



Removal of Trimethoprim and 5-Fluorouracil by UV/Persulfate and UV/VUV Persulfate Methods[†]

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Abstract: The UV, UV/VUV photolysis and their combination with persulfate ($S_2O_8^{2-}$) were studied for the elimination of trimethoprim and 5-fluorouracil. Methods were examined in terms of transformation and mineralization rate and the matrix effect. The relative contribution of the direct UV photolysis and radical-based reactions ($\bullet OH$, $SO_4\bullet^-$) were also investigated. Without $S_2O_8^{2-}$, the efficiency of UV/VUV photolysis highly exceeds that of UV photolysis due to the $\bullet OH$ formation, while in the presence of $S_2O_8^{2-}$, the dominant reaction partner is $SO_4\bullet^-$. However, $SO_4\bullet^-$ -based methods proved to be efficient for both transformation and mineralization; they are sensitive for the matrix components.

Keywords: antibiotics; pharmaceuticals; wastewater; persulfate; energy consumption



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1. Introduction

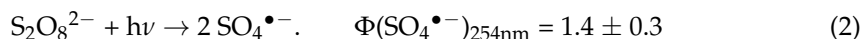
The complete removal of pharmaceutical ingredients from water is one of the most challenging tasks in water purification today. The application of antibiotics remains the primary treatment for bacterial infections for humans and animals. However, the release of pharmaceuticals, especially antibiotics into the environment, has led to the emergence of antibiotic-resistant bacterial strains and created a global health emergency causing at least 700,000 deaths a year. In addition to antibiotics, we must also pay attention to removing other drugs used in large quantities that are difficult to biodegrade. The conventional wastewater treatment renders limited results in pharmaceuticals elimination; thus, additive water treatment processes are required to prevent them exceeding into the environment and decreasing the risk. Advanced oxidation processes (AOPs) are additional water treatment methods that use chemical or photochemical processes to decompose compounds that are not or are only slightly removed by biological water treatment. Most AOPs are based on the highly reactive hydroxyl radical ($HO\bullet$) generation; however, during the last decade, the number of publications relating to the investigation of chlorine species or sulphate radical ion-based processes has been fluently increasing.

The low-pressure mercury vapor (LPM) lamp emitting at 254 nm is a widely used light source for water disinfection, but its effectiveness in eliminating organic pollutants and reducing toxicity is highly limited. The molar absorbance at 254 nm and the quantum yield of the transformation of the target compound determine the efficiency of UV photolysis. The LPM lamps, equipped with special high-purity quartz, emit at 254 and 185 nm and are suitable for high-purity water production due to the $HO\bullet$ via absorption 185 nm VUV light by water:



The efficacy of UV photolysis can be enhanced by using various oxidizing agencies, such as ozone, hydrogen peroxide, or persulfate ion [1]. During persulfate-based processes,

the reaction with sulfate radical ions ($\text{SO}_4^{\bullet-}$) is the primary degradation pathway. Persulfate ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant but can be activated to generate highly reactive $\text{SO}_4^{\bullet-}$ characterized by a higher oxidative potential ($E^0 = 2.6$ V) than that of $\text{S}_2\text{O}_8^{2-}$ ($E^0 = 2.1$ V). The 254 nm UV light-activated persulfate ($\text{S}_2\text{O}_8^{2-}$; $\epsilon_{254\text{ nm}} = 20\text{--}22\text{ M}^{-1}\text{ cm}^{-1}$ [2]) is a clean source for producing $\text{SO}_4^{\bullet-}$ with high quantum yield [2] via the homolytic bond cleavage [3]:



The $\text{SO}_4^{\bullet-}$ is a potent oxidizing agent, similar to the $\text{HO}^{\bullet}$ ($E^0 = 2.8$ V) [3]. The primary reaction mechanism of $\text{SO}_4^{\bullet-}$ initiated transformation of organic substances is the electron transfer opposite to the addition, which is characteristic of $\text{HO}^{\bullet}$ -initiated transformations [4]. Based on the literature so far, the AOP methods based on $\text{SO}_4^{\bullet-}$ are adequate for the degradation and mineralization of organic micropollutants, similar to $\text{HO}^{\bullet}$ -based methods [5,6], especially in the case of the aromatic molecules with an amino group [7]. Comparing the primary reactive radicals, $\text{HO}^{\bullet}$ is less selective and more reactive towards saturated organic substances than $\text{SO}_4^{\bullet-}$. The reaction rate constants of $\text{HO}^{\bullet}$ with TRIM and 5-FU are $7.36 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [8] and $1.52 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [9], respectively, whereas the reaction rate constant with $\text{SO}_4^{\bullet-}$ is only available for TRIM, its value is $3.81 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [10], just slightly lower than with $\text{HO}^{\bullet}$.

