FATE OF SELECTED EMERGING POLLUTANTS AND FORMATION OF TRANSFORMATION PRODUCTS IN ACTIVATED SLUDGE BATCH REACTORS UNDER AEROBIC/ANOXIC/ANAEROBIC CONDITIONS

PSOMA A.K.[1], ATTITI S.[1], ARVANITI O.[2], STASINAKIS A.S.[2] and THOMAIDIS N.S.[1]

[1]National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Analytical Chemistry, Panepistimiopolis Zografou, 15771 Athens, Greece, [2]Water and Air Quality Laboratory, Department of Environment, University of the Aegean, University Hill, Mytilene 81100, Greece.
Email: ntho@chem.uoa.gr

The removal of emerging pollutants during secondary biological treatment due to biosorption and biotransformation is a challenge that current environmental chemists and engineers are facing. In a recent study conducted in the WWTP of Athens, several pharmaceuticals, like diuretics (furosemide, hydrochlorothiazide), antiepileptic drugs (topiramate), opiates (tramadol), psychotropic drugs (citalopram, lidocaine, ephedrine), anti-ulcear drugs (ranitidine), antidiabetics (metformin) and artificial sweeteners (cyclamate) were detected at high concentrations in both influent and effluent samples [1, 2, 3].

As some micropollutants may be more degradable under anoxic/anaerobic than under aerobic conditions and vice versa [4], the aim of this study was to evaluate the parameters for efficient removal of the above mentioned micropollutants in activated sludge bioreactors under aerobic, anoxic and anaerobic conditions. The role of nitrates on biodegradation of target compounds were investigated as well as half-life values and first order kinetics were calculated. The formation of transformation products (TPs) were studied using reverse phase liquid chromatography quadrupole-time-of-flight mass spectrometry (LC-QToF-MS). Hydrophilic interactions liquid chromatography (HILIC) was used complementarily, as many polar TPs presented higher sensitivity and clearer MS/MS spectra under HILIC conditions.

Experiments were conducted in stoppered glass bottles that were constantly agitated on a shaking plate. The working volume in each reactor was 0.2 L and the mixed liquor suspended solids (MLSS) concentration was (2000 ± 100) mg L^{-1}. In aerobic experiments, dissolved oxygen concentrations higher than 4 mg L^{-1} were achieved by using aeration through porous ceramic diffusers. In anoxic experiments, the reactors were initially purged with N_2 gas and a solution of $NaNO_3$ was added to provide an initial concentration of NO_3-N equal to 40 mg L^{-1}.

Removals due to biotransformation were differentiated according to the parent compound and oxygen availability. Under aerobic conditions, ranitidine, citalopram, ephedrine, metformin and tramadol were completely removed. Biodegradation was suppressed by the absence of oxygen and lower removal rates were occurred for the majority of the compounds during anoxic experiments. Topiramate and hydrochlorthiazide did not show any removal under anoxic conditions, while metformin presented the same biotransformation rate under both aerobic and anoxic conditions. Under anaerobic conditions, only ranitidine was almost completely removed (90% after 12 days), compared to the majority of the other compounds that presented poor biotransformation (up to 30% after 12 days) or no removal (furosemide). Several transformation products were identified for the target pharmaceuticals, mainly under aerobic conditions, followed by anoxic conditions. As anaerobic biotransformation did not occur in great extent, only few TPs were identified for ranitidine and citalopram under these conditions.

Keywords: transformation products; HRMS; emerging pollutants; activated sludge; aerobic/anoxic/anaerobic conditions

ACKNOWLEDGMENTS

This research has been co-financed by the European Union and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – ARISTEIA 624 (TREMEPOL project).

REFERENCES

1. Borova V., Maragou E., Gago-Ferrero P., Pistos C. and Thomaidis N.S. (2014), Highly sensitivity determination of 68 psychoactive pharmaceuticals, illicit drugs and related human metabolites in wastewater by liquid chromatography – tandem mass spectrometry, Anal. Bioanal. Chem., **406**, 4273–4285.
2. Thomaidi V.S.,.Stasinakis A.S,.Borova V.L and Thomaidis N.S. (2015), Is there a risk for the aquatic environment due to the existenc eof emerging organic contaminants in treated domestic wastewater ? Greece as a case-study, J. Hazard. Mater., **283**, 740–747.
3. Kokotou M., and Thomaidis N.S. (2013), Determination of Eight Artificial Sweeteners in Wastewater by Hydrophilic Interaction Liquid Chromatography - tandem Mass Spectrometry, Anal. Methods, **5**, 3825-3833.
4. Petrovic M., Barcelo D. and Pérez S (2013), Comprehensive analytical chemistry- analysis, removal, effects and risk of pharmaceuticals in the water cycle occurrence and transformation in the environment, **62**, 2-734, ISBN: 978-0-444-62657-8.