Hindawi
International Journal of Photoenergy
Volume 2018, Article ID 6181747, 6 pages
https://doi.org/10.1155/2018/6181747

Research Article

Albendazole Degradation Possibilities by UV-Based Advanced Oxidation Processes

Davor Ljubas,[1] Mirta Čizmić,[2] Katarina Vrbat,[2] Draženka Stipaničev,[3] Siniša Repec,[3] Lidija Ćurković,[4] and Sandra Babić[2]

[1]*Department of Energy, Power Engineering and Environment, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Ivana Lučića 5, Zagreb, Croatia*
[2]*Department of Analytical Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 20, Zagreb, Croatia*
[3]*Croatian Waters, Central Water Management Laboratory, Ulica grada Vukovara 220, Zagreb, Croatia*
[4]*Department of Materials, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Ivana Lučića 5, Zagreb, Croatia*

Correspondence should be addressed to Davor Ljubas; davor.ljubas@fsb.hr and Mirta Čizmić; mzrncic@fkit.hr

Received 21 June 2018; Accepted 17 October 2018; Published 20 December 2018

Academic Editor: Francesco Riganti-Fulginei

Pharmaceuticals are present in an aquatic environment usually in low (ng/L) concentrations. Their continuous release can lead to unwanted effects on the nontarget organisms. The main points of their collection and release into the environment are wastewater treatment plants. The wastewater treatment plants should be upgraded by new technologies, like advanced oxidation processes (AOPs), to be able to degrade these new pollutants. In this study, the degradation of albendazole (ALB), a drug against parasitic helminths, was investigated using four UV-based AOPs: UV photolysis, UV photocatalysis (over TiO_2 film), UV + O_3, and UV + H_2O_2. The ranking of the degradation process degree of the ALB and its degradation products for studied processes is as follows: UV photolysis < UV photocatalysis with TiO_2 < UV + O_3 < UV + H_2O_2. The fastest degradation of ALB and its degradation products was obtained by UV-C + H_2O_2 process with a degradation efficiency of 99.95%, achieved in 15 minutes.

1. Introduction

Pharmaceuticals are complex molecules with different physicochemical and biological properties and functionalities. Although they are present in the aquatic environment in low (ng/L to μg/L) concentrations, they are continually being released into the environment which can lead to unwanted effects on the living organisms, especially on the nontarget organisms [1–3]. Many studies showed that the main points of collection and subsequent release of pharmaceuticals into the environment are wastewater treatment plants, suggesting that their upgrade and implementation of advanced treatment technologies are required [4, 5].

Research studies now concentrate on diverse categories of pharmaceuticals, e.g., macrolide antibiotics, hormones, endocrine-disrupting compounds, β-blockers, and anthelmintics, as well as their metabolites [6–9].

Anthelmintics are mostly used both for humans and animals, and their focused activity is the treatment of gastrointestinal parasites [10, 11]. A few different anthelmintics are commercially available today. Among them, albendazole, flubendazole, thiabendazole, and fenbendazole are usually the most commonly used ones [12].

Albendazole (ALB), as one of the most widely used benzimidazole anthelmintics, was in focus of this study, since we noticed the lack of reports on the environmental fate of anthelmintics discharged into the water environment. Degradation products and metabolites of ALB that were detected in previous studies [13–15] are albendazole sulfoxide (ALB-SX), albendazole sulfone (ALB-SF), and albendazole-

Table 1: Degradation conditions of ALB in experiment groups A–D.