This research compares and studies the UV photolysis, UV/VUV photolysis-producing $\text{HO}^{\bullet}$, and their combinations with persulfate to eliminate and mineralize two commonly used pharmaceuticals, namely trimethoprim (TRIM), an antibiotic drug, and the 5-fluorouracil (5-FU), a chemotherapeutic agent. Both selected model components are present in detectable concentrations in urban and hospital wastewater [11,12].

2. Materials and Methods

2.1. Photochemical Experiments

Two low-pressure mercury vapor (LPM^{UV} and LMP^{VUV}) lamps were used as light sources. LPM^{UV} emits 254 nm UV photons (GCL307T5L/CELL, produced by LightTech), while LMP^{VUV} (GCL307T5VH/CELL produced by LightTech) emits both 254 nm UV and 185 nm VUV photons. Both lamps have the same electric (15 W) and geometric (227 mm arc length and 20.5 mm diameter) parameters. The envelope of LMP^{VUV} lamp was made from synthetic quartz to transmit the $\text{VUV}_{185\text{ nm}}$ photons. The UV photon flux was determined by ferrioxalate actinometry and found to be the same ($3.70 \times 10^{-6}\text{ mol}_{\text{photon}}\text{ s}^{-1}$) for both LPM lamps. The flux of the 185 nm VUV photons was determined by methanol actinometry and found to be one magnitude lower; $3.23 \times 10^{-7}\text{ mol}_{\text{photon}}\text{ s}^{-1}$. The experiments were carried out in a 500 mL cylindrical glass reactor with a 45 mm inner diameter and 300 mm height. The thickness of the irradiated water layer was 13 mm, which is enough for the complete absorption of 185 nm photons [13]. The initial concentration of TRIM and 5-FU was $1.0 \times 10^{-4}\text{ M}$ in each case.

2.2. Materials and Methods

The concentration of model compounds was performed by Agilent 1100 HPLC system, equipped with a diode array detector (DAD). For the analysis of TRIM ($\geq 99\%$, Sigma-Aldrich) and its degradation products, Gemini 3u C6-phenyl 110A column was used (thermostated at 40°C). The eluent contains 10% methanol (HPLC grade, VWR) and 90% formate buffer ($\geq 99\%$, Sigma-Aldrich); the flow rate was 0.4 mL min^{-1} . In the case of 5-FU ($\geq 99\%$, Sigma-Aldrich), the eluent consisted of $5.0 \times 10^{-3}\text{ M}$ sulfuric acid (HPLC grade, FLUKA), the flow rate was 0.8 mL min^{-1} . The detection wavelength was 275 nm for TRIM and 210 nm for 5-FU.

Total organic carbon (TOC) measurements were performed using an Analytik Jena N/C 3100 analyzer. For the investigation of matrix effect, biologically treated wastewater was used with high ionic ($c(\text{HCO}_3^-) = 526\text{ mg L}^{-1}$ and $c(\text{Cl}^-) = 120\text{ mg L}^{-1}$) and relatively low organic content ($\text{TOC} = 5\text{--}6\text{ mg L}^{-1}$).

3. Results and Discussion

3.1. UV and UV/VUV Photolysis

The efficiency of direct photolysis is determined by the molar absorbance of the target substance at 254 nm and the quantum efficiency of the transformation. However, the molar absorbances of the model compounds have a similar value ($4045 \text{ M}^{-1} \text{ cm}^{-1}$ for TRIM and $5297 \text{ M}^{-1} \text{ cm}^{-1}$ for 5-FU), the transformation of 5-FU is significantly higher, with no more than 10 minutes required for the complete removal in both O_2 -free and O_2 -containing solutions. There is practically no transformation of TRIM in O_2 -free solution, and its transformation starts with a long induction period in the O_2 -containing one.

