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Article

A New Mechanism of the Selective Photodegradation of Antibiotics in the Catalytic System Containing TiO_2 and the Inorganic Cations

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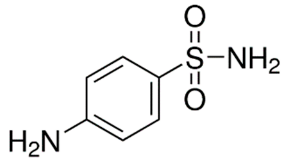
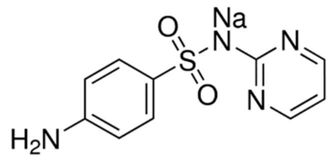
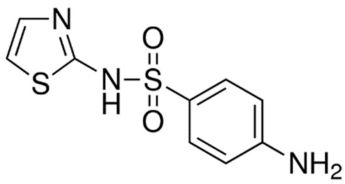
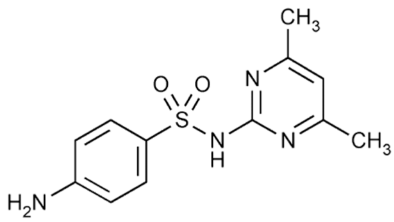
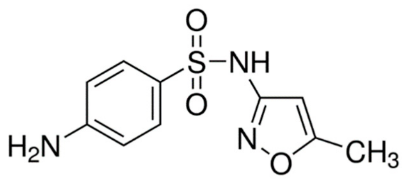
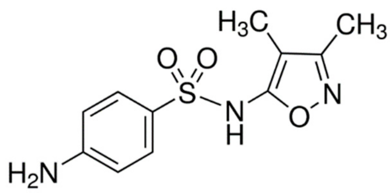
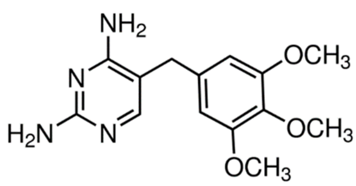
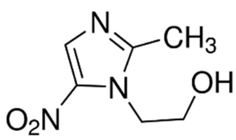
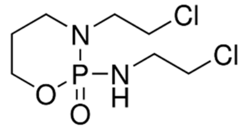
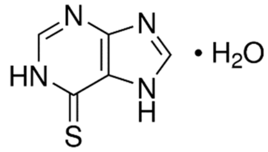
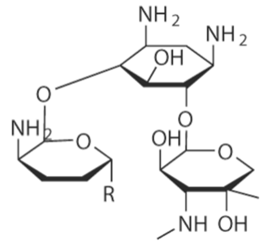
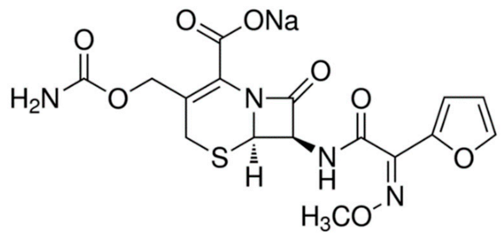
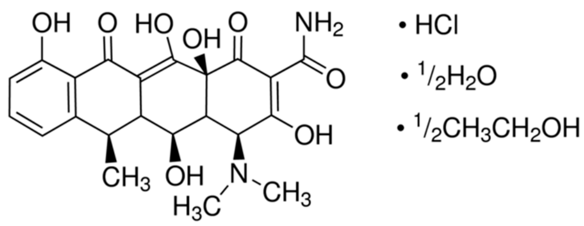
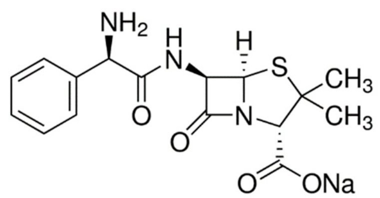
Tables and figures list in Supplementaty Materials

Table S1. Characteristics of the investigated pharmaceuticals used in screening tests.

Name, CAS number	Manufacturer	Chemical purity	Structural formula[1)]
Sulfanilamide 63-74-1	Sigma-Aldrich	>98.0%	
Sulfadiazine sodium salt 547-32-0	Sigma-Aldrich	≥98.0%	
Sulfathiazole 72-14-0	Sigma-Aldrich	≥99.0%	
Sulfamethazine 57-68-1	Sigma-Aldrich	≥99.0%	 [2)]
Sulfamethoxazole 723-46-6	Sigma-Aldrich	≥99.0%	
Sulfisoxazole 127-69-5	Sigma-Aldrich	≥99.0%	
Trimethoprim 738-70-5	Sigma-Aldrich	≥99.0%	
Metronidazole 443-48-1	Supelco		

Ifosfamide 3778-73-2	Sigma-Aldrich	≥98.0%	
6-Mercaptopurine monohydrate 6112-76-1	Sigma-Aldrich	98.0%	
Gentamicin sulfate salt 1405-41-0	Sigma-Aldrich	≥590 µg gentamicin base per mg	 3)
Cefuroxime sodium salt 56238-63-2	Supelco		
Doxycycline hyclate 24390-14-5	Sigma-Aldrich	≥93.5%	
Ampicillin sodium salt 69-52-3	Sigma-Aldrich	≥98%	

1) from the manufacturer's website

2) [63]

3) [64]

