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COMPARISON OF ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF TRIMETHOPRIM AND 5-FLUOROURACIL

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Abstract

Two pharmaceuticals, trimethoprim (TRIM), an antibiotic, and 5-fluorouracil (5-FU), a widely used cytostatic, were applied as target substances to compare the efficiency of various AOPs, such as UV (254 nm), UV/VUV (254/185 nm) photolysis, ozonation, and O_3/UV process. Opposite that, there is no significant difference between the molar absorbance of target substances; TRIM transformed very slowly, while 5-FU degradation was fast in 254 nm radiated solutions. The low-intensity 185 nm VUV photons highly increased the transformation and mineralization rate of both components. Ozonation was highly effective for eliminating both compounds. However, the mineralization was limited due to the formation products being resistant to ozone. The O_3/UV process primarily increased the mineralization rate, but no significant change in the transformation rates was observed. Comparing the individual methods in terms of energy consumption, the O_3, and O_3/UV combination was the most effective for both compounds. The effect of biologically treated wastewater as a real matrix significantly reduced the transformation rate in the case of UV/VUV photolysis, while the matrix effect was moderated for O_3/UV and negligible or even positive for ozonation.

Introduction

Antibiotics are used in huge amounts against bacterial diseases. Due to their frequent use, primarily in animal husbandry, their large quantities are emitted into the wastewater and finally reach the surface waters and groundwater. Consequently, they appear in drinking water sources. The traditional biological water treatment process is not adequate for their complete elimination; thus, it is crucial to investigate and develop additive water treatment processes that can effectively remove these hazardous contaminations.

TRIM, which has been used since the 1960s, is mainly effective in treating urinary tract infections and, at the same time, in the treatment of otitis media and bacterial diseases [1]. Numerous studies report the occurrence of TRIM in the environment, which is a consequence of its relatively low biodegradability; its presence in raw wastewater has been reported by several countries [2, 3]. 5-FU is one of the most frequently used chemotherapeutic antimetabolite [4, 5]. In wastewaters from hospitals, it can be detected in 10-100 μg L^{-1} concentration.

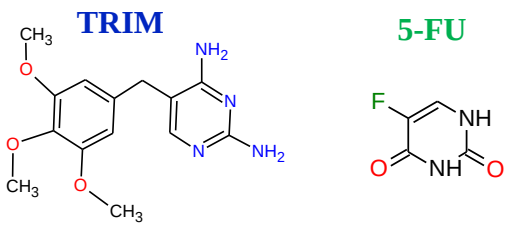

Fig. 1. Chemical structures of TRIM and 5-FU

In this work, the degradability of these two drug substances with different advanced oxidation processes, such as UV (254 nm) photolysis, UV/VUV (254/185 nm) photolysis, ozonation, and O_3/UV combination, was studied. Low-pressure mercury vapor lamps radiating at 254 nm are widely used for disinfection [6]. The same lamp emitting 185 nm VUV photons besides 254 nm UV is used for TOC decrease and produces high-purity water for electronics and pharmaceutical industries. In water and wastewater treatment, ozonation (O_3) is often used as pre- and post-treatment methods [7] and for water disinfection. The efficiency of ozonation is often enhanced by its combination with 254 nm UV radiation due to the increased radical formation rate.

Experimental

Two low-pressure mercury vapor (LPM) lamps were used as light sources. UV lamp emitting at 254 nm (GCL307T5L/CELL, produced by LightTech, having 227 mm arc length) covered by commercial quartz envelope was used for UV photolysis. For UV/VUV photolysis a low-pressure mercury-vapor lamp having the same electric and geometric parameters (GCL307T5VH/CELL produced by LightTech, having 227 mm arc length) was used. The envelope of this lamp was made of synthetic quartz transmitting 185 nm VUV photons besides 254 nm UV light. The UV (254 nm) photon flux was determined by ferrioxalate actinometry and that was the same (3.68×10^{-6} mol_{photon} s^{-1}) for both LPM lamps. The flux of the 185 nm VUV photons was determined by methanol actinometry and found to be 3.23×10^{-7} mol_{photon} s^{-1}. In the case of UV (254 nm), and UV/VUV photolysis, air, oxygen, nitrogen or O_3 containing oxygen was bubbled continuously through the solution. O_3 was produced from O_2 by an Ozomatic Modular 4HC silent electric discharge ozonator. TRIM (Sigma-Aldrich, ≥98.5%) and 5-FU (Sigma-Aldrich, ≥99%) solutions with an initial 1.0×10^{-4} mol L^{-1} solutions were prepared in ultrapure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16), and 500 mL solution was treated in each case.

