INVESTIGATION OF THE EFFECTIVENESS OF THE UV/ClO_2 PROCEDURE FOR THE ELIMINATION OF TRACES OF ORGANIC POLLUTANTS FROM AQUEOUS SOLUTIONS

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The removal of persistent organic pollutants with a biological effect requires the development of a water treatment process that can be used as a supplementary or quaternary process. Most often, chlorine-containing substances, such as HOCl, Cl_2, and less often ClO_2, are used for water disinfection in drinking water production. The combination of chlorination with UV photolysis is called the UV/chlorine process, is one of the Advanced Oxidation Processes (AOPs), and can be used to eliminate trace organic pollutants. The application of ClO_2 is getting more and more attention due to its excellent disinfecting effect, and relatively high oxidation potential. Using ClO_2, the disinfection byproducts (including THMs) formation can be reduced; however, toxic chlorite and chlorate formation and chlorination of organic substances pose a potential risk.
The development of UV-LEDs enables their application in water treatments, especially in the UV/ClO_2 process. The absorption spectra of ClO_2 have a maximum of 359 nm (ε =1250 M^{-1} cm^{-1}). Thus high intensity UV-LED emitting at 367 nm is adequate for the efficient photolysis of ClO_2 to generate radicals. The ClO_2/UV process was investigated in the transformation of two pharmaceuticals, namely trimethoprim (TRIM), an antibiotic, and 5-fluorouracil (5-FU), a chemotherapeutic antimetabolite; both are frequently detected in wastewater and surface waters. The effect of pH (3.0 – 9.0), ClO_2 concentration (up to 14 ppm), and photon flux (4.44×10^{-6}–2.45×10^{-5} $mol_{photon}s^{-1}dm^{-3}$) were studied. ClO_2 was added to the treated solution every 5 minutes until the target substance (1.0×10^{-4} M) was degraded.
The UV radiation decomposes the ClO_2 within 3 minutes, even at the highest 14 ppm dosage and lowest photon flux, and results in a complex radical set in an aqueous solution, including reactive oxygen- (ROS) and chlorine-containing species (RCS), such as $^{\bullet}OH$, $O^{\bullet}$, $O_2^{\bullet-}$, $Cl^{\bullet}$, $ClO^{\bullet}$, and $Cl_2^{\bullet-}$. The UV/ClO_2 method proved to be more effective for TRIM transformation, mainly due to its high reactivity towards RCS. The pH has no effect on ClO_2 transformation but slightly affects the transformation rate 5-FU (pK_a = 8.0), as a consequence of the different reactivity of its protonated and deprotonated forms. The effect of radical scavengers proved that besides ROS and RCS, singlet oxygen ($^1O_2$) has an important role in the transformation.
The ecotoxicity of the treated samples slightly increased, most probably because of the formation of chlorinated organic substances and chlorate ions. Results of AOX and ion chromatography measurements proved the formation of these substances.
Biologically treated domestic wastewater having high Cl^- (120 mg L^{-1}) and HCO_3^- (524 mg L^{-1}) concentration reduced the efficiency of the process for both compounds with different extend. The effect of HCO_3^- is complex, as it changes the pH to 9, and behaves as an RCS scavenger changing the radical set in this way.

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