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Synergistic effects of catalytic and photocatalytic ozonation on four sulfonamides antibiotics degradation in an aquatic solution

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ABSTRACT

The effects of operational parameters including pH, initial antibiotic concentration, ozone concentration, contact time and catalytic concentration on the degradation of four antibiotics were studied through comparing synergistic effects between catalytic and photocatalytic ozonation. Under the optimal conditions: pH = 5, [SCT, STZ, SMX, SDZ]$_0$ = 10 mg/L, ozone concentration = 3.67 mg/min and catalytic concentration = 1 g/L, 100% of the antibiotics were removed at contact times of 45 and 15 min. The values of electrical energy per order (E_{Eo}) increased from 49.79 to 106.9 (SCT), 53.69 to 108.84 (STZ), 55.36 to 111.11 (SMX) and 56.14 to 111.62 (kWh m^{-3}) (SDZ). Increased from 30.67 to 59.18 (SCT), 29.73 to 61.45 (STZ), 30.01 to 62.33 (SMX) and 30.67 to 64.42 (kWh m^{-3}) (SDZ) for catalytic and photocatalytic ozonation when antibiotic concentrations increased from 10 to 40 mg/L, respectively. The mechanism of catalytic and photocatalytic ozonation degradation of the antibiotics is governed by the formation of •OH. 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 the antibiotics identified by GC/MS were organic acids. The untreated antibiotics solution had higher acute toxicity for *Daphnia magna* than the treated solution by photocatalytic ozonation.

Keywords: Antibiotics sulfonamides degradation; Catalytic ozonation; Photocatalytic ozonation; Synergistic effect; Bioassay

1. Introduction

Antibiotics are organic compounds that are synthesized by different industries or generated by organisms including microorganisms, plants, and animals [1,2]. These compounds have the ability to selectively depress or influence the function of organisms at low or even micro level concentrations [1,3]. Over the last six decades, large quantities of antibiotics are being employed worldwide for the prevention and treatment of diseases in both humans and livestock, as well as for various non-therapeutic purposes such as promoting the growth of cattle [1,4]. Antibiotics can enter the environment through irrigation with sewage water, disposal of unused drugs, land application of biosolids, and through animal manure and

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are ubiquitous in a variety of environmental media such as water, sediments, soils, organism excrement, and so on [5]. Freshwater contamination by antibiotics from municipal and industrial streams poses a significant threat to human health as well as ecosystems [5]. For example, sulphonamide antibiotics, which are made from sulphanilic acid, inhibit the synthesis of dihydrofolic acid [6,7]. These antibiotics have a low biodegradability with a reported water range of 0.13–1.9 μg L^{-1} and can be bioaccumulated in a variety of organisms [6,7]. The incomplete elimination of emerging pollutants such as pharmaceuticals by means of conventional treatment methods can also have adverse effects on ecosystems [8]. However, the extent of these adverse effects is still unknown [9].

Thus, in order to enhance the degradation rate of antibiotics, a few new methods such as advanced oxidation processes (AOPs) are needed [10]. A strong oxidant is ozone that, under water treatment conditions, can generate hydroxyl radicals and act in a direct pathway; as a result, a large spectrum of organic materials can be oxidized [11,12]. Nonetheless, when single ozonation is utilized solely, a suitable mineralization rate of organic compounds cannot be attained. Also, refractory by-products are generated, which may be more toxic than their parent compounds. The mineralization rate of organic matters can be improved by means of the UV irradiation with photocatalysts [13,14]. In this method, the photogenerated holes and electrons can enhance removal efficiency. To this end, molecules such as oxygen and water are needed to produce superoxide ($O_2^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$), able to minerlize pollutants into end products of H_2O and CO_2. It should be pointed that a few organic compounds cannot be well degraded photocatalytically in the absence of oxygen or even single photolysis. Thus, to enhance the performance of the method, it is essential to add a compound that acts as electron scavenger. Hence, ozone, which is more reactive than oxygen can work effectually. It can be claimed that the combination of photocatalysis and ozone can cause the removal efficiency to increase [15]. Therefore, the electron–hole recombination declines with ozone because more amount of photogenerated electrons are trapped. As a result, the degradation efficiency rate of contaminants improves. Thus, photogenerated electron–holes pairs on the photocatalyst surface increases, declining electron acceptor or oxidize water and pollutants, when ozonation, heterogeneous catalysis and UV irradiation are combined [16]. In this case, reactive oxygen species, such as hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{\bullet-}$) and ozonide radicals ($O_3^{\bullet-}$) are produced more. By large, photocatalytic ozonation can be considered as promising method for water reclamation. The improvement of antibiotic degradation in the presence of AOPs has previously been reported [1,6,17–19]. But there is not much available information on the removal efficiency and removal kinetics of drug materials with illuminated TiO_2 from synthetic and real water samples.

In the current study, we employed catalytic and photocatalytic ozonation to investigate the effects of solution pH, initial antibiotic concentration, ozone concentration, catalyst concentration, scavenger type, and ion type on the removal of four sulfonamides antibiotics from synthetic and real water. In addition, the kinetic, Langmuir–Hinshelwood models and E_{E0} were calculated to determine the reaction rate and cost efficiency of the two ozonation processes, respectively. Intermediates and the mineralization degradation of the effluent were also examined by GC/MS and total organic carbon (TOC), respectively. The bioassay of the antibiotics was performed by *Daphnia magna* in solutions containing untreated and treated antibiotics via photocatalytic ozonation.

2. Materials and methods

The four antibiotics were purchased from Sigma-Aldrich Co., United States. Potassium iodide, sodium thiosulfate, sodium hydroxide, sulphuric acid, methanol and acid trichloroacetic acid were procured from Merck (Germany). The chemical structures of the sulfonamide antibiotics (sulfacetamide [SCT], sulfathiazole [STZ]), sulfamethoxazole [SMX] and sulfadiazine [SDZ]) have been shown in Table 1. A titanium dioxide nanocatalyst (>99.5% purity) with an anatase and rutile ratio of 80/20 was bought from Degussa Corp., Iran. The specific surface area of the TiO_2 particles was 50 ± 15 m^2/g and the average particle size was 21 nm. Ozone was produced by an ozone generator (Tonglin Technology, AGN-300, China) from high purity oxygen (Fuzhou Lianzhong Industrial Gases Co., Ltd., China). A 150 W high-pressure UVC lamp with wavelengths shorter than 280 nm was served as the light source. The elucidation of antibiotics decomposition pathways was done via a gas chromatography–mass spectroscopy (Varian-GC-MS 4000, Australia) device. A column (HP-5) of 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness was utilized. The initial temperature was kept at 100°C for 5 min and then raised (10°C min^{-1}) to reach 280°C. The interface temperature was kept at 280°C. And, helium was employed as the carrier gas at the rate of 1 mL min^{-1}. The experiment setup for the degradation of sulfonamides antibiotics has been shown in Fig. 1.

2.1. Nano catalyst TiO_2 analyses

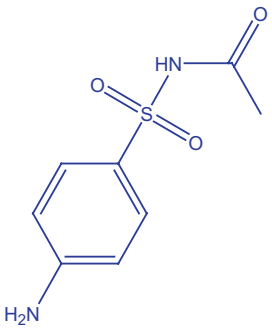
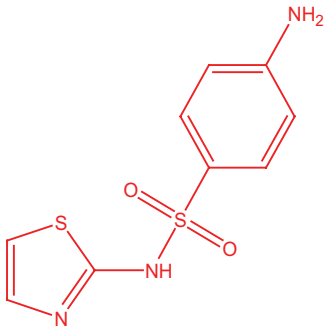
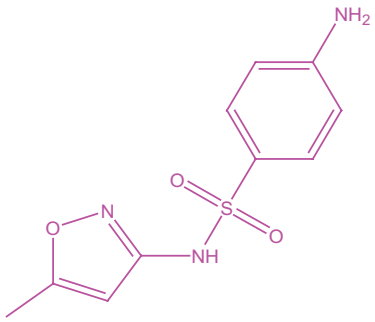
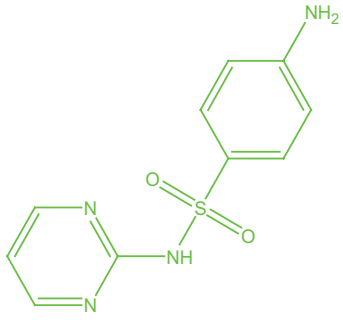
The crystallinity and phase, functional surface groups, and morphological and chemical composition of the sample were measured by X-ray diffraction, Fourier transform infrared spectroscopy, FE-SEM and energy dispersive X-ray spectroscopy, respectively. Details regarding all measurement device models were can be found in our previous article [20]. The average crystalline size of the catalyst was determined by the Debye–Scherrer formula [21]. In order to survey the surface charge properties of the adsorbent, the pH_{pzc} was detected and measured according to the method explained in a previously published work [22].

2.2. Experiments

A stock solution of the antibiotics was prepared with distilled water. The method of one-factor-at-a-time was used to study one key variable while holding the other variables constant. Studied variables in photocatalytic and catalytic ozonation included catalyst concentration (0.1, 0.5, 1 g/L), pH (3, 5, 7, 9, 11), initial antibiotic concentration (10, 20, 40 mg/L), reaction time (5–60 min), ozone concentration (1.67, 2.5, 3.67 mg/min), ion type (carbonate, bicarbonate, sulphate, nitrate and chloride) equal to 200 mg/L and scavenger type

(*t*-butanol and ammonium oxalate). In order to adjust the initial pH of each solution, 0.1 N HCl and 0.1 N NaOH were used with a pH meter. The duration of catalytic and photocatalytic ozonation was 1 h, and the samples were randomly taken from the reactor during these processes for analysis. The antibiotic concentration was quantified by means of high performance liquid chromatography (Waters, USA) with a UV detector at 270 nm and A C18 column (5 ml, 250 mm long × 4.6 mm ID). Chemistation software was used to record the data. The mobile phase consisted of a mixture of trichloro acetic acid acidified at pH 3 by sulphuric acid addition and methyl alcohol at 20/80 (v/v). The flow speed was set at 1.5 mL/min, and 20 μL injection volumes were used. Gas chromatography–mass spectroscopy was used to discern

Table 1
Chemical structure and characteristics of the four 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

