



Article 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

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Abstract: Several ternary- and binary-structured ZnO-based nanocrystallites (Zn₂SnO₄, Zn₂TiO₄, ZnO/SnO₂, ZnO/TiO₂) were synthesized by the solid-state method and first tested as photocatalysts in the removal of fumonisin B₁ (FB₁) under UV irradiation. The phase composition and nanocrystalline dimensions (50–80 nm) were confirmed by X-ray diffraction and Raman analyses. Similar preparation procedures applied in the case of binary structures resulted in their uniform morphology consisting of spherical particles ranging from 100 nm to 1 μ m in size. However, higher synthesis temperatures of ternary oxides contributed to the growth of particles up to 10 μ m. The optical energy bands of the examined photocatalysts were in the range of 3.08–3.36 eV. The efficiency of photocatalysis was compared with the efficiency of direct and indirect (sensitized by UV/H₂O₂ or UV/S₂O₈^{2–}) photolysis. The matrix effect of the different water types (Danube River, ground, and tap water) on the removal efficiency of FB₁ was investigated by applying direct and indirect photolysis, as well as in the presence of the Zn₂SnO₄ photocatalyst. The effects of inorganic anions (Cl⁻, NO₃⁻, HCO₃⁻ and SO₄^{2–}), cations (Ca²⁺ and Mg²⁺), and humic acid were also investigated, since they were identified as a major species in tap, ground, and river water.

Keywords: fumonisin B₁; mycotoxin; photocatalysis; metal oxides; photolysis; matrix environmental and tap water

1. Introduction

Fumonisin B₁ (FB₁) belongs to the group of widespread *Fusarium* mycotoxins [1]. These pollutants were discovered at the end of the 1980s [2], and since then, fumonisins have been extensively studied because of their harmful effects on human and animal health [2]. Their presence in corn is statistically associated with the occurrence of esophageal cancer in humans, and according to the International Agency for Research on Cancer, fumonisins are classified as potentially carcinogenic compounds [3]. They usually contaminate corn and wheat, as well as the products thereof [1,4,5]. The presence of fumonisins in corn, corn-based food, and feed is regulated by the maximum permitted and recommended values [6].

Since their discovery in the 1980s, 30 fumonisins have been isolated and their structures elucidated, while nearly 100 new fumonisins and isomers have been detected by LC-ESI-ITMS and LC-ESI-TOFMS procedures [7]. However, FB₁ is the most toxic and most prevalent in nature. According to its chemical structure, it is a 2*S*-amino-12*S*,16*R*-dimethyl-3*S*,5*R*,10*R*,14*S*,15*R*-penta-hydroxy-eicosane with esterified hydroxyl groups at the C14 and



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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/). C15 positions and a terminal carboxyl group of propane-1,2,3-tricarboxylic acid [8]. The solubility of FB₁ in deionized water was determined to be approximately 20 mg/cm³ [9]. In addition, the stability of this toxin was confirmed in the aquatic environment at ambient temperature [10]. The possibility of fumonisins production in the water matrix [11] as well as the presence of FB₁ in different types of water was proven [12]. The highest concentration (27.4–55.6 ng/dm³) of this mycotoxin was recorded in river water in the period from April to November [12].

Due to the potential risk of the presence of fumonisins in water, the development of methods for their removal is of the highest importance. Advanced oxidation processes (AOPs) are effective in the treatment of waters contaminated with organic pollutants [13]. These processes are mainly based on the formation of highly reactive hydroxyl ($^{\circ}OH$) and sulfate (SO₄^{•-}) radicals that effectively remove many pollutants [14]. Moreover, other types of radicals and reactive oxygen species such as superoxide radical-anion (O₂^{•-}), its conjugated acid form, hydroperoxide radical (HO₂[•]), triplet oxygen ($^{3}O_{2}$), ozone (O₃) as well as organic peroxide radicals (R-O-O[•]) can also occur during AOPs and be involved in the degradation processes [15]. The expected result of the abovementioned interactions between radicals and organic pollutants is the complete pollutant mineralization to CO₂ and H₂O. Although these radicals can cause the oxidation of some living cell components, they do not threaten their activity or viability [13].

A successful AOP of heterogeneous photocatalysis requires the presence of efficient semiconductors as catalysts. Semiconductors of binary metal (II-VI and IV-VI) oxides and their chemically more stable ternary metal (II-IV-VI) oxide compounds are attracting much attention due to their unique properties and diverse applications in electronics, sensing, energy conversion, and environmental heterogeneous photocatalysis [16-21]. In particular, ZnO-based materials are considered to be multifunctional, and their high chemical stability and electrochemical coupling coefficient, wide range of radiation absorption, and high photostability makes them highly desired in photocatalysis [22]. ZnO is a II-IV semiconductor with a covalence between ionic and covalent compounds, a wide band gap (about 3.37 eV), and high thermal and mechanical stability [23,24]. Overcoming the disadvantages of ZnO, such as its significant tendency to agglomerate, motivates numerous researchers to find effective modification procedures to stabilize its surface. The most popular techniques apply another inorganic (Al₂O₃, SiO₂, SnO₂, TiO₂, ZrO₂, CeO₂) and organic (triethanolamine, aminopropyltriethoxysilane, steric acid) compounds or polymer matrices (polyethylene glycol, silane, polymethylmethacrylate) as modifiers for changing the surface area and particle size, reducing agglomeration, and improving its long-term stability and dispersion and overall electrical, thermal, and optical properties [16].

Mechanochemistry has a long history as a standard method for manipulating solid materials and is attracting increased attention especially from the area of production of new composite materials for environmental applications, as it can be performed without hazardous solvents and at a low cost. Zinc oxide forms spinel-type ternary compounds with SnO_2 and TiO_2 , zinc orthostannate Zn_2SnO_4 [25], and zinc orthotitanate Zn_2TiO_4 [26] by mechanochemical synthesis starting at temperatures of 700 °C [27,28]. All of these materials are well-known for their various applications, especially in photocatalysis [26,29]. A modifier in this research, the TiO_2 itself, is one of the most familiar, commercialized, chemically stable, and biologically harmless photocatalysts for the degradation of organic pollutants and is primarily active under UV light [30]. The second modifier, the SnO₂, which shows a wide range of applications in gas sensors, batteries, transistors, and transparent electrodes, has no adverse health effects and is considered a potentially ideal photocatalyst, having a structure, band gap, and chemical stability similar to TiO₂ [31]. Ternary zinc-tin oxide, Zn₂SnO₄, showed significant efficiency in the photodegradation of various organic water pollutants under UV irradiation [32-34]. A recent comprehensive study on the chemical stability of Zn₂SnO₄ in aqueous media [35] proved that Zn₂SnO₄ powder can be used in a variety of applications involving acidic or basic aqueous media. In this study, acidic media resulted in a higher rate of dissolution of Zn²⁺ and Sn⁴⁺ ions compared to basic

media, and Zn^{2+} ions were dissolved by a proton-induced dissolution mechanism in acidic media. Furthermore, the strength of the cationic field in Zn_2SnO_4 caused the differential dissolution of Sn^{4+} and Zn^{2+} ions, which were determined to have a maximum of 0.04% and 0.4%, respectively, and no interaction layer was found on the surface of particles. Thus, it can be soundly concluded that Zn_2SnO_4 powders are chemically stable materials in terms of potential metal leaching from the material during photocatalysis. Zinc–titanium oxide Zn_2TiO_4 is present in binary systems of $ZnO-TiO_2$ as one of the most stable structures, and is particularly attractive due to its cheapness, non-toxicity, and exceptional stability, with optical properties in UV and near-visible light [36]. The high photocatalytic efficiency of $ZnO, SnO_2, TiO_2, Zn_2SnO_4$, and Zn_2TiO_4 structures, which have been established so far, justifies the commitment of many studies to combine these metal-oxide semiconductors as photocatalysts to achieve a synergistic effect and improve photocatalytic degradation processes [32,33,36–40].

