Photodegradation of doxazosin under simulated conditions and products identification

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The group of new pollutants, so called emerging pollutants, includes diverse groups of pharmaceuticals and pharmaceutical active substances used in human and veterinary medicine (such as painkillers, antibiotics, hormones, anti-inflammatory drugs, lipid regulators, beta bolckers, anti-cancer drugs) and personal care products. Continuous release of pharmaceuticals to the environment as complex mixtures can result in higher concentrations, long-term and negative effects on aquatic and terrestrial organisms. For these reasons biological, physical and chemical methods have been developed for removal of pharmaceuticals from aqueous solution.

Doxazosin, a selective alpha blocker, is widely used in medical therapy as an effective antihypertensive agent. It is very frequently prescribed drug and for this reason, environmental and ecotoxicological research is of great importance in terms of exposure and risk for both aquatic species and humans. In this study we focused on photolytic and TiO2 photocatalytic degradation processes of doxazosin under different simulated conditions, with the emphasis on identification of degradation products.

TiO2 photocatalytic and photolytic (without TiO2) experiments were performed in photoreactor equipped with polychromatic low-pressure mercury lamps (1.6 mW/cm2 of UVA (300 - 400 nm)) as well as with UVC gemicidal lamps (254 nm). In the case of photolytic experiments, doxazosin aqueous solution was irradiated for 120 min in the presence and absenсe of oxygen, while photocatalytic degradation of doxazosin aqueous solution have been carried out under constant oxygen flow. Selected samples have been further concentrated for analysis. LC-MS/MS was conducted using a high-resolution quadrupole-time-of-flight mass spectrometer TripleTOF 5600+ (Sciex, Canada). The separation of products was aсhieved by reversed phase liquid chromatography in a gradient elution mode. Ionization was carried out in the positive electrospray mode with further detection by Information Dependent Acquisition (IDA) scanning. This approach allowed observing the formation of several major degradation products depending on the reaction conditions (presence or absence of oxygen, photocatalysis). Based on the exact masses, isotopic distribution, fragmentation pathways, and elemental compositions of the ions in the mass spectrum, the transformation products were identified. Among them, C17H21N5O3 and C17H23N5O4 (cleavage of the dioxane cycle), C23H27N5O5 (hydrogenation of the benzene ring), and C23H25N5O7 (hydroxylation) are dominated. The detailed degradation pathway has been proposed.