Environmental Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t791546829

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Online publication date: 12 February 2010

To cite this Article Lester, Y., Avisar, D. and Mamane, H.(2010) 'Photodegradation of the antibiotic sulphamethoxazole in water with UV/H_2O_2 advanced oxidation process', Environmental Technology, 31: 2, 175 — 183
To link to this Article: DOI: 10.1080/09593330903414238
URL: http://dx.doi.org/10.1080/09593330903414238

Environmental Technology
Vol. 31, No. 2, February 2010, 175–183

Taylor & Francis
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Photodegradation of the antibiotic sulphamethoxazole in water with UV/H_2O_2 advanced oxidation process

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(*Received 30 April 2009; Accepted 14 October 2009*)

Photodegradation of the antibiotic sulphamethoxazole (SMX) in water using a medium-pressure UV lamp combined with H_2O_2 (UV/H_2O_2) was used to generate the advanced oxidation process (AOP). The photodegradation process was steadily improved with addition of H_2O_2 at relatively low to moderate concentrations (5 to 50 mg L^{-1}). However, the addition of H_2O_2 to the photolysis process at higher concentrations (50 to 150 mg L^{-1}) did not improve the degradation rate of SMX (in comparison with 50 mg L^{-1} H_2O_2). Addition of H_2O_2 to the UV photolysis process resulted in several processes occurring concurrently as follows: (a) formation of HO• radicals which contributed to the SMX degradation, (b) decrease in the available light for direct UV photolysis of SMX, and (c) scavenging of the HO• radicals by H_2O_2, which was highly dominant at moderate to high concentrations of H_2O_2. It is clear that these factors, separately and synergistically, and possibly others such as by-product formation, affect the overall difference in SMX degradation in the AOP process at different H_2O_2 concentrations.

Keywords: advanced oxidation process; medium-pressure UV lamp; hydroxyl radicals; photolysis; antibiotic residues

Introduction

Sulphonamides, a group of synthetic antimicrobial agents, are widely used in human therapy and in food-producing animals as growth promoters and as therapeutic and prophylactic drugs for a variety of bacterial and protozoan infections. Sulphamethoxazole (SMX), a sulphonamide antibiotic, is a commonly administrated suphonamide in human medicine [1]. Generally, only a fraction of the active ingredients in the antibiotic drugs is transformed in the body, and consequently antibiotics are excreted via urine and faeces as a mixture of metabolized and unmetabolized forms. For example, approximately 15% of the SMX drug is excreted from the human body unchanged [1], whereas most of the SMX is eliminated from the body via N-acetylation to a water-soluble metabolite and thus appears in the urine in the metabolized form [2].

The excreted drug residues are ultimately discharged into conventional wastewater treatment plants (WWTPs), which are limited in their removal of these antibiotics as many of the drug residues are neither biodegraded nor adsorbed to the sewage sludge. Sulphamethoxazole was detected at concentrations up to 0.472 μg L^{-1} at urban WWTP effluents in Ohio (USA) [3], at concentrations of 0.1–0.09 μg L^{-1} in effluents throughout Europe [4] and at reducing concentration of 2460, 1500–300 and 30–80 ng L^{-1} in primary effluent, secondary effluent and surface water, respectively, in Germany [5]. Sulphamethoxazole was also detected at concentrations of 30 ng L^{-1} in a deep groundwater well located below a field irrigated with secondary effluent [6]. Ingerslev and Halling-Sorensen [7] found that 12 different suphonamides were not readily biodegradable in activated sludge, although other studies concluded that SMX has the potential to be biodegraded during sewage treatment, with great dependence on the wastewater matrix and antibiotic residence time [8]. Given that wastewater effluents are commonly used in crop irrigation or discharged directly into water bodies, there is a growing concern regarding the potential impact of antibiotic residues on the environment. Many studies suggest that antibiotic emissions into the environment can increase the occurrence of resistant bacteria (e.g. [1,9,10]) and enhance the transfer of genes that resist antibiotics between different bacterial taxonomic affiliations [11]. Thus, the wide use of SMX on a regular basis in human therapy and its limited

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ISSN 0959-3330 print/ISSN 1479-487X online

DOI: 10.1080/09593330903414238
http://www.informaworld.com

removal in conventional WWTPs can potentially contribute to an environmental load of SMX.

Only few studies have been conducted to evaluate the effectiveness of more advanced treatment technologies on the removal of antibiotics from drinking water and wastewater effluents. Several studies showed that oxidation with ferrate (VI) [12] and ozonation [13] have great potential in removing sulphonamides, including SMX, from water. Watkinson *et al.* [14] found that microfiltration did not efficiently remove SMX (among other antibiotics) from WWTPs, whereas reverse osmosis reduced its concentration below detection limit.

