biology and life sciences forum

Proceedings

EFFICACY OF FUMONISIN B_1 REMOVAL FROM VARIOUS SIMULATED WATER TYPES USING UV AND UV/H_2O_2 TREATMENTS†

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† Presented at The 2nd International Electronic Conference on Toxins, online, 14–28 July 2023.

Abstract: Fumonisins are secondary metabolites of mold whose presence has been proven in water. Since fumonisin B_1 (FB_1) is highly toxic and has dangerous effects on the health of living organisms, in this study the influence of various water matrix on the effectiveness of UV and UV/H_2O_2 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 FB_1 removal efficiency in simulated water samples, compared to UPW.

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

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Published: date

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]. Authors regarding their distribution, i.e. occurrence in the aquatic environment, 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 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 graminerum* [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 for the first time determined [9]. In Portuguese rivers [11], the highest concentrations of DON were measured during spring (246.1 ng/dm^3) and summer (373.5 ng/dm^3), while ZEA was not detected. The most frequently found mycotoxins in bottled drinking water are: aflatoxin B_2 (AFB_2), followed by aflatoxin B_1 (AFB_1) and aflatoxin G_1 (AFG_1), as well as ochratoxins (OTA), with maximum concentrations of 0.48±0.05 ng/dm^3 AFB_2, 0.70±0.06 ng/dm^3 AFB_1, 0.60±0.02 ng/dm^3 AFG_1 and 0.26±0.06 ng/dm^3 OTA [12]. Also, AFB_1 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/dm^3 [13]. Waśkiewicz et al. [14] were the first to report the presence of fumonisin B_1 (FB_1), which production can be carried out in aquatic environment, in different water systems. It was found that the presence of FB_1 is correlated with the season, where the maximum concentration was 48.2 ng/dm^3 in the period after harvest (during September and October), while the lowest concentration of this toxin was during winter and spring (21.9 ng/dm^3).

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 FB_1 removal using UV and UV/H_2O_2 treatments.

2. Material and Methods

The efficiency of FB_1 (1.39×10^{-6} mol/dm^3) removal was investigated in simulated water types by UV photolysis, as well as using UV/H_2O_2 treatment with a high-pressure mercury lamp (HPL-N, 125W, Philips. To examine the influence of mixture some ions and humic acid (HA) on the efficiency of UV and UV/H_2O_2 treatments of FB_1 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[3]
Hydrogen carbonate (mg/dm^3)	209	768	238	<DL
Chloride (mg/dm^3)	44.02	61.39	16.50	<DL
Sulphate (mg/dm^3)	15.52	0.486	35.0	<DL
Nitrate (mg/dm^3)	3.86	0.099	1.87	<DL
Calcium (mg/dm^3)	0.136	<DL	70.49	<DL
Magnesium (mg/dm^3)	0.078	0.129	20.3	<DL

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

To examine the efficiency of the UV/H_2O_2 treatment, an appropriate volume of H_2O_2 (0.278 mmol/dm^3) was added to the reaction mixture. The removal of FB_1 (20 cm^3) was performed in a photochemical cell (total volume about 40 cm^3, liquid layer thickness 35 mm). Aliquots of the reaction mixture (0.4 cm^3, 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 FB_1 photodegradation [15]. For this purpose, samples were analyzed by liquid chromatograph, Thermo Scientific Dionex UltiMate 3000 Series, with FLD 3100 fluorescence detector, 150×3 mm Hypersil GOLD column, particle size 3 µm, with isocratic elution. Samples were derivatized with *o*-phthaldialdehyde–2-mercaptoethanol before analyzing. Changes in the 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 FB_1 removal, their composition was simulated with 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 FB_1 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 FB_1 decreases slightly indicating that the efficiency of FB_1 removal is small.

