



Proceeding Paper Efficacy of Fumonisin B₁ Removal from Various Simulated Water Types Using UV and UV/H₂O₂ Treatments [†]

Ivana Jevtić^{1,*}, Sandra Jakšić², Daniela Šojić Merkulov³, Szabolcs Bognár³ and Biljana Abramović³

- ¹ Academy of Professional Studies Šabac, Hajduk Veljkova 10, 15000 Šabac, Serbia
- ² Scientific Veterinary Institute Novi Sad, Rumenački put 20, 21000 Novi Sad, Serbia; sandra@niv.ns.ac.rs
 ³ Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia; daniela.sojic@dh.uns.ac.rs (D.Š.M.); sabolc.bognar@dh.uns.ac.rs (S.B.); biljana.abramovic@dh.uns.ac.rs (B.A.)
- * Correspondence: ivana.dabic@yahoo.com
- [†] Presented at the 2nd International Electronic Conference on Toxins, 14–28 July 2023; Available online: https://iect2023.sciforum.net/.

Abstract: Fumonisins are secondary metabolites of mold whose presence has been proven in water. Since fumonisin B_1 (FB₁) is highly toxic and has dangerous effects on the health of living organisms, in this study, the influence of various water matrices on the effectiveness of UV and UV/H₂O₂ treatments for its removal was investigated. Different types of water (Danube River, tap and ground water) were simulated by addition of humic acid and the main ions for each type of water into ultrapure water (UPW). The results showed lower FB₁ removal efficiency in simulated water samples compared to that of UPW.

Keywords: mycotoxins; fumonisin B_1 ; removal; simulated different water types; UV photolysis; UV/ H_2O_2 treatment

1. Introduction

Mycotoxins are secondary metabolites of mold, and several hundred mycotoxins with very different chemical and physicochemical properties have been discovered so far [1]. Previous studies on mycotoxins have mainly focused on their production and presence in cereals. On the other hand, more and more attention is paid to the studies of fungi found in drinking water, where they and their metabolites are considered to be dangerous pollutants due to their toxicity [2,3]. Regarding their distribution, i.e., occurrence in the aquatic environment, various authors made different conclusions. For instance, according to Hartmann et al. [4], the presence of mycotoxins in the water environment is the result of runoff from agricultural land, while some authors believe that fungi are capable of biosynthesizing mycotoxins in water [5]. So far, mycotoxins have been detected in several water types: spring, surface and ground water, water from water supply and water reservoirs, as well as in bottled and tap water [6]. During the examination of the presence of zearalenone (ZEA) in surface (rivers and lakes), ground and waste water in Poland, the measured concentrations were found to be in the range of $0-43.7 \text{ ng/dm}^3$ [7], with the highest concentration measured in river water at the end of October, when the fungal activity is reduced. This also indicates that the presence of ZEA is the result of leaching from arable land contaminated with Fusarium graminearum [8]. According to the results of Kolpin et al. [9], a significant correlation was found between the presence of ZEA and deoxynivalenol (DON) in river waters, whereby DON was detected three times more often than ZEA. Laganà et al. [10] found that the concentration of DON is significantly higher than the concentration of ZEA in drainage waters. The highest concentrations of DON were observed in March (583 ng/dm^3). What is more, their retention in the soil during the winter and their later transport to watercourses after snow melting was determined for the first time [9]. In Portuguese rivers [11], the



Citation: Jevtić, I.; Jakšić, S.; Šojić Merkulov, D.; Bognár, S.; Abramović, B. Efficacy of Fumonisin B₁ Removal from Various Simulated Water Types Using UV and UV/H₂O₂ Treatments. *Biol. Life Sci. Forum* **2023**, *24*, 7. https://doi.org/ 10.3390/IECT2023-14802

Academic Editor: Sarah De Saeger

Published: 17 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). highest concentrations of DON were measured during spring (246.1 ng/dm³) and summer (373.5 ng/dm³), while ZEA was not detected. The most frequently found mycotoxins in bottled drinking water are aflatoxin B₂ (AFB₂), aflatoxin B₁ (AFB₁) and aflatoxin G₁ (AFG₁), as well as ochratoxins (OTA), with maximum concentrations of 0.48 ± 0.05 ng/dm³ AFB₂, 0.70 ± 0.06 ng/dm³ AFB₁, 0.60 ± 0.02 ng/dm³ AFG₁ and 0.26 ± 0.06 ng/dm³ OTA [12]. Also, AFB₁ has been found in drinking water sources such as metro, river, and well water, as well as in water from boreholes and aboveground reservoirs in the concentration range of 0.052–0.075 ng/dm³ [13]. Waśkiewicz et al. [14] were the first to report the presence of fumonisin B₁ (FB₁), the production of which can be carried out in aquatic environment, in different water systems. It was found that the presence of FB₁ is correlated with the season, where the maximum concentration was 48.2 ng/dm³ in the period after harvest (during September and October), while the lowest concentration of this toxin was during winter and spring (21.9 ng/dm³).