Table S2. Chemical composition of the synthetic municipal wastewater (ISO 9887:1992(E)) [62]

Chemicals	Manufacturer	Chemical purity	Concentration (mg/l)
Peptone from animal tissue	Sigma-Aldrich	-	160
Meat extract	Millipore	-	110
Urea	POCH (Poland)	p.a.	30
K_2HPO_4	POCH (Poland)	p.a.	28
NaCl	POCH (Poland)	p.a.	7
$CaCl_2{\cdot}2H_2O$	POCH (Poland)	p.a.	4
$MgSO_4{\cdot}7H_2O$	Chempur (Poland)	p.a.	2

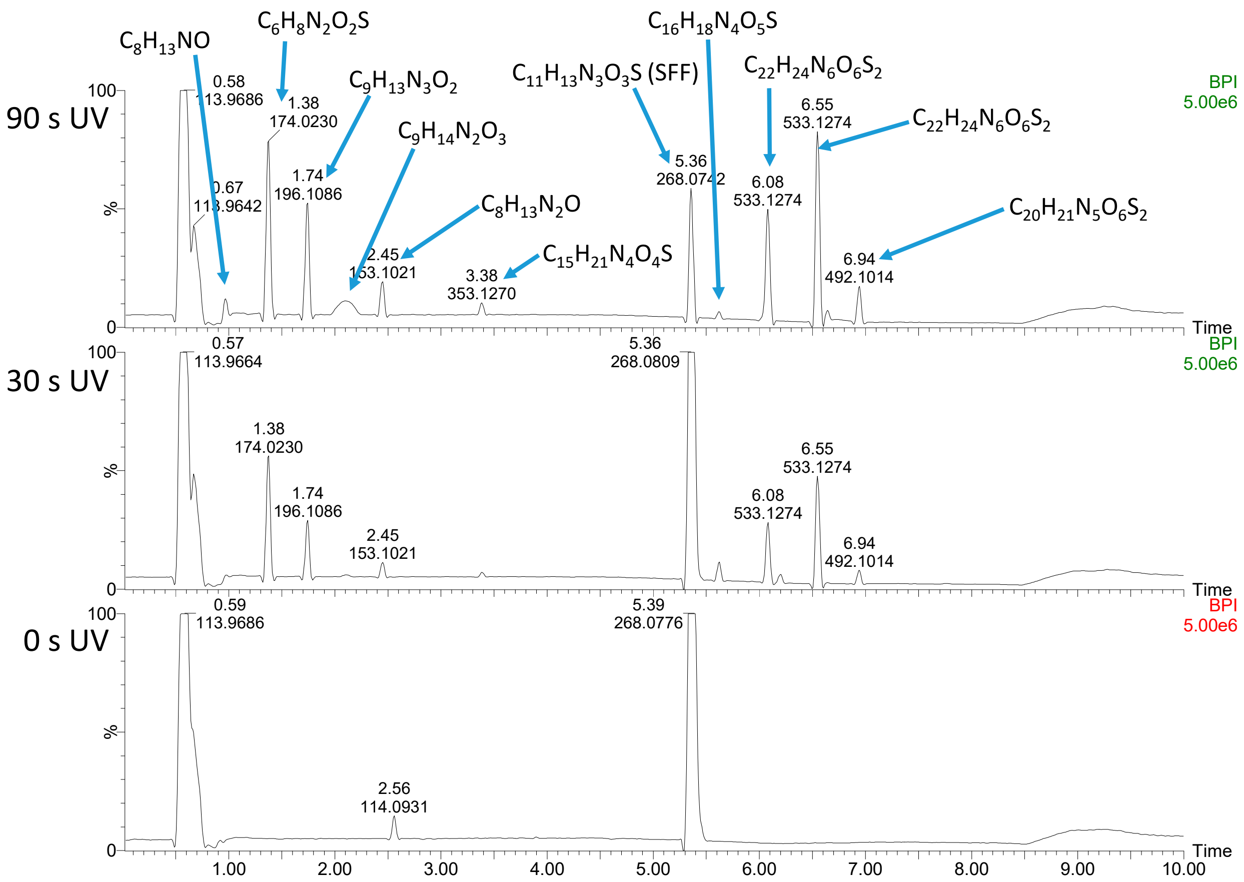


Figure S1a. TOF/BPI chromatograms of SFF solution irradiated for 0, 30 and 90 s in the presence of a $TiO_2/FeCl_3$ mixture