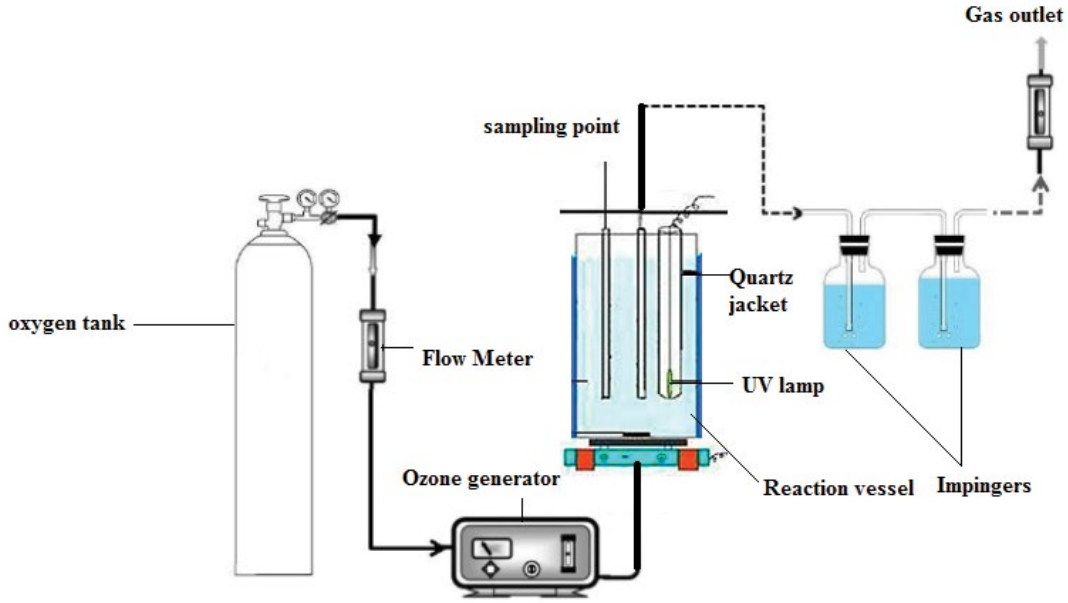


Fig. 1. Schematic diagram of the photocatalytic ozonation reactor.

antibiotic decomposition pathways. In order to determine antibiotic mineralization rates, TOC content was detected using a Shimadzu TOC-VCSH (Japan) analyzer by directly injecting the aqueous solution with 0.05 mL hydrochloric acid. Immobilization tests for *D. magna* were conducted in order to assess acute toxicity by observing mobility. The initial concentration of the antibiotics sample was 10 mg/L. The effluent product from the photocatalytic ozonation process was prepared with a different dilation (V/V%). Ten neonate daphnids were added to the vessel samples at 24, 72 and 96 h in order to determine mortality counts, and LC_{50} and TU values were computed by the Probit analysis.

3. Results and discussion

3.1. Effect of operational parameters on antibiotics removal

3.1.1. Effect of initial pH

The effect of the initial pH on the catalytic ozonation degradation of the antibiotics was investigated by varying pH from 3 to 11 under the following conditions: antibiotic concentration 10 mg/L, influent ozone concentration 3.67 mg/min and catalyst concentration 1 g/L over a period of 45 min. Fig. 2a shows that degradation efficiency enhanced from 95.2%, 94.3%, 95.2%, and 93.1% to 100% for SCT, STZ, SMX, and SDZ by increasing the initial pH from 3 to 5. However, the degradation efficiency decreased to 53.6% (SCT), 51.6% (STZ), 51.7% (SMX), and 50.7% (SDZ) at pH 11. Fig. 2b shows that the degradation efficiency by photocatalytic ozonation through varying the initial pH from 3 to 11 increased from 85.3%, 86.7%, 86.8%, 85.3% to 100% for SCT, STZ, SMX, and SDZ, respectively, under the following conditions: initial antibiotic concentration 10 mg/L, influent ozone concentration 3.67 mg/min, catalyst concentration 1 g/L and contact time 15 min,. However, it decreased to 44.2% (SCT), 45.7% (STZ), 46.2% (SMX), and 46.8% (SDZ) at pH 11. According to the data, the pH_{zpc} of the TiO_2 nanoparticles was determined equal to 4. Nano TiO_2 surface is negatively charged in basic conditions because force of attraction increases the adsorption of positively charged contaminants onto the activated surface, thereby increasing the tendency of subsequent photocatalytic reactions [23]. With an increase in the pH value, sulfonamides will lose a proton and exist in anionic form. Hence, these two negative sulfa pharmaceutical molecules cannot easily be adsorbed onto the surface of TiO_2 with the same negative charges [23]. Under UV illumination, titania shows a high oxidizing power at lower pH. At lower pH, positive holes are believed to be leading species causing oxidation reactions [24]. Tong et al. [25] reported that the pH values for the degradation of sulfosalicylic acid solution by photocatalysis ozonation decreased first within a period of time and then increased subsequently with the mineralization of intermediates. They found that the pH value in the system increased an initial pH of 2.2–2.8 for ozonation within 45 min [25].

3.1.2. Effect of catalyst concentration

The effect of catalyst dosage on the degradation of the antibiotics by the O_3/TiO_2 process was investigated through varying the catalyst dosage (0.1, 0.5, 1 g/L) under the conditions as follows: initial pH 5, initial antibiotic concentration 10 mg/L, ozone concentration 3.67 mg/min and contact time 30 min. Fig. 3a shows that the degradation efficiency enhanced from 86.4% to 94.1% (SCT), 85.9% to 92.7% (STZ), 84.3% to 92.1% (SMX), and 84.1% to 91.7% (SDZ) with increasing the catalyst dosage from 0.1 to 1 g/L. The most effective decomposition rates of the antibiotics were observed at 1 g/L of the nanocatalyst, which were 94.1% (SCT), 92.7% (STZ), 92.1% (SMX), and 91.7% (SDZ); thus, this value of dose was chosen as the optimum amount. Fig. 3b indicates the degradation efficiency of $O_3/UV/TiO_2$ by varying the catalyst

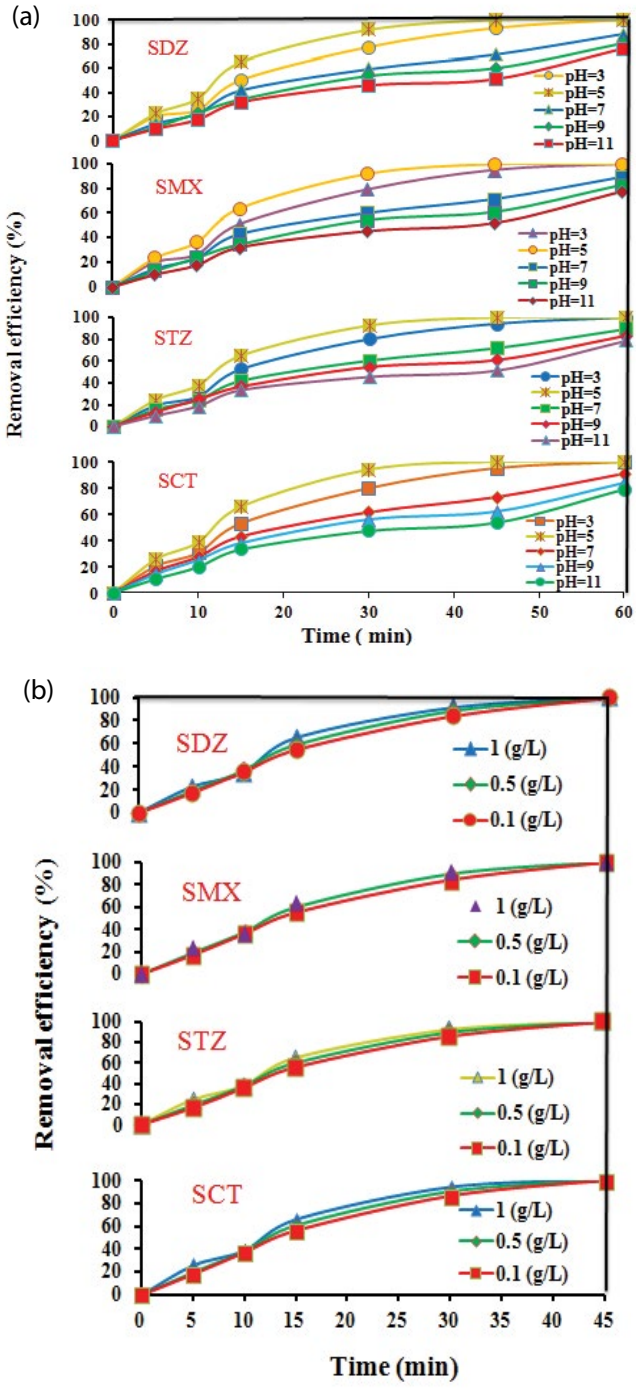


Fig. 2. Effect of initial pH on (a) catalytic ozonation and (b) photocatalytic ozonation of four antibiotics ($[C]_0$ = 10 mg/L, ozone concentration = 3.67 mg/min, catalytic concentration = 1 g/L, contact times = 45 and 15 min, respectively).

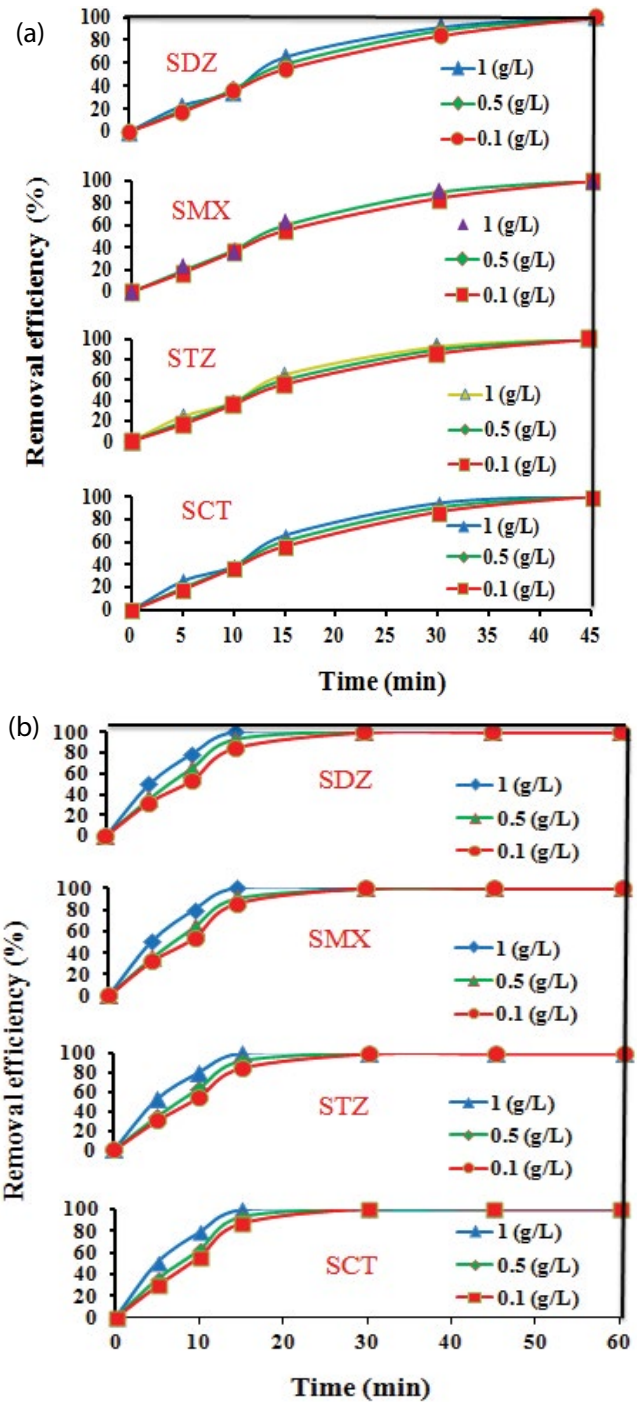


Fig. 3. Effect of catalyst concentration on (a) catalytic ozonation and (b) photocatalytic ozonation degradation of different antibiotics (($[C]_0$ = 10 mg/L, pH = 5, ozone concentration = 3.67 mg/min, contact times = 30 and 15 min, respectively).