UV-Vis spectra of the samples were taken with an Agilent 8453 diode array spectrophotometer. Separation of the aromatic components in the treated solutions was performed by Agilent 1100 type HPLC, equipped with a diode array detector (DAD). For the analysis of TRIM and its degradation products, Kinetex 2.6u XB-C18 100A column (Phenomenex) (flow rate 0.75 mL min^{-1}, the mixture of phosphate buffer and acetonitrile 80-20 v/v%), while for the analysis of 5-FU and its products, Aminex (HPX-87H) column was used to separate 5-FU and its degradation products (flow rate 0.8 mL min^{-1}, mobile phase: 0.005 M sulfuric acid) was used. The wavelength of the detection was 285 nm for TRIM and 265 nm for 5-FU. Total organic carbon (TOC) measurements were performed using an Analytik Jena N/C 3100 analyzer. The amount of energy required is a model developed by Bolton [8]. In this work, biologically treated wastewater was used to study the matrix effect. Its parameters are collected in Table 1.

Table 1: Parameters of biologically treated wastewater

pH	7,8
conductivity (µS cm^{-3})	1258
COD (mg dm^{-3})	24,4
NH_4 – N (mg dm^{-3})	<0,4
HCO_3^- – C (mg dm^{-3})	103,4
NO_3^- – N (mg dm^{-3})	3,37
Cl^- (mg dm^{-3})	120
TOC (mg dm^{-3})	6,9

Results and discussion

The efficiency of direct photolysis is determined by the molar absorbance of the target compound at the irradiation wavelength and the value of the quantum yield for its conversion. The difference between the molar absorbance values of the two compounds at 254 nm is negligible: 3650 M^{-1} cm^{-1} for TRIM and 3506 M^{-1} cm^{-1} for 5-FU. However, 5-FU completely converted in 15 minutes (Fig. 2b), less than 20% of TRIM decomposed within 90 min in dissolved O_2 containing solution (Fig. 2a). The low quantum yield of TRIM transformation is most likely due to its intensive fluorescence around 350 nm, in 254 nm irradiated solutions (Fig. 2c). For 5-FU, no fluorescence was observed, which supports that after the absorption of 254 nm photon, a chemical bond cleavage takes place with quantum yield $\Phi = 0.022$. The intensity of fluorescent light decreases by the dissolved O_2 (Fig. 2c), which suggests that the formation of reactive species ($^1O_2$, $O_2^{\bullet-}$ or $CO_3^{2-\bullet}$) may be responsible for the slight increase of the transformation rate.