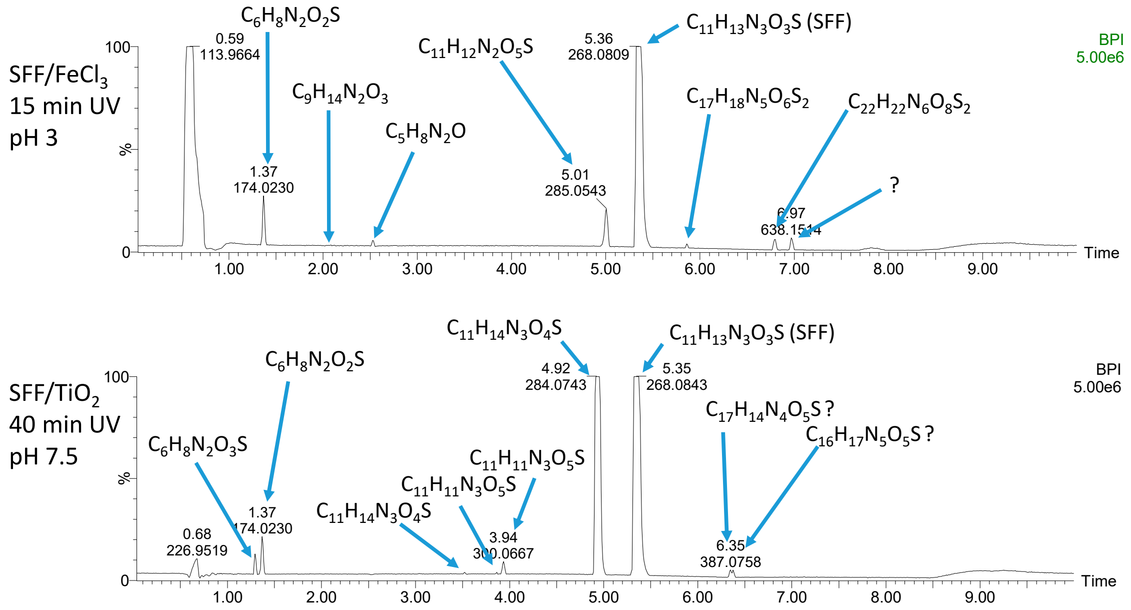


Figure S1b. TOF/BPI chromatograms of SFF solution irradiated for 15 and 40 min separately in the presence of TiO_2 or $FeCl_3$

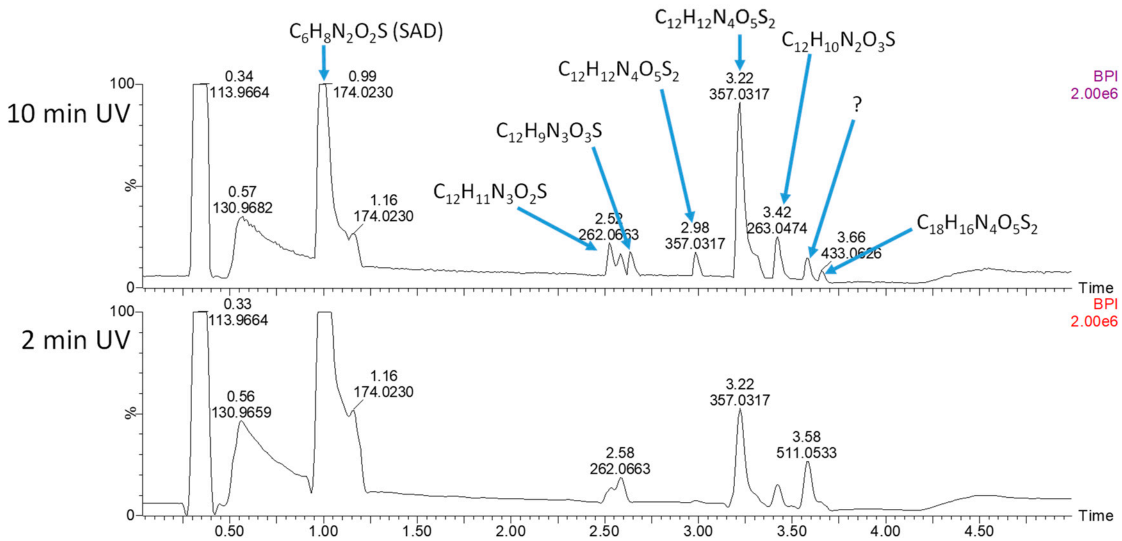


Figure S1c. TOF/BPI chromatograms of SAD solution irradiated for 2 and 10 min in the presence of a TiO_2/$FeCl_3$ mixture