dosage (0.1, 0.5, 1 g/L) at initial pH 5 and initial antibiotic concentration (10 mg/L), ozone concentration (3.67 mg/min) at 15 min. The efficiency increased from 86.4%, 85.2%, 85.9%, and 84.9% to 100% for SCT, STZ, SMX, and SDZ with increasing the catalyst dosage from 0.1 to 1 g/L. The most effective decomposition rate (100%) of the antibiotics was observed at 1 g/L of the nanocatalyst. The higher amount of the catalyst, the better the degradation was; this could be due to an increase in light absorption, which increases the numbers of •OH radicals. However, at quantities higher than the optimal value the degradation did not improve probably due to stronger competition for the incoming light [26]. Cernigoj et al. studied the degradation of thiacloprid using photocatalysts with various surface areas and photocatalytic activities;

they showed that the higher surface area of a photocatalyst increased the degree of synergy between ozonation and photocatalysis. This was due to increased amounts of adsorbed ozone molecules on the surface and their further reactions with photogenerated electrons [27].

3.1.3. Effect of initial antibiotics concentration

We investigated the effect of the initial concentration of the antibiotics (10, 20, 40 ppm) on the degradation of antibiotics under the conditions as follows: initial pH 5, constant catalyst concentration (1 g/L), ozone concentration 3.67 mg/min and contact time 30 min. Fig. 4a shows that the catalytic ozonation degradation of the antibiotics decreased from 94.1% to 73.5% (SCT), 92.7% to 72.8% (STZ), 92.1% to 72.1% (SMX), and 91.7% to 71.9% (SDZ) when in the initial concentration increased from 10 to 40 ppm. Also, the photocatalytic ozonation degradation of the antibiotics also decreased from 100% to 71.9% (SCT), from 100% to 70.5% (STZ), from 100% to 69.8% (SMX) and from 100% to 68.4% (SDZ) when the initial concentration increased from 10 to 40 ppm (Fig. 4b). An increase in the initial concentration of water pollutants resulted in an increase in the saturation of the catalyst surface with pollutants and a decrease in the oxidation rate by photocatalytic ozonation [28,29]. Beltrán et al. [30] described an inverse effect for the photocatalytic ozonation of sulfamethoxazole, which was due to an increase in the initial concentration of this pollutant. However, the light adsorption of the photocatalyst particles is reduced by increasing the amounts of pollutants on the photocatalyst surface [30].

3.1.4. Effect of influent ozone gas concentration

The effect of influent ozone concentration on the catalytic ozonation degradation of the sulfonamides antibiotics was investigated by varying the initial ozone gas concentration from 1.67 to 3.67 mg/min, at initial pH 5, with a constant initial antibiotics concentration (10 mg/L) and constant catalyst concentration (1 g/L). Fig. 5a shows that the catalytic ozonation degradation of the antibiotics increased from 84.3% to 100% (SCT and STZ), 83.5% to 100% (SMX) and 83.1% to 100% (SDZ) per increases in the initial ozone concentration after 45 min. Fig. 5b shows that the photocatalytic ozonation degradation of the antibiotics increased similarly from 80.9% to 100% (SCT), 80.1% to 100% (STZ), 81.6% to 100% (SMX) and 80.7% to 100% (SDZ) when the initial ozone concentration was raised from 1.67 to 3.67 mg/min after 15 min. This increase in ozone concentration led to increased adsorption of ozone molecules [31]. Stabilization of the photogenerated positive holes on the photocatalyst surface was a result of photocatalytic ozonation enhancing reaction between photogenerated electrons and adsorbed ozone molecules and adsorption of pollutants on the positively charged photocatalyst surface [31,32]. The results reported by Beltrán et al. [30] and Rodriguez et al. [33] illustrated that the photocatalytic ozonation of various pharmaceuticals (atenolol, hydrochlorothiazide, ofloxacin, trimethoprim, and sulfamethoxazole) at low ozone concentrations where the ozone was increased up to a critical concentration level is due to hydroxyl radicals and direct ozonation.

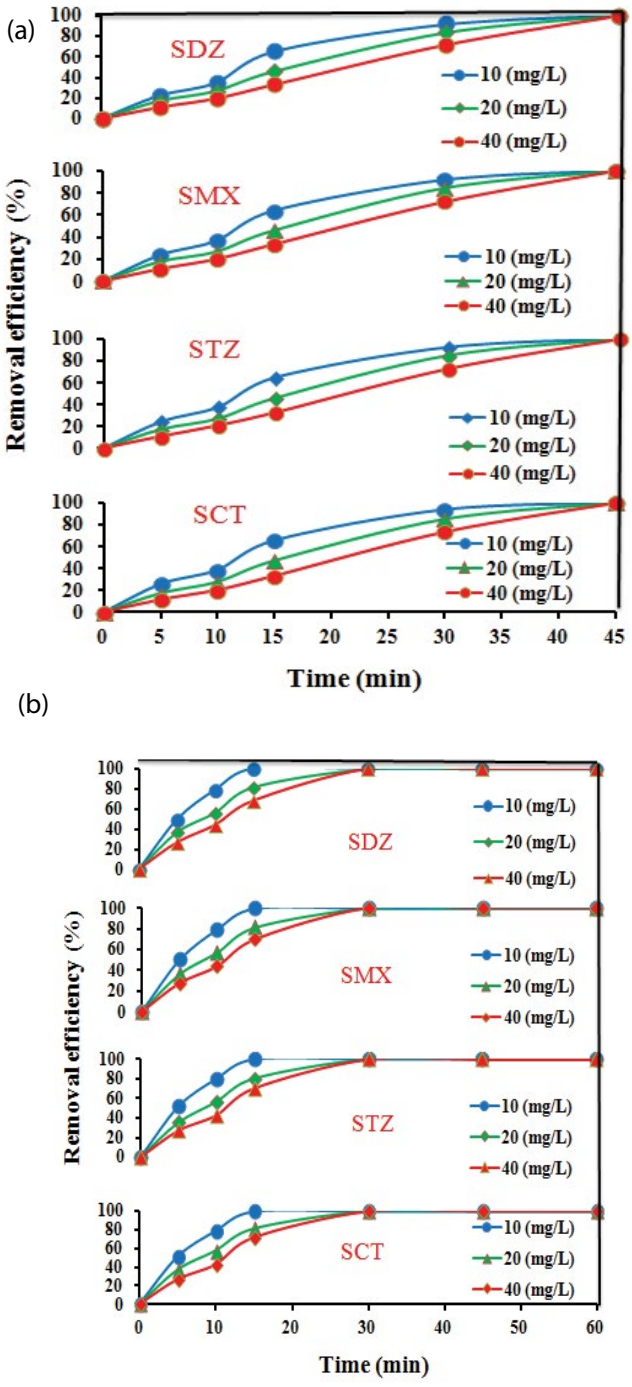


Fig. 4. Effect of initial antibiotic concentration on (a) catalytic ozonation and (b) photocatalytic ozonation of four antibiotics (pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L, contact times = 30 and 15 min, respectively).

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

Experiment results obtained at various reaction times were fitted with the zero, first and second order equations. For catalytic photocatalytic ozonation, the relationship between the initial degradation rate (r) and the initial concentration of antibiotics can be described by the Langmuir–Hinshelwood

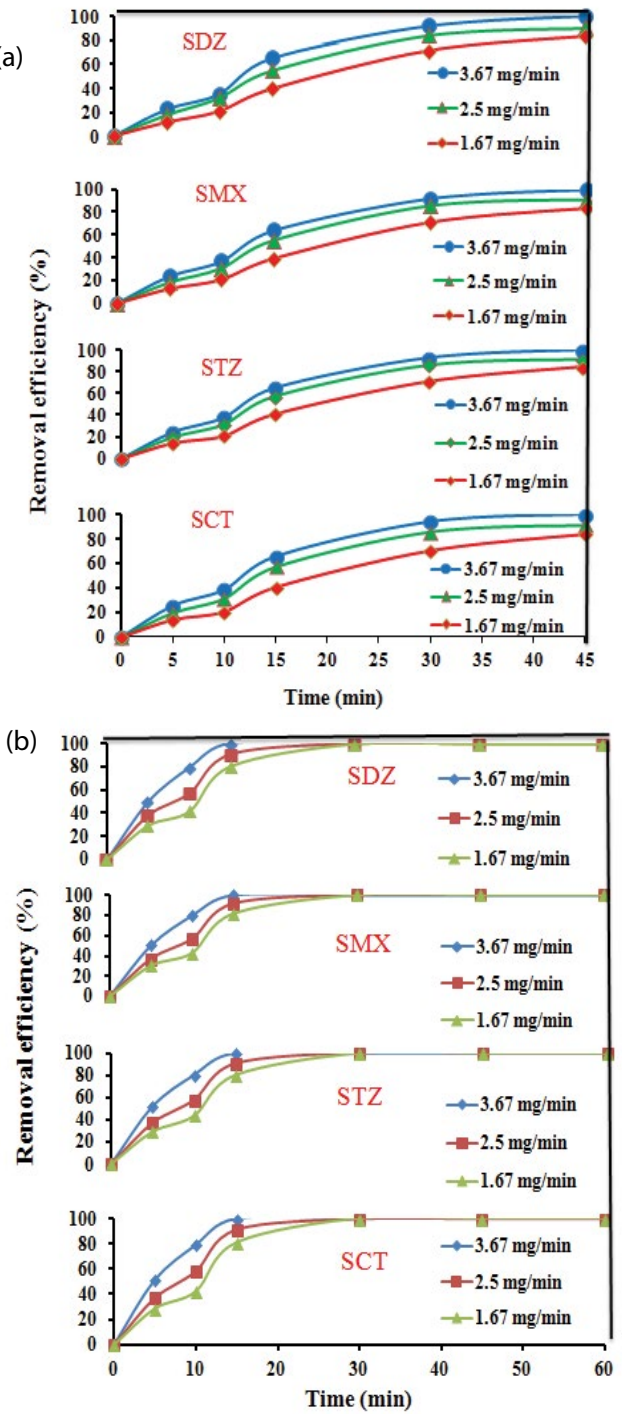


Fig. 5. Effect of influent ozone concentration on (a) catalytic ozonation and (b) photocatalytic ozonation of four antibiotics ($[C]_0$ = 10 mg/L, pH = 5, catalyst concentration = 1 g/L, contact times 45 and 15 min, respectively).