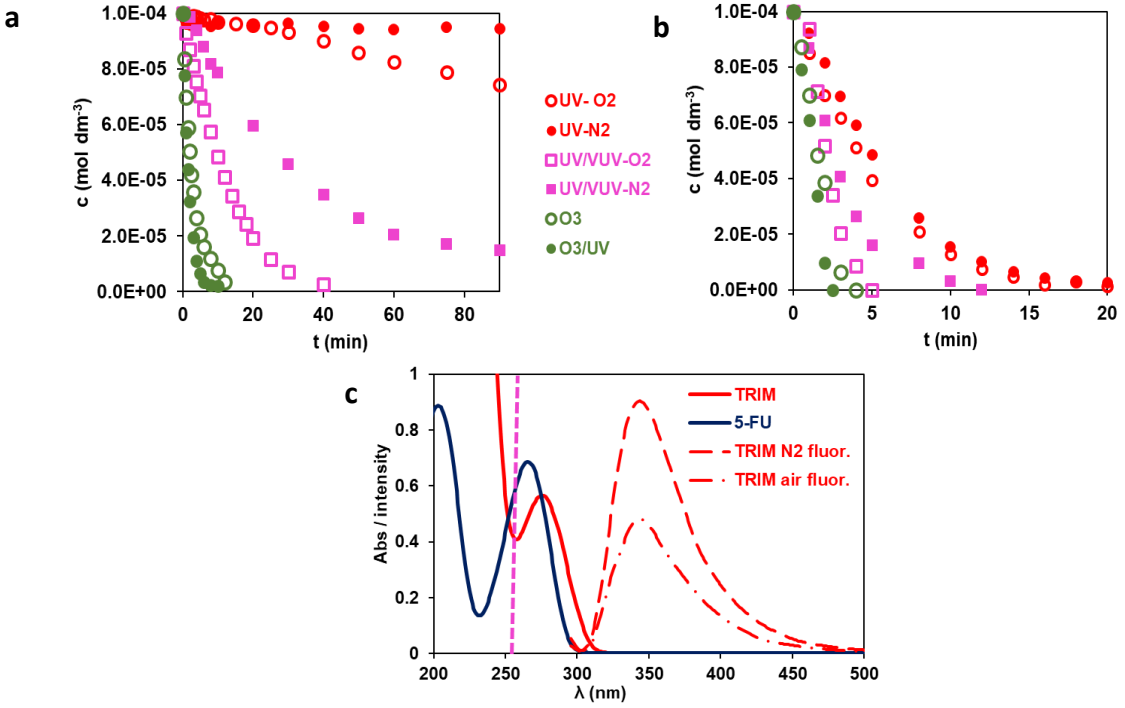

Fig. 2. Kinetics profile of TRIM (a) and 5-FU (b) transformation during UV, UV/VUV, ozonation, and UV/O_3 treatments, absorption spectra, and the effect of O_2 on the emission spectra of TRIM (excitation: 254 nm) (c)

Table 2: Initial transformation rates (r_0), electrical energy per order (E_{EO}), and effect of biologically treated domestic wastewater as matrix on the transformation of TRIM and 5-FU

	r_0^{ref} ($\times 10^{-7}$ M s^{-1})		E_{EO} (kWh m^{-3} $order^{-1}$)		Matrix effect (r_0/r_0^{ref})	
	TRIM	5-FU	TRIM	5-FU	TRIM	5-FU
UV	~0.04	2.00		3.5		
UV/VUV	0.83	3.35	10.6	2.1	0.36	0.42
O_3	4.88	5.75	2.8	0.88	1.47	1.34
O_3/UV	5.28	7.60	2.8	1.4	1.26	0.88

$r_0^{ref.}$: initial transformation rate determined in Milli-Q water; **r_0**: initial transformation rate determined in biologically treated domestic wastewater as matrix

During UV photolysis, the dissolved organic compound absorbs the photons, but the 185 nm VUV photons are adsorbed by water and result in the formation of H• and •OH ($\Phi^{185nm} = 0.33$). The low-intensity 185 nm VUV radiation highly increased the transformation and mineralization rate of both substances, most probably due to the reactions with formed radicals. The effect is much more pronounced for TRIM than for 5-FU because of the relatively high contribution of the UV photolysis to the transformation. A significant effect of dissolved O_2 and 185 nm photons on the absorbance at 257 nm (Fig. 3a and b) indicates that both factors affect the quality and quantity of the aromatic products and are required for efficient mineralization.