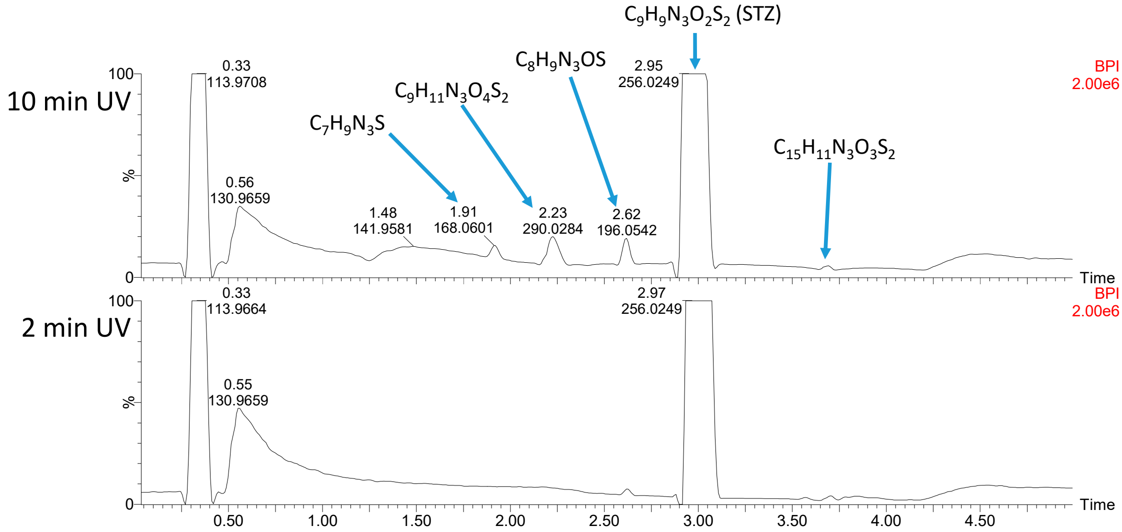


Figure S1d. TOF/BPI chromatograms of STZ solution irradiated for 2 and 10 min in the presence of a $TiO_2/FeCl_3$ mixture

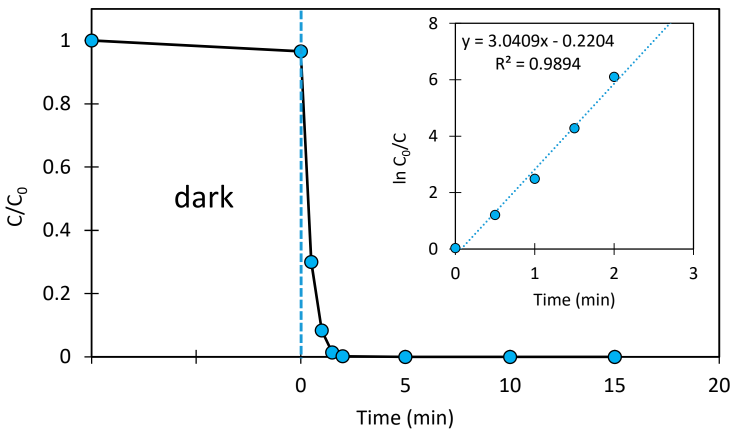


Figure S2. Changes in the concentration of SFF solution in the presence of a mixture of TiO_2 (0.5 g/l)/$FeCl_3$ (1.0 mmol/l) in the dark and irradiated with UVA

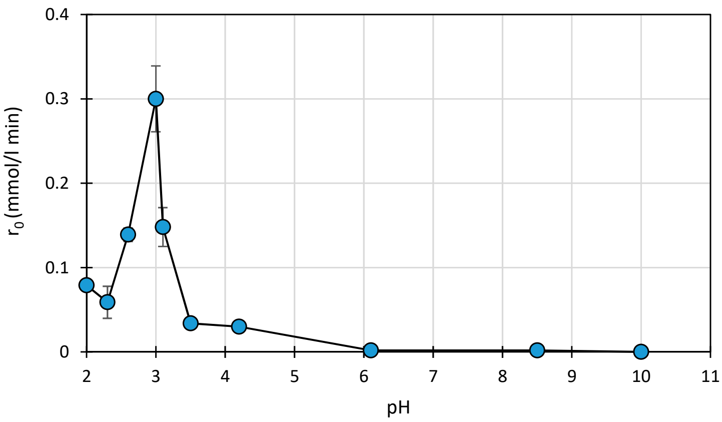
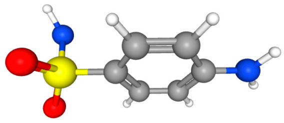
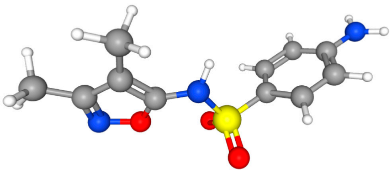
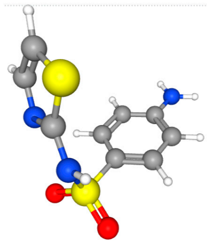
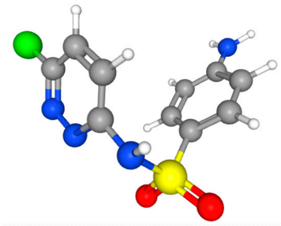
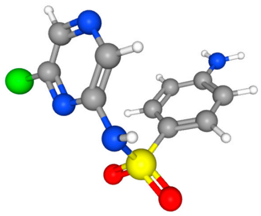


Figure S3. Effect of pH on the photodegradation rate of SFF (0.1 mmol/l) in the presence of a TiO_2 (0.5 g/l)/$FeCl_3$ (1.0 mmol/l) mixture