model. The E_{Eo} values for the catalytic and photocatalytic 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, were evaluated [34]. To obtain kinetic parameters for the catalytic and photocatalytic ozonation degradation of antibiotics, C_0–C_t, ln $[C_0/C_t]$ and $1/C_t$–$1/C_0$ vs. t was plotted. These equations and constants have been summarized in Table 2. The kinetic parameters of the zero, first and second-order reactions for the catalytic and photocatalytic ozonation degradation of the antibiotics at different initial antibiotics concentrations have been summarized in Tables 3 and 4, respectively. The catalytic and photocatalytic ozonation degradation rates of the antibiotics fitted well with the first-order model. As shown in Table 3, the reaction rate of the pseudo-first order kinetic model (k_{obs}) and R^2 decreased from 0.0964 to 0.0449 min^{-1} and 0.968 to 0.9482 for SCT, 0.0894 to 0.0441 min^{-1} and 0.9737 to 0.9517 for STZ, 0.0867 to 0.0432 min^{-1} and 0.9738 to 0.9545 for SMX and 0.0855 to 0.043 min^{-1} and 0.9739 to 0.9533 for SDZ with an increase in the initial antibiotic concentration from 10 to 40 mg/L, respectively. As shown in Table 4, the reaction rate of the pseudo-first order kinetic model (k_{obs}) and R^2 decreased from 0.1565 to 0.0811 min^{-1} and 0.9978 to 0.9386 for SCT, 0.1614 to 0.0781 min^{-1} and 0.9971 to 0.9484 for STZ, 0.1599 to 0.077 min^{-1} and 0.9945 to 0.9588 for SMX and 0.1565 to 0.0745 min^{-1} and 0.9951 to 0.9685 for SDZ with increasing the initial antibiotics concentration from 10 to 40 mg/L, respectively. K_{SCT} and k_c were (17.8 L mg^{-1}) and (2.57 mg/L min^{-1}), K_{STZ} and k_c were (20 L mg^{-1}) and (2.63 mg/L min^{-1}), K_{SMX} and k_c were (20.45 L mg^{-1}) and (2.6) (mg/L min^{-1}), K_{SDZ} and k_c were (21.6 L mg^{-1}) and (2.63 mg/L min^{-1}) by plotting $1/k_{obs}$ vs. the initial antibiotics concentration, for catalytic ozonation, respectively. K_{SCT} and k_c were (25 L mg^{-1}) and (5.2 mg/L min^{-1}), K_{STZ} and k_c were (21.23 L mg^{-1}) and (4.69 mg/L min^{-1}), K_{SMX} and k_c were (19.82 L mg^{-1}) and (4.55 mg/L min^{-1}), K_{SDZ} and k_c were (18.21 L mg^{-1}) and (4.31 mg/L min^{-1}) by plotting $1/k_{obs}$ vs. the initial antibiotic concentration, for photocatalytic ozonation, respectively. E_{Eo} values at different initial antibiotic concentrations have been summarized in Tables 3 and 4, respectively. The E_{Eo} values increased from 49.79 to 106.9 (kWh/m^3) for (SCT), from 53.69 to 108.84 (kWh/m^3) for (STZ), 55.36 to 111.11 (kWh/m^3) for (SMX) and 56.14 to 111.62 (kWh/m^3) for (SDZ) when antibiotic concentrations were raised from 10 to 40 mg/L for catalytic ozonation, respectively. The E_{Eo} values increased from 30.67 to 59.18 (kWh/m^3) for (SCT), from 29.73 to 61.45 (kWh/m^3) for (STZ), 30.01 to 62.33 (kWh/m^3) for (SMX) and 30.67 to 64.42 (kWh/m^3) for (SDZ) with raising antibiotic contents from 10 to 40 mg/L for photocatalytic ozonation, respectively.

3.3. Comparison of reaction rate

The value of the first order kinetic constant was obtained by fitting the experiment data at optimum conditions of systems as shown in Fig. 6. These results, summarized in Table 5, show that the reaction rate of photocatalytic ozonation to be 3.2 times (SCT), 3.4 times (STZ), 3.47 times (SMX), 3.62 times (SDZ) higher than those for the catalytic ozonation process under the optimum conditions. In the presence of TiO_2 under illumination, ozone can generate •OH radicals through the formation of an ozonide radical ($O_3^{\bullet-}$) [35]. In the absence of O_3, dissolved O_2 itself can accept TiO_2 conduction band electron and generate $O_2^{\bullet-}$. Therefore, this species cannot give •OH radicals in a single step and require a total of three electrons for the generation of a single •OH species [35]. Sánchez et al. [36] found that the strategy of

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

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

Table 3
Kinetic parameters and electrical energy per order for the catalytic ozonation of four antibiotics at different initial concentrations (pH = 5, ozone concentration = 3.67 mg/min and catalyst dosage = 1 g/L)

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	0.0819	0.0824	0.0964	10.37	0.968	49.79	0.0568	0.8738
20	–0.1137	0.0331	0.065	15.38	0.9568	73.84	0.011	0.9291
40	–0.0771	0.0035	0.0449	22.27	0.9482	106.9	0.0029	0.9527
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	–0.0789	0.0753	0.0894	11.18	0.9737	53.69	0.0458	0.8949
20	–0.1114	0.0315	0.0645	15.5	0.9539	74.41	0.0109	0.9279
40	–0.0687	0.0028	0.0441	22.67	0.9517	108.84	0.0028	0.9537
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	–0.0774	0.0715	0.0867	11.53	0.9738	55.36	0.0422	0.9009
20	–0.1068	0.0293	0.0633	15.79	0.955	75.82	0.0105	0.9312
40	–0.0599	0.0021	0.0432	23.14	0.9545	111.11	0.0028	0.9546
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	–0.0792	0.0718	0.0855	11.69	0.9739	56.14	0.0403	0.9101
20	–0.1015	0.0266	0.0614	16.28	0.9592	78.17	0.0099	0.938
40	–0.0577	0.0019	0.043	23.25	0.9533	111.62	0.0027	0.9541

Table 4
Kinetic parameters and electrical energy per order for photocatalytic ozonation degradation of the four antibiotics at different initial concentrations (pH = 5, ozone concentration = 3.67 mg/min and catalyst dosage = 1 g/L)

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	0.209	0.183	0.1565	6.38	0.9978	30.67	0.0478	0.9934
20	0.1408	0.0274	0.1089	9.18	0.9711	44.077	0.0169	0.9363
40	0.5464	0.0743	0.0811	12.33	0.9386	59.18	0.0055	0.9473
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	0.199	0.1695	0.1614	6.19	0.9971	29.73	0.0503	0.9902
20	0.15	0.0297	0.1058	9.45	0.9716	45.36	0.0161	0.9427
40	0.5824	0.0861	0.0781	12.8	0.9484	61.45	0.0053	0.9533
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	0.202	0.1626	0.1599	6.25	0.9945	30.01	0.0495	0.9883
20	0.1388	0.0258	0.1089	9.18	0.9682	44.077	0.0169	0.9338
40	0.5936	0.0911	0.077	12.98	0.9588	62.33	0.0052	0.9591
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	0.209	0.171	0.1565	6.38	0.9951	30.67	0.0478	0.9906
20	0.1388	0.0259	0.11	9.09	0.9607	43.63	0.0173	0.9225
40	0.6192	0.0988	0.0745	13.42	0.9685	64.42	0.005	0.9649

Table 5
First order kinetic and contact time for the degradation processes of the four antibiotics

	O_3/TiO_2			$O_3/UV/TiO_2$		
	K (min^{-1})	T (min)	R^2	K (min^{-1})	T (min)	R^2
Sulfacetamide	0.48939	10	0.968	1.565421	10	0.9978
Sulfathiazole	0.474815	10	0.9737	1.61445	10	0.9971
Sulfamethoxazole	0.460449	10	0.9738	1.599488	10	0.9945
Sulfadiazine	0.432323	10	0.9739	1.565421	10	0.9951

ozonation pre-treatment followed by photocatalysis would be a satisfactory route for aniline degradation.

3.4. Comparison of effects of synergistic catalytic and photocatalytic ozonation

The combination of two and three oxidation systems including ozonation and catalysis and ozonation, catalysis, UV radiation for water treatment under optimum conditions are reported to have increased oxidation efficiencies (synergy) compared with the sum oxidation efficiencies of these two and three oxidation systems separately [37]. The results obtained in degradation of sulfonamides antibiotics by the $TiO_2/UV/O_3$ process showed that the synergistic effect was 1.3 (SCT), 1.36 (STZ), 1.36 (SMX), and 1.37 (SDZ) times higher than those of O_3/TiO_2, which were 1.2 (SCT), 1.23 (STZ), 1.2 (SMX), and 1.2 (SDZ; Fig. 7). The synergistic effects of photocatalytic ozonation resulted in an increase in the number of electrons on the surface of titanium dioxide [38,39]. Consequently, a larger number of radicals are

