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Degradation of four antibiotics from aqueous solution by ozonation: intermediates identification and reaction pathways

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ABSTRACT

The effects of some operational parameters like pH, initial antibiotics concentration, ozone concentration, reaction time on the degradation of four antibiotics were studied by ozonation. Under optimal conditions: pH = 5, $[antibiotics]_0$ = 10 mg/L and production of ozone capacity = 0.22 g/h, 100% of antibiotics were removed within 45 min. The values of electrical energy per order (E_{Eo}) increased from 24.7 to 47 (SCT), from 31.1 to 52 (STZ), from 32.5 to 49.7 (SMX) and from 32.5 to 51.5 (kWh m^{-3}) (SDZ) with increasing antibiotics concentration from 10 to 40 mg/L, respectively. The main mechanism for the degradation of all antibiotics were governed by the formation of $^{\bullet}OH$ radicals. In general, the efficacy of the processes in the removal of antibiotics from drinking water decreased due to anion scavenger activity. Intermediate products in the removal of antibiotics identified by GC/MS were organic acids. Mineralization of antibiotics by ozonation after 45 min was 34%.

Keywords: Antibiotics degradation; Ozonation; Aqueous solution; Kinetic models; GC-MS; Mineralization

1. Introduction

Antibiotics are mainly used to improve human health and promote animal growth [1–3]. If there is no an appropriate disposal system for antibiotics, their final destinations would be in the environment [1–3]. As a result they may enter the food chain which could enter the body of aquatic and terrestrial animals [4,5]. Antibiotic resistance is one of the emerging issues due to the release of antibiotic residues in the environment [6]. Due to the polar and hydrophilic nature of Sulfonamides (SAs), a widely used class of antibiotics, they are easily distributed into the aquatic environment [7]. There are eight common sulfonamides currently used: sulfacetamide, sulfadiazine, sulfadoxine, sulfamethizole, sulfamethoxazole, sulfanilamide, sulfasalazine, sulfisoxazole [8]. SAs have been detected extensively in raw sewage, sewage treatment plants (STPs) effluents, surface water, sediments, and groundwater [9–11]. About 16,000 tons of antibiotics are used in the US and SAs constitute 2.3% of this total consumption [12]. In Europe, annual consumption of SAs is about 11–23% [13]. Presence of SAs in water systems and environment is dangerous since it may cause cancer in human, and antibiotic-resistance [14–18]. The current study focuses on the removal of sulfadiazine (SDZ), Sulfacetamide (SCT), sulfamethoxazole (SMZ), and sulfathiazole (STZ) from aqueous solution using ozonation. The major reasons for selection of these SAs are the following: (1) SMZ is the most widely prescribed antibiotics in Iran, US and other developed countries, and hence frequently detected in the environment, (2) some of the SAs can be excreted by the body at high rates, (c) some of the SAs were detected at very high concentrations in the environment (d) all of the SAs were detected in the environ-

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ment, including drinking water, surface water, groundwater, and wastewater treatment plant effluent. The detection of the chemicals in treated drinking water and wastewater treatment plant effluent indicates that they are not effectively removed during conventional water and wastewater treatment [8,19,20].

Therefore, it is necessary to remove them from the aquatic systems. Previous studies have shown that the current methods of water treatments such as coagulation, flocculation, sedimentation, sand filtration, and disinfection with chlorine and wastewater treatment (primary settling, activated sludge or trickling filter, and secondary settling) are not effective for removal of all pharmaceuticals present in raw water and wastewater [21]. Because, these methods have some operational problems like sludge generation, membrane fouling and phase change of the pollutants [22]. Inefficacy of these methods could be related to different structures and physicochemical properties of the antibiotics which affect their rate of removal [23]. Advanced oxidation processes (AOPs) could be used to remove toxic biorefractory organic compounds based on the generation of radicals [24]. Ozone-based AOPs are potentially effective treatment alternatives for reducing or mineralizing refractory organic matter [21].

Ozone is an excellent oxidant and disinfectant, which has been widely used for the pretreatment of drinking water and effective in removal of wide range of organic pollutants through advanced treatment of wastewater [22,25,26]. Besides, ozonation treatment of several environmental pollutants by ozone is noticeably rapid, efficient, and economical, because the raw material for producing ozone is water and oxygen. Ozone can produce hydroxyl radicals in an aquatic environment, and in many ozonation cases, these two elements will work together to degrade organic substances. Many studies have reported ozonation of different types of environmental pollutants [22,25,26]; however, very few studies has been done on the degradation mechanism of antibiotics by ozone, as well as the identification of intermediate products and kinetics study during the ozonation process.

In the current research, we used the ozonation for the four antibiotics removal. The effects of pH solution, initial antibiotics concentration, ozone concentration, scavengers type and ions type on the removal of the four antibiotics from synthetic and real water were investigated. Additionally, kinetic study was conducted and simulated with the zero, first, second and Langmuir-Hinshelwood kinetic models. The electrical energy per order (EE_0) was calculated to evaluate the cost-efficiency of the processes. The intermediates and mineralization degradation of effluent were also followed by GC/MS and TOC, respectively.

2. Materials and methods

2.1. Chemicals

Sulfonamides were purchased from Sigma aldrich company, city, country. Potassium Iodide, sodium thiosulfate, sodium hydroxide, sulfuric acid, methanol, trichloroacetic acid (TCA) were purchased from Merck Co, Darmstadt, Germany. Sulfonamides (sulfacetamide, sulfathiazole, sulfamethoxazole and sulfadiazine) chemical structures were listed in Table 1. The experimental set-up for the degradation of Sulfonamides showed in Fig. 1.

2.2. Experimental procedure and analysis

A total of 1000 mg/L of each antibiotic as stock solution was prepared by dissolving of each in distilled water. This study deals with kinetics using the one-factor-at-a-time (OFAT) approach as well as examines the effect of parameters such as pH (3, 5, 7, 9, 11), initial antibiotics concentration (10, 20, 40 mg/L), reaction time (5–60 min), ozone concentration (0.1, 0.15, 0.22, 0.4 g/h), ions type (carbonate, bicarbonate, sulphate, nitrate and chloride) equal to 200 mg/L and scavengers type (t-butanol and ammonium oxalate) on the ozonation degradation of antibiotics. 0.1 N HCl or 0.1 N NaOH was used to adjust the initial pH of each solution . The pH was measured by pH meter (Metron, Switzerland). Duration of ozonation was 1 h, and the samples were randomly taken from the reactor during ozonation process for analysis. Ozonated solutions were collected at the defined time intervals, and flushed immediately with pure nitrogen for 3 min to remove the residual ozone to quench the reaction. The concentration of the antibiotics was quantified by means of a high performance liquid chromatography (HPLC, Waters, USA) equipped with a UV detector at with a length of 270 nm and a Diamonsil (R) C18 column (5 ml, 250 mm long × 4.6 mm ID) was used. The data were recorded by a Chemistation software. The mobile phase was composed of a mixture of TCA acidified at pH 3 by the Sulfuric acid addition and Methyl alcoholat a ratio of 20/80, V/V. The flow speed was set at 1.5 mL/min and 20-µL injection volumes were used in this study.