Table S3. Characteristics of the investigated SNs

Abbreviation	3D structures [65]	pK_{a1}	Molar fraction

Name, CAS, manufacturer, chemical purity	in the text		pK_{a2} 1)	of the molecular form (SH)1) at pH 3
Sulfanilamide 63-74-1 Sigma-Aldrich, >98.0%	**SAD**		2.46 ± 0.12 10.35 ± 0.21[20]	0.776
Sulfisoxazole 127-69-5 Sigma-Aldrich, ≥99.0%	**SFF**		1.69 ± 0.27 5.00 ± 0.00 [20]	0.944
Sulfathiazole 72-14-0 Sigma-Aldrich, ≥99.0%	**STZ**		2.22±0.27 7.15±0.12 [20]	0.858
Sulfachlorpyridazine 80-32-0 Sigma-Aldrich, 99.7%	**SCP**		1.87±0.30 5.45±0.06 [66]	0.928
Sulfaclozine 23307-72-4 Sigma-Aldrich, 99.8%	**SCL**		~2 5.5 [28]	0.906

1) $SH_2^+ \xleftrightarrow{Ka_1} SH \xleftrightarrow{Ka_2} S^-$,

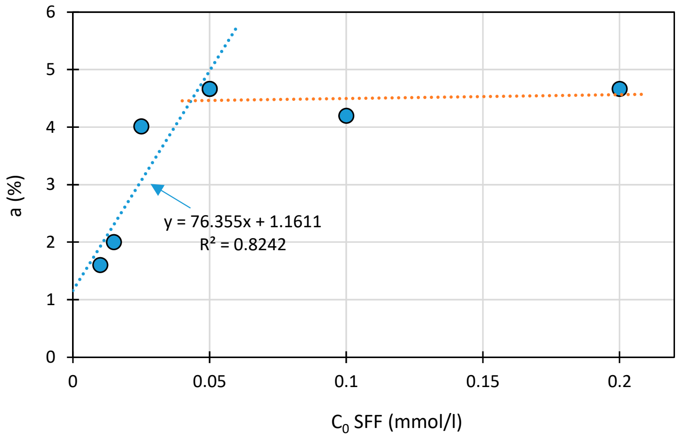


Figure S4. Effect of the initial concentration of SFF on the degree of sorption (before UVA irradiation) in the presence of a TiO_2 (0.5 g/l)/$FeCl_3$ (1.0 mmol/l) mixture

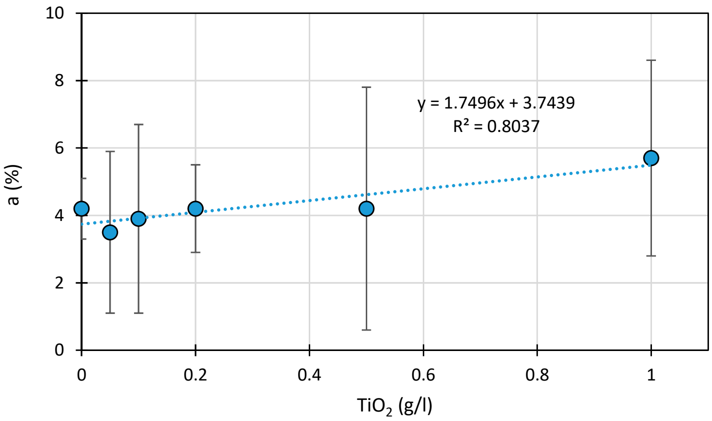


Figure S5. Effect of the amount of TiO_2 on the sorption of SFF (0.1 mmol/l) in the presence of $FeCl_3$ (1.0 mmol/l)

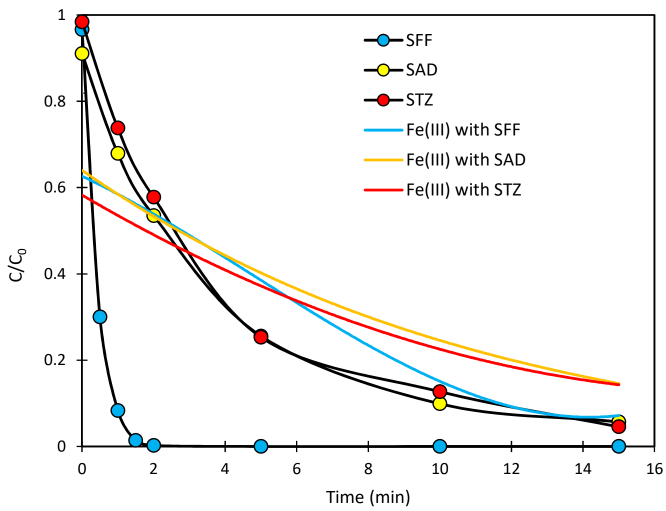


Figure S6. Changes in the concentration of SNs (C_0 0.1 mmol/l) and Fe^{3+} (C_0 1.0 mmol/l) during the photodegradation conducted in the presence of a TiO_2/$FeCl_3$ mixture at pH 3.0±0.1.