This work aimed to examine the efficiency of different binary and ternary ZnO-based semiconductors in the photocatalytic removal of FB₁ prepared by simple, hazard- and solvent-free, and low-cost mixing–calcination and solid-state reaction methods. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman, diffuse-reflectance (DRS), and photoluminescence (PL) spectroscopy were used to characterize the obtained photocatalysts. The matrix effects of various water types on the efficiency of FB₁ removal by photolysis and photocatalysis were also examined using ternary and binary-structured ZnO-based nanocrystallites. Furthermore, we studied the effects of the inorganic anions (Cl⁻, NO₃⁻, HCO₃⁻ and SO₄²⁻), cations (Ca²⁺ and Mg²⁺), and humic acid (HA) as a surrogate for dissolved organic matter, as these were identified as most abundant in tap, ground, and river water. To the best of our knowledge, this is the first study of FB₁ removal in environmental and tap waters.

2. Results and Discussion

2.1. Morphology of ZnO-Based Catalysts

Figures 1 and 2 show the SEM images of binary and ternary ZnO-based catalysts, respectively. The binary sample of zinc–tin oxide (ZnO/SnO₂) is further marked as ZS–1 and zinc–titanium oxide (ZnO/TiO₂) mixture as ZT–1. The ternary sample of zinc orthostannate (Zn₂SnO₄) is hereinafter marked as ZS–2, and zinc orthotitanate (Zn₂TiO₄) is marked as ZT–2. Similar preparation procedures applied in the case of binary catalysts resulted in the formation of agglomerates consisting of uniform spherical particles ranging from 100 nm to 1 µm in size (Figure 1). However, more intense mechanical activation and higher synthesis temperatures of ternary oxides contributed to their rather different morphology with the growth of particles up to 10 µm (Figure 2). While ZS–2 consists of clearly defined closely spaced quite round particles, ZT–2 particles show formation of contact necks, which is characteristic for the initial phases of sintering. However, ZS–2 shows less agglomeration (Figure 2a) as compared to the others (Figures 1a,c and 2c).



Figure 1. SEM images of binary structured (**a**,**b**) ZS–1, and (**c**,**d**) ZT–1 catalysts at the same magnifications (**a**,**c**) \times 1800 and (**b**,**d**) \times 3500 for comparison.

Figure 2. SEM images of ternary structured (**a**,**b**) ZS–2, and (**c**,**d**) ZT–2 catalysts at the same magnifications (**a**,**c**) ×1800 and (**b**,**d**) ×3300 for comparison.

2.2. Crystal Structure Characterization (XRD and Raman) of ZnO-Based Catalysts

Figure 3 shows the XRD diffraction patterns of ZnO-based catalysts. XRD profile analysis was performed using the Rietveld refinement method to identify the phases and estimate their crystallite size and lattice parameters. The obtained values are shown

in Tables 1–3 together with the statistical parameters of Rietveld fitting quality, *R*-factors: weighted profile (R_{WP}), profile (R_P), expected (R_{EXP}), the goodness of fit (GOF = R_{WP}/R_{EXP}). ICDD cards: 2300112, 9007533, 9009086, and 9007432 were used for the identification of ZnO, SnO₂, anatase TiO₂ (hereafter TiO₂ (A)), and rutile TiO₂ (hereafter TiO₂ (R)), respectively, in the ZS–1 (Table 1), ZT–1 (Table 2), and ZT–2 (Table 3). ICDD cards: 1001187 and 9001692 were used to index the peaks of Zn₂SnO₄ and Zn₂TiO₄ phases present in the ZS–2 and ZT–2, respectively (Table 3). Both Zn₂SnO₄ and Zn₂TiO₄ phases crystallized in the face-centered cubic spinel structure. The low-intensity peaks of residual ZnO were found in ZT–2 (Figure 3d), but the % ZnO could not be quantified and was considered an impurity. The crystalline dimensions of all phases present were in the nano range of 50–80 nm (Tables 1–3).

Figure 3. XRD patterns of (a) ZS-1, (b) ZT-1, (c) ZS-2, and (d) ZT-2 catalysts.

Table 1. Phase composition and structure parameters of ZS-1 by Rietveld refinement.

Phase	ZnO	SnO ₂
Phase content (%)	53.94	46.06
Crystallite size (nm)	72.0	50.5
Microstrain (%)	0.034	0.042
а	3.2502	4.7385
b	3.2502	4.7385
С	5.2068	3.1870
R _{WP} (%)	5.51	5.51
R _P (%)	4.39	4.39
R _{EXP} (%)	2.64	2.64
GOF	2.088	2.088

Phase	ZnO	Zn ₂ TiO ₄	TiO ₂ (A)	TiO ₂ (R)
Phase content (%)	43.20	41.42	14.98	0.39
Crystallite size (nm)	69.5	56.9	61.4	82.9
Microstrain (%)	0.033	0.079	0.059	0.08

Table 2. The phase composition, crystallite size, and microstrain of ZT-1 by Rietveld refinement.

Table 3. Structure parameters of ZS–2 and ZT–2 by Rietveld refinement.

Sample	ZS-2	ZT–2
Phase	Zn_2SnO_4	Zn ₂ TiO ₄
Crystallite size (nm)	70.2	71.5
Microstrain (%)	0.07	0.07
a	8.6612	8.4736
b	8.6612	8.4736
С	8.6612	8.4736
R _{WP} (%)	11.62	17.55
R _P (%)	8.06	9.91
R _{EXP} (%)	2.85	2.91
GOF	4.0786	6.0294

Raman spectroscopy of the resulting binary and ternary ZnO-based catalysts obtained by 514 nm excitation is shown in Figure 4. Figure 4a shows the Raman spectrum of ZS–1 with vibrational modes of both ZnO and SnO₂, which is consistent with the percentage of these phases found in ZS–1 (Table 1). The Raman positions of ZS–1 are in good agreement with previous reports [23,39]. However, the Raman spectrum of ZT–1 (Figure 4b) shows vibrational modes of only the anatase TiO₂ structure with a total of five modes found at 144, 197, 397, 515, and 639 cm⁻¹. Similar vibrational behavior of the ZnO/TiO₂ mixture was previously reported [28], except that our experiments did not show vibrations belonging to the ZnO and Zn₂TiO₄ phases found there.

Figure 4c,d show the vibration characteristics of ternary ZS–2 and ZT–2 structures, respectively. According to the factor group analysis, the spinel-type ternary compounds (Zn₂SnO₄ and Zn₂TiO₄) have five allowed Raman-active modes: $A_{1g} + E_g + 3F_{2g}$.

The ZS–2 Raman spectrum shows characteristic cubic inverse-spinel type zinc–tin oxide (Zn₂SnO₄) phonon modes at 381 (F_{2g}), 466 (E_g), 530 (F_{2g}), 577 (F_{2g}), and 670 cm⁻¹ (A_{1g}) [40]. The mode at 622 cm⁻¹ arises when Zn₂SnO₄ is synthesized by the mechanochemical method [41] due to the disorder of Sn and Zn cations over the tetrahedral (in parentheses brackets) and octahedral [in square brackets] of (Zn²⁺)[Sn⁴⁺Zn²⁺]O₄ structure sites. The leakage Raman peaks observed at 111, 136, 163, and 229 cm⁻¹ do not belong to first-order Raman modes of Zn₂SnO₄ and could originate from laser plasma effect, order–disorder in Zn₂SnO₄ structure, or something else.