The presence of mycotoxins in water, especially in drinking water, can be a potential problem that requires monitoring as well as removal of mycotoxins from water with the aim of their degradation or detoxification, without disturbing the physical, chemical, and organoleptic characteristics of water. The aim of this work was to simulate different water types to examine their influence on the efficacy of FB₁ removal using UV and UV/H₂O₂ treatments.

2. Material and Methods

The efficiency of FB₁ ($1.39 \times 10^{-6} \text{ mol/dm}^3$) removal was investigated in simulated water types by UV photolysis, as well as using UV/H₂O₂ treatment with a high-pressure mercury lamp (HPL-N, 125W, Philips). To examine the influence of the mixture of some ions and humic acid (HA) on the efficiency of UV and UV/H₂O₂ treatments of FB₁ removal, their concentrations in the reaction solution were adjusted to the values determined in real water samples (Table 1).

Table 1. The physicochemical characteristics of the analyzed water types.

Parameter	Water Type			
	Danube River	Ground Water	Tap Water	UPW ¹
pH	7.70	7.62	7.30	6.56
Conductivity at 25 °C (µS/cm)	333	466	516	0.055
TOC $(mg/dm^3)^2$	2.30	0.78	1.80	<dl<sup>3</dl<sup>
Hydrogen carbonate (mg/dm ³)	209	768	238	<dl< td=""></dl<>
Chloride (mg/dm ³)	44.02	61.39	16.50	<dl< td=""></dl<>
Sulphate (mg/dm ³)	15.52	0.486	35.0	<dl< td=""></dl<>
Nitrate (mg/dm ³)	3.86	0.099	1.87	<dl< td=""></dl<>
Calcium (mg/dm ³)	0.136	<dl< td=""><td>70.49</td><td><dl< td=""></dl<></td></dl<>	70.49	<dl< td=""></dl<>
Magnesium (mg/dm ³)	0.078	0.129	20.3	<dl< td=""></dl<>

¹ UPW: ultrapure water; ² TOC: total organic carbon; ³ DL: detection limit.

To examine the efficiency of UV/H_2O_2 treatment, an appropriate volume of H_2O_2 (0.278 mmol/dm³) was added to the reaction mixture. The removal of FB₁ (20 cm³) was performed in a photochemical cell (total volume of about 40 cm³, liquid layer thickness of 35 mm). Aliquots of the reaction mixture (0.4 cm³, allowed volume change of 10%) were taken before the irradiation, as well as during irradiation at certain time intervals in order to monitor the kinetics of FB₁ photodegradation [15]. For this purpose, samples were analyzed by a liquid chromatograph, Thermo Scientific Dionex UltiMate 3000 Series, with an FLD 3100 fluorescence detector, a 150 × 3 mm Hypersil GOLD column, particle size of 3 µm, with isocratic elution. Samples were derivatized with *o*-phthaldialdehyde–2-mercaptoethanol before analyzing. Changes in pH during the degradation were monitored by using a combined glass electrode (pH-Electrode SenTix 20, WTW, Thermo Fisher Scientific, Waltham, MA, USA) connected to the pH meter (pH/Cond 340i, WTW).

3. Results and Discussion

In order to evaluate the influence of the matrix of different water types on the efficiency of FB₁ removal, their composition was simulated with the addition of some inorganic ions and HA, whose concentrations were corresponded to their concentration in real water samples. Namely, inorganic ions (calcium, magnesium, chloride, sulfate, hydrogen carbonate and nitrate) and HA were added to ultrapure water (UPW). Figure 1 shows the chromatograms obtained during the removal of FB₁ using UV radiation in simulated tap water. As it can be seen in the period of 90 min of UV irradiation, the peak height of FB₁ decreases slightly, indicating that the efficiency of FB₁ removal is insignificant.



Figure 1. Chromatograms of FB₁ photolysis in simulated tap water using UV radiation.