The fluorescence behavior of the compounds was investigated using 254 nm as excitation wavelength. For 5-FU, no fluorescence was observed, while TRIM emitted an intensive fluorescent light with a maximum intensity at 340 nm. Thus, a significant part of the absorbed photons results in fluorescent light without chemical transformation. Consequently, the quantum yield related to the TRIM transformation is much lower (<0.002), than to the 5-FU transformation (0.08 and 0.061 in aerated and in O_2 -free solutions, respectively). The dissolved O_2 decreased the intensity of fluorescent light, suggesting that O_2 can quench the excited state of TRIM. The formed singlet oxygen is probably responsible for the positive effect of the dissolved O_2 on the transformation of TRIM in the case of UV photolysis.

In the case of UV/VUV photolysis, the low intensity 185 nm photons highly enhanced the transformation rate of TRIM both in aerated and O_2 -free solutions due to the formation of reactive $\text{H}^\bullet$ and $\text{HO}^\bullet$ (1) but only slightly affected the 5-FU transformation (Figure 1a,b). The manifestation of the degree of the positive effect of VUV photons depends on the relative contribution of direct UV photolysis and radical (mainly $\text{HO}^\bullet$)-based transformation. For 5-FU the contribution of direct UV photolysis remains significant even in the presence of VUV light-generated radicals, while for TRIM, the radical-based transformation became the primary way.

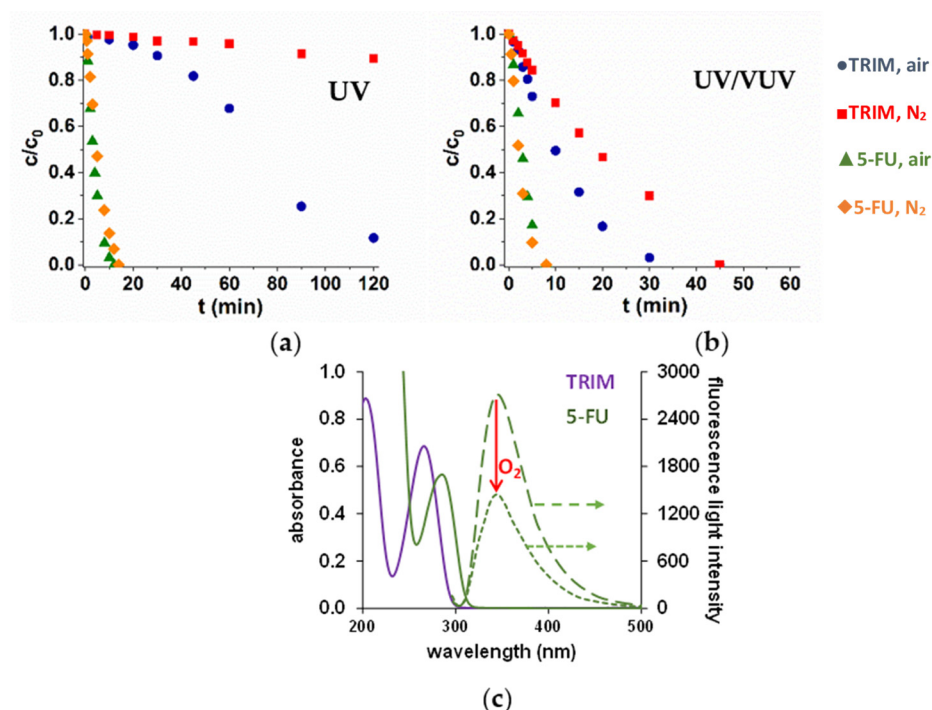


Figure 1. Degradation of TRIM and 5-FU during UV (a) and UV/VUV (b) photolysis and their absorption and emission spectra in O_2 -free and O_2 -containing solutions (c).

The presence of radicals produced by VUV photolysis of water also enhanced the mineralization rate. For TRIM, there is no observable mineralization in UV-radiated solution, while 40% of TOC can be removed for 5-FU (Figure 2). In UV/VUV light-

irradiated O₂-containing solutions about 80% of TOC was removed during 2 h. The results also showed that dissolved O₂ has an essential role in mineralization most probably because of the formation organic peroxy radicals (Figure 2).