The band at 719 cm⁻¹ that dominates the ZT–2 Raman spectrum belongs to the A_{1g} mode of Zn₂TiO₄ structure (Figure 4d), while the much weaker intensity mode at 307 cm⁻¹ has the E_g symmetry. Three other lower-intensity peaks at 246, 363, and 476 cm⁻¹ of the Zn₂TiO₄ first-order Raman modes are indexed as F_{2g} modes [42]. Leakage peaks of the ZT–2 are marked red in Figure 4d.

Figure 4. Raman spectra of (**a**) ZS–1 compared to the ZnO and SnO₂, (**b**) ZT–1 compared to the TiO₂, (**c**) ZS–2, and (**d**) ZT–2.

2.3. UV-Vis DRS and PL Characterization of ZnO-Based Catalysts

DRS spectra (example of ZT-2 is shown in Figure 5a) were used to estimate the optical band gap energy (E_g) by plotting the $(F(R)\cdot h\nu)^{1/n}$ vs. photon energy ($h\nu$), where F(R)is the Kubelka-Munk transformation of the measured diffuse reflectance (%) defined as $(1-R)^2/2R$ (example of ZT–2 is shown in Figure 5b). The estimation of the optical band gap was performed using the model of indirect band gap transition, where the value of n = 2was used in $(F(R) \cdot hv)^{1/n}$ vs. photon energy (hv) plot. The estimated values (summarized in Table 4) were in the range of 3.08–3.36 eV, while the optical absorption thresholds of ZnO-based catalysts calculated as $1240/E_g$ were between 369–402 nm (Table 4), which confirms their UV and Vis absorption photocatalytic capacity. Although the proposed fundamental E_g of Zn_2SnO_4 is 3.6–3.7 eV, previous experimental and theoretical reports on the band gap of Zn_2SnO_4 have shown large variability in the obtained E_g values from 3.32 to 4.1 eV [40]. The lower E_g value of 3.36 eV (ZS-2) estimated in our experiments may be the result of defect traps formed during mechanochemical synthesis. The optical energy band gap of 3.28 eV found for Zn_2TiO_4 (ZT-2) is consistent with the literature data, where, similar to Zn₂SnO₄, different values of the optical energy band gap, caused by different microstructures, the grain sizes, etc., have been reported in the range of 3.0–3.8 eV [43,44]. The estimated E_g of binary ZnO/TiO₂ (ZT–1) is between the E_g of single metal oxides (E_g of ZnO = 3.2 eV is commonly reported for ZnO powder [40]; E_g of anatase TiO₂ = 3.2 eV) and ternary Zn_2TiO_4 (the Zn_2TiO_4 content of 41.42 wt. % is found in ZT-1). However, the E_g of the ZnO/SnO_2 (ZS–1) mixture has the lowest value of 3.08 eV, which is again consistent with previous reports [39,40], and it is lower than single oxides (E_g of ZnO = 3.2 e; E_g of $SnO_2 = 3.9 \text{ eV} [40]$). This lowest value of the optical band gap indicates that the ZS-1 has the highest capacity for visible photocatalysis among these catalysts, but also the close contact-type heterojunction between ZnO and SnO₂ in the binary ZnO/SnO₂ (ZS–1), i.e., their effective coupling [39,40].

Figure 5. UV–Vis diffuse-reflectance and PL excitation spectroscopy of ZT–2 (**a**), Kubelka–Munk estimation of the optical band gap of ZT–2 (**b**), and PL emission spectra of ZT–2 (**c**).

Table 4. Estimated optical band gap energy values of ZS–1, ZT–1, ZS–2, and ZT–2 catalysts and their corresponding absorption edges.

Sample	ZS-1	ZT–1	ZS–2	ZT–2
$E_{\rm g}~({\rm eV})$	3.08	3.27	3.36	3.28
λ (nm)	402	379	369	378

Compatible results were obtained by PL spectroscopy (an example for ZT–2 is shown in Figure 5a–c). The PL excitation spectra of ZT–2 under 521 nm and 640 nm emissions (Figure 5a) confirm the position of the optical absorption edge, as the PL peak at around 378 nm belongs to the optical band gap emission estimated by DRS to 3.28 eV (Table 4). Moreover, the PL emission spectra of ZT–2 shown in Figure 5c with excitations at 365 and 376 nm show green emissions with a band centered at about 520 nm. Semiconductor nanomaterials (such as ZnO, Zn₂SnO₄, SnO₂), often show such green emissions, which are due to oxygen vacancies that induce the formation of new energy levels in the band gap or other similar luminescent center formed during synthesis, as a photo-excited hole with an electron occupying oxygen vacancy yields these green emissions [45].

2.4. Effect of Photocatalyst Type

Figure 6a shows the efficiency of FB₁ removal from reaction suspensions using ZS–1, ZT–1, ZS–2 and ZT–2 nanocrystallites under UV irradiation in ultrapure water (UPW). As can be seen, depending on the catalyst type, the degree of adsorption as well as FB₁ degradation was very different. The degree of FB₁ adsorption on ZS–1 during sonification in the dark was as much as 90%, whereas it was about 50% for ZT–1 and ZT–2, and only 6% for ZS–2 (Figure 6a). The complete removal of FB₁ using ZS–1, ZT–1, and ZT–2 after 20 min of degradation can be explained by the abovementioned high adsorption, while in the system with ZS–2, 90% of FB₁ was removed after 60 min of irradiation. A different degree of FB₁ adsorption on the studied nanocrystallites is probably due to the differences in their chemical composition. Similarly, the tests of the efficiency of ZnO and TiO₂ Degussa

P25 for FB₁ removal revealed the FB₁ adsorption in the dark (15 min) of 90 and 100%, respectively [46]. The somewhat lower FB₁ adsorption in the case of ZT–1 compared to ZnO and TiO₂ [46] was probably due to the presence of about 41% Zn₂TiO₄, while the TiO₂ content was only about 15% (Table 2). Since the least FB₁ adsorption was observed in the system with ZS–2 (Figure 6a), further experiments were carried out in the presence of this catalyst.

Figure 6. Efficiency of FB₁ (1.39 μ mol/dm³) removal at pH ~8 using (**a**) different nanocrystallites (1 mg/cm³) during UV photocatalysis; (**b**) photolysis and photocatalysis by UV irradiation.

By comparing the efficiency of FB₁ photocatalytic removal using ZS–2 with the efficiency of direct (UV) and indirect (UV/H₂O₂ and UV/S₂O₈²⁻) photolysis under optimal conditions [46], it was found that the most efficient removal of FB₁ was achieved by indirect photolysis (Figure 6b). Namely, during the first 30 min of irradiation, 26% of FB₁ was degraded by direct photolysis, 88% by UV/H₂O₂, and 89% by UV/S₂O₈²⁻ (Figure 6b). In the case of photocatalysis, 67% of FB₁ was removed after the same irradiation time. The difference in the efficiency of indirect photolysis and photocatalysis decreases over time, so after 60 min of irradiation, it was about 10%. Under the relevant experimental conditions, the reactions followed pseudo-first-order kinetics. On the basis of the kinetic curves lnc (substrate concentration) vs. *t*, the values of the apparent first-order degradation rate constant (*k*') were calculated (Table S1, from Supplementary Materials). Almost the same values for the degradation rate constant were observed using UV/H₂O₂ and UV/S₂O₈²⁻ treatment (0.071 min⁻¹) where the correlation coefficients were (*r*) ≥ 0.996, while a lower *k*' was obtained using photocatalytic treatment (0.039 min⁻¹, *r* = 0.992).

All tests on the efficiency of FB_1 removal using different treatments were carried out at initial pH ~8, since the different water samples tested in this study had a pH of around 8. In this way, the influence of pH on the efficiency of FB_1 removal was eliminated.