An attractive technology for treatment of organic micropollutants in water is the advanced oxidation process (AOP). Advanced oxidation processes are defined as the chemical oxidation of target organic pollutants in water by a process involving the accelerated production of hydroxyl radicals [15]. The hydroxyl radical (HO•) reacts very quickly with many contaminants, at kinetic constants in the range 10^8 to 10^{10} M^{-1} s^{-1} [16]. The HO• radicals can be generated, for example, by the combined application of ozone (O_3) and hydrogen peroxide (H_2O_2), UV and O_3, O_3 and electron beam, or UV and H_2O_2 [17–20]. In the process involving the application of UV/H_2O_2, hydroxyl radicals are produced by photolysis of H_2O_2, as shown in Equation (1) [18]:

$$H_2O_2 \xrightarrow{h\nu} 2^{*}OH. \quad (1)$$

Direct photolysis (by exposure to UV light) for removal of contaminants was shown to be effective only when the absorption spectrum of the pollutant overlaps the emission spectrum of the UV lamp and the quantum yield (QY) of the photochemical process is reasonably large. However, for most chemicals, direct UV photolysis is not a reasonable process for removal of micropollutants in water, thus addition of H_2O_2 to the UV process is used to enhance the degradation rate. For example, addition of H_2O_2 to the UV-based photodegradation process of two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazole-2-methylthio (MMTD-Me) and 5-methyl-1,3,4-thiadiazole-2-thiol (MMTD)) in water at an initial substrate concentration of 1 mg L^{-1} and H_2O_2/substrate molar ratios of 50/1, 42/1, 34/1 and 23/1 increased the substrate degradation rate in all cases [21]. Other studies showed that UV/H_2O_2 can also be an effective process for degradation of pharmaceuticals such as diclofenac and carbamazepine [20], metronidazole [22] and the endocrine-disrupting compounds 17-β-estradiol (E2) and 17-α-ethinyl estradiol (EE2) [23]. Arslan-Alaton and Dogruel [24] concluded that the low pressure UV/H_2O_2 process has a relatively low potential for the treatment of penicillin formulation in effluent. Kruithof *et al.* [25] integrated a medium-pressure (MP) polychromatic lamp with H_2O_2 in a drinking water treatment plant, for primary disinfection and as a general barrier against organic micropollutants (e.g. pesticides and pharmaceuticals). At an H_2O_2 concentration of 6 mg L^{-1} and an irradiation dose of 540 mJ cm^{-2}, SMX removal was approximately 80% (at an unspecified concentration). However, neither parametric optimization nor kinetic analysis was provided. Thus, even though the UV/H_2O_2 process, using a polychromatic MP UV source, shows high potential for SMX degradation, basic research and detailed kinetic analysis are still lacking. Moreover, SMX is a microcontaminant of increasing concern because of its potential adverse effects on ecosystems and human health [1,9]. Because there are no drinking water standards for many micropollutants, SMX, among others suggested, is considered an indicator for contaminant monitoring, thus its oxidation potential is of practical interest.

The goal of this study was to determine the potential of UV/H_2O_2 for removal of SMX in water using a polychromatic (200–300 nm) UV source and to develop a kinetic model under varying concentrations of H_2O_2 and UV fluences. The UV/H_2O_2 system is a widely researched AOP, with high engineering potential especially when using polychromatic UV light sources for disinfection, making the addition of the oxidant H_2O_2 (with higher UV doses compared with disinfection), for treatment of organic micropollutants, a relatively practical process.

Materials and methods

Chemicals

An SMX standard (99.9% purity) was obtained from Sigma-Aldrich, and ULC-grade acetonitrile and water were obtained from Bio-Lab Ltd (Rehovot, Jerusalem, Israel). A stock solution of SMX was prepared by dissolving the compound in deionized (DI) water (Direct-Q3 UV system, Millipore, Molsheim, France) at a concentration of 100 mg L^{-1}. The molecular structure of the SMX antibiotic is presented in Figure 1. A stock solution of H_2O_2 (30% w/w, extra pure, Merck, Darmstadt, Germany) was prepared by measuring 375 μL of hydrogen peroxide solution into 50 mL DI water, to achieve a final concentration of 73.5 mM H_2O_2 (2500 mg L^{-1}). The compound para-chlorobenzoic acid (pCBA) was obtained from Sigma Aldrich (Rehovot, Israel) and used as a reference compound for the determination of the HO• radical concentration. Para-chlorobenzoic acid is an ideal probe compound for UV AOP study because of its low QY values [26], indicating that direct photolysis will likely be slow compared with the advanced oxidation pathway. A working solution of pCBA was prepared by measuring 5 mg of pCBA into 5 L of DI water to obtain a concentration of approximately 6.4 μM (1 mg L^{-1}). All chemicals were

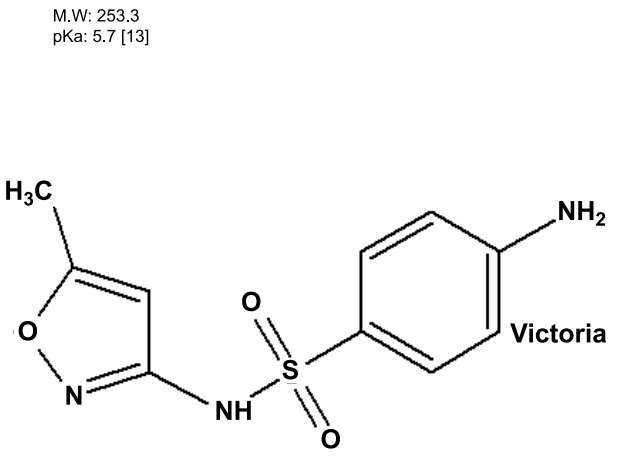

Figure 1. Molecular structure of the SMX antibiotic.

used as obtained and working solutions were prepared with DI water.