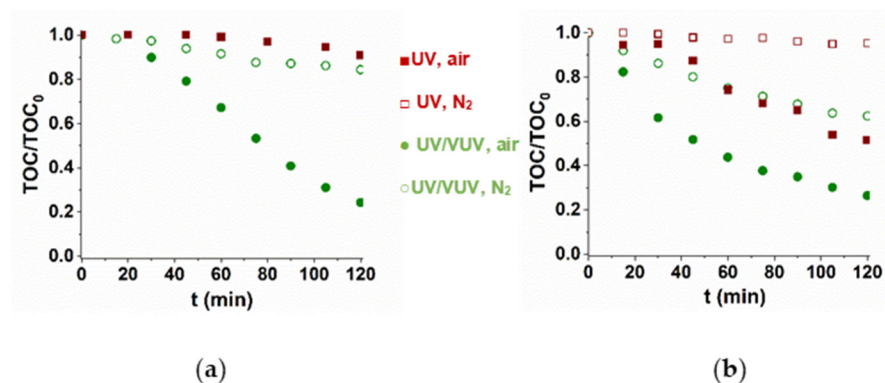


Figure 2. Mineralization of TRIM (a) and 5-FU (b) during UV and UV/VUV photolysis.

3.2. Effect of S₂O₈^{2−}

In the case of both pharmaceuticals and light sources the S₂O₈^{2−} addition enhanced the transformation rate independently on the presence of dissolved O₂, due to the formation of reactive SO₄^{•−} via UV photolysis of S₂O₈^{2−}.

In the case of UV/S₂O₈^{2−} process, the transformation of organic substances can take place via direct UV photolysis or due to the reaction with SO₄^{•−}. For UV/VUV/S₂O₈^{2−}, additionally, the reactions with HO[•] must be taken into consideration. Comparing the molar absorbance of TRIM (4045 M^{−1} cm^{−1}), 5-FU (5297 M^{−1} cm^{−1}), and S₂O₈^{2−} (30 M^{−1} cm^{−1}), the contribution of direct photolysis is likely to remain significant for 5-FU and negligible for TRIM transformation besides SO₄^{•−}- and/or HO[•]-initiated reactions at the given concentrations. Except in the case of UV/S₂O₈^{2−} process for 5-FU elimination, the transformation rate increased linearly with the initial concentration of added S₂O₈^{2−}. In the case of the UV/S₂O₈^{2−} process for the 5-FU elimination, the transformation rate changes exponentially (Figure 3).

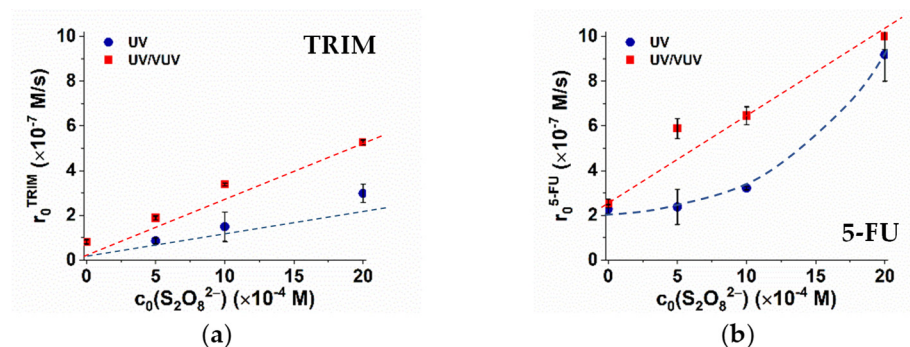


Figure 3. Effect of S₂O₈^{2−} dosage on the degradation of TRIM (a) and 5-FU (b) in the case of UV and UV/VUV photolysis.

For UV/VUV/S₂O₈^{2−}, the transformation rates are higher (approximately doubled) than for the UV/S₂O₈^{2−} process, which suggest that the additive effect due to the VUV light most likely remains important even in the presence of SO₄^{•−} (Table 1). The primary reaction mechanism of SO₄^{•−}-initiated transformation of organic substances (S) is the electron transfer, which results in SO₄[−]. In VUV irradiated solutions, water is the main absorbent because of its high concentration (55 M). However, absorbance of SO₄[−] is not

negligible ($\epsilon_{185\text{nm}} = 160 \text{ M}^{-1} \text{ cm}^{-1}$) and gives a possibility for the VUV photolysis of SO_4^{2-} , regenerating the $\text{SO}_4^{\bullet-}$ [14], with a relatively high quantum yield.