2.5. The Effect of the Matrix of Different Types of Water

Considering the presence of a large number of different ions and organic substances in natural waters and their different composition, the removal rate of FB₁ in different natural types of water (tap, Danube, and ground) was compared using UV photolysis and photocatalysis. As can be seen in Figure 7, the efficiency of FB₁ degradation by direct photolysis increases in tap, Danube, and ground water as compared to UPW. The efficiency of degradation during the first 30 min of irradiation was approximately the same for all four types of water. However, after 90 min of irradiation, the efficiency of FB₁ removal was significantly changed. The efficiency of FB₁ degradation was the highest in Danube water (Figure 7; 68%), which was almost twice as high as in UPW (Figure 7; 36%). On the other hand, the degradation efficiency in tap and ground water was almost the same—52% and 50%, respectively (Figure 7). The degradation rate constants of FB₁ in different types of water are presented in Table S2 (Supplementary Materials). A certain difference in relation to the degradation efficiency is a consequence of determining the degradation rate constant for the first 60 min of irradiation when the linear regression coefficient is the highest. During the photodegradation process, the pH value of the reaction suspension was monitored, and the pH value was increased by 0.5–1 pH units. The largest increase was recorded in Danube water, where the highest efficiency of degradation was determined. This is probably due to the formation of intermediates that increase the pH. During the decomposition in UPW, the pH only changed by about 0.2 pH units.

Figure 7. Efficiency of FB₁ (1.39 μ mol/dm³) degradation in different types of water using UV irradiation at natural pH.

The efficiency/degradation rate constants of indirect photolysis in the degradation of FB₁ in different types of water matrixes were also investigated (Figure 8, Table S3) (Supplementary Materials). The matrix influence on UV/H_2O_2 treatment can be seen in Figure 8a, while the influence on $UV/S_2O_8^{2-}$ treatment is shown in Figure 8b. It is known that the natural water matrix usually reduces the oxidation efficiency of the target pollutant by consuming •OH radicals generated during UV/H₂O₂ treatment, and the pollutant degradation rate is expected to be lower [47]. The same result was observed during $UV/S_2O_8^{2-}$ treatment, where natural waters and various ions also slowed down the degradation of pollutants [48]. Our findings are consistent with previously reported data, as the greatest and fastest degradation of FB₁ was observed in the UPW using UV/H_2O_2 (Figure 8a). Namely, in the first 10 min of treatment, the degradation rates in tap water and UPW were similar; however, during further irradiation, the degradation efficiency started to differ. More importantly, after 90 min of irradiation, 91% and 100% of FB₁ was degraded in tap water and UPW, respectively (Figure 8a). Slightly lower efficiency of FB1 degradation was observed in Danube and ground water during the entire treatment. After 90 min of irradiation, the degradation efficiency of FB₁ in the Danube and ground water was 82% and 85%, respectively (Figure 8a). We obtained similar results in the case of the degradation rate constants of FB_1 (Table S3) (Supplementary Materials). A certain difference in relation to the degradation efficiency is a consequence of determining the degradation rate constant for the first 60 min of irradiation when the linear regression coefficient is the highest. Based on the data obtained during the pH monitoring in the conducted experiments, it can be seen that the initial pH increased by one pH unit in tap water, while in natural waters, it increased by 0.6–0.8 pH units. In the case of UPW, the pH increased to 8.5 during the first 30 min of irradiation, and then decreased to 7.8 after 90 min. The pH change during indirect photolysis could be explained by the formation/disappearance of certain degradation intermediates.

Kinetic curves in Figure 8b show that the complete degradation of FB₁ was achieved in UPW after 60 min of irradiation (Figure 8b), while in other types of water, even 90 min of irradiation was not enough for complete degradation (Figure 8b). A higher FB₁ removal efficiency was observed in tap water, where 95% of FB₁ was degraded after 90 min of irradiation (Figure 8b) as compared to natural waters, where the degradation percentage was about 60% for the same irradiation time (Figure 8b). UV/H_2O_2 and $UV/S_2O_8^{2-}$ treatments acted similarly, as the kinetic of the FB₁ degradation reaction was similar in both mentioned processes. This is also shown by the values for the decomposition rate constant, which are significantly higher in UPW compared to other types of water, regardless of the treatment (Table S3) (Supplementary Materials). In all tested water types, the initial pH was ~8. During the treatment, the pH increased by 0.6–1 pH units in Danube, tap, and ground water, whereas it decreased by 0.6 pH units in UPW. As previously assumed, this is likely due to the formation/disappearance of certain degradation intermediates.

Figure 8. Efficiency of FB₁ (1.39 μ mol/dm³) degradation in different types of water using: (a) UV/H₂O₂ treatment at natural pH~8; (b) UV/S₂O₈²⁻ treatment at pH~8. c(H₂O₂) = 0.278 mmol/dm³, c(S₂O₈²⁻) = 0.140 mmol/dm³.

The photocatalytic efficiency of FB₁ removal in different types of water was also investigated. As can be seen in Figure 9, the highest FB₁ removal efficiency was achieved in UPW, similar to the indirect photolysis. After 30 min of irradiation, about 40% of FB₁ was removed from tap and ground water, while the removal rate in Danube water was 25%. On the other hand, about 70% of FB₁ was removed from the UPW after the same time of irradiation. After 60 min of treatment, the percentage of FB₁ removal from UPW was 90%, while significantly lower removal rates were observed for other types of water for the same treatment period, being 40% for ground water, 35% for tap water, and 20% for Danube water. The degradation rate constants of FB₁ in different types of water are presented in Table S4 (Supplementary Materials). Furthermore, a significant increase in pH (by about one pH unit) was also observed in these waters, while there was no significant change in the initial pH in UPW. Bearing in mind that the removal efficiency is higher at a lower pH value [46], besides the water matrix effect, increased pH during the treatment probably further reduces the efficiency of FB₁ removal from the tap, Danube, and ground water.

Figure 9. Efficiency of FB₁ (1.39 μ mol/dm³) removal in different types of water using ZS–2 photocatalyst (1 mg/cm³) using UV irradiation at pH~8.

2.6. Effect of Species in the Solution Matrix on FB₁ Removal Efficiency Using UV and UV/H₂O₂ 2.6.1. Effect of Cations

Since the content of calcium and magnesium ions was the highest compared to the other cations present in the tested waters, the influence of these cations on the efficiency of direct photolysis of FB₁ was investigated by adding their chloride salts $MgCl_2$ and

CaCl₂ to the reaction suspension (Figure 10a; Table S5) (Supplementary Materials). The mass concentrations of added Mg^{2+} and Ca^{2+} ions were 20.30 mg/dm³ and 70.49 mg/dm³, respectively, which were also their maximum concentrations in the tested waters (Table S8). To determine the effect of chloride on photodegradation efficiency, NaCl was added to the tested samples, and the obtained results are shown in Figure 10a, where the chloride concentration was the same as that obtained with MgCl₂, while chloride concentration was doubled with CaCl₂. The addition of NaCl resulted in 93% degradation of FB₁ after 90 min of irradiation, which was about 2.5 times the degradation efficiency in UPW (Figure 10a). Compared to NaCl, a slightly lower efficiency was observed with the addition of MgCl₂ when 81% of FB₁ was degraded, while in the presence of CaCl₂, 73% of FB₁ was degraded, which was almost double the degradation efficiency as compared to UPW (Figure 10a).

Figure 10. Effect of different ions and HA on the efficiency of FB₁ (1.39 μ mol/dm³) degradation at pH 7.7–9.0: (**a**,**b**) using UV irradiation; (**c**,**d**) using UV/H₂O₂treatment. c(H₂O₂) = 0.278 mmol/dm³.

