Photo-removal of sulfamethoxazole (SMX) by photolytic and photocatalytic processes in a batch reactor under UV-C radiation ($\lambda_{\text{max}} = 254 \text{ nm}$)

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ABSTRACT

In this study, photolytic and photocatalytic removal of the antibiotic sulfamethoxazole (SMX) under UVC radiation ($\lambda = 254 \text{ nm}$) was investigated. The light intensity distribution inside the batch photoreactor was characterized by azoxybenzene actinometry. The intensity of incident radiation was found to be a strong function of position inside the reactor. 12 mg L^{-1} of SMX was completely removed within 10 min of irradiation under UVC photolysis, compared to 30 min under TiO_2 photocatalysis. COD measurement was used as an indication of the mineralization efficiency of both processes and higher COD removal with photocatalysis was shown. After 6 h of reaction with photolysis and photocatalysis, 24% and 87% removal of COD was observed, respectively. Two of the intermediate photo-products were identified as sulfanilic acid and 3-amino-5-methylisoxazole by direct comparison of the HPLC chromatograms of standards to those of treated solutions. Ecotoxicity of treated and untreated solutions of SMX towards *Daphnia magna* was also investigated. It was found that a 3:1 ratio of sample to standard freshwater and a high initial concentration of 60 mg L^{-1} of SMX were used to obtain reliable and reproducible results. The photo-products formed during photocatalytic and photolytic processes were shown to be generally more toxic than the parent compound.

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1. Introduction

Contamination of natural waters by pharmaceuticals and personal care products (PPCPs) is a rising issue of global concern. After their use, usually these substances are excreted only partially metabolized and end up in the sewage system. A great portion of these compounds are not removed by classical sewage and wastewater treatment plants and are eventually discharged into receiving waters [1,2]. It has been found that there are significant amounts of pharmaceuticals present in the aquatic environments at up to the $\mu\text{g L}^{-1}$ level [3–8]. Even though these compounds are detected at very low concentrations in nature, it is highly likely for aquatic organisms to experience toxicity via concentration addition effect due to decades of unregulated discharge [9,10].

Sulfamethoxazole (SMX, Fig. 1) is a synthetic antibiotic commonly used in humans for treatment of bronchitis and urinary tract infections and as well as veterinary medicine. It is generally prescribed in combination with trimethoprim. In the year 2007, it was the 6th most commonly prescribed antibiotic combination in Canada [11]. Even though no direct effects on human health have been associated with this compound, concerns for increase in bacterial resistance to the antibiotic agents were also reported [12].

Due to the antibacterial nature of this compound, it shows resistance to conventional biological water treatment methods and is often found in sewage treatment plant effluents and wastewater plant effluents [13,14], as well as in natural wastewaters [8].

Advanced oxidation processes (AOPs) have received great interest in recent years as complementary methods to conventional water treatment or as alternative treatment strategies for industrial wastewater prior to discharge into sewage or into aquatic environments. Among these AOPs; ozonation [15–19], fenton and photo-fenton oxidation [20–22]; photolysis and H_2O_2 enhanced photolysis [23–25]; heterogeneous photocatalysis [26,27] were frequently studied. During advanced oxidation of pharmaceutical compounds, intermediate compounds are formed that might show more toxic effects than the parent compound; therefore overall goal of treatment processes should be complete mineralization rather than just removal of the parent compounds or at least the transformation into non-toxic products.

Photolysis relies on the absorption of artificial or natural sunlight by a target molecule to undergo direct degradation to intermediates which can potentially further decompose to lead to mineralization. Ultraviolet (UV) radiation (especially UVC, $\lambda < 280 \text{ nm}$) is usually used for disinfection of drinking water and is increasingly used for sterilization of wastewater. Recent research employing only UV radiation (generally UVA, $320 < \lambda < 400 \text{ nm}$ and UVB, $280 < \lambda < 320 \text{ nm}$) focuses generally on the understanding of photochemistry involved in the persistence

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Fig. 1. Chemical structure of sulfamethoxazole (SMX).

and fate of pharmaceuticals in the natural aquatic environments [24].