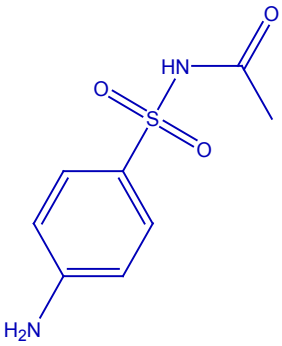
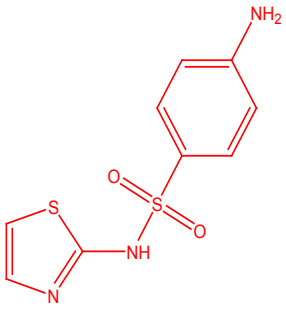
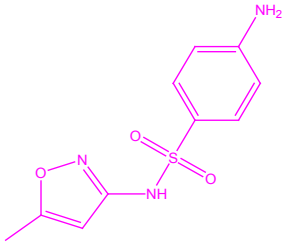
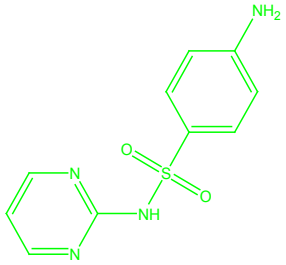
The elucidation of antibiotics decomposition pathways was performed by gas chromatography–mass spectroscopy (Varian-GC-MS 4000) instrument. In this study, in order to investigate the rates of mineralization of the antibiotics, total organic carbon (TOC) contents were detected using a Shimsdzu TOC-VCSH analyzer by directly injecting the aqueous solution.

3. Results and discussion

3.1. Effect of initial pH

Effect of initial pH on the ozonation degradation of different antibiotics was investigated by varying the initial pH from 3 to 11, at constant initial antibiotics concentration of 10 mg/L and influent ozone concentration of 0.22 g/h. Fig. 2 shows that degradation efficiency was enhanced 85.3%, 82.3%, 81.7% and 100% for SCT, STZ, SMZ and SDZ, respectively by increasing the initial pH from 3 to 5. However, the degradation efficiency decreased to 44.6% (SCT), 46.8% (STZ), 45.2% (SMZ) and 47.3% (SDZ) at pH 11. At pH lower than 4, sulfonamides antibiotics in their non-protonated form [27]. On the contrary, at pH 7, species present in water was the protonated one [27]. Direct reactivity of non-protonated organic amine species with ozone is higher than the protonated ones [27]. However, free radical oxidation is negligible in ozone processes at pH lower than 5 [27]. In unbuffered solutions antibiotics were removed from direct ozonation. In buffered solutions direct ozonation is also likely the main mechanism of oxidation but free radical oxidation cannot be discarded [27].

Table 1
Chemical structure and characteristics of antibiotics

Compound	Chemical structure	Molecular formula	M_w (g/mol)	pK_{a1}	pK_{a2}	Solubility in water (g/L)
Sulfacetamide		$C_8H_{10}N_2O_3S$	214.243	2.5	5.27	12.5
Sulfathiazole		$C_9H_9N_3O_2S_2$	255.3	2	7.1	0.48
Sulfamethoxazole		$C_{10}H_{11}N_3O_3S$	253.3	1.7	5.6	0.281
Sulfadiazine		$C_{10}H_{10}N_4O_2S$	250.3	2	6.4	0.13

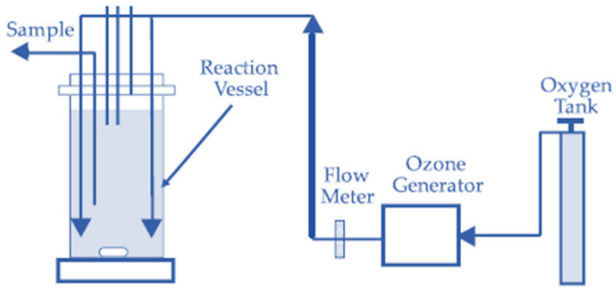


Fig. 1. Schematic diagram of the make up of the ozonation reactor.

3.2. Effect of initial antibiotics concentration

The removal of different antibiotics was investigated at three different concentrations (10, 20, 40 mg/L), at initial pH 5 and influent ozone concentration (0.22 g/h) (Fig. 3). Fig. 3 shows that antibiotics degradation efficiency decreased as initial antibiotics concentration increased. The ozonation degradation of different antibiotics was decreased from 100% to 90.7% for SCT, from 100% to 89.7% for STZ, from 100% to 88.4% for SMZ and from 100% to 86.2% for SDZ with increasing the initial antibiotics concentration from 10 to 40 mg/L, respectively. Increasing the initial concentration of pollutants in water led to an increased oxidation rate by ozonation, which was due to increased availability

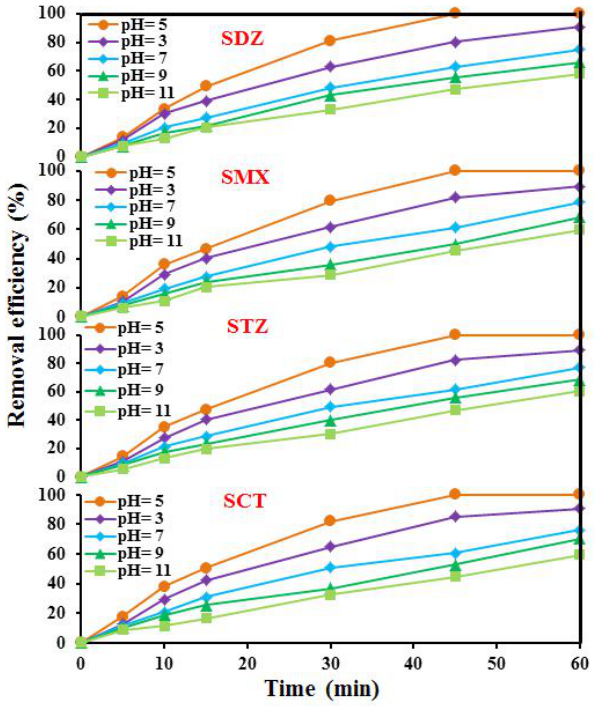


Fig. 2. The effect of initial pH on the degradation of different antibiotics ($[C]_0$ = 10 mg/L, Ozone concentration = 0.22 g/h).

