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UVA or UVC Activation of H_2O_2 and $S_2O_8^{2-}$ for Estrogen Degradation towards an Application in Rural Wastewater Treatment Plant

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Abstract : The presence of micropollutants in surface waters has been widely reported around the world, particularly downstream from wastewater treatment plants (WWTPs). Rural WWTPs constitute more than 90 % of the total WWTPs in France. Like conventional ones, they are not able to fully remove micropollutants. Estrogens are excreted by human beings every day and several studies have highlighted their endocrine disruption properties on river wildlife. They are mainly estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). Rural WWTPs require cheap and robust tertiary processes. UVC activation of H_2O_2 for HO· generation, a very reactive molecule, has demonstrated its effectiveness. However, UVC rays are dangerous to manipulate and energy-consuming. This is why the ability of UVA rays was investigated in this study. Moreover, the use of $S_2O_8^{2-}$ for SO_4·- generation as an alternative to HO· has emerged in the last few years. Such processes have been widely studied on a lab scale. However, pilot-scale works constitute fewer studies. This study was carried out on a 20-L pilot composed of a 1.12-L UV reactor equipped with a polychromatic UVA lamp or a monochromatic (254 nm) UVC lamp fed in recirculation. Degradation rates of a mixture of spiked E1, E2 and EE2 (5 µM each) were followed by HPLC-UV. Results are expressed in UV dose (mJ.cm-2) received by the compounds of interest to compare UVC and UVA. In every system, estrogen degradation rates followed pseudo-first-order rates. First, experiments were carried out in tap water. All estrogens underwent photolysis under UVC rays, although E1 photolysis is higher. However, only very weak photolysis was observed under UVA rays. Preliminary studies on both oxidants have shown that $S_2O_8^{2-}$ photolysis constants are higher than H_2O_2 under both UVA and UVC rays. Therefore, estrogen degradation rates are about ten times higher in the presence of 1 mM of $S_2O_8^{2-}$ than with one mM of H_2O_2 under both radiations. In the same conditions, the mixture of interest required about 40 times higher UV dose when using UVA rays compared to UVC. However, the UVA/$S_2O_8^{2-}$ system only requires four times more UV dose than the conventional UVC/H_2O_2 system. Further studies were carried out in WWTP effluent with the UVC lamp. When comparing these results to the tap water ones, estrogen degradation rates were more inhibited in the $S_2O_8^{2-}$ system than with H_2O_2. It seems that SO_4·- undergo higher quenching by a real effluent than HO·. Preliminary experiments have shown that natural organic matter is mainly responsible for the radical quenching and that HO and SO_4 both had similar second-order reaction rate constants with dissolved organic matter. However, E1, E2 and EE2 second-order reaction rate constants are about ten times lower with SO_4 than with HO. In conclusion, the UVA/$S_2O_8^{2-}$ system showed encouraging results for the use of UVA rays but further studies in WWTP effluent have to be carried out to confirm this interest. The efficiency of other pollutants in the real matrix also needs to be investigated.

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