Experiment group	Experiment label	Experiment description
A	A1	UV illumination (photolysis) with predominant wavelengths 185/254 nm (UV-C)
	A2	UV illumination (photolysis) with predominant wavelength 365 nm (UV-A)
B	B1	UV illumination in the presence of sol-gel TiO_2 film (photocatalysis) with predominant wavelengths 185/254 nm(UV-C), with continuous purging with air (O_2)
	B2	UV illumination in the presence of sol-gel TiO_2 film (photocatalysis) with predominant wavelengths 365 (UV-A) nm, with continuous purging with air (O_2)
C	C1	Ozone dosage via concentrated O_3 solution (prepared according to [24]), low dosage of O_3: 0.5 mg/L
	C2	Ozone dosage via concentrated O_3 solution (prepared according to [24]), high dosage of O_3: 1.5 mg/L
	C3	High dosage of O_3: 1.5 mg/L + UV-C radiation
	C4	High dosage of O_3: 1.5 mg/L + UV-A radiation
D	D1	H_2O_2 dosage via concentrated (30%) solution, high dosage of H_2O_2: 320 mg/L H_2O_2
	D2	H_2O_2 dosage via concentrated (30%) solution, high dosage of H_2O_2: 320 mg/L H_2O_2 + UV-C radiation
	D3	H_2O_2 dosage via diluted (1 : 4) 30% solution, low dosage of H_2O_2: 64 mg/L H_2O_2 + UV-C radiation
	D4	H_2O_2 dosage via concentrated (30%) solution, high dosage of H_2O_2: 320 mg/L H_2O_2 + UV-A radiation

2-aminosulfone (ALB-2-ASF). In addition to ALB, ALB-SX is also an important factor in the potential adverse environmental impact on organisms in the environment [15].

One of the possible solutions for the degradation and/or removal of pharmaceuticals from the wastewaters is the use of advanced oxidation processes (AOPs) as an additional treatment step. AOPs can be defined as aqueous phase oxidation methods where highly reactive species such as hydroxyl radicals are responsible for the destruction of target pollutants, e.g., pharmaceutic molecules. They can be used either alone or coupled with other physicochemical and biological processes [16–18], especially as a tertiary treatment in wastewater treatment plants [19]. Extensively investigated AOPs for the degradation of pharmaceuticals include the UV irradiation combined with H_2O_2 or O_3 as strong oxidants, the Fenton and the photo-Fenton oxidation, and the heterogeneous photocatalysis over titanium dioxide or titania (TiO_2) [20–23].

In this study, the degradation of ALB was investigated in lab-scale experiments using four UV-based processes (with 185/254 and 365 nm radiation sources): (A) UV photolysis, (B) UV photocatalysis (UV light + TiO_2 nanofilm), (C) UV + O_3 process, and (D) UV + H_2O_2 process. Screening of ALB degradation was performed using liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) and with ultra-high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS).

Calculation of energy use and total cost of every treatment option, as well as their comparison, will be evaluated in continuous work that will follow this study.

2. Methods and Materials

The analytical standard of ALB was obtained from Veterina Animal Health (Kalinovica, Croatia). For chromatographic analysis methanol (J. T. Baker, Deventer, Netherlands), acetonitrile (J. T. Baker, Deventer, Netherlands), and formic acid (Merck, Darmstadt, Germany) were used. All solvents used were HPLC-grade. Ultrapure water was prepared by a Millipore Simplicity UV system (Millipore Corporation, Billerica, MA, USA) and was used for all experiments. The concentration of aqueous solution of ALB was 1 mg/L. The solutions for experiments were prepared in quantities of 1 L and kept in the dark at 4°C.

Concentrated ozone stock solutions were produced by O_2 gas through an ozone generator through ultrapure water that was cooled in an ice bath, following a procedure described in [24].

Hydrogen peroxide (H_2O_2) concentrated solution (30%) was purchased from Kemika (Zagreb, Croatia) and kept in the dark, at 4°C.

All experiments were carried out in the 0.11 L borosilicate glass cylinder reactor (with 200 mm in height and 30 mm in diameter). A scheme of the reactor set-up was published elsewhere [25]. The TiO_2 nanostructured film was deposited on an inner reactor surface by the sol-gel method and dip-coating technique, described in details elsewhere [26]. Two different UV-radiation lamps were used: model Pen-Ray 90-0019-04, with $\lambda_{max} = 365$ nm and incident photon flux $N_p = 4.295 \times 10^{-6}$ Einstein/s (UV-A lamp), and model Pen-Ray 90-0004-07 with $\lambda_{max} = 254/185$ nm (UV-C lamp) and incident photon flux $N_p = 1.033 \times 10^{-6}$ Einstein/s (UVP, Upland, CA, USA). The lamp was placed in the center of the reactor, and the UV radiation reaches the inner wall of the reactor through the solution, causing the photolytic/photocatalytic oxidation process in the reactor as described elsewhere [27]. During the experiments, samples for chromatographic analysis were taken from the reactor at particular time intervals and stored in the dark under 4°C until analysis. Only by experiments with ozone, samples were analyzed immediately (since ozone alone reacts with ALB in solution).