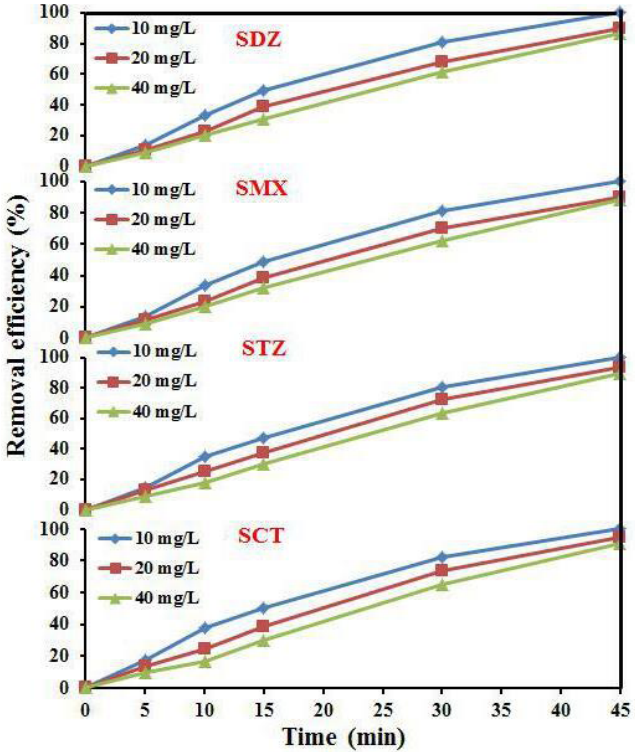


Fig. 3. Effect of initial antibiotics concentration on the degradation of different antibiotics (pH = 5, Ozone concentration = 0.22 g/h).

of pollutants for oxidative reactions with active oxidizing species [28]. Similar results were reported by Beltran et al. for the photocatalytic ozonation of sulfamethoxazole [29].

3.3. Effect of influent ozone gas concentration

The effect of influent ozone concentration on the ozonation degradation of Sulfonamides antibiotics by changing the initial ozone gas concentration from 0.1 to 0.22 g/h, an initial pH 5 and constant initial antibiotics concentration (10 mg/L) was investigated. Fig. 4 shows that degradation efficiency was enhanced with increasing the initial ozone concentration. Because an increase in the influent ozone gas concentration results in an increase in aqueous ozone concentration which either directly reacts with the sulfonamides or decomposes to produce •OH which in turn reacts with the sulfonamides[8].

3.4. Kinetics and electrical energy per order (E_{Eo}) studies

Experimental results obtained at different reaction times were fitted with zero, first and second order equations. For ozonation degradation process, relationship between initial degradation rate (r) and initial concentration of antibiotics can be described by Langmuir-Hinshelwood model. The E_{Eo} value for the ozonation degradation of antibiotics, defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m^3 of contaminated water, was evaluated. To obtain kinetic parameters for the ozonation degradation of antibiotics , $C_0 - C_t$, $\ln[C_0/C_t]$ and $1/C_t - 1/C_0$vs. t was plotted. The used equations and constants are summarized in Table 2.

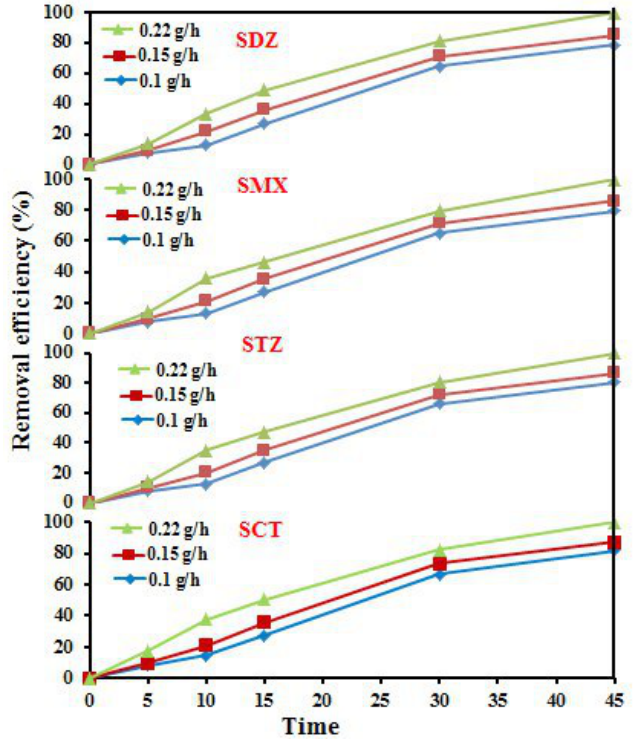


Fig. 4. Effect of influent ozone gas concentration on the degradation of different antibiotics ($[C]_0$ = 10 mg/L, pH = 5).

The kinetic parameters of zero, first and second-order reactions for the ozonation degradation of antibiotics at different initial antibiotics concentrations and pHs are summarized in Tables 3 and 4, respectively. Ozonation degradation rate of antibiotics was fitted well with the first-order model. As can be seen from Table 3, reaction rate of the pseudo-first

Table 2
Kinetics models, electrical energy per order equations and parameters for the degradation of antibiotics

Kinetic models	Electrical energy per order	Parameters
Zero-order $C_0 - C_t = k_0 t$	$E_{EO} = \frac{38.4 \times P}{V \times k_{obs}}$	C_0 (mg/L), C_t (mg/L), (mol L^{-1} min^{-1}), k_{obs} (1/min), (L mol^{-1} min^{-1}), $[C]_0$ (mg/L), k_c (mg L^{-1} min^{-1}), K_C^* (L mg^{-1}), P (kW), V (L), E_{Eo} (kWh /m^3)
First-order $\ln\frac{C_0}{C_t} = k_{obs} t$	$E_{EO} = \frac{p \times t \times 1000}{V \times 60 \times \log\left(C_i / C_f\right)}$	
Second-order $\frac{1}{C_t} - \frac{1}{C_0} = k_2 t$		
Langmuir–Hinshelwood $-\frac{d[C]}{dt} = \frac{k_c K_C [C]}{1 + K_C [C]_0} = k_{obs}[C]$ $\frac{1}{k_{obs}} = \frac{1}{k_c K_C} + \frac{[C]_0}{k_c}$		

*$K_{SCT,}$ $K_{STZ,}$ $K_{SMZ,}$ K_{SDZ}=K_c

Table 3
Kinetic parameters and electrical energy per order for the degradation of different antibiotics at different initial concentrations (pH = 5 and ozone concentration = 0.22 g/h)