Table S4. Characteristics of the radicals and cations [1)]

Radical	Chemical name	Redox potential	Recombination	Reaction constant rate

		(V)	constant rate (mol/l s)	with other compounds (mol/l s)
$HO^{\bullet}$	hydroksyl	2.7 [67]	4.7×10^9 [68]	9.7×10^8 (methanol) [45]
		2.8 [69]	5.5×10^9 [45]	7.9×10^9 (benzene) [45]
		2.33 [70]	6×10^9 [43]	3.1×10^9 2-butanol [45]
		2.34 [71]	5.2×10^9 [72]	1.6×10^7 (acetic acid) [45]
			5.3×10^9 [73]	8.6×10^9(aniline) [74]
			4.2×10^9 [75]	8.2×10^9 (sulfanilic acid) [74]
				1.6×10^8 (pyrimidine) [74]
				3.5×10^9 (isoxazole) [74]
				$\leq 3.5 \times 10^9$ (SNs) [74]
				$0.66 - 1.8 \times 10^{10}$ (phenol) [75]
				$7.8 - 8.5 \times 10^9$ (SNs) [76]
				5.5×10^9 (SMX) [77]
				$10^9 – 10^{10}$ (lipid) [78]
				$2.8 \times 10^9 - 3.4 \times 10^{10}$ (aliphatic alcohols) [79]
				2.7×10^7 (H_2O_2) [80]
$O_2^{\bullet -}$	superoxide radical	0.94 [70,71]]	2.33×10^6 [72]	$< 10^2$ [71]
		-0.33 [67,71]		$10^5 - 10^9$ (ascorbate) [71]
				1.0×10^9 (Fe^{3+}) [43]
$HO_2^{\bullet}$	hydroperoxyl	1.48 [71]	$(8.3 \pm 0.7) \times 10^5$ [45]	$1.18 - 3.05 \times 10^3$ (fatty acids) [71]
		1.7 [81]		$10^9 – 10^{10}$ (lipids) [78]
			1.8×10^6 [43]	
			2.33×10^6 [72]	
			8.5×10^5 [73]	
$Cl^{\bullet}$	chlorine radical	2.5 [45,79]	$1.35 \cdot 10^7$	1.0×10^9 (methanol) [45]
		1.36 [44]	8.8×10^7 [45]	5.0×10^9 (butanol 2) [45]
				2.0×10^8 (acetic acid) [45]
				9.0×10^9 (benzene) [45]
				2.5×10^8 (phenol) [45]
				9.4×10^2 (SMX) [77]
$SO_4^{\bullet -}$	sulfate radical anion	2.60 – 3.10 [79]	7.0×10^8 [45]	$5.6 \times 10^6 - 9.9 \times 10^7$ (alkans) [79]
			$(6.1 \pm 0.15) \times 10^8$ [82]	$5.9 \times 10^7 - 1.4 \times 10^9$ (aliphatic alcohols) [79]
$CH_2OH^{\bullet}$	hydroxymethyl	-0.75 [83]	5.3×10^{10} [84]	6.1×10^9 (benzoquinone) [85]
		-0.90-1.18 [87]		$10^4 – 10^5$ (formaldehyde) [85]
				1.75×10^5 (H_2O_2) [88]
$C_4H_8OH^{\bullet}$	2-hydroxy-2-methylpropyl	0.09 [86]	-	2.2×10^5 (H_2O_2) [88]
Fe^{3+}/Fe^{2+}	-	0.77 [89]	-	-
Fe^{4+}/Fe^{3+}	-	~3.4 [90]	-	-
Cu^{2+}/Cu^{+}	-	0.159 [89]	-	-

Cr^{3+}/Cr^{2+}	-	-0.42 [89]	-	-
$2Cr^{3+}/Cr_2O_7^{2-}$	-	-1,33 [89]	-	-

[1)] not bonded cations, only standard values

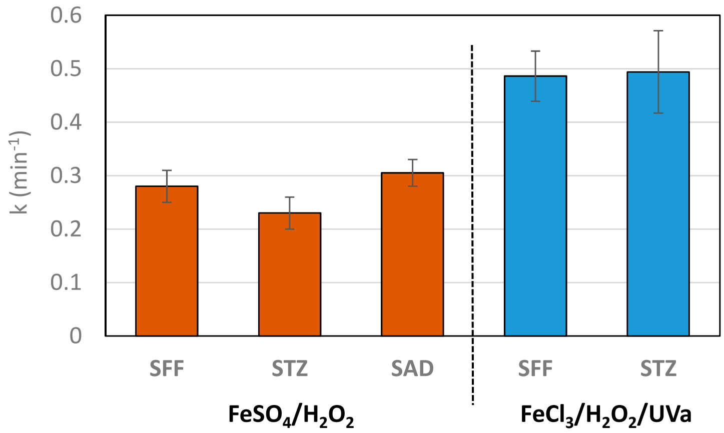


Figure S7. Comparison of the degradation rate constants od the selected SNs (0.1 mmol/l) during the Fenton process (0.15 mmol $FeSO_4$/l and 0.5 mmol H_2O_2/l) and Fenton-like reactions (photo Fenton, 1.0 mmol $FeCl_3$/l and 2.0 mmol H_2O_2/l)