Experimental set-up

Photolysis experiments were carried out using a 0.45 kW polychromatic (200–300 nm) medium-pressure (MP) Hg vapour lamp (Ace-Hanovia Lamp Cat. No. 7830-61 from Ace Glass Inc., Vineland, NJ, USA), housed in a quasi-collimated beam apparatus. Experiments were designed to examine if the removal of SMX in water resulted from H_2O_2, direct UV irradiation, or the combined UV/H_2O_2 process. Thus, the conditions tested in this study were: polychromatic UV source (without added H_2O_2), H_2O_2 (without UV exposure) and the combined UV/H_2O_2 on removal of SMX in water. For all UV and UV/H_2O_2 experiments, 150 mL DI water samples at pH 6.00 ± 0.01 (pH remained steady throughout the experiment duration) were spiked with SMX to achieve a starting concentration of 3.2 μM (1 mg L^{-1}). The SMX initial concentration was higher than that found in natural aquatic environments; however, it allowed the direct analysis of SMX and the determination of the degradation kinetics for the antibiotic. Different concentrations of H_2O_2 were added to the solution in the range of 0–4.41 mM (common H_2O_2 values for UV/H_2O_2 treatments). Residual H_2O_2 was measured by the KI-thiosulphate method outlined in Klassen *et al.* [27]. Catalase (Cat. No. 219001, Calbiochem, Darmstadt, Germany) was added to destroy residual H_2O_2 prior to analysis. Irradiation was performed with gentle stirring in an 8.5 × 5 cm crystallization dish (56.8 cm^2 surface area, solution depth approximately 2.7 cm) open to the atmosphere. Samples of 0.5 mL were withdrawn at appropriate intervals for chromatography analysis. The average irradiance was calculated using the solution spectral absorbance, the spectral incident irradiance obtained from a calibrated spectroradiometer (with spectral range at 200–390 nm and resolution of 0.45 nm FWHM; USB4000, Ocean Optics, Florida, USA) placed in the same position as the centre of the crystallization dish, the reflection at the sample surface and the measured petri-factor for the dish [28]. The UV fluence was calculated by multiplying the average irradiance by exposure time. The UV absorption coefficient of the SMX and pCBA solution at different H_2O_2 concentrations was measured via UV-Vis spectrophotometry (Varian, Cary 100BIO, Victoria, Australia), and the molar (decadic) absorption coefficients for SMX and pCBA were further determined. Relative emission spectra of the UV lamp and UV light absorption spectrum of SMX and H_2O_2 are shown in Figure 2.

For the pCBA experiments (determination of HO• radical concentration), a volume of 150 mL of the pCBA working solution was injected with a known H_2O_2 concentration. The sample was irradiated under the polychromatic collimated beam apparatus conditions for an exposure time up to 10 min, and 0.5 mL samples were withdrawn at 1 min intervals for pCBA concentration analysis by HPLC detector.

Analytical methods

Sulphamethoxazole and pCBA were detected and quantified by an HPLC Agilent 1100 series (limit of detection 1 μg l^{-1}), consisting of a binary pump, a micro vacuum degasser, a diode array detector and a thermostatic column compartment, using an ACE-RP C18 column, 2.5 × 250 mm. The column temperature was 28 °C, the flow rate was 0.5 mL min^{-1} and the volume injected was 100 μL. The UV absorption of SMX was recorded at 260 and 280 nm, while pCBA was recorded at 240 nm. An HPLC mobile phase consisting of water (A) and acetonitrile (B) was used for both SMX and pCBA, adjusted to pH 3.3 for SMX and pH 2.1 for pCBA by the addition of formic acid. The eluent gradient for SMX started with 65% of eluant A followed by a 2 min linear gradient to 15% of eluant A, a 3 min isocratic elution and a 2 min linear gradient back to 65% of eluant A, which was maintained for 17 min to equilibrate the column (adapted from Lester *et al.* [29]). For pCBA, the elution started with 55% eluant A, then a 2 min linear gradient to 5% of eluant A, a 2 min isocratic elution and a 2 min linear gradient back to 55% of eluant A, which was maintained for 10 min for column equilibration.