The experiments for ALB degradation were carried out at a temperature of 25 ± 0.2°C without adjustment of pH. Starting pH of 1 mg/L solution was in interval 5.95–6.10, using different conditions that can be seen in Table 1.

Samples from the photolytic and photocatalytic experiments were analyzed on an Agilent Series 1200 HPLC system (Santa Clara, CA, USA) connected to a triple quadrupole mass spectrometer Agilent 6410 with an ESI interface. The column used for chromatographic separation of the degradation products was Synergi Polar C18 (100 mm × 2.0 mm, particle size 2.5 μm) supplied by Phenomenex (Torrance, CA, USA). The mobile phase was MilliQ water acidified with 0.1% formic acid (A) and acetonitrile acidified with also 0.1% formic acid (B) as it was used in [27]. The gradient elution was started with 8% of B which was held for 3 min. During the next 12 min, the percentage of B was increased linearly to 95% and was held for 5 min. During 0.01 min, it was set at 0% of B and was held for 10 min for the equilibration of the column. The analyses were performed in the positive ion (PI) mode. The conditions of the ion source of the mass spectrometer were drying gas temperature 350°C, capillary voltage 4 kV, drying gas flow 11 L min^{-1}, and nebulizer pressure 35 psi. Injection volume was 5 μL. For acquisition and data processing, Agilent MassHunter software version B.01.03 was used as described elsewhere [27].

HPLC-MS and MS/MS experiments for the identification of photodegradation products in experiments with UV-H_2O_2 and UV-O_3 processes were performed on an LTQ-Orbitrap Velos™ coupled with the Aria TLX-1 HPLC system (Thermo Fisher Scientific Inc., USA). The sample mixture was loaded (20 μL injection volume) on an Acquity UPLC HSS T_3 (2.1 mm × 50 mm, 1.8 μm particle size, Waters UK) column where the chromatographic separation was achieved using an 8 min linear gradient from 5% to 95% methanol in 0.1% formic acid at the flow rate of 200 μL·min^{-1}. The sample injection, separation, and spectra acquisition were carried out automatically. The electrospray capillary voltage was set at 4 kV, the capillary temperature was at 300°C, *m/z* range from 100 to 1000, the instrument resolution was 100,000 at 400 m/*z*, and mass accuracy was within the error of ±5 ppm. Tandem mass spectrometry experiments were performed using collision-induced dissociation. Mass range was from 100 to 600 m/*z*, isolation width was 1 Da with a normalized collision energy of 35 V, and activation time was 30 ms. Nitrogen was used as the collision gas. The acquisition software was set up in auto MS/MS mode using three precursor ions with active exclusion on (precursor exclusion after 5 MS/MS spectra for 20 s). Data extraction and analysis were done using Thermo Xcalibur 2.2 SP1.48 (Thermo Fisher Scientific Inc., USA).

Ozone was produced from O_2 gas (purity 99.995%, purchased by MESSER, Croatia) with ozone generator 500 M (Fischer Technology, Germany).

Concentrations of O_3 and H_2O_2 in stock solutions were controlled, due to their tendency to spontaneously degrade, by a UV-VIS spectrophotometer (HEWLETT PACKARD, Model HP 8453, USA) at 254 and 240 nm, respectively, by using a 1 cm quartz cell. The dose of H_2O_2 was prepared using the Beer-Lambert law and the established value for $\varepsilon = 401/(\text{M}\bullet\text{cm})$, as it is described in [28].