Based on the obtained results, it can be concluded that the influence of tested compounds on the efficiency of FB₁ degradation decreases in the following order: NaCl > MgCl₂ > CaCl₂. This indicates that positive effect of chloride on the degradation efficiency was strongly evident. However, it should be emphasized that the concentration of chloride in the presence of NaCl (Figure 10a) was twice as low as in the case of CaCl₂. Lower FB₁ degradation efficiency in the presence of Mg²⁺ and especially Ca²⁺ ions is probably due to the formation of complexes of these ions with FB₁. Namely, the carboxyl groups of FB₁ in neutral conditions have an affinity to form complexes with metal ions [49], which can cause a decrease in the degradation rate of FB₁. The more pronounced inhibitory effect of Ca²⁺ ions than that of Mg²⁺ is probably due to the formation of a more stable complex with FB₁.

The initial pH in the presence of NaCl and CaCl₂ was 8.2 and decreased to 7.6 during irradiation. Slightly lower initial pH was measured in the presence of MgCl₂ (7.6) and during the degradation; it increased by about 0.4 pH units, while the pH returned to the initial value (7.6) after 90 min of irradiation.

Experiments were also conducted to compare the effect of different water matrixes (Figure 7) with the effect of cations (Figure 10a) on the efficiency of FB₁ degradation. Our findings indicated the same degradation trend. However, the influence of the water matrix

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was less pronounced, which was probably due to the presence of other components that had an inhibiting influence.

Given that the UV/H_2O_2 treatment proved to be very effective in fumonisin degradation, the effect of cations was also examined using this treatment. The results are shown in Figure 10c, and degradation rate constants of FB₁ using UV/H_2O_2 treatment are presented in Table S6 (Supplementary Materials). As can be seen, both ions (Mg²⁺ and Ca²⁺) had an inhibitory effect, since the degradation efficiency of FB₁ was lower compared to the degradation in UPW (Figure 10c). It is interesting to note that kinetics curves in the presence of Mg^{2+} and Ca^{2+} have a similar shape, where 85% and 75% of FB₁ was degraded in the presence of Mg²⁺ and Ca²⁺, respectively, after 90 min of irradiation. In the same time, FB₁ was completely removed from UPW. For these reasons, the efficiency of FB₁ degradation using UV/H_2O_2 was also investigated in the presence of Cl^- , and the obtained data are shown in the same figure (Figure 10c). Based on our findings, it can be seen that chloride showed an inhibitory effect, yet it was less pronounced as compared to the reaction mixtures containing Mg²⁺ and especially Ca²⁺ ions. Namely, in the presence of NaCl, about 88% of FB1 was degraded after 90 min of irradiation. According to these results, it can be concluded that Mg²⁺ and Ca²⁺ ions had an inhibitory effect on both indirect and direct photolysis of FB₁. The addition of these cations did not significantly change the pH during FB₁ degradation. The pH of the reaction mixture in the presence of NaCl decreased during irradiation by about 0.3 pH units, while in the presence of MgCl₂ and CaCl₂, there was practically no pH change during the treatment.

2.6.2. Effect of Anions

Given that different anions can also be found in the aqueous environment, their influence on the efficiency of FB₁ degradation was also investigated in different water samples. The following inorganic anions were added to UPW: Cl^- , HCO_3^- , SO_4^{2-} , and NO_3^- ions. Their final concentrations were equal to the real concentration of the mentioned anions in the tested types of water.

Effect of chloride: As can be seen in Figure 10b, the presence of Cl^- increased efficiency of direct photolysis, and 93% of FB₁ was degraded after 90 min of irradiation, which is about 2.5 times higher compared to UPW. This phenomenon could be explained by the possible formation of $Cl_2^{\bullet-}$ radicals, although there is little chance of this process happening because of applied radiation. Moreover, higher degradation efficiency may also be due to a higher ionic strength in the presence of NaCl [50]. We obtained similar results in the case of the degradation rate constants of FB₁ (Table S5) (Supplementary Materials). During the treatment, the pH was monitored, revealing a decrease in pH value by 0.6 units compared to the initial value.

On the other hand, oxidation reactions can also take place between the Cl⁻ ion and H₂O₂, leading to the production of Cl[•] radicals, but this only happens in an acidic environment, usually at pH < 5 (reactions 1 and2) [51]. In the next step, the Cl[•] radical reacts with the Cl⁻ ion. Since the Cl₂^{•-} ion is less reactive than the •OH-radical (Cl₂•⁻/2Cl⁻ 2.13 V) [52], the inhibition of photodegradation can be related to the reduced •OH-radical concentrations (reaction 2). If the reaction takes place in a neutral or basic medium, the inhibition of photodegradation is not very pronounced because the reactions are reversible and flow to the reactants.

$$^{\bullet}OH + Cl^{-} \rightleftarrows HOCl^{\bullet -} \tag{1}$$

$$HOCl^{\bullet-} + H^+ \rightleftharpoons Cl^{\bullet} + H_2O \tag{2}$$

As previously stated, the efficiency of FB_1 degradation by direct photolysis was increased in the presence of Cl^- ; however, during indirect UV/H_2O_2 photolysis in the presence of Cl^- , the opposite effect was obtained. As can be seen in Figure 10d, decreased FB_1 degradation rate was observed in the presence of chloride compared to UPW. After 90 min of irradiation, 88% of FB_1 was degraded, whereas the efficiency of FB_1 degradation in the absence of chloride was 100%. The degradation rate constants of FB_1 using UV/H_2O_2 treatment are presented in Table S6 (Supplementary Materials). These results are consistent with data published by AlHamedi et al. [53], where the addition of all investigated anions (Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) in the presence of H₂O₂ inhibited the degradation, but this effect, similar to our research, was less pronounced with chloride. The possible inhibitory effect of Cl⁻ has been earlier explained in detail [51].

Effect of nitrates: Experiments were also carried out to determine the effect of NO₃⁻ ions. Based on our findings (Figure 10b), it can be concluded that these anions, similarly to Cl⁻ions, increased the efficiency of FB₁ photolytic degradation at natural pH (about 8.2). These results are in accordance with published results, where NO_3^- ions at low concentrations improved the efficiency of pollutant degradation [54,55]. This phenomenon originates from the UV irradiation of NO_3^- ions, which generate additional $\bullet OH$ radicals that can be used for efficient pollutant removal. Our results show that 72% of FB₁ is degraded after 90 min of irradiation, which is twice the degradation efficiency in UPW. Similar results were obtained when examining the effect of nitrates on the degradation rate constant of FB₁ (Table S5) (Supplementary Materials). The pH value was monitored throughout the degradation process and did not change significantly, except for a slight drop in the pH value after 30 min of irradiation followed by an increase to 8.6. By the end of the photodegradation, i.e., after 90 min of irradiation, the pH value was about 0.3 pH units higher compared to the initial value (8.5). Since the pH value during the whole process was similar to the treatment in UPW, it can be concluded that the efficiency of FB_1 degradation was only influenced by the addition of NO_3^- ions.