Results and discussion

UV/H_2O_2 advanced oxidation

The time-based degradation of SMX by the UV and UV/H_2O_2 processes, for different hydrogen peroxide

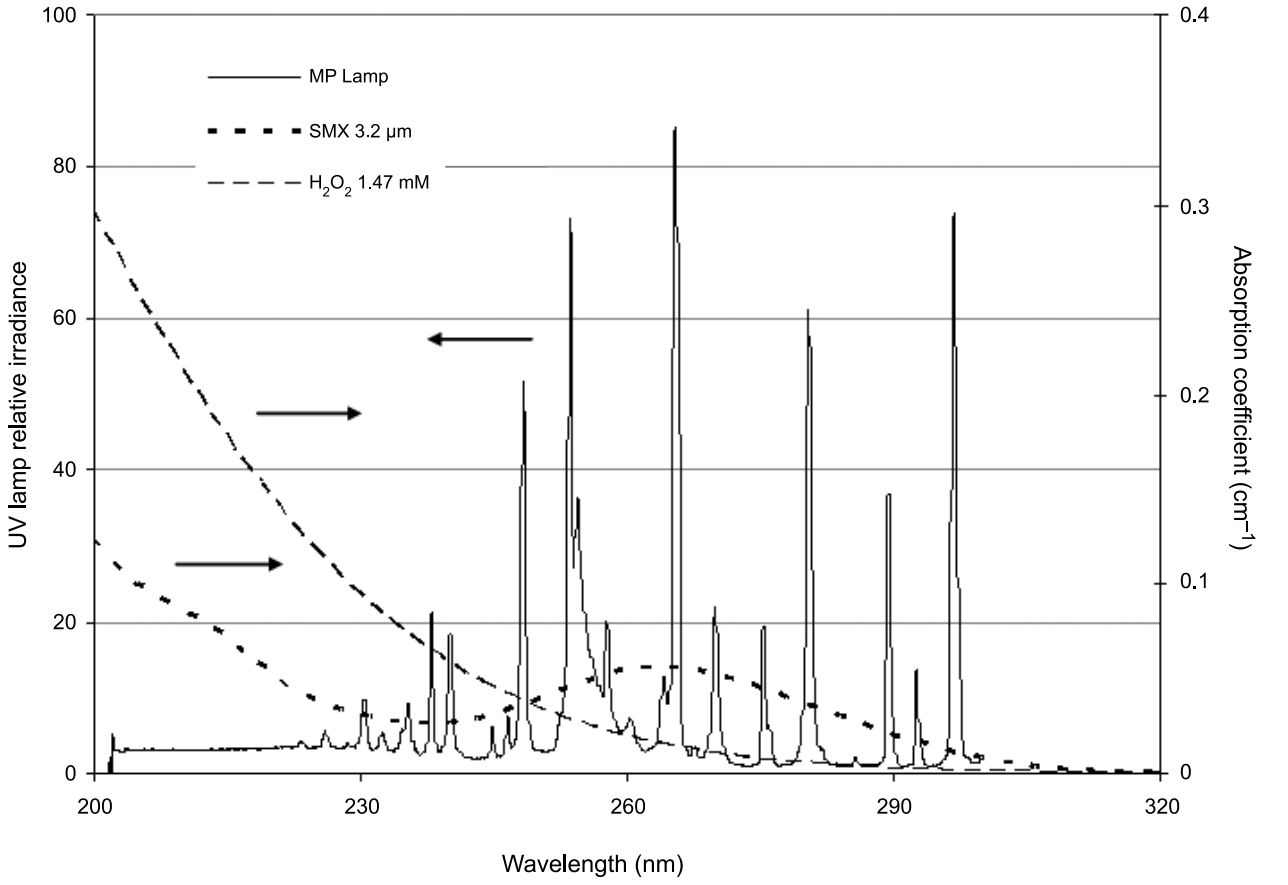

Figure 2. Emission spectra of the UV lamp and absorption spectrum of SMX (3.2 µM) and H_2O_2 (1.47 mM) in DI water (pH 6.0).

concentrations, was plotted by the natural logarithm of $[SMX]_t/[SMX]_0$ as a function of exposure time t (s), where $[SMX]_0$ and $[SMX]_t$ are the initial antibiotic concentration and the concentration after exposure time t, respectively. Representative data for the degradation by UV/H_2O_2 are shown in Figure 3, where linear regression was used to fit the curves to the general Equation (2), indicating first-order kinetics for SMX decay. The slope of the curves reflects the difference in degradation rate between samples:

$$\ln[SMX]_t / [SMX]_0 = k_T t \qquad (2)$$

where k_T is the total first-order decay rate constant (s^{-1}).

Figure 4 illustrates the pseudo-first-order decay rate constants (s^{-1}) for the UV/H_2O_2 process as a function of H_2O_2 concentration. The sensitivity of SMX to the UV/H_2O_2 process in DI water followed a decreasing order of: 4.41 ≈ 2.94 ≈ 1.47 > 0.74 > 0.29 > 0.15 > 0 mM H_2O_2. Thus, it is clear that adding relatively small to moderate amounts of hydrogen peroxide to the photolysis process, resulting in an indirect photolytic process for SMX, leads to a significant increase in SMX degradation rate (two-fold). However, at high concentrations of H_2O_2 the degradation rate remains relatively constant. As a control experiment, the impact of H_2O_2 alone as the single oxidant (no UV irradiation) on the degradation of SMX was evaluated. No degradation was observed when H_2O_2 was used at concentrations of 0–4.41 mM and target contact times of up to 48 hours.