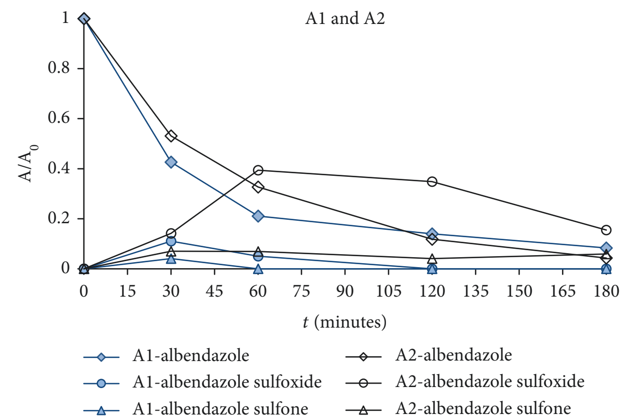

Figure 1: Photolytic degradation of ALB: A1—with UV-C radiation; A2—with UV-A radiation.

3. Results and Discussion

In following figures, the obtained results are presented as the integrated area of the chromatographic peak of specific analyte (ALB or its degradation products) at the specific time (*A*) divided by the integrated area of the chromatographic peak of ALB at $t = 0$ min (A_0). Three DPs were identified using high-resolution MS; they are known as ALB metabolites. All the experiments were performed in duplicate, and the final results are the average of the two replications.

Figure 1 shows the results of photolytic degradation of ALB, using only UV-C (185/254 nm radiation peaks) or UV-A (365 nm radiation peak).

Degradation with UV-C radiation was slightly more efficient than UV-A in ALB degradation, but the degradation of degradation products (albendazole sulfoxide (ALB-SX) and albendazole sulfone (ALB-SF)) is much faster: in 120 minutes, they completely disappeared with UV-C. With UV-A radiation, there is still a significant concentration of the degradation products in the solution even after 180 min of radiation exposure.

According to the studies [13, 14], ALB and its metabolites are sensitive to UV (i.e., solar) radiation and it is to expect that sunlight at the surface of a flat water body could degrade ALB by 50% per clear summer/early autumn day. However, it is not to expect, too, that every run-off from wastewater system to natural water could be exposed to the natural solar radiation at daytime, and that is the reason why wastewaters that contain ALB and its metabolites should be additionally treated.

Experiments performed "in the dark", i.e., with the lamp switched-off and with the additional aluminum foil for protection of light penetration into the reactor, confirmed that the effects of adsorption of ALB on the surface of TiO_2 catalyst film were negligible in the overall ALB degradation process. Figure 2 shows the photocatalytic degradation of ALB with two different lamps in the reactor.

It is obvious that the process UV-C + TiO_2 is much faster in ALB degradation compared to UV-A + TiO_2. However, degradation product, ALB-SX, remains in significant concentration after 120 minutes. In experiment B1 in $t = 10$ and 15

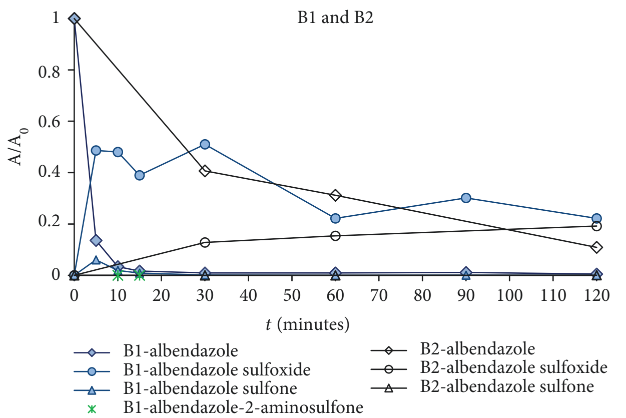

FIGURE 2: Photocatalytic degradation of ALB over TiO_2 film: B1—with UV-C radiation; B2—with UV-A radiation.

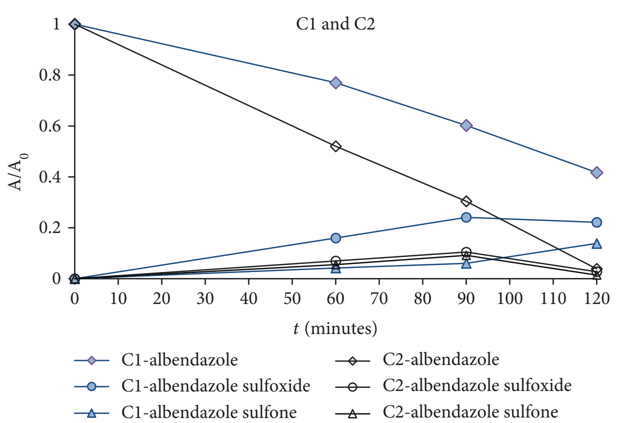

FIGURE 3: UV-based degradation of ALB with ozone: C1—ozone only, small dosage (0.5 mg/L O_3); C2—ozone only, high dosage (1.5 mg/L O_3).