Heterogeneous photocatalysis involves the absorbance of UV-light ($\lambda < 390$ nm) by a semi-conducting material to produce electron/hole pairs which are responsible for the reduction/oxidation reactions that occur on the surface of the catalyst [28–30]. Titanium dioxide (TiO_2) is the most frequently used semiconductor in photocatalysis since it is biologically and chemically inert, cheap and non-toxic [31]. The oxidizing species generated during photocatalysis and responsible for degradation of compounds of interest are hydroxyl radicals ($\cdot\text{OH}$), holes (h_{vb}^+) and superoxide radicals ($\text{O}_2^{\cdot-}$). Generally, a source of oxygen is required to scavenge for electrons, in order to reduce recombination of electron and holes.

There have been numerous reports on the heterogeneous photocatalysis of SMX using UV lamps emitting radiation either in the UVA and UVB range [32–39]. Very little work has been done on the efficiency or synergistic effects of photolysis to photocatalytic processes for SMX during UVC radiation. Higher effectiveness of radiation at 254 nm compared to that at 350 nm towards the removal of salicylic acid and phenol was demonstrated by Matthews and McEvoy [40]. Similar results for phenol [41] and for 2-chlorophenol [42] were also reported.

The majority of the related work focuses on the advantages of coupling solar radiation with photocatalysis in order to establish inexpensive treatment methods. However, in areas such as the case of Quebec, Canada, there is less availability of solar power but electricity is cheaper when compared to other parts of the world, thus making it necessary to study the applicability of artificial radiation sources such as the case of UV-C radiation by germicidal lamps. This type of treatment could be applicable as a pretreatment step to industrial or hospital wastewater before their release to municipal treatment facilities. Since UVC radiation is commonly used as a sterilization method in various treatment facilities, this research also allows to study the fate of pharmaceuticals during the sterilization and possible enhanced benefits if coupled with TiO_2 photocatalysis. The focus of this research is to show the parallel effects of photolysis and photocatalysis on photo-removal efficiency of SMX during UV-C radiation. The effect of initial concentration of SMX during photolytic removal is investigated. The effect of the presence of oxidizing species and dissolved oxygen is also studied to understand the major mode of removal of SMX. Residual toxicity and the extent of COD removal are measured to compare the two treatment methods. Finally several of the photoproducts are identified.

2. Materials and methods

2.1. Reagents

Sulfamethoxazole ($\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$, >99%), benzoquinone (>99%), azoxybenzene (>98%) and sodium dihydrogen phosphate were obtained from Sigma-Aldrich, Canada. Aqueous stock solution (60 mg L^{-1} SMX) was prepared in reverse osmosis (RO) water and kept at 4°C in the dark until the time of treatment. Commercial TiO_2 Degussa P25 (70% anatase and 30% rutile) was used as catalyst with an average particle size of 30 nm and BET surface area of

$50 \text{ m}^2 \text{ g}^{-1}$, according to the manufacturer (Evonik Degussa Canada Inc.). HPLC grade methanol, acetonitrile and isopropanol were purchased from Fisher Scientific, Canada. 95% ethanol was purchased from Commercial Alcohols (Boucherville, Quebec, Canada). All the chemicals were used as received without purification.

2.2. UV-C irradiation experimental setup

Irradiation experiments were carried out in 2 L capacity cylindrical acrylic photoreactor (215 mm height, 108 mm diameter). The reactor walls were covered by aluminum foil to avoid exposure to UV radiation. 1.6 L of an aqueous solution of SMX was charged in the reactor for each experiment. The solution was irradiated by a Hg–Ar (Germicidal UV-C) lamp (Atlantic Ultraviolet Corp. GPH212T5L) located in the center of the reactor and protected in a quartz sleeve (maximum output at 254 nm) and mixing was achieved by magnetic stirring. Before each experiment required amount of titanium dioxide particles (0.01 , 0.03 , 0.05 and 0.5 g L^{-1}) were suspended in RO water and sonicated for 30 min to reduce agglomeration and create a more stable suspension. In photolytic degradation experiments no titanium dioxide was added to the reaction mixture.

Various concentrations of SMX ranging from 3 to 12 mg L^{-1} were tested for adsorption onto TiO_2 at a fixed concentration of 0.5 g L^{-1} . For adsorption experiments, Erlenmeyer flasks were filled with TiO_2 and SMX at the desired concentrations and were placed inside an incubator shaker set at 20°C . After 24 h, withdrawn samples were analyzed with HPLC and compared to the controls containing only SMX. The adsorption flasks and control flasks showed no difference in concentration concluding that the SMX is not adsorbed onto the TiO_2 under dark conditions.