To test whether the differences in slopes (i.e. kinetic rate constants) are statistically significant, the analysis of covariance (ANCOVA) method can be used to capture the interaction of the first-order regression slope with a main effect such as exposure time for each treatment. In this study, this method was accomplished by introducing the interaction between the natural log inactivation of SMX and time for each treatment. The difference in degradation rate constants between the 1.47 and 4.41 mM H_2O_2 concentrations is not significant as the P value for the interaction is above 0.05 ($F(1,24) = 2.5700$, $P = 0.1246$). On the other hand, the difference between the 0 mM H_2O_2 and 0.15 mM H_2O_2 treatments is significant at $P < 0.05$ ($F(1,41) = 5.3564$, $P = 0.0263$), indicating that adding up to 1.47 mM H_2O_2 does affect SMX degradation rate.

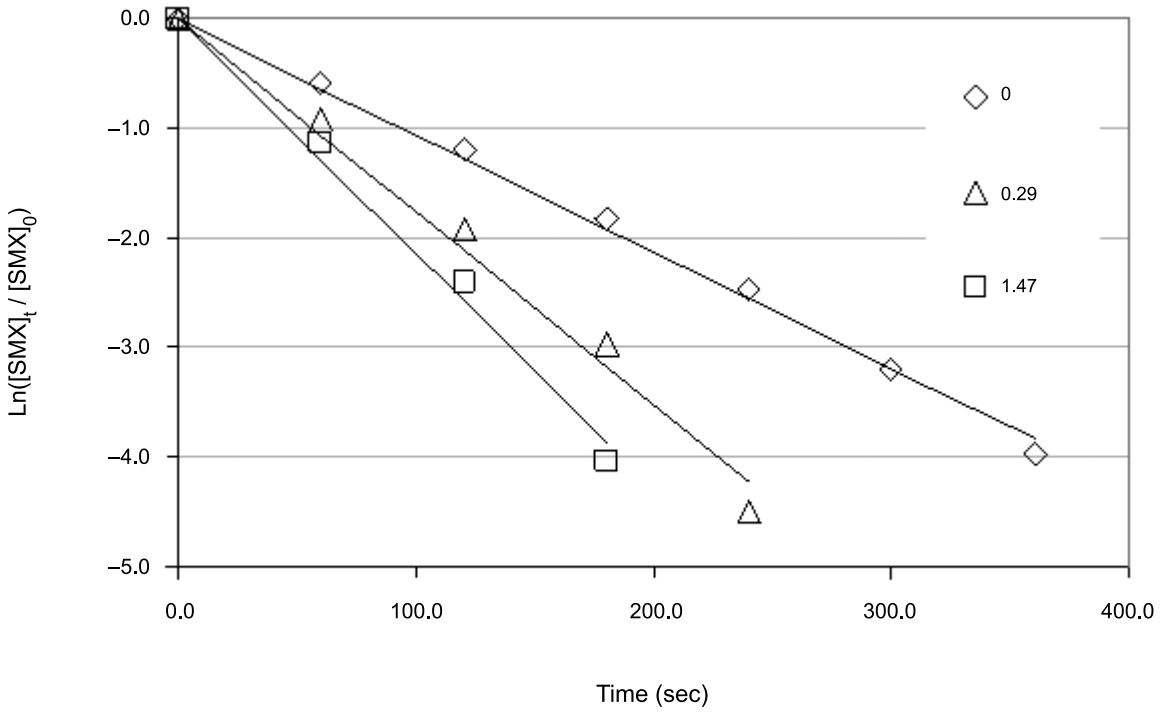

Figure 3. Degradation of 3.2 μM SMX with UV/H_2O_2 by the MP lamp at different H_2O_2 concentrations in DI water. Numbers in the legends (0, 0.29 and 1.47) refer to H_2O_2 concentration in mM. Water pH was approximately 6.0.