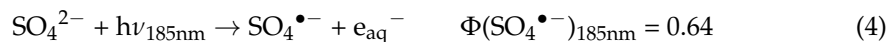


Table 1. The initial transformation rate of TRIM and 5-FU using various processes ($c(\text{S}_2\text{O}_8^{2-}) = 1.0 \times 10^{-3} \text{ M}$).

Process	$r_0 (\times 10^{-7} \text{ M s}^{-1})$	
	TRIM	5-FU
UV/air	–	2.28
UV/N ₂	–	1.54
UV/air/S ₂ O ₈ ^{2−}	1.49	3.22
UV/N ₂ /S ₂ O ₈ ^{2−}	1.39	4.23
UV/VUV/air	0.82	2.53
UV/VUV/N ₂	0.50	3.92
UV/VUV/air/S ₂ O ₈ ^{2−}	3.38	6.45
UV/VUV/N ₂ /S ₂ O ₈ ^{2−}	3.28	7.12

In many cases, the intermediates formed in the transformation of pharmaceuticals still have biological activity, so it is particularly important to study not only the conversion of the parent compound but also its mineralization. The mineralization was investigated with three different $\text{S}_2\text{O}_8^{2-}$ concentrations (Figure 4). Both dissolved O_2 and $\text{S}_2\text{O}_8^{2-}$ enhanced the mineralization rate. The additive positive effect of VUV light is well manifested not only for transformation but also for mineralization efficiency. Using UV radiation, the mineralization rate increased with $\text{S}_2\text{O}_8^{2-}$ concentration, but in UV/VUV irradiated solutions it was practically independent on that. At $1.0 \times 10^{-3} \text{ M}$ $\text{S}_2\text{O}_8^{2-}$ concentrations, using UV radiation, the mineralization efficiency is close to that measured in UV/VUV photolysis.

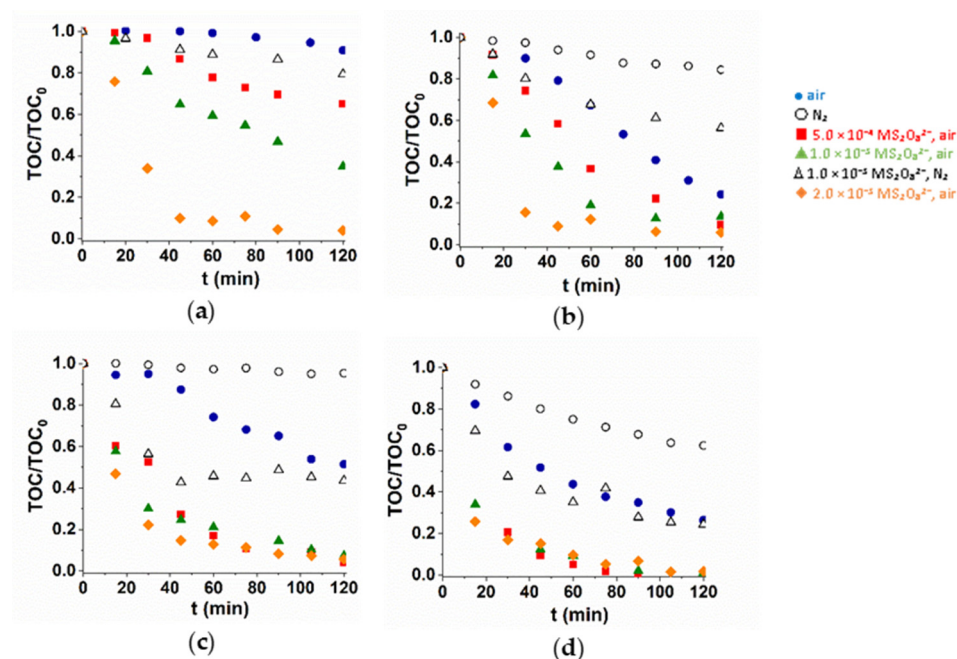


Figure 4. Mineralization of TRIM (a,b) and 5-FU (c,d) during UV (a,c) and UV/VUV photolysis (b,d).