For the UV/H₂O₂ treatment, in the presence of NO₃⁻ ions, 78% of FB₁ was removed after 90 min of irradiation (Figure 10d), which is 22% less compared to UPW (Figure 10d). This effect was also reported by Liu et al. [56] during the degradation of the antibiotics florfenicol and thiamphenicol using UV/H₂O₂ treatment. The authors stated that NO₃⁻ ions act as •OH radical scavengers (reactions 3 and 4), which reduces the concentration of •OH, and thus the rate of antibiotic degradation. Similar results were obtained when examining the effect of nitrate on degradation rate constant of FB₁ (Table S6) (Supplementary Materials). The addition of NO₃⁻ ions did not significantly affect the pH value, since the initial value was 8.2 being 8.3 at the end of the treatment.

$$NO_3^- + H^+ \to HNO_3 \tag{3}$$

$$\bullet OH + HNO_3 \to H_2O + NO_3^{\bullet} \tag{4}$$

Effect of hydrogencarbonate: Unlike the previous two anions, the addition of HCO_3^- reduced the efficiency of FB₁ degradation by direct UV photolysis (Figure 10b, Table S5) (Supplementary Materials), which is accordance with data in the literature on this effect [57]. After 90 min of irradiation in the presence of HCO_3^- ions, only 16% of FB₁ was degraded, which is about two times less than in UPW. Moreover, HCO_3^- ions act as scavengers of •OH radicals (reaction 5) and thereby inhibit the photodegradation reaction of FB₁. The low efficiency of degradation can also be a consequence of a higher initial pH. Similar results were obtained when examining the effect of hydrogencarbonate on the degradation rate constant of FB₁ (Table S6) (Supplementary Materials). Still, this effect is not very pronounced, since after addition of HCO_3^- ions, the initial pH value was 9.0, and during the treatment, it increased by 0.5 pH units to reach 9.5 after 90 min of irradiation.

$$HCO_3^- + \bullet OH \to CO_3^{\bullet -} + OH^-$$
(5)

Similar to UV direct photolysis, the presence of HCO_3^- ions also inhibited the indirect photolysis of FB₁ under UV/H₂O₂ treatment (Figure 10d, Table S6) (Supplementary Materials). During this process, no significant results in the degradation of FB₁ were achieved. This result is in accordance with the data of Li et al. [56], where the inhibition of clofibic acid was recorded when HCO_3^- ion was added, this being due to the trapping of •OH radicals. During the degradation of FB₁, the pH value changed by about two pH units from the initial 8.0 to the final 10.0.

Effect of sulphate: From Figure 10b and Table S5 (Supplementary Materials), it can be seen that SO_4^{2-} ions increased the efficiency of photolytic degradation of FB₁. Under these experimental conditions, 62% of FB₁ was degraded after 90 min of irradiation, while no significant variations in pH (7.7–8.0) were detected. Higher efficiency of FB₁ degradation by direct UV photolysis in the presence of stable SO_4^{2-} ions can be explained by the increased ionic strength of the solution, which also plays a role in the degradation of organic molecules [50].

Furthermore, similar to the already examined ions, the presence of SO_4^{2-} ions inhibits FB₁ degradation by UV/H₂O₂ treatment as compared to direct photolysis. As can be seen in Figure 10d, the degradation of FB₁ after 90 min of irradiation was 86%, which is similar to the results obtained with the addition of NaCl. However, the inhibitory effect of SO_4^{2-} ions on the FB₁ degradation efficiency at the beginning of the treatment was somewhat more pronounced. The inhibitory effect of $SO_4^{\bullet-}$ ions was probably due to the reduced concentration of \bullet OH radicals (reaction 6). In spite of the formation of $SO_4^{\bullet-}$ radicals, which can further oxidize organic molecules, the FB₁ degradation efficiency was lower compared to UPW (Table S6) (Supplementary Materials). Similar results were obtained by AlHamedi et al. [53], who investigated the influence of the SO_4^{2-} ions on the efficiency of rhodamine B degradation using UV/H₂O₂ treatment. The initial pH value during FB₁ degradation was slightly lower (7.5) and did not change significantly during the treatment (7.8).

$$SO_4^{2-} + \bullet OH \rightarrow SO_4^{\bullet-} + OH^- \tag{6}$$

2.6.3. Effect of Humic Acid

Based on the obtained results, it can be concluded that HA (Figure 10a), similar to chloride and nitrate ions, increased the rate of direct FB₁ photolysis using UV radiation (Figure 10b). During the first 20 min of irradiation with the addition of HA, 17% of FB₁ was degraded. After 90 min of irradiation in the presence of HA, 69% of FB₁ was degraded, while 36% of FB₁ was removed from UPW (Figure 10a). Similar results were obtained when examining the effect of HA on the degradation rate constant of FB₁ (Table S5) (Supplementary Materials). The obtained results are in accordance with the data in the literature, where the addition of HA led to more efficient degradation of pollutants [58,59]. However, Ren et al. [59] found that HA can improve the degradation efficiency up to a certain concentration, after which it acts as a scavenger of reactive oxygen species, thus reducing the efficiency of photolysis. The pH was also monitored and a slight decrease of about 0.8 units was noted.

Figure 10c shows the efficiency of FB₁ degradation using UV/H₂O₂ treatment with the addition of HA. HA showed an inhibitory effect, as 70% of FB₁ was degraded after 90 min of irradiation, which is 30% less than in the case of indirect photolysis of FB₁ in UPW. Similar results were obtained when examining the effect of HA on degradation rate constant of FB₁ (Table S6) (Supplementary Materials). The obtained results are in agreement with published data [55], where the inhibitory effect of HA on UV/H₂O₂ treatment was also confirmed. In addition to the fact that HA acid can act as a scavenger of free •OH radicals (reaction 7), higher concentrations of HA can also reduce the penetration of UV light through the irradiated solution [55]. Moreover, a slight change in pH was also observed during the treatment, as the pH increased from 7.6 to 7.9.

$$\bullet OH + HA \to HA \bullet + H_2 O \tag{7}$$

2.7. Effect of Species in the Solution Matrix on FB₁ Removal Efficiency Using Zn_2SnO_4

Similar to the direct and indirect photolysis of FB₁, the effect of the water matrix on the efficiency of FB₁ removal using ZS–2 photocatalyst and UV irradiation was also investigated (Figure 11). The degradation rate constants of FB₁ in different types of water are presented in Table S7 (Supplementary Materials).

Figure 11. Effect of different cations and HA (**a**) and anions (**b**) on the FB₁ (1.39 μ mol/dm³) removal efficiency using photocatalyst ZS–2 and UV irradiation at pH~8.

2.7.1. Effect of Cations

Similar to photolysis, Ca²⁺ and Mg²⁺ cations have an inhibiting effect on the efficiency of photocatalytic removal of FB₁ using Zn₂SnO₄ by UV irradiation. To eliminate the influence of chloride (whose salts of cations are added), the influence of NaCl on the FB_1 removal efficiency was also examined. As can be seen in Figure 11a, the FB_1 removal efficiency in the presence of NaCl was 27% lower than in UPW. Slightly lower removal percentage (about 50%) was recorded with MgCl₂ (Figure 11a). On the other hand, in the presence of CaCl₂, the photocatalysis occurred somewhat faster than in UPW during the first 30 min, while after 60 min of irradiation, the FB_1 removal was lower by about 5% (Figure 11a). Similar results were obtained in the case of determination of the degradation rate constants of FB_1 (Table S7) (Supplementary Materials). A certain difference in relation to the degradation efficiency is a consequence of determining the degradation rate constant for the first 20 min of irradiation when the linear regression coefficient is the highest. These results are in agreement with the data of Burns et al. [60], who consider that Ca^{2+} and Mg^{2+} ions cannot be scavengers of radicals or holes because they are in their maximum oxidation state. Potential inhibition can be explained by the formation of an ionic bridge, which leads to a more intense aggregation of nanoparticles [61]. In general, multivalent cations (Ca^{2+} and Mg^{2+}) have a more negative effect on removal than monovalent cations (Na⁺) [62]. The pH of the suspension with addition of these cations did not change significantly (up to 0.3 pH units).

2.7.2. Effect of Anions

Effect of chloride: Data on the influence of Cl^- ions on the FB₁ degradation in the presence of ZS–2 nanocatalyst are shown in Figure 11b. During the first 20 min of suspension irradiation, about 55% of FB₁ was degraded, which is the same as in the case of UPW (Figure 11b). On the other hand, at the end of the process, the removal efficiency was much lower compared to UPW, being around 67%. Based on the obtained results, it can be concluded that the addition of Cl⁻ ion inhibits the FB₁ removal. Similar results were obtained in the case of determination of the degradation rate constants of FB₁ in the presence of Cl⁻ for the first 20 min of irradiation (Table S7) (Supplementary Materials). The influence of Cl⁻ ion can be twofold: it can act as a scavenger of (i) •OH radicals [63] and (ii) holes [64]. During this treatment, the initial pH was 7.9, and there was no change in pH.