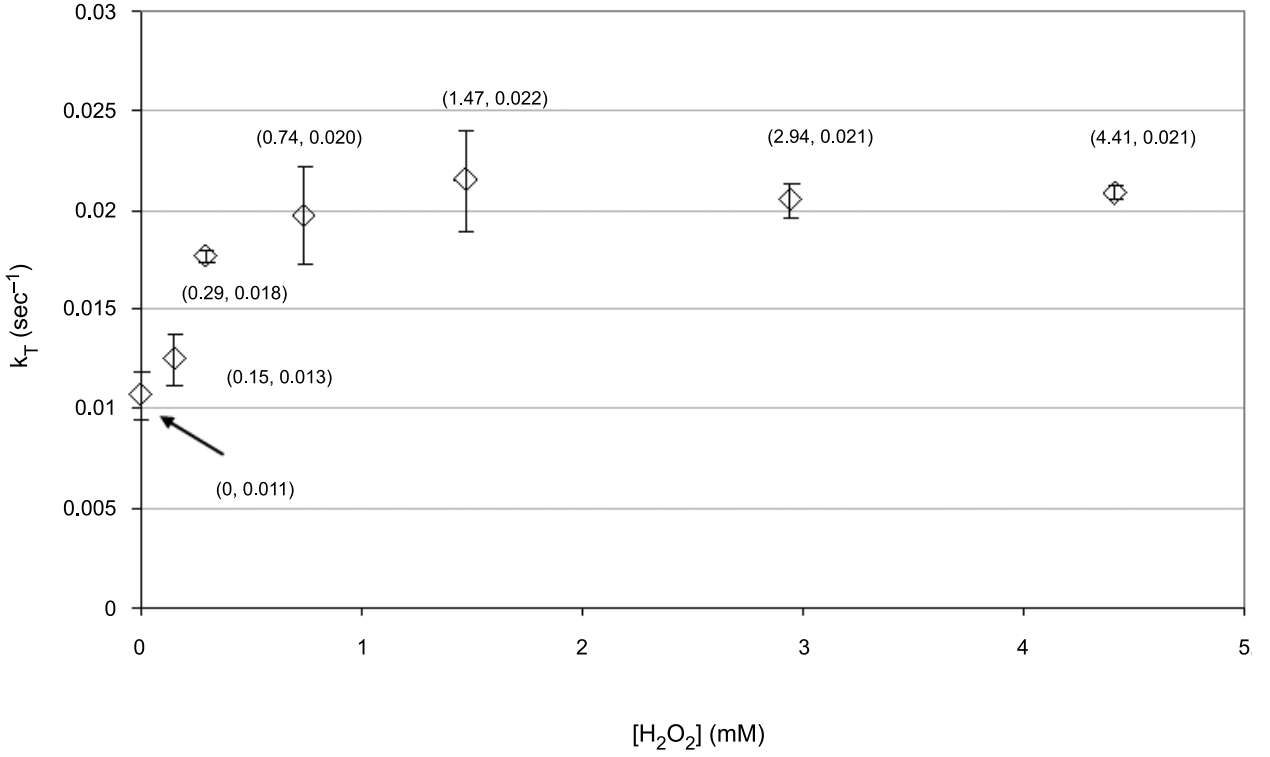

Figure 4. Time-based degradation rate of 3.2 μM SMX at different H_2O_2 concentrations. Values in parentheses are the H_2O_2 concentration (mM) and SMX degradation rate, k_T, respectively, in DI water (s^{-1}).

The observed kinetic response at low and high H_2O_2 concentrations in the UV/H_2O_2 process (Figure 4) is in good agreement with previous studies [30–32] and can be explained by several underlying processes: (a) an increase in H_2O_2 concentration leads to a higher HO• radical concentration in the solution (Equation (1)), (b) at high H_2O_2 concentration a competitive reaction between H_2O_2 and HO• radicals becomes significant; thus, H_2O_2 may act as an HO• radical scavenger (Equation (3), Christensen *et al.* [33]),

$$H_2O_2 + HO\bullet \xrightarrow{k=2.7\times10^7\,M^{-1}s^{-1}} HO_2\bullet + H_2O \qquad (3)$$

(c) H_2O_2 may effectively absorb UV light, and at high concentrations may provide a screening effect that reduces the direct photolysis rate of SMX.

Kinetic study

Degradation of SMX by the UV/H_2O_2 process is expressed through Equations (4) and (5) [34], and involves the following reactions: (a) direct UV photolysis of SMX governed by the absorption spectrum and QY of the target compound and emission of the UV lamp, and (b) indirect photo-oxidation reaction between SMX and hydroxyl radicals generated by photolysis of the peroxidic bond within hydrogen peroxide.

$$-\frac{d[SMX]}{dt} = \phi k_s[SMX] + k_{OH\bullet SMX}[HO\bullet][SMX] \qquad (4)$$

$$k_s = \sum_{200-300} \frac{10^{-3}\times E^0{}_p(\lambda)\varepsilon(\lambda)\left[1-10^{-a(\lambda)Z}\right]}{a(\lambda)z} \qquad (5)$$

where [SMX] and [HO•] are the concentrations of SMX and HO• radicals, respectively (M), Φ is the quantum yield (QY) for removal (mol Einstein^{-1}), k_s is the specific rate of light absorption by SMX (Einstein mol^{-1} s^{-1}), $k_{HO\bullet,SMX}$ is the second-order rate constants of SMX with the HO• radical (M^{-1} s^{-1}), $E^0{}_p(\lambda)$ is the incident photon irradiance (Einstein cm^{-2} s^{-1}), (λ) is the molar (decadic) absorption coefficient of SMX (M^{-1} cm^{-1}), $a(\lambda)$ is the solution absorption coefficient (cm^{-1}) and z is the depth of solution (cm).