Figure 2 shows the efficiency of FB₁ removal using UV photolysis in simulated water samples. As it can be seen, in the case of all simulated water types, the efficiency of FB₁ removal was lower than that of UPW, where 36% of FB₁ was removed. Namely, after 90 min of irradiation, FB₁ was most efficiently removed in simulated tap water (22%), while in other types of water that percentage was less than 10% (Figure 2). Comparing the obtained results with simulated waters with the results of FB₁ photolysis in real water samples, it was found that the removal efficiency of FB₁ was lower in the simulated waters. Namely, in real waters, the highest efficiency was recorded in the Danube River water (68%) [15], which is almost six times greater than in simulated water. On the other hand, the efficiency of removal in tap and ground water was almost the same, 52%, and 50%, respectively [15]. The pH values during this treatment change from 0.2 to 1.5 pH in simulated waters. Namely, the initial pH values of simulated waters were in the range of 7.5–7.8, which is slightly lower than those in real waters and were higher, i.e., in the range of 8.7–9.3 with the addition of FB₁ [15].



Figure 2. Kinetics of FB₁ removal (1.39 μ mol/dm³) from various water types using UV photolysis.

Given that in previous research [16], the UV/H_2O_2 treatment has proven to be very effective in removing FB₁, this treatment was also applied to simulated waters (Figure 3). However, while in UPW, 100% of FB₁ was removed after 90 min of UV irradiation, among the investigated simulated water samples the highest removal efficiency was reached in tap water, when 50% of FB₁ was removed after the same duration of irradiation. Lower degradation efficiency was observed in simulated Danube River water (37%), as well as in ground water (33%). These findings implicate that this treatment in simulated waters (Figure 3) showed a lower FB_1 removal efficiency compared to that in UPW as well as to real ones [15]. Similar results were also obtained in the case of real water samples using UV/H_2O_2 treatment [15]. In these systems, the highest FB₁ removal efficiency was recorded in tap water (91%), which is almost two times higher compared to that in simulated waters. The removal of FB₁ in ground water (85%) and the Danube River water (82%) is about 2.5 times higher than that in simulated water [15]. The initial pH values in the simulated waters were in the range of 8.2–8.4, and during the 90 min irradiation, the values increased by about 1.2 pH units. Similar change in pH value was observed in real waters, where the initial values ranged from 7.3 to 8.6 with the addition of FB_1 and pH increased by 0.3 to 1.0 pH unit in 90 min [15].



Figure 3. Kinetics of FB₁ removal (1.39 μ mol/dm³) from various water types using UV/H₂O₂ treatment, c(H₂O₂) = 0.278 mmol/dm³.

4. Conclusions

In the samples of simulated Danube River, tap and ground water, a lower efficiency of UV photolysis of FB₁ was observed compared to removal in UPW. However, in the case of UV/H_2O_2 treatment in simulated waters, the removal efficiency was significantly lower compared to that in UPW. In the case of real waters, with UV and UV/H_2O_2 treatments, the efficiency of FB₁ removal was higher than that in simulated water types. This is probably due to the presence of other matrix components that affect the degradation efficiency. These results provide insight into the influence of the matrix of different water types on the efficiency of FB₁ removal and contribute to the development of adequate water purification methods for potentially carcinogenic fumonisin removal.