Effect of nitrate: The addition of NO_3^- ion also slightly inhibited the removal of FB₁ (Figure 11b). Kinetics curves in the presence of NaNO₃ have almost the same shape as that of UPW (Figure 11b). In the first 20 min of irradiation, the difference was very small (see also Table S7), and with further irradiation up to 60 min, the removal percentage of FB₁ was lower by 10% compared to UPW. After 60 min of treatment in the presence of NO₃⁻ ions, about 80% of FB₁ was removed, and this was the highest degradation efficiency with anions. The inhibition of photocatalysis in the presence of NO₃⁻ ions was reported by Farner Budarz et al. [65], where these ions acted as •OH radical scavengers. No change in pH value was observed during this treatment.

Effect of hydrogencarbonate: The reduced removal efficiency of FB₁ was registered in the presence of HCO_3^- ions (Figure 11b). As can be seen, the kinetics curve has an irregular shape, where the highest removal rate (62%) was achieved after 30 min of irradiation, and after 60 min of treatment, that percentage was about 50%. Based on the degradation rate constant (Table S7) (Supplementary Materials), it can also be concluded that the inhibitory effect of HCO_3^- is not pronounced for the first 20 min of irradiation. According to Matthews [63], the HCO_3^- ion also acts as a scavenger of •OH radicals, whereby a strong surface complex with the catalyst is not formed. During the treatment, the pH value changed by about one pH unit (from 8.1 to 9.2).

Effect of sulphate: Photocatalysis of FB₁ in the presence of SO_4^{2-} ions was shown to be the least efficient compared to other anions. During this treatment, only 37% of FB₁ was removed in 60 min of irradiation (Figure 11b). SO_4^{2-} ions, just like other anions, act as scavengers of °OH radicals and thus reduce the rate of pollutant degradation [66]. Further, depending on pH, inorganic layers can form on the surface of the catalyst, which interfere with the pollutants and slow down the degradation [67]. Based on the data in Table S7 (Supplementary Materials), it can also be concluded that the inhibitory effect of SO_4^{2-} is the most pronounced compared to other anions. The initial pH of this solution was 7.8, and at the end of the treatment, it increased by about 0.5 pH units (8.3).

2.7.3. Effect of Humic Acid

Humic acid showed a very low effect on the efficiency of photocatalytic degradation of FB₁. In the first 30 min of treatment, the percentage of FB₁ removal as well as the shape of the kinetic curves were almost the same for the systems with and without HA (Figure 11a, Table S7) (Supplementary Materials). However, during further irradiation of up to 60 min, HA inhibited the removal of FB₁, and the final removal efficiency using ZT–2 was 77%. Similar results were obtained by Šojić Merkulov et al. [68], who also observed a minor effect of HA on photocatalysis efficiency. During the treatment, no significant change in pH was recorded (about 0.4 pH units).

3. Material and Methods

3.1. Chemical and Solutions

A stock solution of FB₁ was prepared by dissolving 1 mg of solid FB₁ (from *Fusari-ummoniliforme*, approx. 98% TLC, Sigma-Aldrich F1147, St. Louis, MO, USA) in 100 cm³ of ultrapure water. Working solutions were prepared by diluting the stock solution with ultrapure water to a concentration of 1.39 μ mol/dm³ for FB₁. The aqueous solution of FB₁ (1.39 μ mol/dm³) was found to be stable in the dark for more than 500 days at 4 °C to 8 °C.

Methanol (HPLC gradient grade, LiChrosolv, Merck, Darmstadt, Germany) and 0.1 mol/dm³ NaH₂PO₄ (extra pure, Merck, Darmstadt, Germany) were used as components of the mobile phase, where the pH was adjusted with H₃PO₄ (p.a, Centrohem, Stara Pazova, Serbia). To prepare the means for derivatizationo-phthaldialdehyd (min. 99%, Sigma, Darmstadt, Germany), 0.1 mol/dm³ Na₂B₄O₇ (p.a., Zorka, Šabac, Serbia), and 2-mercaptoethanol (min 99%, Serva, Heidelberg, Germany) were used. H₂O₂ (30%, Sigma-Aldrich, St. Louis, MO, USA) and (NH₄)₂S₂O₈ (p.a. Merck-Alkaloid, Skopje, North Macedonia) were used in the experiments of indirect photolysis. The solutions for adjusting the initial pH were obtained by dilution of 70% HClO₄ (99.999% trace metals basis, Merck-Alkaloid, Skopje, North Macedonia), and 30% NaOH (Suprapur[®], Sigma-Aldrich, St. Louis, MO, USA). All chemicals were used without further purification.

Physicochemical characteristics of the Danube River (Novi Sad, Serbia), ground water (Štrand, Novi Sad, Serbia), and tap water (Novi Sad, Serbia) together with UPW are given in Table S8. Samples of all water types were filtered through a filter paper (Whatman, diameter 125 nm, pore size 0.1 μ m) and stored at 4 °C.

To examine the influence of individual ions and HA on the efficiency of direct and indirect photolysis as well as photocatalysis, their concentrations in the reaction solution/suspension were adjusted to the highest values determined in real water samples. The following chemicals were used to simulate the effects of ions and organic matter: NaCl and HCO₃⁻ (ZorkaPharm, Šabac, Serbia), NaNO₃ (Kemika, Zagreb, Croatia), Na₂SO₄ (MPhemija, Belgrade, Serbia), MgCl₂ and CaCl₂ (Merck, Darmstadt, Germany), and humic acid (p.a, Fluka, St Louis, MO, USA).

3.2. Preparation of ZnO-Based Catalysts

ZS-1 and ZT-1 samples were prepared by a three-step mixing-calcination method in solid-state, when starting precursors (ZnO, TiO₂, and SnO₂, purity 99.9%, particle size $\leq 1 \mu m$, Sigma-Aldrich, St. Louis, MO, USA) in a molar ratio of $ZnO:SnO_2 = 2:1$ and ZnO:TiO₂ = 2:1 were ground in an agate mortar, annealed at 700 $^{\circ}$ C in the air for 2 h, and ground again. ZS-2 and ZT-2 samples were prepared by multi-step-mechanochemical processing, when starting precursors (ZnO, TiO₂, and SnO₂, purity 99.9%, particle size $\leq 1 \mu m$, Sigma-Aldrich, St. Louis, MO, USA) were first mixed in stoichiometric amounts in a ball mill (Retsch GmbH PM100, Haan, Germany) using a zirconia vial and 5 mm diameter zirconia balls in ethanol for 4 h. A standard ball-to-powder mass ratio of 10:1 was used, followed by drying. The next step was mechanical activation of stoichiometric ZnO/SnO₂ powder mixture for 160 min (speed 320 rpm) for the synthesis of ZS-2 and of stoichiometric ZnO/TiO_2 powder mixture for 90 min (speed 320 rpm) for the synthesis of ZT-2. Both ZS-2 and ZT-2 powder mixtures were afterward ground in ethanol for 10 min (speed 100 rpm) for homogenization. After drying, the mechanically activated mixture of ZS-2 was annealed at 1200 °C to synthesize Zn₂SnO₄, while the mechanically activated mixture of ZT–2 was annealed at 1000 $^{\circ}$ C to obtain Zn₂TiO₄ for 120 min in an air atmosphere. The choice of these synthesis conditions was made based on previous experimental results and data from the literature [17-20,25-28,39,40].