In order to determine if the major removal mode of SMX is due to photolysis or to the presence of oxidizing species generated during photocatalysis the effect of dissolved oxygen concentration and scavenging of oxidizing species experiments were performed. Different concentrations of dissolved oxygen were obtained by bubbling air (8.8 mg L^{-1}) or pure oxygen (42 mg L^{-1}) to the reaction mixture. For close to anoxic conditions, the dissolved oxygen in the reaction mixture was purged off by continuously bubbling nitrogen for 2 h before turning on the lamp and the flow of nitrogen was maintained through out the reaction time to maintain low dissolved oxygen levels (0.5 mg L^{-1}). In all cases, gases were introduced into the system by continuous bubbling through a sparger located at the bottom of the reactor.

The method of scavenging and concentrations of scavenging compounds were based on the results reported by Palominos et al. [26]. Isopropanol has been described as one of the best hydroxyl radical quencher due to its high reaction rate constant with the radical ($1.9 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$) [43]. In this work, scavenging of hydroxyl radicals was achieved by adding isopropanol to the reaction mixture (12 mg L^{-1} SMX and 0.05 g L^{-1} TiO_2) at a molar concentration which was three orders of magnitude larger than the initial concentration of SMX. Benzoquinone is also commonly used to trap superoxide radicals by a simple electron transfer mechanism [26]. In the present work, it was introduced into the reaction mixture at a molar concentration ten times that of SMX.

2.3. Determination of incident light intensity distribution in the reactor

In order to quantify the intensity of incident radiation, azoxybenzene was used as a chemical actinometer. The method was modified from the technique developed by Bunce et al. [44]. A quartz cuvette with dimensions ($1 \text{ cm} \times 1 \text{ cm} \times 3.8 \text{ cm}$) was filled with 3 mL of 5 mM azoxybenzene in 95% ethanol. The cuvette was sealed by a stopper attached at the end of a 30 cm long rod and was

then immersed inside the reactor at a desired height from the bottom of the reactor (5–15 cm) and at a desired distance (0.7–2.5 cm) away from the lamp. The solution was irradiated for a desired time of 0–8 min. At this point azoxybenzene is photorearranged to 2-hydroxyazobenzene. Three drops of 0.1 M KOH solution in 95% ethanol was added to convert the photoproduct to its anion form. The absorbance of the sample was taken at a wavelength of 458 nm. The molar extinction coefficient, ε for the product was $7800 \text{ L mol}^{-1} \text{ cm}^{-1}$. Using Beer–Lambert's law

$$A = \varepsilon Pl \quad (1)$$

where A is the absorbance measured, P is the concentration of the product (M) and l is the optical path length (equivalent to length of the cuvette, 1 cm) the concentration of the product was determined. The following equation provided by Bunce et al. [44] describes the relationship between the intensity of incident radiation per unit volume, I_0 ($\text{Einstein L}^{-1} \text{ min}^{-1}$) to the concentration of product P , where A_0 is the initial concentration of azoxybenzene (5 mM), t is time and φ_r is the quantum yield of azoxybenzene determined experimentally at 254 nm ($\varphi_r = 0.017$).

$$A_0 \ln \left[1 - \left(\frac{P}{A_0} \right) \right] = -\varphi_r I_0 t \quad (2)$$

The slope of the line $-\ln(1-(P/A_0))$ against t is used to calculate the intensity of incident radiation per unit volume. This value is converted to intensity of incident radiation (Einstein min^{-1}) by multiplying with the volume of the solution irradiated in the cuvette (3 mL).