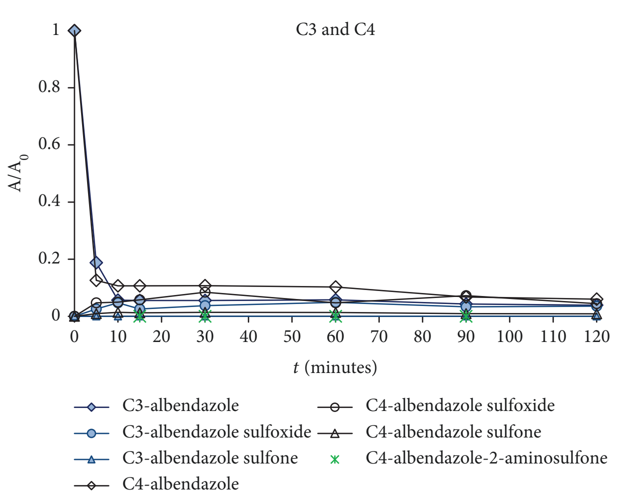

FIGURE 4: UV-based degradation of ALB with ozone: C3—ozone high dosage (1.5 mg/L O_3) with UV-C radiation; C4—ozone high dosage (1.5 mg/L O_3) with UV-A radiation.

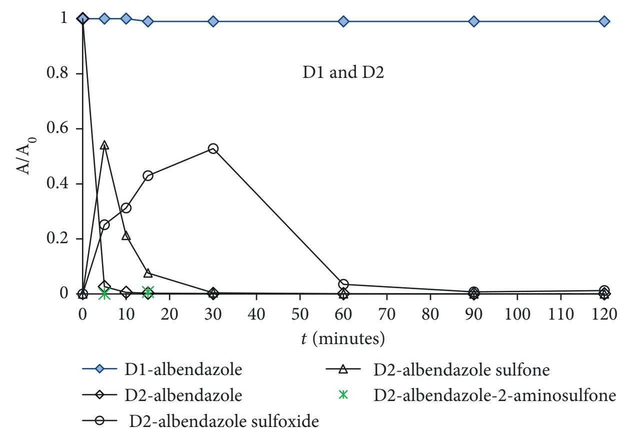

FIGURE 5: UV-based degradation of ALB with H_2O_2: D1—H_2O_2 only; D2—H_2O_2 high dosage + UV-C.

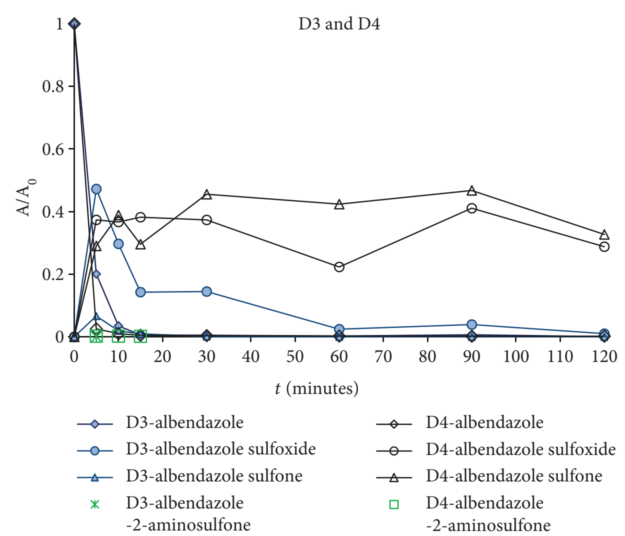

FIGURE 6: UV-based degradation of ALB with H_2O_2: D3—H_2O_2 low dosage + UV-C; D4—H_2O_2 high dosage + UV-A.

minutes, the traces of the 3rd degradation product of ALB was observed—ALB-2-ASF. Due to the fast degradation of ALB, there is a possibility for the formation of all three metabolites. The experiments B1 and B2 are faster in ALB degradation in comparison to the photolytic experiments A1 and A2 with the same radiation sources due to most probably hydroxyl radical formation over the TiO_2 film and its additional attack on the ALB molecule. It is especially observable when energy-higher UV-C radiation (in B1) was used.