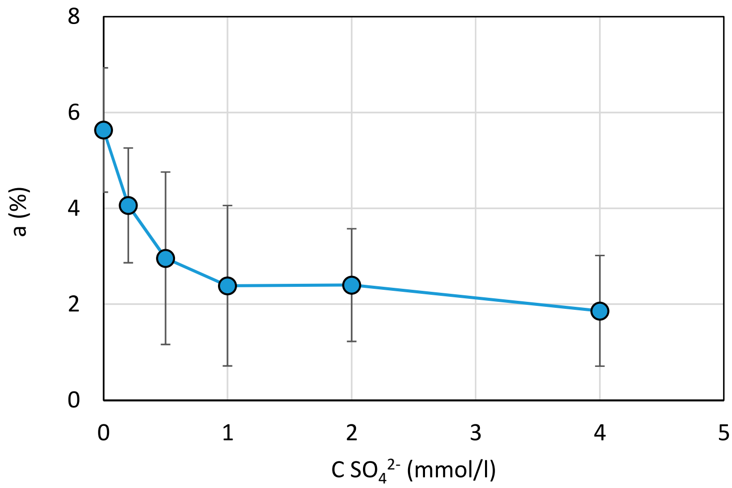


Figure S8. Effect of the SO_4^{2-} concentration on the sorption of SFF (0.1 mmol/l) on the catalytic system (0.5 g TiO_2/l /1.0 mmol $FeCl_3$/l) at pH 3.0±0.1

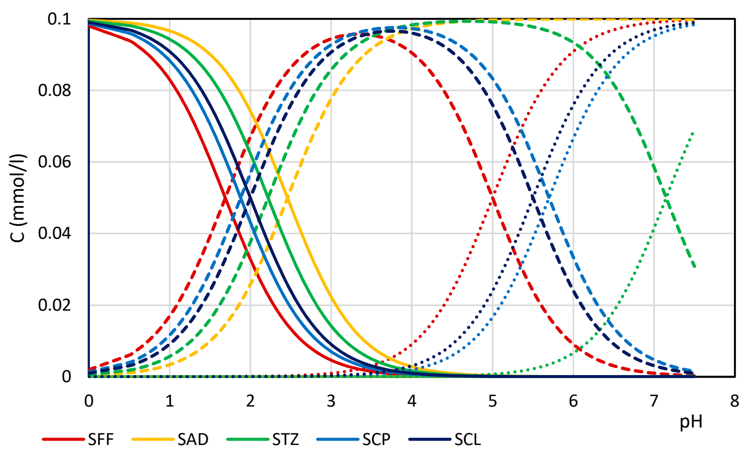


Figure S9. Effect of the pH on the dissociation and the concentration of molecular form of SNs (0.1 mmol/l) in aqueous solution: cationic form (SH_2^+) – solid line, neutral form (SH) – dashed line, anionic form (S^-) – dotted line

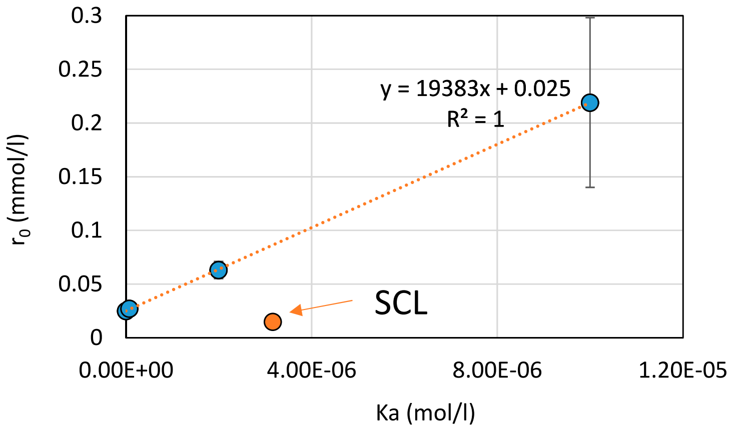


Figure S10. Relationship between the photodegradation rate of SNs (0.1 mmol/l) in the presence of a TiO_2(0.5 g/l)/$FeCl_3$(1.0 mmol/l) mixture and their dissociation constants (K_a)

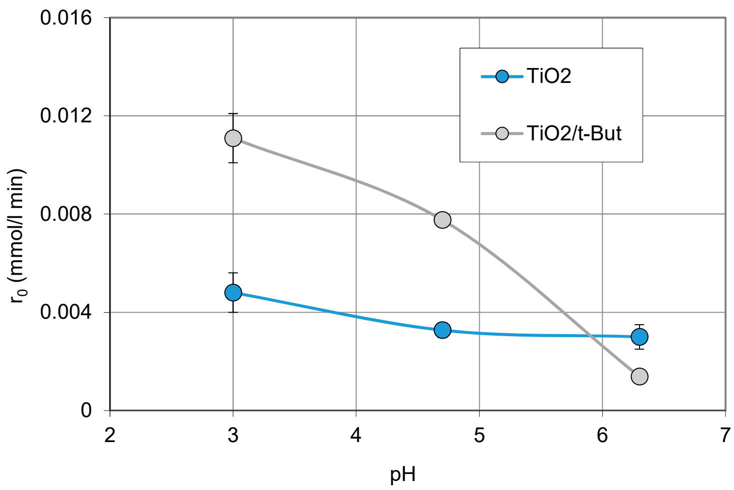


Figure S11. Effect of the pH on the initial rate of SFF photodegradation (0.1 mmol/l) in the presence of TiO_2 (0.5 g/l) or a TiO_2 (0.5 g/l)/t-But (10 mmol/l) mixture