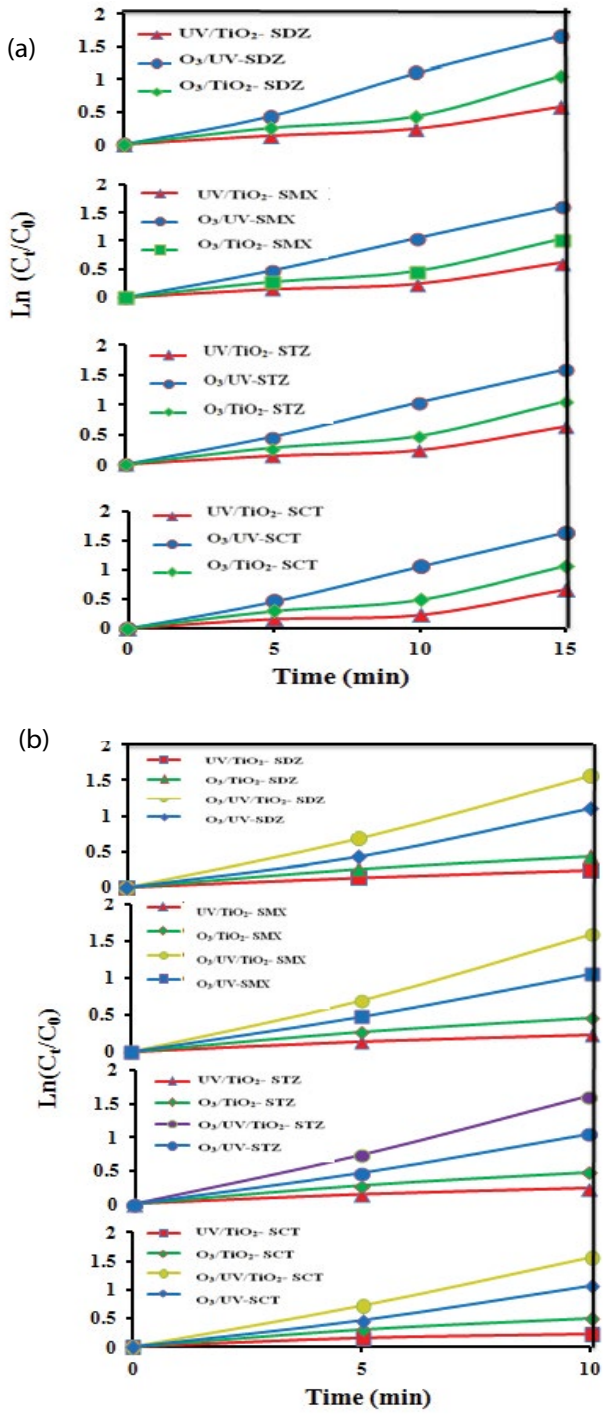


Fig. 6. Comparison of first order kinetic constant reaction rate (a) catalytic ozonation and (b) photocatalytic ozonation of four antibiotics (pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L, contact time = 10 min).

produced, thereby accelerating the photocatalytic reaction [40]. In the study by Rajeswari and Kanmani [41], who investigated the degradation of a pesticide carbaryl, it was found that the oxidation rate constant using TiO_2/UV/O_3 was 2.3 and 4.4 times higher than those of O_3/UV and TiO_2/UV, respectively.

3.4.1. Effect of different inorganic ions

To assess the effect of different inorganic ions on the photocatalytic ozonation degradation of the antibiotics, equal amounts of inorganic ions (sulphate, sodium, carbonate, phosphate, bicarbonate, and nitrate) were added to the reactor before initiating the O_3/UV/TiO_2 process. The concentration of each inorganic ion was adjusted at 200 mg/L while the initial antibiotics concentration, influent ozone concentration, catalyst concentration, and initial pH were constant at 10 mg/L, 3.67 mg/min, 1 g/L, and 5, respectively (Fig. 8). The presence of inorganic ions reduces the active surface of the semiconductor and exerts a scavenging effect on hydroxyl radical oxidation [42,43]. Phosphate ions have an inhibitory influence on the photocatalytic ozonation of sulfamethoxazole and diclofenac in water [44]. This influence is due to the reaction of the ions with hydroxyl radicals (as a scavenger) as well as the role of ions in the deactivation of the photocatalyst surface [44,45].

3.4.2. Effect of different scavengers and possible mechanism

To understand the efficacy of active species in the catalytic ozonation degradation of antibiotics, some experiments were run by means of different scavengers such as benzoquinone (as a $O_2^{\bullet-}$ trapping), of *t*-butanol (as a •OH trapping) and ammonium oxalate (as a h^+ trapping). As shown in Fig. 9, when no scavenger was added to the system, the removal efficiency was 100%. The figure indicates that the removal rates of four antibiotics declined after the addition of scavengers such as benzoquinone and *t*-butanol. This result illustrated that •OH and h^+were the main active species in the catalytic ozonation process. The high decrease in degradation of antibiotics in the presence of tert-butanol verifies the generation of •OH. Because of the high reaction rate constant ($6 \times 10^8\ M^{-1}\ s^{-1}$) of tert-butanol with •OH [46], when it was added to the catalytic ozonation processes (COPS), it actively competed with the antibiotics molecules to react with •OH in the solution bulk and hindered the oxidation of antibiotics [47].

The levels of the removal efficiency of the antibiotics in the current study and in other similar studies in which catalytic and photocatalytic ozonation were used have been compared in Table 6.

The comparison of the methods illustrated that the antibiotics could completely be decomposed. As displayed in Table 6, the efficiency observed in catalytic and photocatalytic ozonation cannot be explained by the simple summation of the single ozonation and photolysis processes. Thus, it is expected a higher generation of hydroxyl radicals in the photocatalytic system when ozone is present in the media. Ozone is capable of trapping photocatalytically generated electrons more efficiently than oxygen, avoiding the recombination of the electron–hole pair according to the following mechanism (Eqs. (1)–(4)) [55].

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$\left.\begin{aligned} O_2 + e^- &\rightarrow O_2^{\bullet-} \\ O_3 + e^- &\rightarrow O_3^{\bullet-} \end{aligned}\right\} \text{Electron trapping} \quad (2)$$

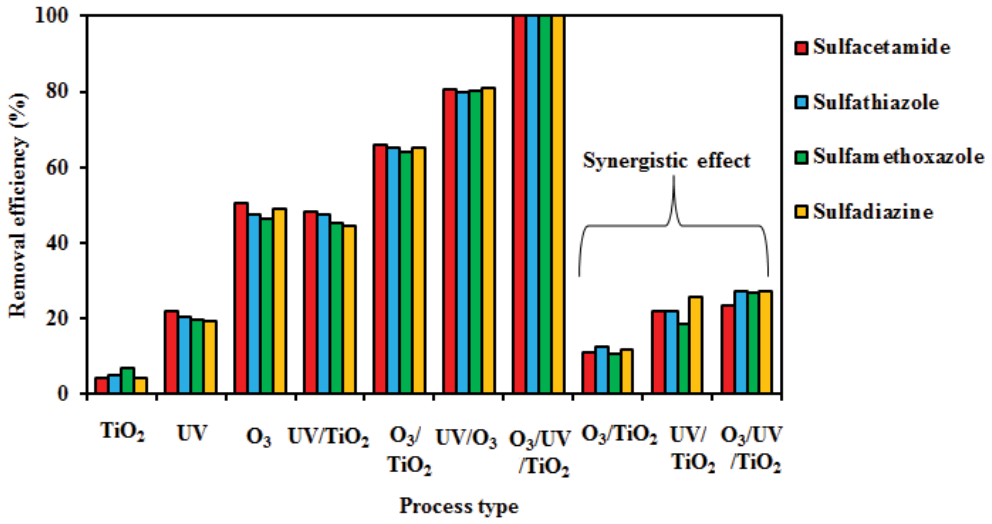


Fig. 7. Contribution of each process and of and synergetic effect of combined processes in degradation of four antibiotics (pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L, contact time = 15 min).

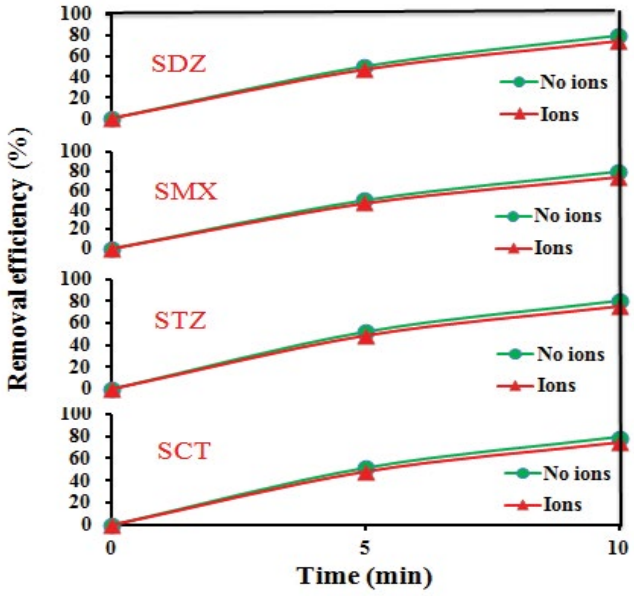


Fig. 8. Effects of different anions on the photocatalytic ozonation of four antibiotics ([C]$_0$ = 10 mg/L, pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L).

$$\left.\begin{aligned} &O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \xrightarrow{+HO_2^{\bullet}} O_2 + H_2O_2 \xrightarrow{+O_2^{\bullet-}} O_2 + HO^{\bullet} + OH^{\bullet} \\ &O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \rightarrow O_2 + HO^{\bullet} \\ &h^+ + H_2O_2 \rightarrow H^+ + HO^{\bullet} \end{aligned}\right\} \quad HO^{\bullet} \text{ generation} \tag{3}$$

$$\left.\begin{aligned} &e^- + R \rightarrow \text{Products} \\ &HO^{\bullet} + R \rightarrow \text{Products} \\ &h^+ + R \rightarrow \text{Products} \end{aligned}\right\} \text{Parent compounds initial reactions} \tag{4}$$

In the above mechanism, one molecule of ozone necessitates only one electron to produce one hydroxyl radical, compared with three electrons required by oxygen to get the same •HO yield.