In Figure 3, the degradation potential of ALB with ozone is shown. Ozone alone, both in high or low dosage, possesses relatively low potential for ALB and its DP degradation.

Nevertheless, when UV radiation was combined with O_3, again as in B group of experiments, due to hydroxyl radical formation, the degradation rate of ALB was increased (Figure 4). Rather a fast degradation of ALB, in 15 minutes, it reached around 90% of ALB removal, followed by very slow additional degradation of ALB, which implicates that the dosage of O_3, dosed by stock solution, was completely spent

Table 2: Removal efficiencies of ALB and formation quantities of ALB-SX and ALB-SF of all experiments at specific time intervals.

Experiment label	After 15 min			After 60 min			After 120 min		
	ALB, removal efficiency, %	ALB-SX, formation quantity, %	ALB-SF, formation quantity, %	ALB, removal efficiency, %	ALB-SX, formation quantity, %	ALB-SF, formation quantity, %	ALB, removal efficiency, %	ALB-SX, formation quantity, %	ALB-SF, formation quantity, %
A1	n.a.*	n.a.	n.a.	78.89	5.06	0.00	86.05	0.00	0.00
A2	n.a.	n.a.	n.a.	67.30	39.39	6.97	88.15	34.87	4.06
B1	98.37	38.95	0.88	99.08	22.14	0.02	99.50	22.20	0.02
B2	n.a.	n.a.	n.a.	68.85	15.40	0.03	89.12	19.20	0.04
C1	n.a.	n.a.	n.a.	23.01	16.00	4.20	58.29	22.15	13.86
C2	n.a.	n.a.	n.a.	48.03	7.01	5.52	96.15	2.74	1.41
C3	94.47	2.55	0.003	94.22	4.90	0.003	96.11	3.56	0.00
C4	89.31	5.79	1.22	89.72	4.72	1.37	93.99	4.44	0.9
D1	0.00	0.06	0.01	1.00	0.06	0.01	1.00	0.06	0.01
D2	99.75	42.98	7.61	99.93	3.47	0.05	99.95	1.21	0.00
D3	99.39	14.25	0.94	99.77	5.96	0.08	99.95	0.98	0.00
D4	99.50	38.21	29.60	99.77	22.30	42.40	99.82	28.76	32.72

on direct reactions with ALB or reactions to the hydroxyl radical formation, and it should be probably beneficiary to dose additional quantities of O_3 after 10 or 15 minutes.

When H_2O_2 was added to ALB solution, no reaction was observed, as can be seen in Figure 5.

In all UV-H_2O_2 processes (Figures 5 and 6), the 3rd degradation product, ALB-2-ASF, was shortly formed and after 15 minutes it disappeared, indicating that when the process of ALB degradation is fast, all three main degradation products of ALB can be observed.

Looking at all D processes, the fastest degradation of all components, ALB and its degradation products, was reached by the D2 process: in 90 minutes, practically, the water is almost free from contaminants. The D3 process is very close to D2 by its efficiency, especially when additional cost and energy requirements will be included in the evaluation of the processes.

Table 2 represents, in a short form, a comparison between all experiments, showing the ratios of the ALB and its degradation products during the treatment. It will be the base for continuing evaluation of these technologies.

4. Conclusions

The fastest degradation of ALB and its degradation products, for both UV-C radiation and UV-A radiation, was obtained by the UV-C + H_2O_2 process with removal efficiency of ALB higher than 99%, achieved in 15 minutes. However, degradation product removal requires extended time, up to 90 minutes.