3.3. Structure, Morphology, and Optical Characterization of ZnO-Based Catalysts

XRD analysis was performed on a MiniFlex600 (Rigaku, Japan) X-ray diffractometer with Cu-K_{α} radiation ($\lambda = 1.5406$ Å) at a tube voltage of 40 kV and a tube current of 15 mA, a step size of 0.02°, and a counting time of 1°/min in the angular range 2 θ from 10° to 80°. The morphology of the obtained powder samples was examined with scanning electron microscopy SEM (JEOL JSM 7001F, Tokyo, Japan). Raman spectra were obtained on a Renishaw confocal Raman microscope InviaTm, (Gloucestershire, UK) with excitation of 514 nm argon-ion laser at ambient temperature. A laser beam of 514 nm was focused with a50x objective, and Raman signal was collected by a CCD camera up to 1400 cm⁻¹ with a spectral resolution of 2 cm⁻¹ and accumulation time of 3s. Photoluminescence (PL) spectra were recorded by Horiba Fluorolog[®]-3 spectrofluorometer (model FL3-22) equipped with a 450W ozone-free xenon lamp as a light source (Tokyo, Japan). DRS was obtained using an Ocean Optics QE65000 (Dunedin, FL, USA) spectrometer at room temperature.

3.4. Photodegradation Procedure

Degradation of FB₁ (20 cm³) was performed in a photochemical cell (total volume about 40 cm³, liquid layer thickness 35 mm) by focusing the light beam on the plain window of the cell [69]. To examine the efficiency of the indirect photolysis, an appropriate volume of H₂O₂ (0.278 mmol/dm³) or (NH₄)₂S₂O₈ (0.140 mmol/dm³) was added to the reaction mixture. Based on our previous research [39,40], to study the efficiency of photocatalysis, 20 mg of photocatalyst (1.0 mg/cm³) was added. Thereafter, the reaction suspension with the catalyst was sonicated (50 Hz) in the dark for 15 min to evenly distribute the photocatalyst particle and achieve the adsorption–desorption equilibrium. Then, the photochemical cell was placed on a magnetic stirrer (with continuous stirring in a stream of O₂, 3.0 cm³/min) and thermostated at 25 ± 0.5 °C. As a source of artificial UV radiation, a high-pressure mercury lamp (HPL-N, 125W, Philips, Brussel, Belgium, emission bands in the range of UVB (290, 293, 296, 304, and 314 nm) and UVA (335 and 366 nm) with emission maximum at 366 nm) together with a corresponding concave mirror were used.

A solution of FB₁ with a concentration of 2.78 μ mol/dm³ was prepared to test the effect of the matrix of several types of water on the photodegradation efficiency of FB₁. In the photocell, 10.00 cm³ of this FB₁ solution and 10.00 cm³ of each of the tested types of water (Danube River, ground, tap water, and UPW water) were measured, so that the concentration of the FB₁ solution was 1.39 μ mol/dm³. When examining the individual influence of ions and HA, 100 μ L of solution (NaCl, NaNO₃, Na₂SO₄, or HA) or the corresponding mass (MgCl₂, CaCl₂, or NaHCO₃) of the salt of the investigated ion was added to the photochemical cell containing the fumonisin solution.

Since the pH value in the investigated types of water was around pH 8.0, in the experiments where the pH was different (e.g., in indirect photolysis $UV/S_2O_8^{2-}$, photolysis, photocatalysis with different types of water and with the addition of some ions), NaOH or HClO₄ (0.10 mol/dm³) were added before the treatment to exclude the effect of pH on the removal efficiency [46]. 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 pHmeter (pH/Cond 340i, WTW).

3.5. FB_1 Determination

Aliquots of the reaction mixture (0.4 cm^3 , allowed volume change of 10%) were taken before the start of irradiation as well as during irradiation at certain time intervals in order to monitor the kinetics of FB₁ photodegradation. Suspensions containing the catalyst were filtered through a membrane filter (SartoriusTM MinisartTM, cellulose acetate, sterile, 0.45 µm, Goettingen, Germany). The absence of fumonisin adsorption on the filter was confirmed by the HPLC–FLD system.

For FB₁ derivatization prior to HPLC–FLD determination, an aliquot of 0.1 cm³ of the reaction mixture was mixed with 0.1 cm³ of OPA–MCE reagent at room temperature and stirred for 1 min. Then, 10 μ L of the derivatized solution was injected into the HPLC–FLD system. Liquid chromatography equipment consisted of a Thermo Scientific DionexUltiMate3000 Series HPLC–FLD system with FLD 3100 fluorescence detector, WPS-3000 autosampler, degasser, quaternary pump, and Hypersil GOLD column 150 × 3 mm, particle size 3 μ m (Thermo Scientific, Germering, Germany). The mobile phase consisted of MeOH–0.1 mol/dm³ NaH₂PO₄ (77:23, *v*/*v*), pH value adjusted to 3.35 with H₃PO₄, with isocratic elution, flow rate of 0.8 cm³/min, excitation wavelength of 335 nm, and emission wavelength of 440 nm. The temperatures of the analytical column and the fluorescent detector were 30 °C and 50 °C, respectively.

4. Conclusions

In this study, two ternary $(Zn_2SnO_4 \text{ and } Zn_2TiO_4)$ and two binary $(ZnO/SnO_2 \text{ and }$ ZnO/TiO_2) structured nanocrystallites were investigated as photocatalysts in the heterogeneous photocatalysis of FB_1 using UV irradiation in UPW. Since, in the case of ternary Zn_2SnO_4 , the adsorption of FB₁ was the least pronounced and the photodegradation efficiency was the highest, this nanocatalyst was used for further tests. Upon comparing the efficiency of direct and indirect photolysis with photocatalysis using Zn_2SnO_4 as a photocatalyst in the removal of FB₁, it was found that indirect photolysis and photocatalysis were significantly more effective treatments than direct photolysis. Photolysis of FB_1 in tap, ground, and river waters was inhibited as compared to UPW. Based on our findings, it can be concluded that the inhibition effect of different water samples was more pronounced in the case of indirect photolysis with UV/H_2O_2 and $UV/S_2O_8^{2-}$. Namely, in the case of direct photolysis, the efficiency of FB₁ removal was higher in tested waters (about 1.3 to 2 times) than in ultrapure water, while in the case of indirect photolysis, as well as in photocatalysis, the rate of FB_1 removal was significantly reduced (about 1.3 to 4 times). The positive influence of the studied ions on photolysis was established, except in the case of hydrogencarbonate ions. On the other hand, the inhibitory influence of ions on FB₁ degradation was confirmed in the system with UV/H_2O_2 . The efficiency of FB₁ photocatalysis

also depends on the presence of the tested ions, and the least inhibition was observed for Ca^{2+} and NO_3^{-} ions, as well as HA.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal13020375/s1: Table S1: Effect of photolysis and photocatalysis using UV irradiation at pH ~8 on degradation rate constant of FB₁ (1.39 µmol/dm³); Table S2: Effect of different types of water on degradation rate constant of FB₁ (1.39 µmol/dm³) using UV irradiation at pH ~8; Table S3: Effect of different types of water on degradation rate constant of FB₁ (1.39 µmol/dm³) using UV irradiation rate constant of FB₁ (1.39 µmol/dm³) using indirect photolysis at pH ~8; Table S4: Effect of different types of water on degradation rate constant of FB₁ (1.39 µmol/dm³) using ZS-2 photocatalyst at pH ~8; Table S5: Effect of different ions and HA on degradation rate constant of FB₁ (1.39 µmol/dm³) at pH 7.7–9.0 using UV irradiation; Table S6: Effect of different ions and HA on degradation rate constant of FB₁ (1.39 µmol/dm³) at pH 7.7–9.0 using UV/H₂O₂ treatment; Table S7: Effect of different ions and HA on degradation rate constant of FB₁ (1.39 µmol/dm³) at pH 7.7–9.0 using ZS-2 photocatalyst; Table S8: The physicochemical characteristics of the analyzed water types.

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