3.5. Removal of antibiotics from natural water samples

In order to investigate the efficiency of photocatalytic ozonation degradation in removal of the antibiotics from natural water, 10 ppm of the antibiotics was added to a natural water sample that was obtained from the municipal water distribution network in Tehran, Iran. The characteristics of the natural water have been presented in Table 7. Generally, the natural water contains anions such as sulphates, carbonates and bicarbonates. The removal of the antibiotics from natural water was compared with synthetic water (Fig. 10). Ion inhibition is due to the ability of ions to act as hydroxyl radical scavengers, based on the following reactions [56]:

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + OH^- \tag{5}$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + HO^- \tag{6}$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \tag{7}$$

The reaction between •OH and carbonate and bicarbonate ions produces a carbonate radical ($CO_3^{\bullet-}$) which in turn reacts with a hydroperoxide ion (HO_2^-) [49]. This hydroperoxide ion is produced as a result of aqueous ozone decomposition and results in the generation of •OH through a series of radical–radical reactions [56]. Although the generated radical anions have been shown to be oxidants themselves, their oxidation potential is less than that of hydroxyl radicals [56]. The pH of natural water containing antibiotics increased from 7.27 to 7.81 after photocatalytic ozonation. Due to sub-neutral pH conditions, inorganic carbon exists primarily in the form of bicarbonate and is found in surface

Table 6
Comparison of removal different of the four antibiotics by catalytic ozonation and photocatalytic ozonation

pH	Antibiotics type	Catalyst type	[catalytic concentration]$_0$ g/L	O_3 influent (mg/L)	Time (min)	Removal efficiency (%)	k_{obs} (min $^{-1}$)	R^2	Reference
7	Sulfamethoxazole	γ-Al_2O_3/O_3	–	20	6–10	100	0.60	–	[48]
7	Sulfamethoxazole	$Co/Al_2O_3/O_3$	–	20	6–10	100	0.69	–	[49]
4.8	Sulfamethoxazole	$MWCNTs/O_3$	100 mg/L	50 g/m^3	30	36	–	–	[50]
4.8	Sulfamethoxazole	AC/O_3	100 mg/L	50 g/m^3	180	46	–	–	[50]
7	Sulfamethoxazole	carbon Darco12-20 /O_3	1	20	10	30	0.0035	–	[51]
8	Sulfamethoxazole	Fe(II)–Mt/O_3	1.91	–	20	98–99	0.24	0.965	[52]
8	Sulfamethoxazole	Co(II)–Mt/O_3	1.91	–	20	97	0.24	0.965	[52]
8	Sulfamethoxazole	Ni(II)–Mt/O_3	1.91	–	20	95	0.24	0.965	[52]
8	Sulfamethoxazole	Cu(II)-Mt/O_3	1.91	–	20	92	0.24	0.965	[52]
4.8	Sulfamethoxazole	$CeO_2/AC/O_3$	0.14	50 g/m^3	180	73	–	–	[50]
7	Sulfamethoxazole	Goethite/O_3	0.2	15	120	48	–	–	[53]
6.8	Sulfamethoxazole	AC1(LH2c20/48),	0.5	5–10	60	50	2.2	0.989	[54]
		AC2(WH2c8/32),					2.5	0.996	
		AC3(WH5c8/32) /O_3					3	0.975	
6.8	Sulfamonomethoxine	AC1(LH2c20/48),	0.5	5–10	60	50	2.3	0.995	[54]
		AC2(WH2c8/32),					1.9	0.998	
		AC3(WH5c8/32)/O_3					3.3	0.994	
6.8	Sulfadimidine	AC1(LH2c20/48),	0.5	5–10	60	50	2.7	0.97	[54]
		AC2(WH2c8/32),					2.8	0.992	
		AC3(WH5c8/32)/O_3					2.5	0.993	
6.8	Sulfadimethoxine	AC1(LH2c20/48),	0.5	5–10	60	50	2.6	0.941	[54]
		AC2(WH2c8/32),					2.5	0.991	
		AC3(WH5c8/32)/O_3					2.1	0.991	
7	Sulfamethoxazole	TiO_2/O_3/UV	0.5	10	15	90	1.5	–	[49]
5	Sulfacetamide	TiO_2/O_3	1	0.22 g/h	45	100	0.0964	0.968	In study
5	Sulfacetamide	O_3/UV/TiO_2	1	0.22	15	100	0.1565	0.9978	In study
5	Sulfathiazole	O_3/TiO_2	1	0.22	45	100	0.0894	0.9737	In study
5	Sulfathiazole	O_3/UV/TiO_2	1	0.22	15	100	0.1614	0.9971	In study
5	Sulfamethoxazole	O_3/TiO_2	1	0.22	45	100	0.0867	0.9738	In study
5	Sulfamethoxazole	O_3/UV/TiO_2	1	0.22	15	100	0.1599	0.9945	In study
5	Sulfadiazine	O_3/TiO_2	1	0.22	45	100	0.0855	0.9739	In study
5	Sulfadiazine	O_3/UV/TiO_2	1	0.22	15	100	0.1565	0.9951	In study

and ground water at concentrations typically in the range of 50–200 mg/L [57]. Higher concentrations may be encountered in high alkaline water reducing the degree of photocatalytic ozonation [58]. The specific conductivity of this solution decreases from 403 to 392 following photocatalytic ozonation degradation. Bicarbonate ions in reactions with hydroxyl radicals in competition with refractory organic pollutants are the principal consumers of hydroxyl radicals [43,59]. Bicarbonate radicals act as an oxidation species and have a much lower reaction rate constant than hydroxyl radicals for the oxidation of organic micropollutants [59].

3.6. Determination of by-products and mineralization

In this study, intermediates were identified from the catalytic and photocatalytic ozonation degradation of the antibiotics by GC-MS under the following conditions: pH = 5, [antibiotics]$_0$ = 10 mg/L, influent ozone concentration = 3.67 mg/min and catalytic concentration = 1 g/L. The rate of antibiotics mineralization was performed by the TOC analysis. The probable degradation pathways of the antibiotics during catalytic ozonation and photocatalytic ozonation were proposed based on C–S bond cleavage to form C1 and aniline, S–N bond cleavage to form C2 and sulfanilic acid, hydroxylation of the aniline moiety to form C4 and further oxidation of the amino group attached to benzene ring to form C3 as shown in Fig. 11. C4 could be a hydroxylated (–OH) derivative of the aniline moiety of sulfonamides. C3 contained the 5-methylisoxazole moiety and oxygenation forms of the aniline group of sulfonamides referring to the addition of –OH and the formation of nitroso group (–N=O). It was also reported that the amino

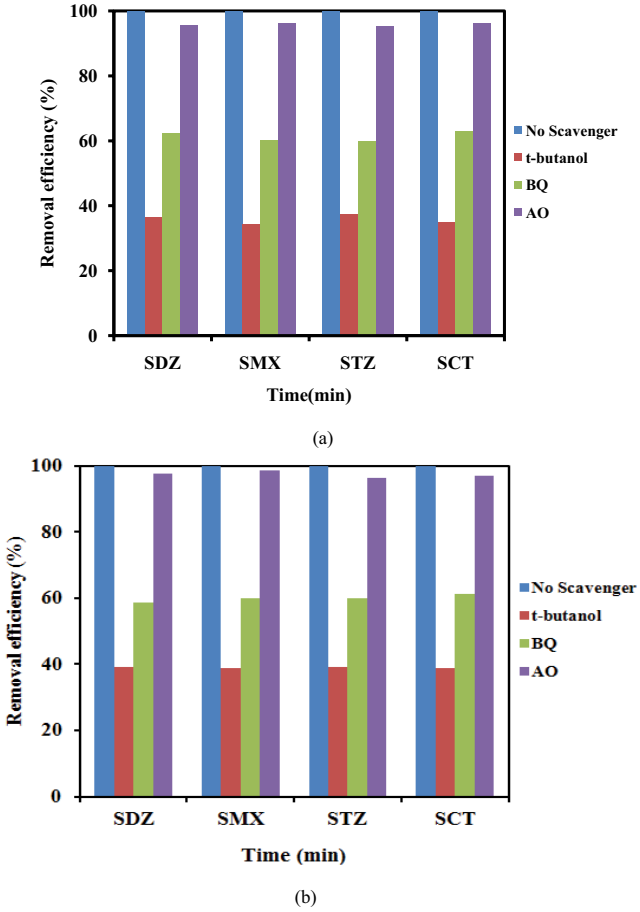


Fig. 9. Effects of different scavengers on (a) catalytic ozonation and (b) photocatalytic ozonation of four antibiotics ($[C]_0$ = 10 mg/L, pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L).

Table 7
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)	1,416
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

group could be transformed to the nitroso group when sulfonamides were oxidized by ozone [17]. The initial attack on the amino group of sulfonamides probably occurred by single electron-transfer from the amino group to O_3. Then, the formed aminyl radical cation evolved into a radical by N–H deprotonation, which could couple with O_3 and oxygen

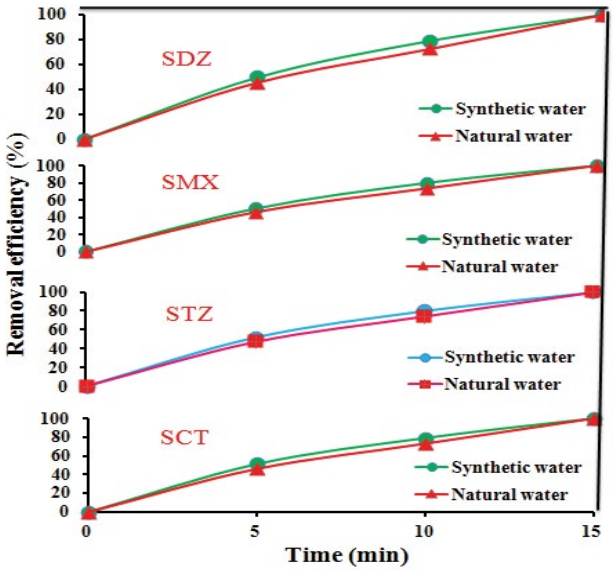


Fig. 10. Investigation of the efficiency of the photocatalytic ozonation on the degradation of four antibiotics from actual water ($[C]_0$ = 10 mg/L, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L).

to form hydroxylamine. The hydroxylamine could be further oxidized to form the nitroso group. The oxidation of excessive O_3 led to the formation of carboxylic acids such as (oxamic acid, pyruvic acid, oxalic acids, and maleic acid) [60]. The results of the TOC analysis revealed that the removal efficiency rates were 87.09% and 85.5% after 45 and 15 min, respectively (Fig. 12). Mineralization (95%) of the photocatalytic ozonation degradation of pharmaceutical mixtures including acetaminophen (Actmph), norfloxacin (Norfx), metoprolol (Metp), caffeine (Caff), antipyrine (Antpy), sulfamethoxazole (SMX), ketorolac (Ketor), hydroxybiphenyl (Hdxbiph), and diclofenac (Diclof) was achieved in 120 min [61]. Also, Beltrán et al. [45] indicated that 90% of TOC was removed by catalytic ozonation with SMX.