In some cases, ALB was degraded more than 99% after 120 minutes but degradation products, especially ALB-SX, remained in high concentration. Such processes are characterized as not efficient enough because they do not efficiently remove all unwanted compounds that could potentially present a threat to the environment.

The ranking of the degradation process degree of the ALB and its degradation products for studied processes is as follows: UV photolysis < UV photocatalysis with TiO_2 < UV + O_3 < UV + H_2O_2. Although the slowest degradation of ALB was obtained using UV-A processes, they have a potential for practical use: they could use natural solar radiation as a source of UV-A radiation and therewith significantly reduce the cost of the treatment step.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Some parts of the study were presented as a poster titled "UV-Based Advanced Oxidation Processes for Albendazole Degradation" at *4th International Symposium on Environmental Management Towards Circular Economy* held in Zagreb, Croatia, December 7-9, 2016.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This study has been supported by the Croatian Science Foundation under the project "Fate of pharmaceuticals in the environment and during advanced wastewater treatment" (PharmaFate) (IP-09-2014-2353).

References

[1] W. C. Li, "Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil," *Environmental Pollution*, vol. 187, pp. 193–201, 2014.

[2] S. E. Jorgensen and B. Halling-Sorensen, "Drugs in the environment," *Chemosphere*, vol. 40, no. 7, pp. 691–699, 2000.

[3] F. A. Caliman and M. Gavrilescu, "Pharmaceuticals, personal care products and endocrine disrupting agents in the environment - a review," *CLEAN - Soil, Air, Water*, vol. 37, no. 4-5, pp. 277–303, 2009.

[4] M. Petrović, S. Gonzalez, and D. Barceló, "Analysis and removal of emerging contaminants in wastewater and drinking water," *TrAC Trends in Analytical Chemistry*, vol. 22, no. 10, pp. 685–696, 2003.

[5] K. Ikehata, N. Jodeiri Naghashkar, and M. Gamal El-Din, "Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review," *Ozone: Science & Engineering*, vol. 28, no. 6, pp. 353–414, 2006.

[6] S. Babić, L. Ćurković, D. Ljubas, and M. Čizmić, "TiO_2 assisted photocatalytic degradation of macrolide antibiotics," *Current Opinion in Green and Sustainable Chemistry*, vol. 6, pp. 34–41, 2017.

[7] J. C. Van De Steene, C. P. Stove, and W. E. Lambert, "A field study on 8 pharmaceuticals and 1 pesticide in Belgium: removal rates in waste water treatment plants and occurrence in surface water," *Science of The Total Environment*, vol. 408, no. 16, pp. 3448–3453, 2010.

[8] X. Yang, R. C. Flowers, H. S. Weinberg, and P. C. Singer, "Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant," *Water Research*, vol. 45, no. 16, pp. 5218–5228, 2011.

[9] M. Bistan, T. Tišler, and A. Pintar, "Ru/TiO_2 catalyst for efficient removal of estrogens from aqueous samples by means of wet-air oxidation," *Catalysis Communications*, vol. 22, pp. 74–78, 2012.

[10] B. P. S. Capece, G. L. Virkel, and C. E. Lanusse, "Enantiomeric behaviour of albendazole and fenbendazole sulfoxides in domestic animals: pharmacological implications," *The Veterinary Journal*, vol. 181, no. 3, pp. 241–250, 2009.

[11] A. Hall and Q. Nahar, "Albendazole as a treatment for infections with *Giardia duodenalis* in children in Bangladesh," *Transactions of the Royal Society of Tropical Medicine and Hygiene*, vol. 87, no. 1, pp. 84–86, 1993.

[12] W.-J. Sim, H. Y. Kim, S. D. Choi, J. H. Kwon, and J. E. Oh, "Evaluation of pharmaceuticals and personal care products with emphasis on anthelmintics in human sanitary waste, sewage, hospital wastewater, livestock wastewater and receiving water," *Journal of Hazardous Materials*, vol. 248-249, pp. 219–227, 2013.

[13] C. A. Weerasinghe, D. O. Lewis, J. M. Mathews, A. R. Jeffcoat, P. M. Troxler, and R. Y. Wang, "Aquatic photodegradation of albendazole and its major metabolites. 1. Photolysis rate and half-life for reactions in a tube," *Journal of Agricultural and Food Chemistry*, vol. 40, no. 8, pp. 1413–1418, 1992.