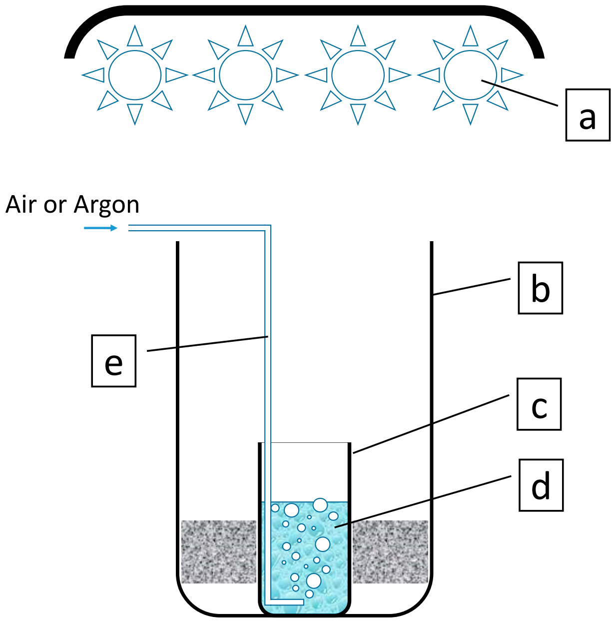


Figure S12. Test stand for the photocatalytic experiments under aerobic and anaerobic conditions, (a) UVa lamps; (b) a glass beaker (5000 ml); (c) a glass beaker (250 ml) (d) SN solution (150 ml, 0.1 mmol/l) with the selected catalyst system; (e) a glass tube (drain)

Table S5. Concentrations of substances used in studies of the photocatalytic degradation of SNs

Chemicals	Concentration (mmol/l)
tert-Butanol (t-But)	10
methanol	10
$CrCl_3 \cdot 6H_2O$	1.0
$AlCl_3 \cdot 6H_2O$	1.0
$CuCl_2 \cdot 2H_2O$	1.0
Na_2SO_4	3.0

Table S6. Detailed data for the UPLC procedure (gradient table).

	Time (min)	Flow rate (ml/min)	%A H_2O with 0.01% HCOOH	%B CH_3CN with 0.01% HCOOH
for SFF,SCL and SCP; ACQUITY UPLC BEH C18 column (130Å, 1.7 µm, 2.1 mm x 100 mm)				
1.	0	0.350	95.0	5.0
2.	3.5	0.350	80.0	20.0
3.	6.5	0.350	50.0	50.0
4.	7.5	0.350	50.0	50.0
5.	8.5	0.350	95.0	5.0
for SAD and STZ; ACQUITY UPLC BEH C18 column (130Å, 1.7 µm, 2.1 mm x 50 mm)				
1.	0	0.350	95.0	5.0
2.	3.0	0.350	60.0	40.0
3.	3.3	0.350	20.0	80.0
4.	3.5	0.350	95.0	5.0

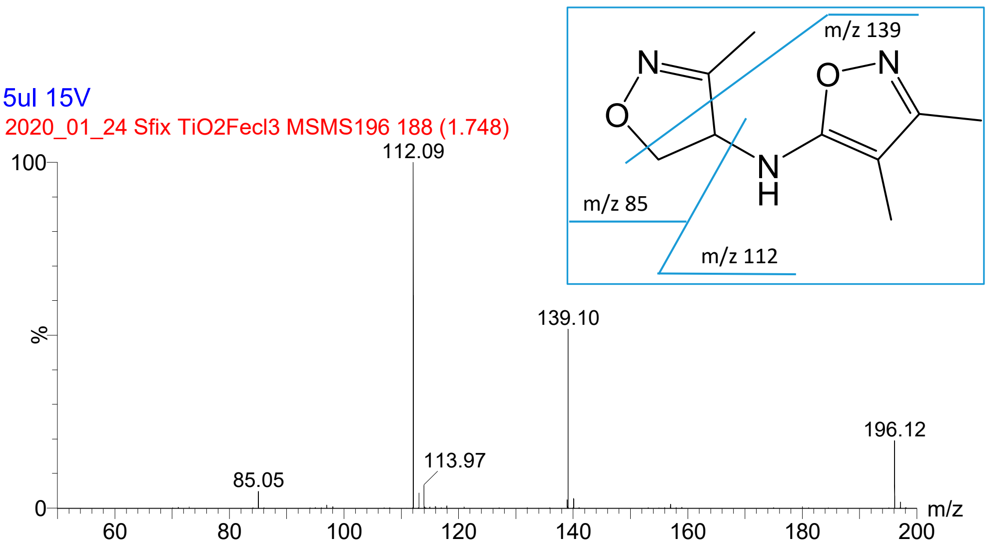


Figure S13. MSMS spectrum and a possible formula of compound with m/z 196.1086 Da occurred in SFF solution after irradiation for 90 s in the presence of a $TiO_2/FeCl_3$ mixture