3.7. Bioassays experiments

In order to assess the toxicity caused by compounds produced before and after the photocatalytic ozonation, the acute toxicity of the untreated sulfonamides solution and solutions submitted to photocatalytic ozonation during 15 min were evaluated by Microtox bioassays. The results presented in Fig. 13 and Table 8 were obtained after 15 min of exposition by calculation of percentage of mortality in the *D. magna* caused by each sample. Ten *Daphnia* were added to each experimental beaker. In the next stage, 0.5, 5, 10, 25, 50 and 100 effluent dilutions (V/V%) were prepared and observations were made after 24, 48, 72 and 96 h. At the end of the test, the number of live neonates was recorded. The toxicity experiments were investigated by the value of LC50, a concentration of the compounds causing death to 50% of *Daphnia* during incubation with toxic matter. The results showed an increase in the mortality percentage of *D. magna* before the photocatalytic ozonation process than the next have

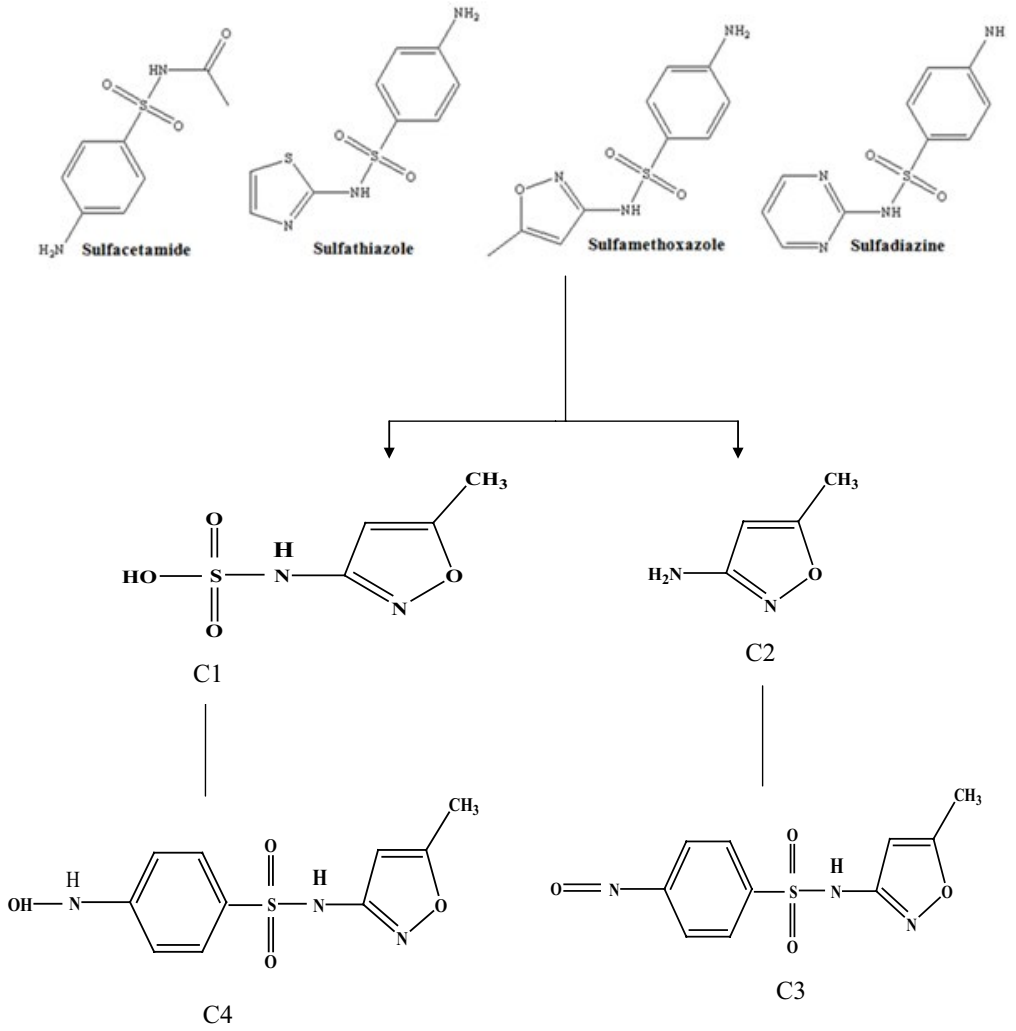


Fig. 11. Determination of by-products of decomposition of four antibiotics by GC-MS at temperature of 280°C.

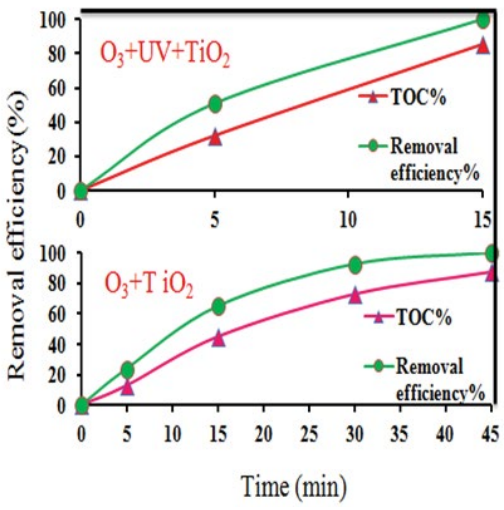


Fig. 12. Mineralization of four antibiotics by means of catalytic ozonation and photocatalytic ozonation ($[C]_0$ = 10 mg/L, pH = 5, ozone concentration = 3.67 mg/min, catalyst concentration = 1 g/L).

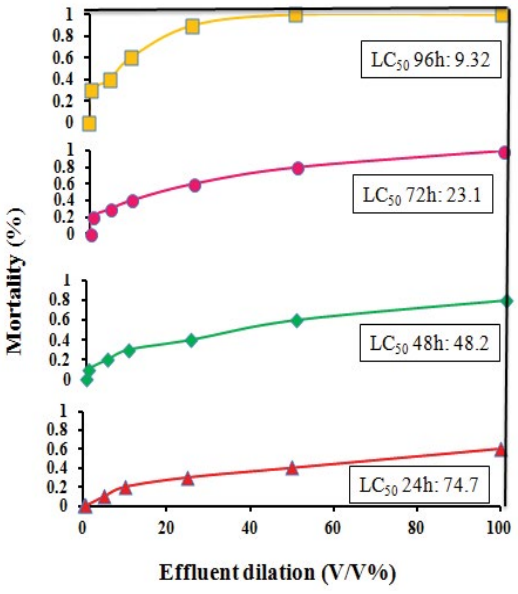


Fig. 13. Bioassay of the antibiotics by *Daphnia magna*.

Table 8
Data of the toxicity of antibiotics on *D. magna* using samples of $UV/O_3/TiO_2$ process ($[C_0]$ = 10 mg/L, pH = 5, catalyst concentration = 1 g/L, ozone concentration = 3.67 mg/min)

Effluent dilation (V/V%)	Number of *D. magna* tested	Number of *D. magna* death during the experiments (number per hour)			
		24 (h)	48 (h)	72 (h)	96 (h)
100	10	6	8	10	–
50	10	4	6	8	10
25	10	3	4	6	9
10	10	2	3	4	6
5	10	1	2	3	4
0.5	10	0	1	2	3
0	10	0	0	0	0

increased; that is, the intermediates formed in this period, in the presence photocatalytic ozonation, have less acute toxicity than the sulfonamides untreated solution. Shang et al. [62] reported a toxicity increase during the early stages of the ozonation of chlorophenols that could be attributed to the formation of chlorocatechols, chloromuconic acids and other hydroxylated or chlorinated compounds.

4. Conclusion

The degradation of the four antibiotics by the TiO_2/O_3 and $TiO_2/UV/O_3$ processes was examined. The synergistic effects of the two processes showed that the photocatalytic ozonation removal efficiency was greater during shorter contact times than that of the catalytic ozonation. All investigated sulfonamides were toxic to *D. magna*. It was determined that the lowest LC_{50} value was 0.63 mg/L at 96 h with a maximum toxicity unit of 158.73. The effect of various anions on the performance of the photocatalytic ozonation was also investigated. Inorganic ions had an inhibitory effect on the antibiotics. In addition, the active species reaction mechanisms were proposed following the identification of scavengers in TiO_2/O_3 and $TiO_2/UV/O_3$ processes. The catalytic and photocatalytic ozonation performed best in the removal of antibiotics at pH 5. By-products were identified as oxamic acid, pyruvic acid, oxalic acids and maleic acid. Mineralization rates resulting from the catalytic ozonation and photocatalytic ozonation were 87.09% and 85.5% within 45 and 15 min, respectively.

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References

[1] G. Lofrano, R. Pedrazzani, G. Libralato, M. Carotenuto, Advanced oxidation processes for antibiotics removal: a review, Curr. Org. Chem., 21 (2017) 1054–1067.
[2] M. Xu, J. Li, Y. Yan, X. Zhao, J. Yan, Y. Zhang, B. Lai, X. Chen, L. Song, Catalytic degradation of sulfamethoxazole through peroxymonosulfate activated with expanded graphite loaded $CoFe_2O_4$ particles, Chem. Eng. J., 369 (2019) 403–413.
[3] L. Lai, J. Yan, J. Li, B. Lai, Co/Al_2O_3-EPM as peroxymonosulfate activator for sulfamethoxazole removal: performance, biotoxicity, degradation pathways and mechanism, Chem. Eng. J., 343 (2018) 676–688.
[4] J. Yan, J. Li, J. Peng, H. Zhang, Y. Zhang, B. Lai, Efficient degradation of sulfamethoxazole by the CuO@ Al_2O_3 (EPC) coupled PMS system: optimization, degradation pathways and toxicity evaluation, Chem. Eng. J., 359 (2019) 1097–1110.
[5] G. Ritu, S. Thhatikkonda, Antibiotic pollution in the environment: a review, Clean Soil Air Water, 43 (2015) 479–489.
[6] 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.
[7] T. Aissani, I. Yahiaoui, F. Boudrahem, S. Ait Chikh, F. Aissani-Benissad, A. Amrane, The combination of photocatalysis process (UV/TiO_2(P25) and UV/ZnO) with activated sludge culture for the degradation of sulfamethazine, SS&T, 53 (2018) 1423–1433.
[8] A.G. Trovó, R.F.P. Nogueira, A. Agüera, C. Sirtori, A.R. Fernández-Alba, Photodegradation of sulfamethoxazole in various aqueous media: persistence, toxicity and photoproducts assessment, Chemosphere, 77 (2009) 1292–1298.
[9] 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.
[10] J.F. Gomes, I. Leal, K. Bednarczyk, M. Gmurek, M. Stelmachowski, M. Diak, M.E. Quinta-Ferreira, R. Costa, R.M. Quinta-Ferreira, R.C. Martins, Photocatalytic ozonation using doped TiO_2 catalysts for the removal of parabens in water, ScTEn, 609 (2017) 329–340.
[11] J.F. Gomes, K. Bednarczyk, M. Gmurek, M. Stelmachowski, A. Zaleska-Medynska, F.C. Bastos, M.E. Quinta-Ferreira, R. Costa, R.M. Quinta-Ferreira, R.C. Martins, Noble metal–TiO_2 supported catalysts for the catalytic ozonation of parabens mixtures, Process Saf. Environ. Prot., 111 (2017) 148–159.
[12] R.C. Martins, R.M. Quinta-Ferreira, Catalytic ozonation of phenolic acids over a Mn–Ce–O catalyst, Appl. Catal., B, 90 (2009) 268–277.
[13] M.N. Chong, B. Jin, C.W. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res., 44 (2010) 2997–3027.
[14] J.F. Gomes, I. Leal, K. Bednarczyk, M. Gmurek, M. Stelmachowski, A. Zaleska-Medynska, M.E. Quinta-Ferreira, R. Costa, R.M. Quinta-Ferreira, R.C. Martins, Detoxification of parabens using UV-A enhanced by noble metals—TiO_2 supported catalysts, J. Environ. Chem. Eng., 5 (2017) 3065–3074.
[15] Z. Xiong, B. Lai, P. Yang, Insight into a highly efficient electrolysis-ozone process for N, N-dimethylacetamide degradation: quantitative analysis of the role of catalytic ozonation,