[14] C. A. Weerasinghe, J. M. Mathews, R. S. Wright, and R. Y. Wang, "Aquatic photodegradation of albendazole and its major metabolites. 2. Reaction quantum yield, photolysis rate, and half-life in the environment," *Journal of Agricultural and Food Chemistry*, vol. 40, no. 8, pp. 1419–1421, 1992.

[15] L. Prchal, R. Podlipná, J. Lamka et al., "Albendazole in environment: faecal concentrations in lambs and impact on lower development stages of helminths and seed germination," *Environmental Science and Pollution Research*, vol. 23, no. 13, pp. 13015–13022, 2016.

[16] M. Klavarioti, D. Mantzavinos, and D. Kassinos, "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes," *Environment International*, vol. 35, no. 2, pp. 402–417, 2009.

[17] V. Naddeo, D. Ricco, D. Scannapieco, and V. Belgiorno, "Degradation of antibiotics in wastewater during sonolysis, ozonation, and their simultaneous application: operating conditions effects and processes evaluation," *International Journal of Photoenergy*, vol. 2012, Article ID 624270, 7 pages, 2012.

[18] S. Norzaee, E. Bazrafshan, B. Djahed, F. Kord Mostafapour, and R. Khaksefidi, "UV activation of persulfate for removal of Penicillin G antibiotics in aqueous solution," *The Scientific World Journal*, vol. 2017, Article ID 3519487, 6 pages, 2017.

[19] A. Bernabeu, R. F. Vercher, L. Santos-Juanes et al., "Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents," *Catalysis Today*, vol. 161, no. 1, pp. 235–240, 2011.

[20] M. M. Huber, S. Canonica, G.-Y. Park, and U. von Gunten, "Oxidation of pharmaceuticals during ozonation and advanced oxidation processes," *Environmental Science & Technology*, vol. 37, no. 5, pp. 1016–1024, 2003.

[21] S. Babić, M. Zrnčić, D. Ljubas, L. Ćurković, and I. Škorić, "Photolytic and thin TiO_2 film assisted photocatalytic degradation of sulfamethazine in aqueous solution," *Environmental Science and Pollution Research*, vol. 22, no. 15, pp. 11372–11386, 2015.

[22] W. H. Glaze, J.-W. Kang, and D. H. Chapin, "The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation," *Ozone: Science & Engineering*, vol. 9, no. 4, pp. 335–352, 1987.

[23] C. Pablos, J. Marugán, R. van Grieken, and E. Serrano, "Emerging micropollutant oxidation during disinfection processes using UV-C, UV-C/H_2O_2, UV-A/TiO_2 and UV-A/TiO_2/H_2O_2," *Water Research*, vol. 47, no. 3, pp. 1237–1245, 2013.

[24] M. S. Elovitz and U. von Gunten, "Hydroxyl radical/ozone ratios during ozonation processes. I. The R_{ct} concept," *Ozone: Science & Engineering*, vol. 21, no. 3, pp. 239–260, 1999.

[25] L. Ćurković, D. Ljubas, S. Šegota, and I. Bačić, "Photocatalytic degradation of Lissamine Green B dye by using nanostructured sol–gel TiO_2 films," *Journal of Alloys and Compounds*, vol. 604, pp. 309–316, 2014.

[26] S. Šegota, L. Ćurković, D. Ljubas, V. Svetličić, I. F. Houra, and N. Tomašić, "Synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films," *Ceramics International*, vol. 37, no. 4, pp. 1153–1160, 2011.

[27] M. Čizmić, K. Vrbat, D. Ljubas, L. Ćurković, and S. Babić, "Photocatalytic degradation of macrolide antibiotic azithromycin in aqueous sample," *Proceedings of the 15th International Conference on Environmental Science and Technology (CEST 2017)*, D. F. Lekkas, Ed., , pp. 1–4, Diagramma, Athens, 2017.

[28] U. Von Gunten and Y. Oliveras, "Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems," *Water Research*, vol. 31, no. 4, pp. 900–906, 1997.