2.4. Ecotoxicity test with *Daphnia magna*

For toxicity testing of SMX solutions in RO water before and after UV treatment, *Daphnia magna* immobilization essays were carried out. Acute toxicity *Daphnia* tests were conducted using the commercial test kit DAPHTOXKIT FTM (MicroBioTests Inc., Gent, Belgium) following the procedures described in the kit. The control to test the viability of the supplied *Daphnia* population consisted of only standard freshwater (SFW). The organisms were considered viable as long as less than 10% of daphnia immobilized in the control. The test plate then was covered and incubated at 20 °C under dark. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was the reference chemical used. An EC_{50} 24 h of 1.23 mg L^{-1} was obtained for the reference compound which is within the range of the 0.6–2.1 mg L^{-1} stipulated in the ISO 6341 to ensure test validity (International Organization for Standardisation, 1996). For the toxicity determination of the samples taken during photolysis and photocatalysis, a dilution ratio of 3 to 1 (treated sample to SFW) was used. After 24 and 48 h of exposure, dead or immobilized daphnids were counted and results were tabulated as % effect (percentage of immobilized organisms). Because the SMX solutions that were treated in the photolysis and photocatalytic experiments were made using RO water, the same ratio of 3 to 1 (RO water to SFW) was used for comparison and no inhibition was observed for the daphnids at this ratio.

2.5. Analytical methods

Prior to any chemical analysis including toxicity tests, samples taken from the reactor were filtered by $0.22 \mu\text{m}$ syringe filters. SMX concentration was determined by an Agilent 1100 series high performance liquid chromatograph (HPLC) equipped with a Zorbax Eclipse C-8 column ($3.5 \mu\text{m}$, $4.6 \text{ mm} \times 150 \text{ mm}$). Eluents consisted of 20 mM sodium dihydrogen phosphate (NaH_2PO_4) buffer and acetonitrile using an eluent gradient from 30% acetonitrile to 50% over 10 min at a constant flow rate of 0.8 mL min^{-1} . The buffer was adjusted to a pH of 2.8 with phosphoric acid. Detection was made

Table 1

MRM ion transitions, de-clustering potential (DP) and collision energies for analysis.

Standards	Chemical formula	Polarity	MRM transition	DP (V)	Collision energy (eV)
Sulfanilic acid	$\text{C}_6\text{H}_7\text{NO}_3\text{S}$	Negative	171.5 → 79.8	–103	–25
3-Amino-5-methylisoxazole	$\text{C}_4\text{H}_6\text{N}_2\text{O}$	Positive	98.9 → 43.9	110	28

with a diode array detector (DAD) at wavelengths of 262 nm for SMX and 225 nm for the intermediates. COD testing of the samples was performed using a COD reactor (HACH DRB 200) and a spectrophotometer (HACH DR 2500). The method adapted by HACH from the ASTM D 1252–95. Dissolved oxygen and pH was measured by Thermo Scientific Orion 3-Star Benchtop pH and DO Meter. Absorbance of chemical actinometry solutions were determined by a UV–vis spectrophotometer (Thermo Electron Corporation Evolution 3000).

Fractions collected on the HPLC Agilent 1200 were analyzed by mass spectroscopy by comparison with standards corresponding to products previously identified by Zhou and Moore [45]. Analyses were performed with an MDS/Sciex QTrap 500 mass spectrometer (Concord, ON, Canada) equipped with a Turbolon spray (i.e. ESI) ionization source operated in positive and negative ion mode. Acquisition was performed in multiple reaction monitoring (MRM) mode. Nitrogen was used as the curtain, nebulizer, auxiliary, and collision gases. The MRM ion transitions for both standards and selected optimized operating conditions for MS/MS are listed in Table 1. All data were acquired and processes using Analyst 1.4 software.

3. Results and discussion

3.1. Characterization of reactor conditions

Fig. 2a shows the distribution of light inside the empty reactor as a function of distance from the bottom of the reactor at a horizontal distance of 0.7 cm away from the lamp (shortest available distance). The effect of radial distance from the lamp on light intensity was studied in water which is the reaction medium. From the results presented in Fig. 2b there is about 70% reduction in light intensity if the distance from the lamp is increased from 0.7 cm to 2.5 cm at a vertical distance of 10 cm from the bottom of the reactor.

In order to assess the participation of photolysis during heterogeneous photocatalysis of SMX, the amount of light absorbed by the photocatalyst, TiO_2 was measured. Fig. 3 shows the effect of having the photocatalyst in suspension on light intensity distribution inside the reactor. The maximum available light intensity in water occurs when no TiO_2 is present in the reaction mixture. As it is clearly observed from these results, almost all the available light is absorbed by the photocatalyst at a concentration of 0.5 g L^{-1} even at the location closest to the lamp. This result indicates that due to the presence of the titanium dioxide no significant amount of light would be available for SMX for it to undergo direct photolysis and also that the majority of the reactor operates in UV-dark.