Sulfacetamide (SCT)								
$[C]_0$ (mg L^{-1})	Zero-order			First-order			Second-order	
	k_0 (mol L^{-1} min^{-1})	R^2	k_{obs} (1/min)	$1/k_{obs}$ (min)	R^2	E_{Eo} (kWh/m^3)	k_2 (L mol^{-1} min^{-1})	R^2
10	0.219	0.9556	0.193585	5.16	0.9942	24.79	0.0013	0.1095
20	0.4302	0.9874	0.141564	7.06	0.9429	33.9	0.0196	0.7497
40	0.8326	0.9946	0.102033	9.8	0.9373	47.043	0.005	0.7827
				Sulfathiazole (STZ)				
$[C]_0$ (mg L^{-1})	Zero-order			First-order			Second-order	
	k_0 (mol L^{-1} min^{-1})	R^2	k_{obs} (1/min)	$1/k_{obs}$ (min)	R^2	E_{Eo} (kWh/m^3)	k_2 (L mol^{-1} min^{-1})	R^2
10	0.2221	0.9675	0.154317	6.48	0.9949	31.1	0.0043	0.2085
20	0.4227	0.9895	0.1381	6.48	0.9487	34.75	0.0154	0.7687
40	0.8273	0.9931	0.091019	10.98	0.9396	52.7	0.0045	0.7911
Sulfamethoxazole (SMX)								
$[C]_0$ (mg L^{-1})	Zero-order			First-order			Second-order	
	k_0 (mol L^{-1} min^{-1})	R^2	k_{obs} (1/min)	$1/k_{obs}$ (min)	R^2	E_{Eo} (kWh/m^3)	k_2 (L mol^{-1} min^{-1})	R^2
10	0.2241	0.9641	0.1473	6.78	0.9964	32.57	0.0046	0.1994
20	0.4087	0.9848	0.1244	8.03	0.9726	38.57	0.0096	0.831
40	0.8114	0.9908	0.096	10.36	0.9443	49.7	0.0039	0.8034
Sulfadiazine (SDZ)								
$[C]_0$ (mg L^{-1})	Zero-order			First-order			Second-order	
	k_0 (mol L^{-1} min^{-1})	R^2	k_{obs} (1/min)	$1/k_{obs}$ (min)	R^2	E_{Eo} (kWh/m^3)	k_2 (L mol^{-1} min^{-1})	R^2
10	0.2241	0.9641	0.1473	6.78	0.9964	32.57	0.0046	0.1994
20	0.4056	0.9855	0.1142	8.74	0.9698	41.99	0.0091	0.8267
40	0.7985	0.987	0.093	10.72	0.9547	51.49	0.0033	0.8328

Table 4
Kinetic parameters for the degradation of different antibiotics at different pHs (initial concentrations = 10 mg/L and ozone concentration = 0.22 g/h)

Sulfacetamide (SCT)						
pH	Zero-order		First-order		Second-order	
	k_0	R^2	k_1	R^2	k_2	R^2
	(mol L^{-1} min^{-1})		(1/min)		(L mol^{-1} min^{-1})	
3	0.1524	0.9363	0.041	0.9926	0.016	0.9175
5	0.1689	0.8932	0.0229	0.9913	0.0022	0.1011
7	0.1222	0.9665	0.0193	0.9741	0.0049	0.9317
9	0.1125	0.956	0.0143	0.9879	0.0037	0.9324
11	0.0951	0.9907	0.0619	0.9942	0.0023	0.9515
Sulfathiazole (STZ)						
pH	Zero-order		First-order		Second-order	
	k_0	R^2	k_1	R^2	k_2	R^2
	(mol L^{-1} min^{-1})		(1/min)		(L mol^{-1} min^{-1})	
3	0.1508	0.9458	0.0382	0.9944	0.0135	0.912
5	0.1727	0.9066	0.0237	0.9919	0.0022	0.1298
7	0.1252	0.9759	0.0183	0.9877	0.0052	0.9218
9	0.1098	0.9701	0.015	0.9877	0.0033	0.9278
11	0.0989	0.9932	0.0589	0.9949	0.0024	0.9508
Sulfamethoxazole (SMX)						
pH	Zero-order		First-order		Second-order	
	k_0	R^2	k_1	R^2	k_2	R^2
	(mol L^{-1} min^{-1})		(1/min)		(L mol^{-1} min^{-1})	
3	0.1494	0.944	0.0377	0.9948	0.0132	0.9102
5	0.1727	0.9083	0.0246	0.9831	0.0022	0.137
7	0.128	0.9842	0.0184	0.9615	0.0056	0.8886
9	0.111	0.947	0.0146	0.9823	0.0033	0.9273
11	0.0969	0.9917	0.0618	0.9964	0.0023	0.942
			Sulfadiazine (SDZ)			
pH	Zero-order		First-order		Second-order	
	k_0	R^2	k_1	R^2	k_2	R^2
	(mol L^{-1} min^{-1})		(1/min)		(L mol^{-1} min^{-1})	
3	0.1496	0.9485	0.0389	0.9925	0.0147	0.8593
5	0.1735	0.9017	0.023	0.9960	0.0023	0.1181
7	0.1244	0.9755	0.0184	0.9924	0.0048	0.9551
9	0.1122	0.966	0.0158	0.9866	0.0033	0.9856
11	0.1014	0.9951	0.0618	0.9964	0.0026	0.9396

order kinetic model (k_{obs}) and R^2 were decreased from 0.19 to 0.1 min^{-1} and 0.9942 to 0.9373 for SCT, from 0.15 to 0.09 min^{-1} and 0.9949 to 0.9396 for STZ, from 0.14 to 0.096 min^{-1} and 0.9964 to 0.9443 for SMZ and from 0.14 to 0.093 min^{-1} and 0.9964 to 0.9547 for SDZ with increasing the initial concentration of antibiotic from 10 to 40 mg/L, respectively. K_{SCT} and k_c were 24.9 L mg^{-1} and 6.57 mg/L min^{-1}, K_{STZ} and k_c were 26.3 L mg^{-1} and 6.23 mg/L min^{-1}, K_{SMZ} and k_c were 47.2 L mg^{-1} and 8.41 mg/L min^{-1}, K_{SDZ} and k_c were 45.68 L mg^{-1} and 7.89 mg/L min^{-1} by plotting $1/k_{obs}$ versus initial concentration of antibiotics, respectively. E_{Eo} values at different initial antibiotics concentrations are summarized in Table 3. E_{Eo} value was increased from 24.79 to 47.043 kWh/m^3 for (SCT), from 31.1 to 52.7 kWh/m^3 for (STZ), from 32.57 to 49.7 kWh/m^3 for (SMZ) and from 32.57 to 51.49 kWh/m^3 for (SDZ) with increasing antibiotics concentration from 10 to 40 mg/L.