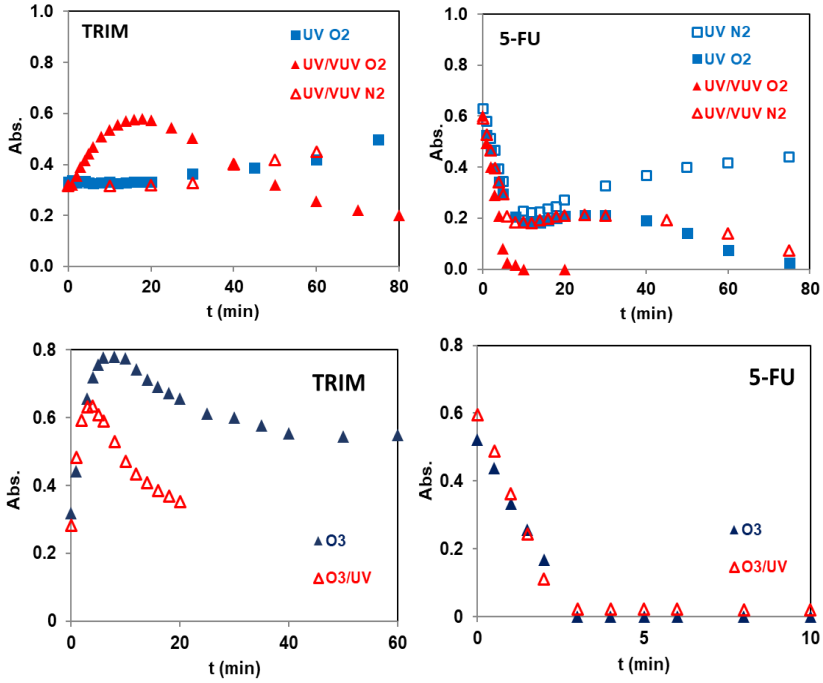

Fig. 3. The absorbance of the treated solutions determined at 257 nm versus time of treatment

Using ozonation, the transformation rate of both components exceeds that determined for UV/VUV photolysis (Fig. 2a,b and Table 2), but ozonation was less effective for mineralization than UV/VUV photolysis (Fig. 4). At the given pH, mainly molecular O_3, a quite selective oxidizing agent reacts with organic substances. Thus, the TOC content remained constant after a fast drop of TOC value; finally, no more than 15% TOC can be removed. In contrast, during UV/VUV photolysis, the decrease in TOC is continuous despite the slower conversion rate. The combination of ozonation and UV photolysis generally enhances efficiency due to non-selective and highly reactive •OH formation via UV photolysis of O_3. The O_3/UV combination did not increase the transformation rate but highly enhanced the mineralization with the formation and transformation of intermediates (Fig. 3).

Regarding energy efficiency (E_{EO}), UV/VUV photolysis, ozonation, and O_3/UV combination proved effective, partly depending on the target compound. In these cases, we also examined the matrix effect using biologically treated domestic wastewater. For UV/VUV photolysis, the matrix decreased the transformation rate, while for ozonation increased that.

The most plausible explanation is that for UV/VUV photolysis, the dominant reaction partner is the non-selective •OH, thus the competition between the matrix components and target substances decreases the transformation rate. While for ozonation matrix components can behave as promotors and enhance the transformation of O_3 and consequently the formation of

reactive oxygen-containing species and transformation of TRIM and 5-FU. In the case of O_3/UV a slightly negative effect for 5-FU degradation was observed since, in this case, both O_3 and radical-based transformation are significant.

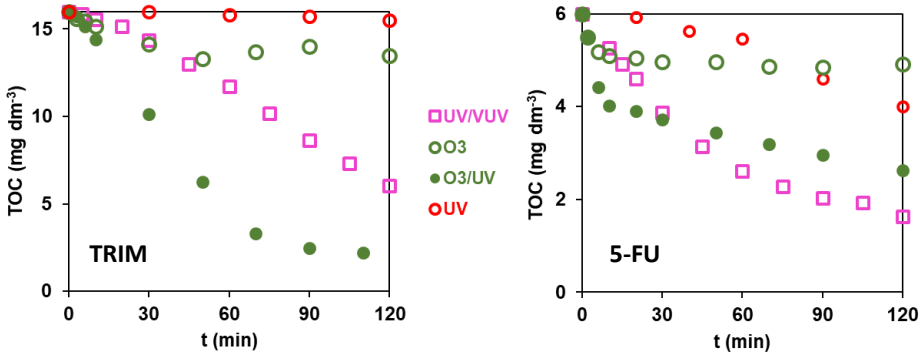

Fig. 4. TOC content versus time of treatment

Conclusion

In the present work, two pharmaceuticals, trimethoprim (TRIM), an antibiotic, and 5-fluorouracil (5-FU), a widely used cytostatic, were applied as target substances to compare the efficiency of various AOPs, such as UV (254 nm), UV/VUV (254/185 nm) photolysis, ozonation, and O_3/UV process. The low-intensity VUV light highly enhanced the transformation and mineralization rates. Ozonation was the most efficient for transforming target substances, but it was pretty inefficient for mineralization. In terms of transformation, mineralization, and electrical energy efficiency, the O_3/UV treatment was the most efficient. Moreover, biologically treated wastewater as a matrix just slightly affected the efficiency of this method, opposite to the UV/VUV photolysis.

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