3.2. Evolution of SMX concentration during photolysis and photocatalysis

Fig. 4 shows that the SMX removal rate diminishes as TiO_2 concentration increases under UVC radiation ($\lambda = 254 \text{ nm}$). By far the fastest removal is observed in the absence of the catalyst suggesting that the main mode of removal is photolysis. In order to distinguish the effect of photolysis and photocatalysis on the removal of SMX, the emission spectrum of the UVC lamp and the UV absorbance of SMX were compared in Fig. 5. SMX absorbs up to 315 nm with a

Fig. 2. Light intensity measured: (a) in air vertically as a function of distance from the bottom of the reactor at a radial distance of 0.7 cm away from the lamp and (b) in RO water as a function of the vertical distance from the bottom of the reactor and of radial distance from the lamp. Height of the reactor = 21.5 cm. Position of the UVC lamp = 1.9–21.5 cm.

Fig. 3. Light intensity measured as a function of catalyst concentration at 10 cm from the bottom of the reactor and at two radial distances.

Fig. 4. Effect of TiO_2 concentration on removal of SMX ($C_0 = 12 \text{ mg/L}$).

Fig. 5. Comparison of the emission spectrum of UV-C lamp used with UV absorbance of SMX.

maximum absorbance at 262 nm, which is the region overlapping with the maximum radiation supplied by the lamp at a wavelength of 254 nm. Although the addition of TiO_2 seems to act as an inner filter, the beneficial effects of the presence of TiO_2 are discussed later.

3.3. Effect of initial concentration on SMX removal during photolysis

The effect of the initial concentration of SMX on the removal rate in photolysis is shown in Fig. 6a. The exponential decay observed in Fig. 5 and Fig. 6a suggests the decomposition of SMX follows first order kinetics; however, the initial reaction rate data (Fig. 6b) obtained from the derivatives estimated at the start do not support this observation as the reaction rates eventually reach a plateau at higher concentrations. This is further confirmed by the kinetic rate constants, k (min^{-1}) which were calculated by assuming first order reaction kinetics with respect to the SMX concentration and tabulated in Table 1. The decrease in the values of k with increasing SMX concentration is also an indication that the reaction of SMX with light is not first order. This plateau can be explained by the fact that at the higher concentrations of SMX, the available light becomes limiting. As shown by the azoxybenzene actinometry experiments light is absorbed by the target compound as well as by the produced intermediates.

The initial minimum apparent quantum efficiency for SMX, $\Phi_{\text{app}}^{\text{min}}$ (mol Einstein^{-1}) can be determined by normalizing the initial reaction rate, r_0 ($\text{mol L}^{-1} \text{min}^{-1}$) with the maximum incident photon

Fig. 6. Effect of initial concentration of SMX on removal kinetics during photolysis: (a) evolution of SMX concentration at different initial SMX concentrations and (b) calculated initial reaction rates.

Table 2

Calculated minimum apparent quantum efficiencies of photolytic removal of SMX.

Type of treatment	Catalyst concentration (g L ⁻¹)	Initial concentration of SMX (mg L ⁻¹)	Initial $r \times n$ rate, r_0 (mg L ⁻¹ min ⁻¹)	Initial $r \times n$ rate, r_0 (μ M min ⁻¹)	1st order $r \times n$ rate constant, k (min ⁻¹)	Apparent quantum efficiency Φ_{app} (mol Einstein ⁻¹)
UVC	0	1.5	1.43	5.6	1.41	0.42
UVC	0	3	2.28	9.0	1.23	0.67
UVC	0	6	3.17	12.5	0.87	0.93
UVC	0	12	3.80	15.2	0.52	1.14
UVC	0	24	4.76	18.8	0.29	1.41

flux per unit volume I_0 (Einstein min⁻¹ L⁻¹). Maximum incident photon flux per unit volume was measured at the mid section of the reactor at the closest available distance from the lamp and the value was approximately 1.3×10^{-3} Einstein min⁻¹ L⁻¹.

As shown in Table 1, Φ_{app}^{min} ranges from 0.41 to 1.41 mol Einstein⁻¹ for some of the studied conditions. Quantum yield for photolysis has been reported as high as 7.9 mol Einstein⁻¹ [34]. The values obtained in the present work fall in the same order of magnitude. It should be noted values presented here are a conservative estimate for the quantum efficiency. The intensity value in our calculations is the maximum value measured at a very close position to the lamp. The volume averaged light intensity the solution experiences would be much lower, thus increasing the calculated quantum yield values significantly.

