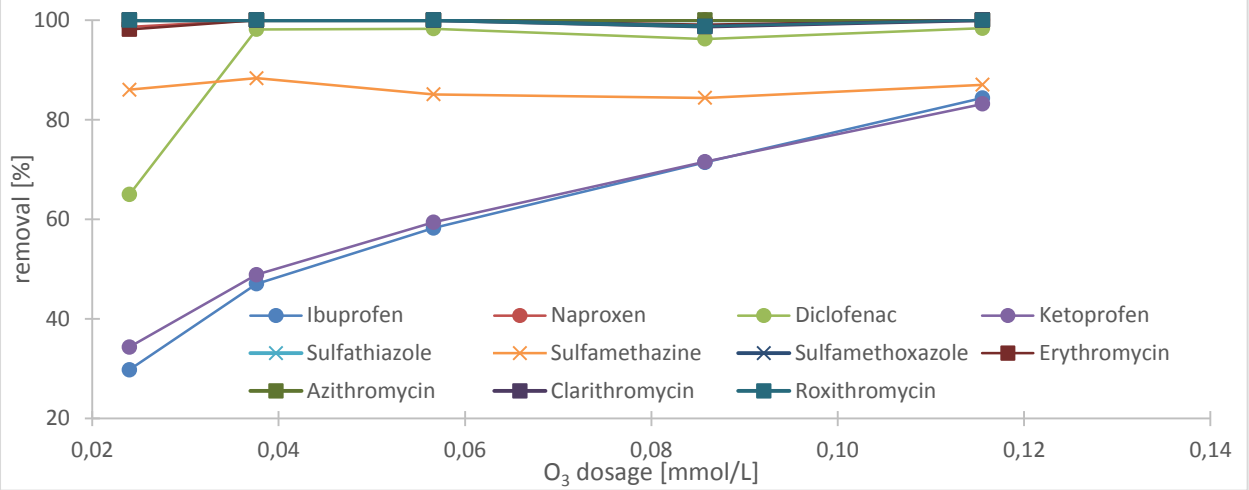

Figure 2. Removal of studied pollutants by simple ozonation

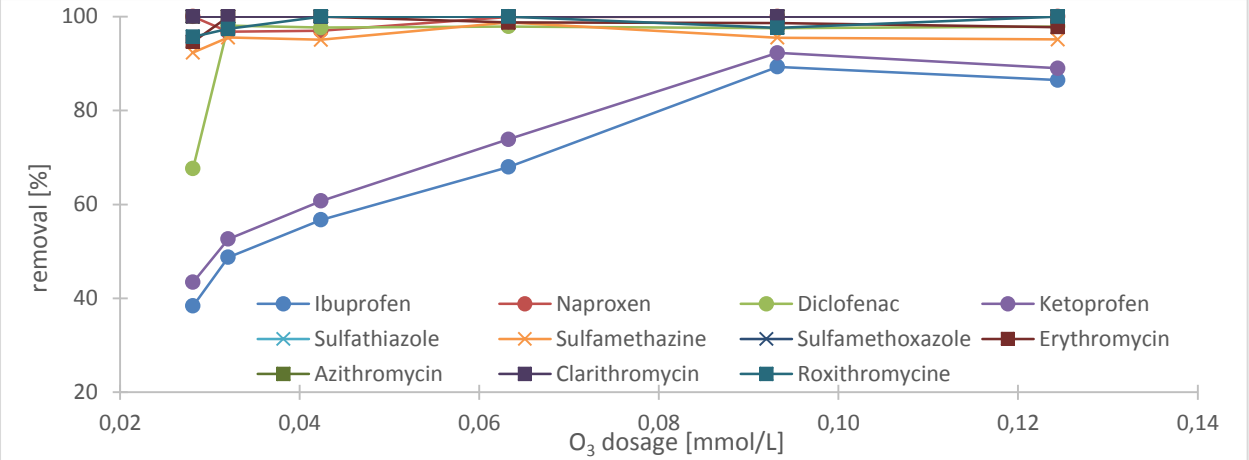

Figure 3. Removal of studied pollutants by ozonation combined with H_2O_2

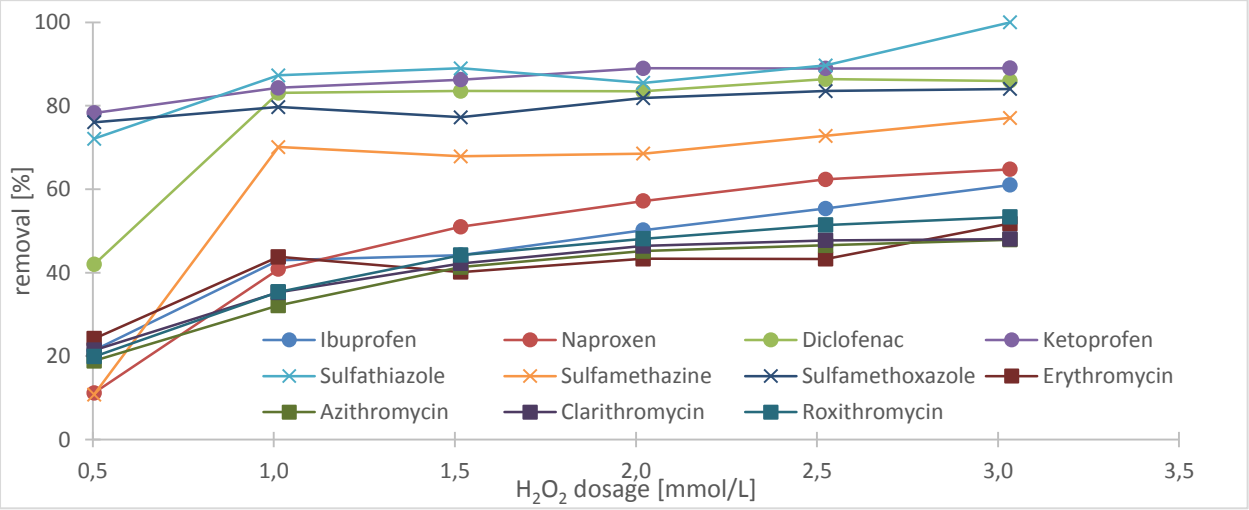

Figure 4. Removal of studied pollutants by dosing hydrogen peroxide combined with UV-C

4. Summary and conclusions

As results show, sufficient removal rate of studied pollutants was reached only by using ozone based processes. Hydrogen peroxide processes at 24 times higher dosage of H_2O_2 against O_3 have not reached comparable results. From tested combinations of oxidation processes, the H_2O_2/O_3 combination was the most efficient at removing of studied pollutants, where removal rate of all pollutants was above 90% and most of them were removed completely.

5. Acknowledgements

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