3.3. Radical Scavenger

The role of $\text{HO}^\bullet$ radical was investigated with a commonly used $\text{HO}^\bullet$ scavenger, tert-butanol (t-BuOH). The t-BuOH reacts three orders of magnitude faster with $\text{HO}^\bullet$ ($k_{\text{HO}^\bullet} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [15] than with $\text{SO}_4^{\bullet-}$ ($k_{\text{SO}_4^{\bullet-}} = 4.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [16]. Applying $3.0 \times 10^{-2} \text{ M}$ t-BuOH ensured that 95% of $\text{HO}^\bullet$ and no more than 3% of $\text{SO}_4^{\bullet-}$ reacts with t-BuOH. At first, the effect of radical scavenger was investigated in the case of UV/VUV photolysis and found to be significant for TRIM, while for 5-FU the effect was moderated because of the relatively high contribution of the direct photolysis to the transformation (Table 2). During $\text{S}_2\text{O}_8^{2-}$ -based processes, the t-BuOH just slightly inhibited the transformation, which means that the $\text{SO}_4^{\bullet-}$ is the dominant reaction partner. It also confirmed that, in the presence $\text{S}_2\text{O}_8^{2-}$, the positive effect of VUV is most probably attributable to the regeneration of $\text{SO}_4^{\bullet-}$ (4) and not to the $\text{HO}^\bullet$ formation, opposite to the simple UV/VUV photolysis.

Table 2. Effect of t-BuOH ($3.0 \times 10^{-2} \text{ M}$) on the degradation of TRIM and 5-FU.

	$r_0 (\times 10^{-7} \text{ M/s})$	
	TRIM	5-FU
UV	–	2.28
UV/ $\text{S}_2\text{O}_8^{2-}$	1.49	3.22
UV/ $\text{S}_2\text{O}_8^{2-}$ /tBuOH	1.59	5.40
UV/VUV	0.82	2.53
UV/VUV/tBuOH	0.21	2.18
UV/VUV/ $\text{S}_2\text{O}_8^{2-}$	3.38	6.45
UV/VUV/ $\text{S}_2\text{O}_8^{2-}$ /tBuOH	2.88	5.00

3.4. Matrix Effect

In the development of additive water treatment processes, it is important to examine the effect of matrices and energy consumption because of several practical reasons. In this study, a biologically treated domestic wastewater was used, having low organic content ($5\text{--}6 \text{ mg L}^{-1}$) and relatively high Cl^- ($3.4 \times 10^{-3} \text{ M}$) and HCO_3^- ($8.6 \times 10^{-3} \text{ M}$) concentration.

The biologically treated domestic wastewater has no significant absorbance at 254 nm, thus, it has no effect on the UV photolysis (Figure 5). For UV/VUV photolysis, the organic content and HCO_3^- behaves as an $\text{HO}^\bullet$ scavenger ($k = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, [16]) and inhibits the transformation and mineralization. The effect of Cl^- is not completely clarified. It can react with $\text{HO}^\bullet$ ($k = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, [17]), but several studies described that no significant radical scavenging effect of Cl^- because of the fast backward reaction.

The negative effect of matrix manifested well for UV/ $\text{S}_2\text{O}_8^{2-}$ process (Figure 5). For TRIM, the transformation and mineralization were completely inhibited after a short period, while in MilliQ water, both were extremely fast. For 5-FU in terms of transformation, the effect is moderated, however, mineralization is inhibited similarly to TRIM. For UV/VUV/ $\text{S}_2\text{O}_8^{2-}$ similar trends were observed, but the inhibitory effect of the matrix is less strong than for UV/ $\text{S}_2\text{O}_8^{2-}$.