3.5. Effect of different inorganic ions

To assess the effect of different inorganic ions on the ozonation degradation of antibiotics, constant amounts of inorganic ions (sulphate, sodium, carbonate, bicarbonate and nitrate) were added to the reactor before initiating the process. The concentration of each inorganic ions was adjusted to 200 mg/L while the initial antibiotics concentration, influent ozone concentration, and initial pH were constant at 10 mg/L, 0.22 g/h, and 5, respectively (Fig. 5). These data suggest that any type of inorganic ions show inhibition effect on the antibiotics. The negative effects on the degradation of antibiotics might be due to these anions may react with •OH to produce less active oxidants such as sulphate, sodium, carbonate, bicarbonate and nitrate [30]. Thus, competition among oxidants and antibiotics brought out the deterioration of degradation efficiency. According to the previous research, sulphate, carbonate and bicarbonate are well-known free radical inhibitors and have been widely used for •OH scavenging [31]. Similar results were reported by Feng, et al. for the removal fluoroquinolone antibiotics from aqueous solution by ozonation [30]. Gao et al. reported significant inhibitory effect on SMX degradation was observed for HCO_3^- anion while studying the degradation of Ametryn using UV/H_2O_2 treatment which is similar in the current study [32].

3.6. Effect of different scavengers and possible mechanism

The free radicals scavenging experiments were conducted by adding active scavenger species using ozonation degradation of antibiotics at constant initial antibiotics concentration (10 mg/L), influent ozone concentration (0.22 g/h) and initial pH 5 as the model reaction. Briefly, the ozonation degradation of antibiotics was repeated by adding 200 mg/L of t-butanol, as a hydroxyl radical scavenger (•OH) and 200 mg/L of ammonium oxalate (AO) as a hole (h^+) scavenger. As shown in Fig. 6, the ozonation of antibiotics was apparently inhibited when t-butanol was added, while there was no obvious ozonation reduction with the addition of (AO). This phenomenon gives evidence that the degradation of antibiotics is dominated by the oxidation reaction of •OH radical oxidation. Efficiency of antibiotics removal in the current study and the other similar studies which used ozonation has been compared in Table 5.

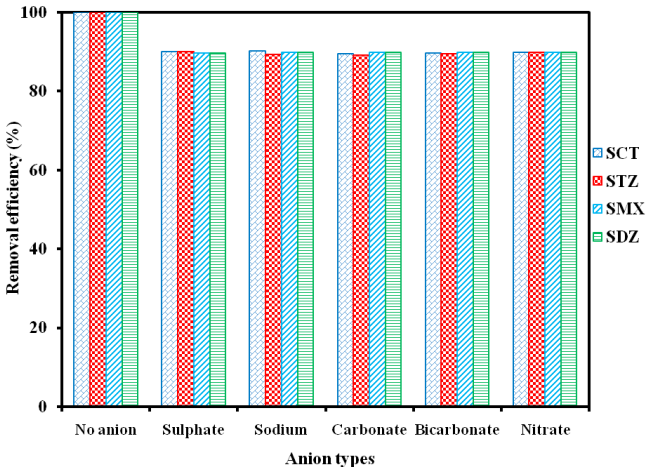


Fig. 5. Effects of different anions on the degradation of different antibiotics ([C]$_0$ = 10 mg/L, pH = 5, Ozone concentration = 0.22 g/h).

3.7. Removal of antibiotics from real water samples

In order to investigate the efficiency of ozonation degradation in removal of antibiotics from real water, 10 ppm of antibiotics was added into a real water sample that was obtained from water distribution network in Tehran, Iran. The characteristics of the real water are presented in the Table 6. Generally, real water contains anions such as sulphate, carbonate and bicarbonate. Removal of antibiotics in real water was compared with synthetic water and shown in Fig. 7. As shown in Fig. 7,the efficiency of antibiotic removal reduced in real water compared to synthetic water. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers by the following reaction:

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + OH^- \quad (1)$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \quad (2)$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \quad (3)$$

The reaction between •OH and carbonate and bicarbonate ions produce carbonate radical ($CO_3^{\bullet-}$) which in turn reacts with hydroperoxide ion (HO_2^-). Hydroperoxide ion

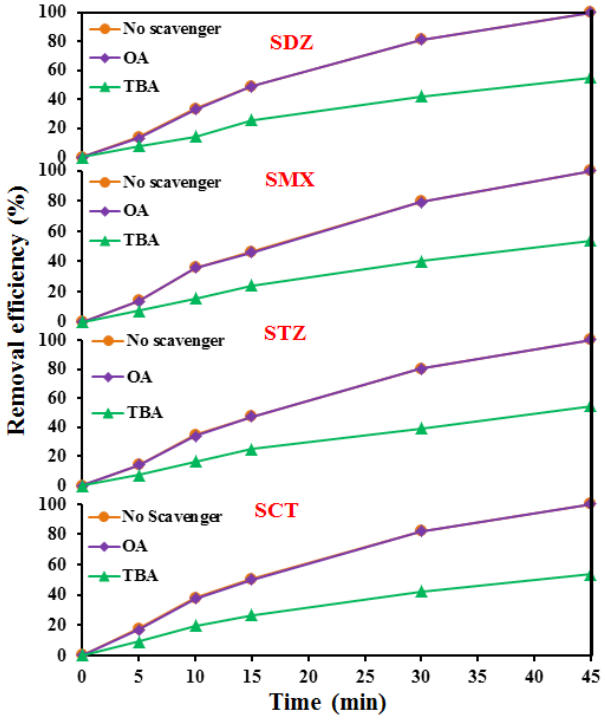


Fig. 6. Effects of different scavengers on the degradation of different antibiotics ([C]$_0$ = 10 mg/L, pH = 5, Ozone concentration = 0.22 g/h).

