

ABSTRACT

The presence of pharmaceuticals and phthalates has been confirmed in the surface waters, soils, sediments and other components of the natural environment. Classic wastewater treatment plants (WWTPs) are not designed for removing them, therefore WWTPs are a source of secondary pollution of the environment with pharmaceuticals and phthalates. Accidents are a special case, during which pollutants are released into the environment in an uncontrolled manner without neutralizing them.

The presented doctoral dissertation was prepared on the basis of two overarching research objectives, which were: the analysis of the possibility of using constructed wetlands to remove pharmaceuticals and phthalates in municipal wastewater treatment plants and the assessment of the degree of contamination of the Vistula with pharmaceutical residues and phthalates after the emergency sewage discharges as a result of the damage to transmission systems which took place in 2019 and 2020 at the Wastewater Treatment Plant "Czajka".

In order to realize the first of the goals, a municipal wastewater treatment plant in Sochaczew was selected, which has been successfully using constructed wetland for 2^o of sewage treatment (biological treatment sector) for the removal of biogens for years, while the effectiveness of using this system for the elimination of pharmaceuticals and phthalates has not been known. Firstly, a method for the determination of pharmaceuticals in plant material was developed using the ASE-SPE-GC-MS(SIM) technique, while the determination of analytes in wastewater was carried out using the SPE-GC-MS(SIM) method. Regarding the phthalates, it proved effective to apply the combined UAE-SPE extraction technique and gas chromatography together with mass spectrometry for the analysis of these compounds in macrophytic plants (UAE-SPE-GC-MS(SIM) method). For the determination of phthalates in wastewater samples, a method based on SPE and GC-MS(SIM) was proposed.

The conducted research proved that the combination of a classic wastewater treatment system with a constructed wetland allows the elimination of some pharmaceuticals from the wastewater stream with an efficiency sometimes reaching almost 100%. Similar

conclusions were drawn with regard to phthalates, because some of them were removed with the efficiency of 70 - 98% in the tested system.

The developed methods were also used to achieve the second research goal. It has been shown that the accident at the Wastewater Treatment Plant "Czajka", which took place in 2019, led to the release of significant amounts of ibuprofen, naproxen, paracetamol and diclofenac to the waters of the Vistula River. The phenomenon of deposition of diclofenac in the river bottom sediments was also observed, and its concentration was maintained at a high level even 48 days after the accident.

The failure of the same treatment plant in 2020 was one of the largest failures of its kind in the world. The leaking sewage introduced significant amounts of phthalates into the Vistula River, for example the concentrations of two of them (DOP, DEHP) on the 22nd day of the accident were above 100,000 ng/L. The ability of these compounds to migrate to sediments was also observed. The concentrations of DMP, DEP, DBP, BBP, and DOP observed 36 days after the failure were higher than in the previous days. This phenomenon may significantly affect the content of phthalates in water and cause secondary pollution of the aquatic environment.

The conducted research proved that the combination of classic wastewater treatment systems with relatively cheap and simple technologies of constructed wetlands allows to increase the efficiency of removing pharmaceuticals and phthalates in municipal wastewater treatment plants. In turn, the analysis of the degree of contamination of the Vistula with pharmaceutical residues and phthalates after emergency wastewater discharges in 2019 and 2020 at the "Czajka" Sewage Treatment Plant conducted for the first time for this type of event, provided reliable data on the scale of the threat and the negative impact of untreated wastewater on the natural environment.

Keywords: constructed wetland, municipal wastewater treatment plants, pharmaceuticals, phthalates, macrophytes, assisting the removal process, wastewater treatment plant failure