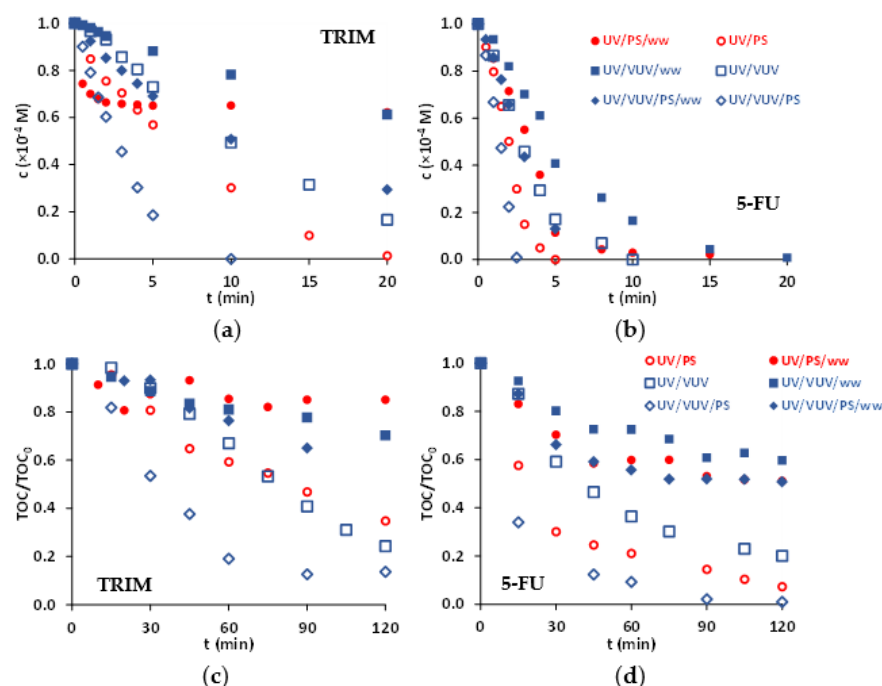
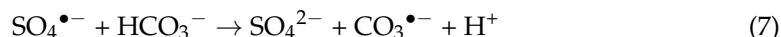


Figure 5. Effect of biologically treated domestic wastewater (ww) as matrix of the transformation (a,b) and mineralization (c,d) of TRIM (a,c) and 5-FU (b,d) ($c(\text{S}_2\text{O}_8^{2-}) = 1.0 \times 10^{-3}$ M).

For $\text{S}_2\text{O}_8^{2-}$ -based processes, the main reaction partner is $\text{SO}_4^{\bullet-}$. The $\text{SO}_4^{\bullet-}$ reacts moderately quickly with both Cl^- ($k = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and HCO_3^- ($k = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) via electron transfer reaction:



The further transformation of $\text{Cl}_2^{\bullet-}$ can finally result in $\text{HO}^{\bullet}$ at a neutral pH from the $\text{Cl}^{\bullet}/\text{Cl}_2^{\bullet-}$ reaction with water. The formed $\text{CO}_3^{\bullet-}$ is a quite selective reactive species, its reaction rate constant with TRIM is $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [18]. By increasing the concentration of persulfate, good efficiency can be obtained even in such a complex matrix, as the biologically treated wastewater. The required PDS concentration is determined by the analytical parameters of the matrix, especially the TOC content and the inorganic ion concentration.

4. Conclusions

In this work, UV (254 nm) and UV/VUV (254 and 185 nm) photolysis was combined with persulfate ($\text{S}_2\text{O}_8^{2-}$) addition. Commonly used drugs, trimethoprim (TRIM) and 5-fluorouracil (5-FU), were used as target substances. Opposite to the similar molar absorbances, UV photolysis was effective only for 5-FU transformation, while the low intensity VUV photons enhanced the transformation and mineralization rates of both components. The addition of $\text{S}_2\text{O}_8^{2-}$ highly enhanced the transformation and mineralization efficiencies and linearly with the $\text{S}_2\text{O}_8^{2-}$ concentration. The effect of t-BuOH as a radical scavenger proved that the main reaction partner the $\text{SO}_4^{\bullet-}$, even in the case of the UV/VUV/ $\text{S}_2\text{O}_8^{2-}$ process. In biologically treated domestic wastewater as a matrix, the efficacy of UV/ $\text{S}_2\text{O}_8^{2-}$ and UV/VUV/ $\text{S}_2\text{O}_8^{2-}$ processes are significantly reduced, partly due to the organic matter and mainly due to the reaction of $\text{SO}_4^{\bullet-}$ with inorganic ions.

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