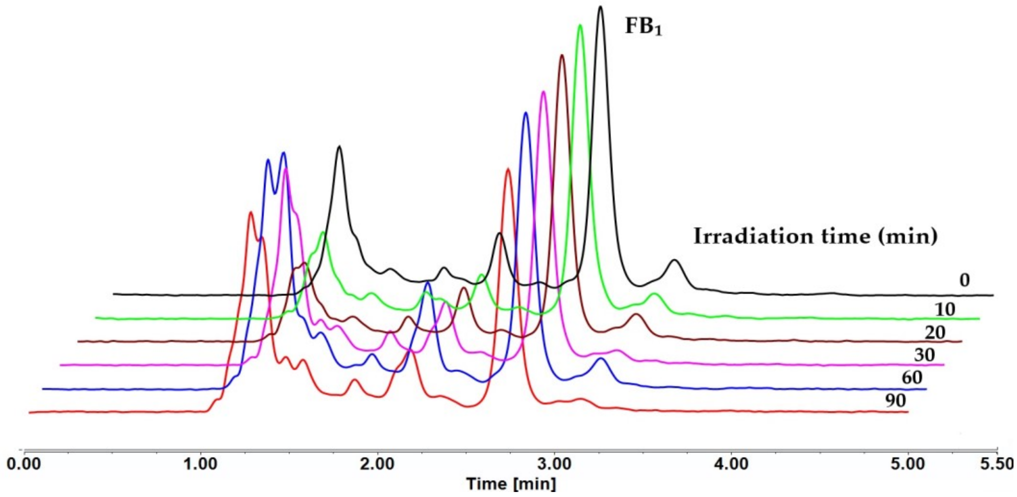

Figure 1. Chromatograms of FB_1 photolysis in simulated tap water using UV radiation.

Figure 2 shows the efficiency of FB_1 removal using UV photolysis in simulated water samples. As it can be seen, in the case of all simulated water types, the efficiency of FB_1 removal was lower compared to UPW, where 36% of FB_1 was removed. Namely, after 90 min of irradiation, FB_1 was most efficiently removed in simulated tap water (22%), while in other types of water that percentage was less than 10% (Figure 2). If the obtained results with simulated waters are compared with the results of FB_1 photolysis in real water samples, the removal efficiency of FB_1 was lower in simulated waters. Namely, in real waters, the highest efficiency was recorded in Danube River water (68%) [15], which is almost six times more 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 changes from 0.2 to 1.5 pH value in simulated waters. Namely, the initial pH values of simulated waters were in the range of 7.5–7.8, which are slightly lower values than those in real waters. Also, even after 90 min of irradiation, the pH values differed from those in real waters and were higher, i.e. in the range of 8.7–9.3 with the addition of FB_1 [15].

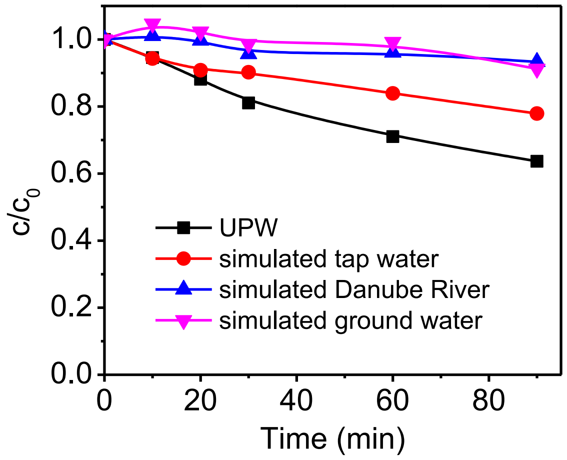

Figure 2. Kinetics of FB_1 removal (1.39 μmol/dm^3) from various water types using UV photolysis.

Given that in previous research [16] the UV/H_2O_2 treatment has proven to be very effective in removing of FB_1, this treatment was also applied to simulated waters (Figure 3). However, while in UPW 100% of FB_1 was removal after 90 min of UV irradiation, among the investigated simulated water samples the highest removal efficiency was reached in tap water, when 50% of FB_1 was removed after the same time 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 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 FB_1 removal efficiency was recorded in tap water (91%), which is almost two times higher compared to simulated waters. The removal of FB_1 in ground water (85%) and 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 7.3–8.6 with the addition of FB_1 and pH increased by 0.3 to 1.0 pH unit in 90 min [15].

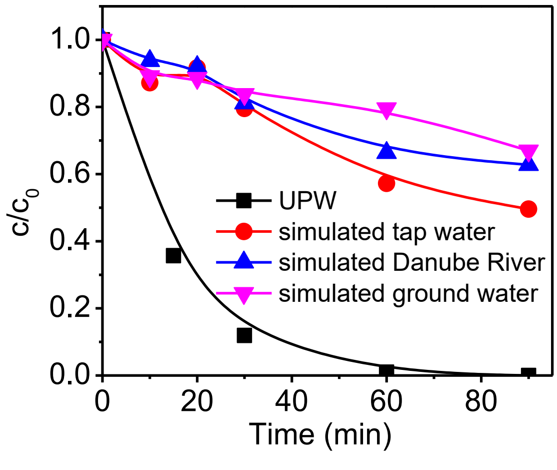

Figure 3. Kinetics of FB_1 removal (1.39 μmol/dm^3) from various water types using UV/H_2O_2 treatment, c(H_2O_2) = 0.278 mmol/dm^3.

4. Conclusion

In the samples of simulated Danube River, tap and ground water, a lower efficiency of UV photolysis of FB_1 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 as in UPW. In the case of real waters, using UV and UV/H_2O_2 treatments the efficiency of FB_1 removal was higher in comparison with 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 FB_1 removal and contribute to the development of adequate water purification methods for potentially carcinogenic fumonisins 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.

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