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ROZPRAWA DOKTORSKA

Porównanie efektywności wybranych procesów fizykochemicznych w aspekcie usuwania estrogenów i ksenoestrogenów z oczyszczonych ścieków komunalnych

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SUMMARY

The presence of organic micropollutants, especially the compounds interfering hormonal processes in surface waters is a potential threat to the health and life of organisms, including humans. Dangerous biological activity of these compounds (including toxicity) and high resistance to biodegradation creates a need for research on their removal in an unconventional water and wastewater treatment processes. Advanced oxidation processes and pressure membrane techniques are considered as an effective method of eliminating micropollutants because their effectiveness is not affected by toxic nature of the removing compounds, as it is in case of biological methods.

The aim of this study was to compare the effectiveness of selected physicochemical processes (advanced oxidation processes and membrane processes ie. ultra- and nanofiltration) in terms of removal of estrogens (17β-estradiol, 17α-ethinylestradiol) and xenoestrogens (bisphenol A) from model and actual treated municipal wastewater. Deionized water solution with the addition of testing compounds was used as a comparative matrix. Oxidation processes (photolysis, photolysis-ozonation, photocatalysis and photocatalysis assisted with activated carbon) was carried out in a batch reactor. Membrane filtration was carried out in the dead-end system using commercial flat membranes used for ultrafiltration and nanofiltration. During ultrafiltration process there were also used own membranes modified with nanomaterials. Solutions were characterized in terms of the toxicological potential using three tests ie. an enzymatic Microtox®, survival Daphtoxit F® and growth Lemna minor.

The effectiveness of decomposition of micropollutants during ozonation and photolysis dependent on both the operational conditions of the process (ozonation - the dose of ozone from 1 to 10 mg/dm^3, the reaction time from 1 to 10 min, and pH value in the range from 4 to 9, photolysis - exposure time from 0 to 30 min), the kind of the compound (bisphenol A, 17β-estradiol, 17α-ethinylestradiol) and also the aqueous matrix solution (deionized water, model and real outflow). It was determined that for the tested estrogen (17β-estradiol and 17α-ethinylestradiol) the use of both processes UV and UV/O_3 (ozone dose of 3 mg/dm^3) allowed for a similar degree of decomposition. However, in case of need to eliminate the micropollutants less susceptible to degradation such as bisphenol A, preferred was to use complex systems (UV/O_3). Decomposition of xenoestrogen during actual outflow treatment when using UV/O_3system exceeded 90%. To achieve high decomposition efficiency

of bisphenol A in case of a single exposure process it was necessary to apply a long time irradiating. In turn, reduction of the tested compound concentration during ozonation process is clearly dependent on the applied dose of an oxidant.

Comparing the process of eliminating micropollutants during photocatalysis process (with TiO_2 at a concentration of 100 mg/dm^3) operated with and without the addition of activated carbon (dose of 1-20 mg/dm^3) determined that it is preferable to operate the process with the addition of the adsorbent. Effectiveness of a single photocatalytic process depend on a plenty of factors (time of the process, treated matrix type) and the physicochemical properties of micropollutants. Furthermore, it was also shown that the dose of active carbon should be selected empirically. Too small dose of active carbon is not allowed to achieve synergies and too much interfere with the process of purification.

Based on the study it has been determined that the degree of decomposition of the tested compounds were higher in case of the actual outflow (characterized by the highest concentration of contaminations) than it has been shown for the solution of deionized water and model outflow in each implemented advanced oxidation process. Probably this was related to the photosensitizers presence in the actual outflow of wastewater, which supported the process of decomposition of micropollutants.

Furthermore, it was found that the elimination of micropollutants during pressure membrane processes depend on the type of process (ultrafiltration - ΔP of 2.0 to 0.1 MPa, nanofiltration - ΔP = 2.0 MPa), but the more effective was the nanofiltration process. In the study the possibility to create a ultrafiltration membrane has been documented (membranogenic material polyethersulfone PES modified with a mixture of carbon nanotube SWCNT and MWCNT-COOH) with separation properties similar to nanofiltration membrane. It was also found that during both membrane processes the adverse membrane fouling phenomenon paradoxically increases retention of micropollutants.

In the last stage of the study it was shown that the toxicity of post-process solutions depend on the type or configuration of oxidation processes (UV, UV/O_3, UV/TiO_2 and UV/TiO_2-AC). There were also observed different sensitivities of indicator organisms in this field. However, in any of the tested oxidation processes the toxic by-products were generated.