Table 5
Comparison of removal different antibiotics by ozonation

pH	Antibiotics type	$[Concentration)]_0$	O_3 influent (mg/L)	Time (min)	Removal efficiency (%)	Mineralization (%)	k_{obs} (min^{-1})	R^2	Reference
7	Oxazepam	0.1 µg/L	1.5	–	96	–	1	–	[33]
7	Gabapentin	–	1.5	–	95	–	2.2×10^4	–	[33]
7	Levetiracetam	–	1.5	–	83	–	<1	–	[33]
7	Mefenamic acid	–	1.5	–	100	–	6.4×10^6	–	[33]
7	Sulfapyridine	–	1.5	–	100	–	2×10^5	–	[33]
7	Sotalol	–	1.5	–	100	–	1.4×10^4	–	[33]
7	Valsantan	–	1.5	–	96	–	38	–	[33]
7	Gemfibrozil	–	–	–	–	–	5×10^4	–	[34]
7	Meprobamate	–	–	–	–	–	<1	–	[34]
7	Trimethoprim	–	–	–	–	–	3×10^5	–	[34]
8	Tramadol (Analgesic)	100 µM	0.5 mg/L	–	90	–	4×10^3	–	[35]
7	Phenytoin	–	–	–	–	–	<10	–	[34]
2	Ketorolac	30 ppm	12g/h	60	60	58	4.4×10^5	0.99	[36]
2	Flumequine	30 ppm	12g/h	60	60	58	6.4	0.97	[36]
2	Caffeine (stimulant)	30ppm	12g/h	60	60	58	2.5×10^3	0.98	[36]
2	Acetominophen	30 ppm	12g/h	60	60	58	2.5×10^5	0.99	[36]
3	Sulfaquinoxaline	500 µg/L	2.8	15	99	–	6.36	–	[8]
6.5	Fenofibric acid	15 ppm	–	–	–	–	3.43	–	[37]
5	Sulfacetamide	10 ppm	0.22 g/h	45	100	66	0.19	0.99	In study
5	Sulfathiazole	10 ppm	0.22 g/h	45	100	66	0.15	0.99	In study
5	Sulfamethoxazole	10 ppm	0.22 g/h	45	100	66	0.14	0.99	In study
5	Sulfadiazine	10 ppm	0.22 g/h	45	100	66	0.14	0.99	In study

Table 6
Characteristics of real water

Parameters	Value
pH	7.6
Sulfate concentration (mg/L SO_4^{2-})	263
Chloride concentration (mg/L Cl^-)	169
Specific conductivity (µmhos/cm)	1416
Nitrate concentration (mg/L NO_3^-)	47.43
Nitrite concentration (mg/L NO_2^-)	0.00021
Total dissolved solids(TDS) (mg·L^{-1})	707
Sodium concentration (mg/L Na^+)	187
Potassium concentration (mg/L K^+)	2.35
Bicarbonate hardness (mg/L $CaCO_3$)	282.5

produced as a result of aqueous ozone decomposition and results in the generation of •OH through series of radical–radical reactions [38–40]. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals. pH of real water containing antibiotics increased from 7.27 to 7.81 after ozonation degradation of antibiotics. Because of neutral pH conditions, the inorganic carbon exists mainly in the form of bicarbonate, and found in surface and ground waters at concentrations typically in the range of 50–200 mg/L [41]. Higher concentrations may be encoun-

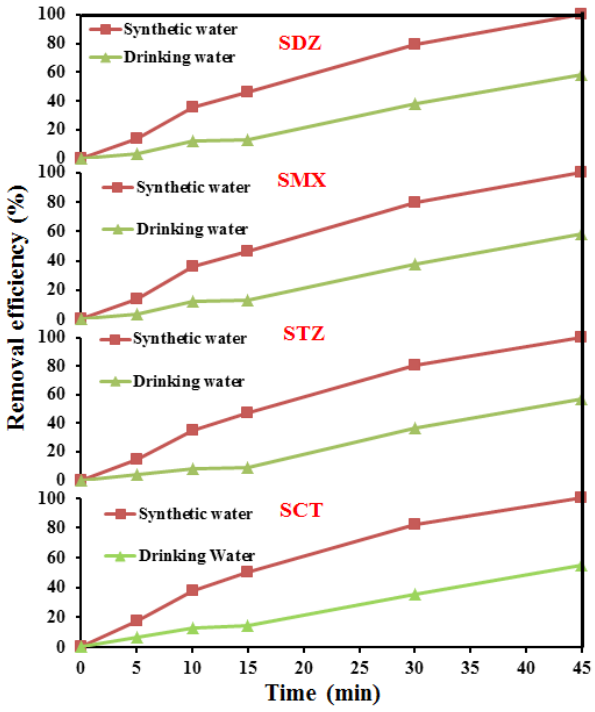


Fig. 7. Investigation of the efficiency of the ozonation on the degradation of different antibiotics from actual water ($[C]_0$ = 10 mg/L, Ozone concentration = 0.22 g/h).

tered in high alkalinity waters that decrease of degree ozonation [41]. Specific conductivity of solution decrease from 403 to 392 after ozonation degradation. Bicarbonate ion in reactions with hydroxyl radicals in competition with refractory organic pollutants is the principal consumer of the hydroxyl radicals [42]. Bicarbonate radicals act as a oxidation species and which have a much lower reaction rate constant than hydroxyl radicals for the oxidation of organic micropollutants [42].

3.8. Determination of by-products and mineralization

The intermediates and byproducts were identified by GC-MS under the following conditions: pH = 5, [antibiotics]$_0$ = 10 mg/L and influent ozone concentration(0.22 g/h). And, the rate of antibiotics mineralization was performed by means of the TOC analysis. A probable degradation pathway of antibiotics during the ozonation process was proposed (Fig. 8). First, Sulphonamides antibiotics is converted to hydroxy sulphonamides via •OH radical attack on the aromatic ring [43]. Next, Benzeneacetaldehyde is created through oxido/reductive attack on the S–N bond with the breaking of the molecule and the release of sulphur atom as sulphate ions [43]. Then, 4-aminodihydro-2(3H)-furanone by the introduction of methoxy groups and sulphur atom in the ring via activating it toward an •OH attack and a further oxidation of the molecule is generated intermediate of thiocyanic acid and butyric acid [43]. In turn, acids like benzoic acid, 1,2-benzenedicarboxylic acid and acetic acid are formed. The results of the TOC analysis illustrated 33.7% mineralization after 45 min (Fig. 9). Baran et al. (2009) indicated that ozonation removed 34% of TOC with SMX (0.198 mM at pH 4.8) degradation after 180 min [44].

4. Conclusion

The degradation of antibiotics by ozonation process was examined. The effect of various anions on the performance of ozonation was also investigated. Inorganic ions show inhibitory effect on the antibiotics. In addition, the

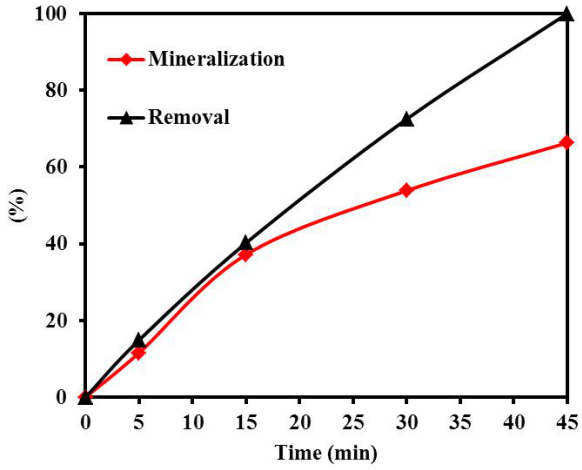


Fig. 9. Mineralization of antibiotics by ozonation ([C]$_0$ = 10 mg/L, pH = 5, Ozone concentration = 0.22 g/h).