3.4. Effect of dissolved oxygen and oxidizing species on photocatalytic removal of SMX

The effect of the presence of oxidizing species such as hydroxyl radicals, superoxide radicals and holes on removal of SMX was studied by carrying out experiments to scavenge these species. Removal profiles when hydroxyl radicals and superoxides were scavenged are shown in Fig. 7a. When the superoxide radicals were scavenged after 10 min of reaction time 32.2 (± 1.7)% of the initial SMX concentration was found to remain in solution. Scavenging of hydroxyl radicals lead to 26.2 (± 1.5)% of SMX remaining in solution after 10 min. When both oxidizing species were present (i.e. control) 24.2 (± 1.8)% of initial SMX was still present. Overlapping of the standard errors between hydroxyl radical scavenging and the control experiment suggests that there is no inhibitory effect on the removal of SMX due to scavenging of hydroxyl radicals, only slight inhibitory effects were observed when superoxides were scavenged.

Results of the effect of dissolved oxygen on the removal of SMX during photocatalysis are presented in Fig. 7b. Experiments were carried out in the presence of air, pure oxygen and nitrogen corresponding to dissolved oxygen concentrations of 8.8, 42 and 0.5 mg L⁻¹. After 10 min of reaction 24.2 (± 1.8)%, 26.3 (± 1.2)% and 32.3 (± 2.0)% of initial SMX remained in solution when air, nitrogen and oxygen were introduced, respectively. Overlapping of the standard errors between air and nitrogen purging reveals that the presence of dissolved oxygen does not contribute to the removal of SMX significantly. Contrary to what would be expected the introduction of oxygen did not improve the removal of SMX rather lead to a lower final removal than cases with lower dissolved oxygen concentrations.

Lack of considerable deviation from the general removal profile of SMX during photocatalysis when the above mentioned scavenging and dissolved oxygen experiments are performed, strongly suggests that the main mechanism of removal of SMX is by direct UVC irradiation (i.e. photolysis). Lower removal after 10 min of reaction observed when oxygen is used might be due to higher concentration of products (initial rate of removal during oxygen is higher than nitrogen purging) accumulating as reaction proceeded, thus decreasing light availability for direct reaction with SMX.

Fig. 7. (a) Effect of hydroxyl radicals and superoxides on removal of SMX during photocatalysis. (b) Effect of dissolved oxygen concentration on removal of SMX during photocatalysis. Control consists of 12 mg L⁻¹ of SMX and 0.05 g L⁻¹ of TiO₂ under air purge.

3.5. Evolution of photoproducts formed and degree of COD removal

The persistence of the degradation products was determined by running irradiation experiments for longer times (up to 6 h) under photolytic and photocatalytic conditions. The initial SMX concentration for both cases was 12 mg L⁻¹ and the TiO₂ concentration was 0.05 g L⁻¹ for photocatalysis. Photoproducts with similar retention times were observed for both types of photodegradation methods studied as seen in chromatograms in Fig. 8 suggesting that the mechanism of degradation of SMX is not altered by the presence of TiO₂. The intermediates formed during the initial stages of photolysis are resistant to further decomposition (Fig. 8a). In contrast when TiO₂ is present, SMX is removed at a much slower rate (Table 2); however the intermediates formed are removed from the system. Chemical oxygen demand (COD) can be used as an indication of the extent of mineralization. The hypothesis that photoproducts are more resistant to UV but are easily removed during photocatalysis can also be supported by analyzing the evolution of COD removal during the two treatment methods, as presented in Fig. 9. Approximately 87% of the initial COD is removed during photocatalysis; however only about 24% reduction was observed for photolysis even after 360 min of irradiation.

Fig. 8. HPLC chromatograms showing the evolution of intermediates with increasing irradiation time during removal of 12 mg L^{-1} SMX by (a) UVC and (b) UVC + TiO_2 .

Fig. 9. COD removal during UVC and UVC + TiO_2 treatments of 12 mg L^{-1} SMX.

Fig. 10. HPLC chromatograms of UVC, UVC + TiO_2 treated SMX, untreated solutions of 40 mg L^{-1} sulfanilic acid and 25 mg L^{-1} 3-amino-5-methylisoxazole.