Fenton-like and peroxone reactions, Water Res., 140 (2018) 12–23.
[16] T.E. Agustina, H.M. Ang, V.K. Vareek, A review of synergistic effect of photocatalysis and ozonation on wastewater treatment, J. Photochem. Photobiol., C, 6 (2005) 264–273.
[17] W. Ben, Y. Shi, W. Li, Y. Zhang, Z. Qiang, Oxidation of sulfonamide antibiotics by chlorine dioxide in water: kinetics and reaction pathways, Chem. Eng. J., 327 (2017) 743–750.
[18] J. Jung, Y. Kim, J. Kim, D.-H. Jeong, K. Choi, Environmental levels of ultraviolet light potentiate the toxicity of sulfonamide antibiotics in *Daphnia magna*, Ecotoxicology, 17 (2008) 37–45.
[19] L. Wollenberger, B. Halling-Sørensen, K.O. Kusk, Acute and chronic toxicity of veterinary antibiotics to *Daphnia magna*, Chemosphere, 40 (2000) 723–730.
[20] M. Gholami, M. Shirzad-Siboni, J.-K. Yang, Application of Ni-doped ZnO rods for the degradation of an azo dye from aqueous solutions, Korean J. Chem. Eng., 33 (2016) 812–822.
[21] A.L. Patterson, The Scherrer formula for X-ray particle size determination, PhRv, 56 (1939) 978–982.
[22] M. Naimi-Joubani, M. Shirzad-Siboni, J.-K. Yang, M. Gholami, M. Farzadkia, Photocatalytic reduction of hexavalent chromium with illuminated ZnO/TiO_2 composite, J. Ind. Eng. Chem., 22 (2015) 317–323.
[23] A.Ö. Yıldırım, Ş. Gül, O. Eren, E. Kuşvuran, A comparative study of ozonation, homogeneous catalytic ozonation, and photocatalytic ozonation for C.I. Reactive Red 194 azo dye degradation, Clean Soil Air Water, 39 (2011) 795–805.
[24] M.J. Farré, M.I. Franch, S. Malato, J.A. Ayllón, J. Peral, X. Doménech, Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, Chemosphere, 58 (2005) 1127–1133.
[25] S.-p. Tong, D.-m. Xie, H. Wei, W.-p. Liu, Degradation of sulfosalicylic acid by O_3/UV O_3/TiO_2/UV, and O_3/V-O/TiO_2: a comparative study, OzSE, 27 (2005) 233–238.
[26] S. Nishimoto, T. Mano, Y. Kameshima, M. Miyake, Photocatalytic water treatment over WO3 under visible light irradiation combined with ozonation, CPL, 500 (2010) 86–89.
[27] U. Černigoj, U.L. Štangar, P. Trebše, Degradation of neonicotinoid insecticides by different advanced oxidation processes and studying the effect of ozone on TiO_2 photocatalysis, Appl. Catal., B, 75 (2007) 229–238.
[28] J.K. Challis, J.C. Carlson, K.J. Friesen, M.L. Hanson, C.S. Wong, Aquatic photochemistry of the sulfonamide antibiotic sulfapyridine, J. Photochem. Photobiol., A, 262 (2013) 14–21.
[29] T. Sekimoto, S. Nishihama, K. Yoshizuka, R. Maeda, Adsorptive removal of sulfamethoxazole with shell-core chitosan immobilized metal ion, SS&T, 53 (2018) 1116–1123.
[30] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water, Water Res., 43 (2009) 1359–1369.
[31] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int., 35 (2009) 402–417.
[32] F. Madjene, N. Yeddou-Mezenner, Design and optimization of a new photocatalytic reactor with immobilized ZnO for water purification, SS&T, 53 (2018) 364–373.
[33] E.M. Rodríguez, G. Márquez, E.A. León, P.M. Álvarez, A.M. Amat, F.J. Beltrán, Mechanism considerations for photocatalytic oxidation, ozonation and photocatalytic ozonation of some pharmaceutical compounds in water, J. Environ. Manage., 127 (2013) 114–124.
[34] M. Shirzad-Siboni, A. Khataee, B. Vahid, S.W. Joo, Synthesis, characterization and immobilization of ZnO nanosheets on scallop shell for photocatalytic degradation of an insecticide, Sci. Adv. Mater., 7 (2015) 806–814.
[35] M. Mehrjouei, S. Müller, D. Möller, Catalytic and photocatalytic ozonation of tert-butyl alcohol in water by means of falling film reactor: kinetic and cost–effectiveness study, Chem. Eng. J., 248 (2014) 184–190.
[36] L. Sánchez, J. Peral, X. Domènech, Aniline degradation by combined photocatalysis and ozonation, Appl. Catal., B, 19 (1998) 59–65.
[37] R.R. Giri, H. Ozaki, T. Ishida, R. Takanami, S. Taniguchi, Synergy of ozonation and photocatalysis to mineralize low concentration 2,4-dichlorophenoxyacetic acid in aqueous solution, Chemosphere, 66 (2007) 1610–1617.
[38] 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.
[39] O. Turkay, H. Inan, A. Dimoglo, Experimental and theoretical study on catalytic ozonation of humic acid by ZnO catalyst, SS&T, 52 (2017) 778–786.
[40] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, A. Oropesa, Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water, Water Res., 42 (2008) 3799–3808.
[41] R. Rajeswari, S. Kanmani, A study on synergistic effect of photocatalytic ozonation for carbaryl degradation, Desalination, 242 (2009) 277–285.
[42] T. Garoma, S.K. Umamaheshwar, A. Mumper, Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation, Chemosphere, 79 (2010) 814–820.
[43] A. Jonidi-Jafari, M. Gholami, M. Farzadkia, A. Esrafili, M. Shirzad-Siboni, Application of Ni-doped ZnO nanorods for degradation of diazinon: kinetics and by-products, SS&T, 52 (2017) 2395–2406.
[44] G.-A.J. F., B.F. J., A. Almudena, Diclofenac removal from water by ozone and photolytic TiO_2 catalysed processes, J. Chem. Technol. Biotechnol., 85 (2010) 798–804.
[45] F.J. Beltrán, A. Aguinaco, A. Rey, J.F. García-Araya, Kinetic studies on black light photocatalytic ozonation of diclofenac and sulfamethoxazole in water, Ind. Eng. Chem. Res., 51 (2012) 4533–4544.
[46] H. Li, B. Xu, F. Qi, D. Sun, Z. Chen, Degradation of bezafibrate in wastewater by catalytic ozonation with cobalt doped red mud: efficiency, intermediates and toxicity, Appl. Catal., B, 152 (2014) 342–351.
[47] G. Moussavi, A. Alahabadi, K. Yaghmaeian, M. Eskandari, Preparation, characterization and adsorption potential of the NH_4Cl-induced activated carbon for the removal of amoxicillin antibiotic from water, Chem. Eng. J., 217 (2013) 119–128.
[48] P. Pocostales, P. Álvarez, F.J. Beltrán, Catalytic ozonation promoted by alumina-based catalysts for the removal of some pharmaceutical compounds from water, Chem. Eng. J., 168 (2011) 1289–1295.
[49] F.J. Beltrán, P. Pocostales, P.M. Álvarez, F. López-Piñeiro, Catalysts to improve the abatement of sulfamethoxazole and the resulting organic carbon in water during ozonation, Appl. Catal., B,92 (2009) 262–270.
[50] A.G. Gonçalves, J.J.M. Órfão, M.F.R. Pereira, Catalytic ozonation of sulphamethoxazole in the presence of carbon materials: catalytic performance and reaction pathways, J. Hazard. Mater., 239–240 (2012) 167–174.
[51] J.P. Pocostales, P.M. Alvarez, F.J. Beltrán, Kinetic modeling of powdered activated carbon ozonation of sulfamethoxazole in water, Chem. Eng. J., 164 (2010) 70–76.
[52] D. Shahidi, A. Moheb, R. Abbas, S. Larouk, R. Roy, A. Azzouz, Total mineralization of sulfamethoxazole and aromatic pollutants through Fe^{2+}-montmorillonite catalyzed ozonation, J. Hazard. Mater., 298 (2015) 338–350.
[53] Z. Bai, Q. Yang, J. Wang, Catalytic ozonation of sulfamethazine using $Ce_{0.1}Fe_{0.9}OOH$ as catalyst: mineralization and catalytic mechanisms, Chem. Eng. J., 300 (2016) 169–176.
[54] S. Fukahori, T. Fujiwara, R. Ito, N. Funamizu, pH-Dependent adsorption of sulfa drugs on high silica zeolite: modeling and kinetic study, Desalination, 275 (2011) 237–242.
[55] R.R. Solís, F.J. Rivas, O. Gimeno, J.L. Pérez-Bote, Photocatalytic ozonation of clopyralid, picloram and triclopyr. Kinetics, toxicity and influence of operational parameters, J. Chem. Technol. Biotechnol., 91 (2016) 51–58.
[56] X. Liu, T. Garoma, Z. Chen, L. Wang, Y. Wu, SMX degradation by ozonation and UV radiation: a kinetic study, Chemosphere, 87 (2012) 1134–1140.

[57] A. Rey, J. Carbajo, C. Adán, M. Faraldos, A. Bahamonde, J.A. Casas, J.J. Rodriguez, Improved mineralization by combined advanced oxidation processes, Chem. Eng. J., 174 (2011) 134–142.
[58] 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.
[59] P.E. Stackelberg, E.T. Furlong, M.T. Meyer, S.D. Zaugg, A.K. Henderson, D.B. Reissman, Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant, ScTEn, 329 (2004) 99–113.
[60] M.C. Dodd, C.-H. Huang, Transformation of the antibacterial agent sulfamethoxazole in reactions with chlorine: kinetics, mechanisms, and pathways, Environ. Sci. Technol., 38 (2004) 5607–5615.
[61] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, Kinetic modelling of TOC removal in the photocatalytic ozonation of diclofenac aqueous solutions, Appl. Catal. B, 100 (2010) 289–298.
[62] N.-C. Shang, Y.-H. Yu, H.-W. Ma, C.-H. Chang, M.-L. Liou, Toxicity measurements in aqueous solution during ozonation of mono-chlorophenols, J. Environ. Manage., 78 (2006) 216–222.