Author Contributions: Conceptualization, I.J., S.J. and B.A.; methodology, I.J. and S.J.; validation, I.J., S.J. and B.A.; formal analysis, I.J., S.J. and S.B.; data curation, I.J., S.J. and S.B.; writing—original draft preparation, I.J., S.J., D.Š.M., S.B. and B.A.; writing—review and editing, S.J., D.Š.M., B.A.; supervision, I.J., S.J., D.Š.M. and B.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Science Fund of the Republic of Serbia (Grant No. 7747845, In situ pollutants removal from waters by sustainable green nanotechnologies-CleanNanoCatalyze).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Schenzel, J.; Hungerbühler, K.; Bucheli, T.D. Mycotoxins in the environment: II. Occurrence and origin in Swiss river waters. Environ. Sci. Technol. 2012, 46, 13076–13084. [CrossRef] [PubMed]
- Hedayati, M.T.; Pasqualotto, A.C.; Warn, P.A.; Bowyer, P.; Denning, D.W. Aspergillus flavus: Human pathogen, allergen and mycotoxin producer. *Microbiology* 2007, 153, 1677–1692. [CrossRef] [PubMed]
- Al-gabr, H.M.; Zheng, T.; Yu, X. Occurrence and quantification of fungi and detection of mycotoxigenic fungi in drinking water in Xiamen City, China. *Sci. Total Environ.* 2014, 466–467, 1103–1111. [CrossRef] [PubMed]
- Hartmann, N.; Erbs, M.; Wettstein, F.E.; Schwarzenbach, R.P.; Bucheli, T.D. Quantification of estrogenic mycotoxins at the ng/L level in aqueous environmental samples using deuterated internal standards. *J. Chromatogr. A* 2007, 1138, 132–140. [CrossRef] [PubMed]
- 5. Oliveira, B.R.; Mata, A.T.; Ferreira, J.P.; Barreto Crespo, M.T.; Pereira, V.J.; Bronze, M.R. Production of mycotoxins by filamentous fungi in untreated surface water. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 17519–17528. [CrossRef] [PubMed]
- Jevtić, I. Direct and Indirect Photolysis of Fumonisins in the Aquatic Environment as well as Assessment of their Toxicity. Ph.D. Thesis, University in Novi Sad, Faculty of Sciences, Novi Sad, Serbia, 2022. Available online: https://nardus.mpn.gov.rs/handle/ 123456789/19078 (accessed on 25 May 2022). (In Serbian)
- Gromadzka, K.; Waśkiewicz, A.; Goliński, P.; Świetlik, J. Occurrence of estrogenic mycotoxin—Zearalenone in aqueous environmental samples with various NOM content. *Water Res.* 2009, 43, 1051–1059. [CrossRef] [PubMed]
- 8. Bucheli, T.D.; Wettstein, F.E.; Hartmann, N.; Erbs, M.; Vogelgsang, S.; Forrer, H.-R.; Schwarzenbach, R.P. *Fusarium* mycotoxins: Overlooked aquatic micropollutants? *Agric. Food Chem.* **2008**, *56*, 1029–1034. [CrossRef] [PubMed]
- Kolpin, D.W.; Hoerger, C.C.; Meyer, M.T.; Wettstein, F.E.; Hubbard, L.E.; Bucheli, T.D. Phytoestrogens and mycotoxins in Iowa streams: An examination of under investigated compounds in agricultural basins. *J. Environ. Qua.* 2010, 39, 2089–2099. [CrossRef] [PubMed]
- 10. Laganà, A.; Bacaloni, A.; De Leva, I.; Faberi, A.; Fago, G.; Marino, A. Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters. *Anal. Chim. Acta* 2004, 501, 79–88. [CrossRef]
- 11. Ribeiro, A.R.; Maia, A.; Santos, M.; Tiritan, M.E.; Ribeiro, C.M.R. Occurrence of natural contaminants of emerging concern in the Douro River estuary, Portugal. *Arch. Environ. Contam. Toxicol.* **2015**, *70*, 361–371. [CrossRef] [PubMed]
- Mata, A.T.; Ferreira, J.P.; Oliveira, B.R.; Batoréu, M.C.; Barreto Crespo, M.T.; Pereira, V.J.; Bronze, M.R. Bottled water: Analysis of mycotoxins by LC–MS/MS. Food Chem. 2015, 176, 455–464. [CrossRef] [PubMed]
- 13. Banu, N.; Malaikumar, B.; Pavithra, S. Enumeration of terrestrial mycobiota and aflatoxin in drinking water. *Asian Jr. Microbiol. Biotech. Env. Sc.* **2016**, *18*, 207–217.
- 14. Waśkiewicz, A.; Bocianowski, J.; Perczak, A.; Goliński, P. Occurrence of fungal metabolites—Fumonisins at the ng/L level in aqueous environmental samples. *Sci. Total Environ.* 2015, 524–525, 394–399. [CrossRef] [PubMed]
- 15. Jevtić, I.; Jakšić, S.; Šojić Merkulov, D.; Bognár, S.; Abramović, B.; Ivetić, T. Matrix effects of different water types on the efficiency of fumonisin B₁ removal by photolysis and photocatalysis using ternary-and binary-structured ZnO-based nanocrystallites. *Catalysts* **2023**, *13*, 375. [CrossRef]
- 16. Jevtić, I.; Jakšić, S.; Simin, D.Č.; Uzelac, M.; Abramović, B. UV-induction of photolytic and photocatalytic degradation of fumonisins in water: Reaction kinetics and toxicity. *Environ. Sci. Pollut. Res.* **2021**, *28*, 53917–53925. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.