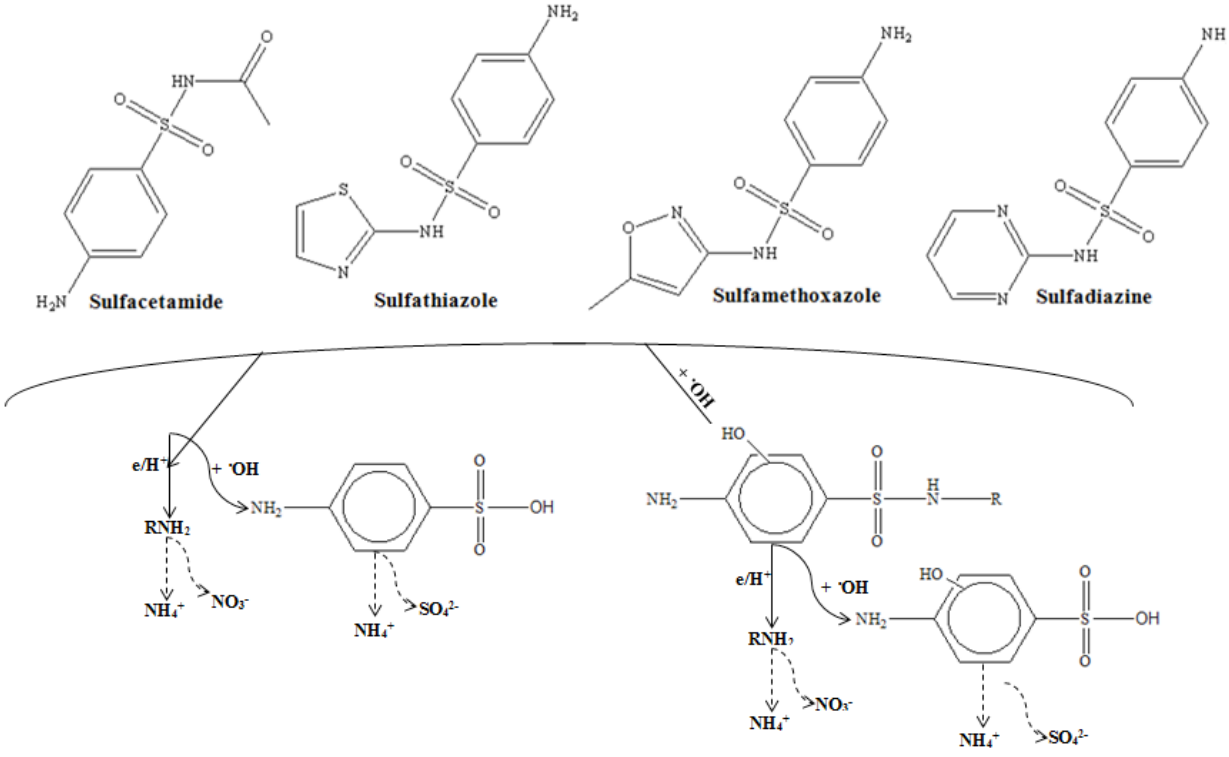


Fig. 8. Determination of by products of decomposition antibiotics decomposition by GC-MS at temperature 280°C.

reaction mechanisms were proposed via identification of scavengers in the process. Ozonation process has exhibited the best performance in removal of antibiotics at pH 5. Byproducts were identified as acids like benzoic acid, 1,2-benzenedicarboxylic acid and acetic acid. Mineralization using this process reached to 33.7% at the end of the process (45 min).