Fig. 11. Mass spectra of (a) compound I and (b) compound III obtained in negative ionization mode.

Two of the five major photoproducts observed (Fig. 8) were identified by comparing them with standards corresponding to products previously identified by Zhou and Moore [45]: sulfanilic acid and 3-amino-5-methylisoxazole. As a first confirmation, HPLC chromatograms of UVC treated SMX were compared to HPLC chromatograms of the two standards. Matching retention times were observed, as shown in Fig. 10. Mass spectrums, presented in Fig. 11a and b with matching MRM transitions selected for the standards (Table 1), confirmed the nature of these two products.

3.6. Ecotoxicological effect of photolysis and photocatalysis of SMX on *Daphnia Magna*

The majority of the photolytic and photocatalytic experiments were performed with an initial SMX concentration of 12 mg L^{-1} . At

Fig. 12. Toxicity of SMX ($C_0 = 60 \text{ mg L}^{-1}$) towards *Daphnia magna* during UVC and UVC+TiO₂ treatments: (a) after 24 h of exposure and (b) after 48 h of exposure.

Fig. 13. Evolution of major products of SMX ($C_0 = 60 \text{ mg L}^{-1}$) detected by HPLC during (a) UVC and (b) UVC+TiO₂ treatments.

this initial concentration of SMX with a dilution of 3 to 1 (sample to SFW), it was difficult to obtain reproducible values of mortality. At the high concentration of 60 mg L^{-1} untreated SMX with a 3 to 1 ratio (sample to SFW), all three replicates showed reproducible values of mortality of daphnia, approximately 30% and 50% at 24 and 48 h of exposure, respectively. Toxicity of UV treated solutions of SMX with an initial concentration of 60 mg L^{-1} with a 3 to 1 dilution ratio (sample to SFW) are presented in Fig. 12 below. According to results not presented here, 30 min and 60 min of irradiation are required to completely remove 60 mg L^{-1} SMX with photolysis and photocatalysis, respectively. Therefore, the toxicity data presented in Fig. 12 are solely due to the presence of photoproducts rather than the presence of the target compound. The increase in toxicity with increasing irradiation time is observed for both UVC only (i.e. photolysis) and UVC coupled with TiO₂ oxidation (i.e. photocatalysis) processes. Such effects were expected for the initial stages of irradiation however, the persistence of toxicity after longer irradiation times during photocatalysis was not expected since further removal of the products were achieved in the presence of TiO₂; in fact, a decrease in toxicity would be the more probable expectation for the photocatalytic treatment.

Fig. 13 shows the evolution of the HPLC peak areas of major photoproducts detected. The detected products for both types of treatment (UV and UV/TiO₂) are present at high concentrations but their removal starts by photocatalysis only after 360 min of irradiation. The major photoproducts are removed during photocatalysis and only a small portion of compound I (i.e. sulfanilic acid) remains

after 13 h of irradiation. The lack of reduction of toxicity can be attributed to two reasons; either the presence of sulfanilic acid even at the concentrations encountered at the end of 13 h of photocatalytic treatment are still too high for *D. magna* or there are photoproducts present which are highly toxic but are not detected by the HPLC method. From the data currently presented here, treating SMX with UVC or UVC/TiO₂ processes leads to formation of more toxic species than the original target compound.

4. Conclusions

Removal of the antibiotic sulfamethoxazole (SMX) by photolytic and photocatalytic processes was investigated in a pure water matrix. Following conclusions can be drawn from the work presented here:

- Photolysis is the dominant mode of removal of SMX during photocatalysis when operated under UV-C radiation.
- Two of the major photoproducts formed during UV-C treatment were identified as sulfanilic acid and 3-amino-5-methylisoxazole by LC–MS analysis. Especially sulfanilic acid is persistent against further removal by UVC however; it is susceptible to removal by oxidizing species generated during photocatalysis due to the presence of TiO₂.
- Considerably higher COD removal is observed during photocatalysis. Even though with photolysis SMX is removed faster, presence of TiO₂ leads to removal of the persistent products formed.
- Both UVC treatments of SMX lead to generation of products which are more toxic than the parent compound towards *D. Magna*. These results underline the fact that analysis of toxicity of treated samples is necessary in any research that deals with treatment of contaminants.

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