Direct photolysis and quantum yield

The QY for SMX degradation via direct photolysis was calculated for wavelengths between 200 and 300 nm, using Equations (4) and (5) (where [HO•] = 0) and the experimental degradation results in Figure 3. The QY was found to be 0.054 mole Einstein^{-1} and is similar to a value of 0.051 obtained by Canonica *et al*., [35] using an MP lamp at pH 7. Boreen *et al.* [36] calculated a value of 0.09 mole Einstein^{-1} for SMX under natural sunlight at pH 6.9. The direct photolysis contribution to the UV/H_2O_2 degradation process (left component on the right side of Equation (4)) highly depends on the amount of UV light available for the SMX photodegradation. The fraction of light directly absorbed by SMX is represented by the specific rate of light absorption (k_s), and is recalculated when solution spectral absorbance varies. For example, increasing the concentration of H_2O_2 in the solution will lead to an increase in spectral absorbance and a decrease in the k_s value, thus decreasing the relative contribution of direct photolysis to the total SMX degradation rate.

HO• radical steady state concentration

The HO• radical concentration can be indirectly determined by the rate of consumption of the probe compound pCBA. Figure 5 illustrates the pCBA UV/H_2O_2 degradation results, plotted by the natural logarithm of $[pCBA]_t/[pCBA]_0$ and the exposure time for different H_2O_2 concentrations.

The QY for pCBA direct photolysis was calculated in this study, and a value of 0.0182 mole Einstein^{-1} was obtained. This value is in agreement with the value of 0.018 previously obtained by Rosenfeldt and Linden [37] under similar conditions. The HO• radical concentration was calculated using Equations (4) and (5) (modified for pCBA), where the second-order time-based rate constant between HO• and pCBA ($k_{HO\bullet,pCBA}$) was reported to be 5×10^9 M^{-1} s^{-1} [38]. Figure 6 presents the HO• radical concentration as a function of H_2O_2 concentration.

As expected, addition of hydrogen peroxide to the UV-irradiated solution generates HO• radicals. The concentration of HO• radicals as a function of H_2O_2 concentration varies in the range of 6.0×10^{-13} to 2.5×10^{-12} M. Wu *et al.* [32] calculated values for HO• radicals in the range of 1.0×10^{-12} to 12.0×10^{-12} M for H_2O_2 concentrations of 5–250 mg L^{-1}. It is clear from Figure 6 that, whereas the steady-state concentration of HO• radicals increases rapidly at low to moderate concentrations of H_2O_2 (0.15–1.47 mM), its concentration becomes steady or even decreases at higher concentrations of H_2O_2 (within the examined concentration range). The cause for this trend, as mentioned earlier and was observed elsewhere [32,39], is the competitive reaction of hydrogen peroxide to consume hydroxyl radicals (Equation (3)).