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References

[1] Y. Zhang, J. Xu, Z. Zhong, C. Guo, L. Li, Y. He, W. Fan, Y. Chen, Degradation of sulfonamides antibiotics in lake water and sediment, Environ. Sci. Pollut. Res., 20 (2013) 2372–2380.
[2] K. Kümmerer, Antibiotics in the aquatic environment – A review – Part I, Chemosphere, 75 (2009) 417–434.
[3] K. Kümmerer, Antibiotics in the aquatic environment – A review – Part II, Chemosphere, 75 (2009) 435–441.
[4] F. Liu, G.-G. Ying, R. Tao, J.-L. Zhao, J.-F. Yang, L.-F. Zhao, Effects of six selected antibiotics on plant growth and soil microbial and enzymatic activities, Environ. Pollut., 157 (2009) 1636–1642.
[5] M.H. Farkas, E.-R.E. Mojica, M. Patel, D.S. Aga, J.O. Berry, Development of a rapid biolistic assay to determine changes in relative levels of intracellular calcium in leaves following tetracycline uptake by pinto bean plants, Analyst, 134 (2009) 1594–1600.
[6] S. Kim, D.S. Aga, Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants, J. Toxicol. Environ. Health, Part B, 10 (2007) 559–573.
[7] W.-h. Xu, G. Zhang, S.-c. Zou, X.-d. Li, Y.-c. Liu, Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry, Environ. Pollut., 145 (2007) 672–679.
[8] T. Garoma, S.K. Umamaheshwar, A. Mumper, Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation, Chemosphere, 79 (2010) 814–820.
[9] X. Peng, Z. Wang, W. Kuang, J. Tan, K. Li, A preliminary study on the occurrence and behavior of sulfonamides, ofloxacin and chloramphenicol antimicrobials in wastewaters of two sewage treatment plants in Guangzhou, China, ScTEn, 371 (2006) 314–322.
[10] X.-S. Miao, F. Bishay, M. Chen, C.D. Metcalfe, Occurrence of antimicrobials in the final effluents of wastewater treatment plants in Canada, Environ. Sci. Technol., 38 (2004) 3533–3541.
[11] S. Managaki, A. Murata, H. Takada, B.C. Tuyen, N.H. Chiem, Distribution of macrolides, sulfonamides, and trimethoprim in tropical waters: ubiquitous occurrence of veterinary antibiotics in the Mekong Delta, Environ. Sci. Technol., 41 (2007) 8004–8010.
[12] A. Fabiańska, A. Białk-Bielińska, P. Stepnowski, S. Stolte, E.M. Siedlecka, Electrochemical degradation of sulfonamides at BDD electrode: Kinetics, reaction pathway and eco-toxicity evaluation, J. Hazard. Mater., 280 (2014) 579–587.
[13] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere, 65 (2006) 725–759.
[14] W. Baran, E. Adamek, J. Ziemiańska, A. Sobczak, Effects of the presence of sulfonamides in the environment and their influence on human health, J. Hazard. Mater., 196 (2011) 1–15.
[15] F.C. Cabello, Heavy use of prophylactic antibiotics in aquaculture: a growing problem for human and animal health and for the environment, Environ. Microbiol., 8 (2006) 1137–1144.
[16] S. Fletcher, Understanding the contribution of environmental factors in the spread of antimicrobial resistance, Environ. Health Prevent. Med., 20 (2015) 243–252.
[17] L. Gao, Y. Shi, W. Li, J. Liu, Y. Cai, Occurrence, distribution and bioaccumulation of antibiotics in the Haihe River in China, J. Environ. Monit., 14 (2012) 1247–1254.
[18] P. Gao, D. Mao, Y. Luo, L. Wang, B. Xu, L. Xu, Occurrence of sulfonamide and tetracycline-resistant bacteria and resistance genes in aquaculture environment, Water Res., 46 (2012) 2355–2364.
[19] M.J. Focazio, D.W. Kolpin, K.K. Barnes, E.T. Furlong, M.T. Meyer, S.D. Zaugg, L.B. Barber, M.E. Thurman, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II) Untreated drinking water sources, ScTEn, 402 (2008) 201–216.
[20] L.E. Nicolle, Urinary tract infection: traditional pharmacologic therapies, Amer. J. Medicine, 113 (2002) 35–44.
[21] D. Nasuhoglu, V. Yargeau, D. Berk, Photo-removal of sulfamethoxazole (SMX) by photolytic and photocatalytic processes in a batch reactor under UV-C radiation (λ_{max} = 254 nm), J. Hazard. Mater., 186 (2011) 67–75.
[22] R. Qu, B. Xu, L. Meng, L. Wang, Z. Wang, Ozonation of indigo enhanced by carboxylated carbon nanotubes: performance optimization, degradation products, reaction mechanism and toxicity evaluation, Water Res., 68 (2015) 316–327.
[23] N.M. Vieno, H. Härkki, T. Tuhkanen, L. Kronberg, Occurrence of Pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant, Environ. Sci. Technol., 41 (2007) 5077–5084.
[24] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, Chemosphere, 93 (2013) 1268–1287.
[25] S. Wang, X. Wang, J. Chen, R. Qu, Z. Wang, Removal of the UV filter benzophenone-2 in aqueous solution by ozonation: kinetics, intermediates, pathways and toxicity, OzSE, 40 (2018) 122–132.
[26] M. Bourgin, E. Borowska, J. Helbing, J. Hollender, H.-P. Kaiser, C. Kienle, C.S. McArdell, E. Simon, U. Von Gunten, Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O_3/H_2O_2: Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water, Water Res., 122 (2017) 234–245.
[27] N.P. Xekoukoulotakis, C. Drosou, C. Brebou, E. Chatzisymeon, E. Hapeshi, D. Fatta-Kassinos, D. Mantzavinos, Kinetics of UV-A/TiO_2 photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole in aqueous matrices, Catal. Today, 161 (2011) 163–168.
[28] M. Mehrjouei, S. Müller, D. Möller, A review on photocatalytic ozonation used for the treatment of water and wastewater, Chem. Eng. J., 263 (2015) 209–219.
[29] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water, Water Res., 43 (2009) 1359–1369.
[30] M. Feng, L. Yan, X. Zhang, P. Sun, S. Yang, L. Wang, Z. Wang, Fast removal of the antibiotic flumequine from aqueous solution by ozonation: influencing factors, reaction pathways, and toxicity evaluation, ScTEn, 541 (2016) 167–175.
[31] X. Liu, T. Zhang, Y. Zhou, L. Fang, Y. Shao, Degradation of atenolol by UV/peroxymonosulfate: kinetics, effect of operational parameters and mechanism, Chemosphere, 93 (2013) 2717–2724.
[32] N.-y. Gao, Y. Deng, D. Zhao, Ametryn degradation in the ultraviolet (UV) irradiation/hydrogen peroxide (H_2O_2) treatment, J. Hazard. Mater., 164 (2009) 640–645.

[33] Y. Lee, L. Kovalova, C.S. McArdell, U. von Gunten, Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent, Water Res., 64 (2014) 134–148.
[34] Y. Lee, U. von Gunten, Quantitative structure–activity relationships (QSARs) for the transformation of organic micropollutants during oxidative water treatment, Water Res., 46 (2012) 6177–6195.
[35] S.G. Zimmermann, A. Schmukat, M. Schulz, J. Benner, U.v. Gunten, T.A. Ternes, Kinetic and mechanistic investigations of the oxidation of tramadol by ferrate and ozone, Environ. Sci. Technol., 46 (2012) 876–884.
[36] F.J. Rivas, J. Sagasti, A. Encinas, O. Gimeno, Contaminants abatement by ozone in secondary effluents. Evaluation of second-order rate constants, J. Chem. Technol. Biotechnol., 86 (2011) 1058–1066.
[37] R. Rosal, M.S. Gonzalo, A. Rodríguez, E. García-Calvo, Catalytic ozonation of fenofibric acid over alumina-supported manganese oxide, J. Hazard. Mater., 183 (2010) 271–278.
[38] D. Behar, G. Czapski, I. Duchovny, Carbonate radical in flash photolysis and pulse radiolysis of aqueous carbonate solutions, J. Phys. Chem., 74 (1970) 2206–2210.
[39] R.E. Buehler, J. Staehelin, J. Hoigne, Ozone decomposition in water studied by pulse radiolysis. 1. Perhydroxyl (HO_2)/hyperoxide (O_2-) and HO_3/O_3- as intermediates, J. Phys. Chem., 88 (1984) 2560–2564.
[40] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ·OH/·O– in aqueous solution, J. Phys. Chem. Ref. Data, 17 (1988) 513–886.
[41] J. Ma, N.J.D. Graham, Degradation of atrazine by manganese-catalysed ozonation—influence of radical scavengers, Water Res., 34 (2000) 3822–3828.
[42] J.L. Acero, U.R.S. Von Gunten, Characterization of oxidation processes: ozonation and the AOP O_3/H_2O_2, J. AWWA, 93 (2001) 90–100.
[43] P. Calza, C. Medana, M. Pazzi, C. Baiocchi, E. Pelizzetti, Photocatalytic transformations of sulphonamides on titanium dioxide, Appl. Catal. B: Environ., 53 (2004) 63–69.
[44] W. Baran, E. Adamek, A. Sobczak, A. Makowski, Photocatalytic degradation of sulfa drugs with TiO_2, Fe salts and TiO_2/$FeCl_3$ in aquatic environment—Kinetics and degradation pathway, Appl. Catal. B: Environ., 90 (2009) 516–525.