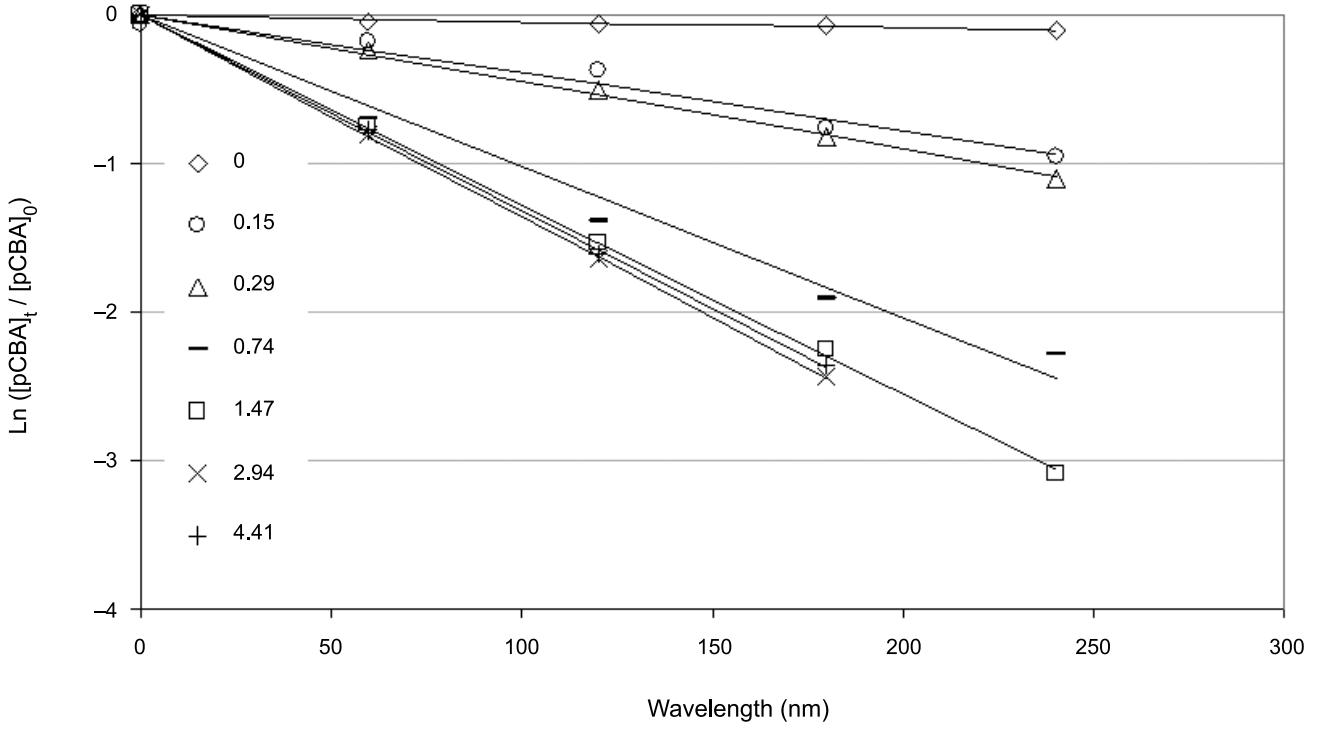

Figure 5. Time-based degradation of 6.4 μM pCBA with UV/H_2O_2 by MP lamp at different H_2O_2 concentrations in DI water. Numbers in the legend refer to H_2O_2 concentration in mM.

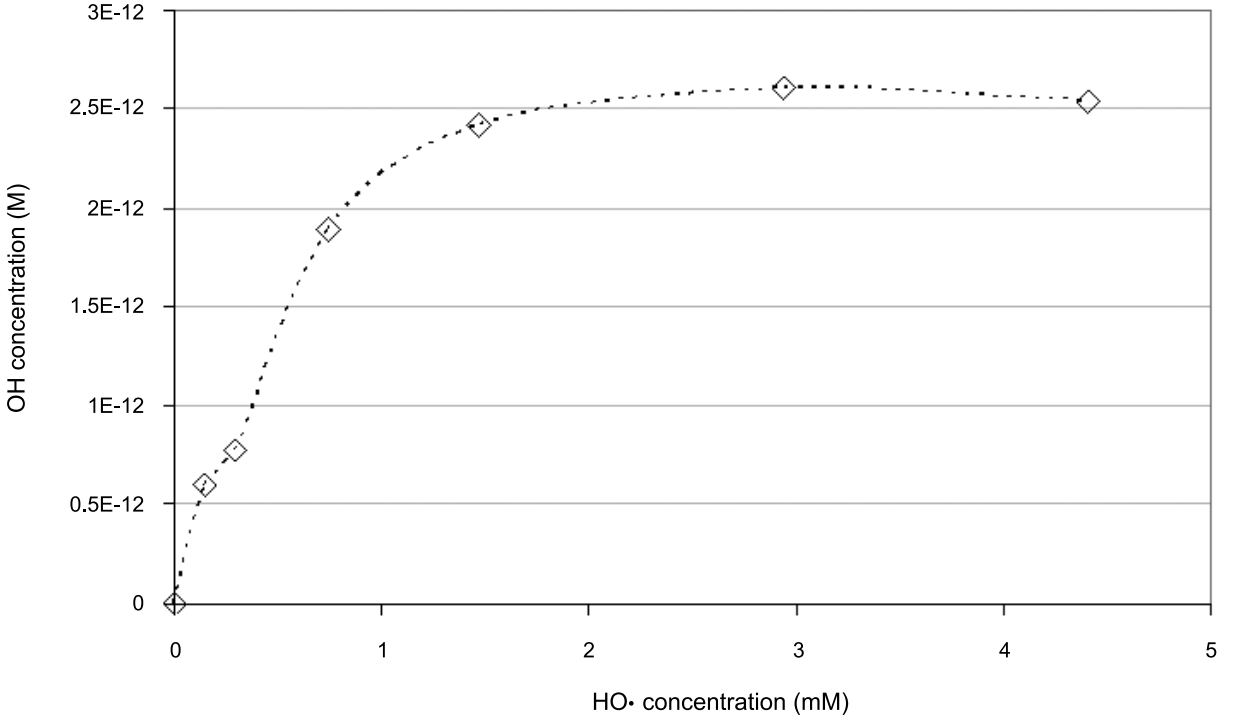

Figure 6. The HO• radical concentration in DI water as a function of H_2O_2 concentration.

Rate constant of reaction of HO• radicals with SMX

Once the direct photolysis rate of SMX has been calculated and the total degradation rate of SMX by the UV/H_2O_2 process has been experimentally measured, the second-order rate constants of SMX with the HO• radical ($k_{HO•,SMX}$) can be quantified using Equations (4) and (5). To verify the kinetic analysis, $k_{HO•,SMX}$ was calculated for each H_2O_2 concentration in the experiment and was found to vary mainly in the range $3.5–6.8 \times 10^9$ M^{-1} s^{-1} (with the exception of 9.6×10^9 M^{-1} s^{-1} for 10 mg L^{-1} H_2O_2). This data was reported elsewhere to be 5.5×10^9 M^{-1} s^{-1} using ozone as the radical generator and competition kinetic [13] and 8.5×10^9 M^{-1} s^{-1} using a combination of electron pulse radiolysis/absorption spectroscopy and steady-state radiolysis/high-performance liquid chromatography measurements [40].

Acknowledgements

The authors gratefully acknowledge Mr. Igal Gozlan, researcher at IMI Tami, Institute for R&D Ltd., Israel for his assistance in the chemical aspects of this research.

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