A Simple Device for the On-Site Photodegradation of Pesticide Mixes Remnants to Avoid Environmental Point Pollution

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Featured Application: The prototype developed in this work can rapidly detoxify agrochemical solutions directly at farms, allowing for their safe disposal in the environment or water reuse.

Abstract: The worldwide increase in the number and use of agrochemicals impacts nearby soil and freshwater ecosystems. Beyond the excess in applications and dosages, the inadequate management of remnants and the rinsing water of containers and application equipment worsen this problem, creating point sources of pollution. Advanced oxidation processes (AOPs) such as photocatalytic and photo-oxidation processes have been successfully applied in degrading organic pollutants. We developed a simple prototype to be used at farms for quickly degrading pesticides in water solutions by exploiting a UV–H_2O_2-mediated AOP. As representative compounds, we selected the insecticide imidacloprid, the herbicide terbuthylazine, and the fungicide azoxystrobin, all in their commercial formulation. The device efficiency was investigated through the disappearance of the parent molecule and the degree of mineralization. The toxicity of the pesticide solutions, before and during the treatment, was assessed by *Vibrio fischeri* and *Pseudokirchneriella subcapitata* inhibition assays. The results obtained have demonstrated a cost-effective, viable alternative for detoxifying the pesticide solutions before their disposal into the environment, even though the compounds, or their photoproducts, showed different sensitivities to physicochemical degradation. The bioassays revealed changes in the inhibitory effects on the organisms in agreement with the analytical data.

1. Introduction

Pesticides, herbicides, fertilizers, plant growth regulators, and other agrochemicals play a decisive role in agriculture, protecting crops and improving yields, but the current main challenge is the development of profit-gaining agriculture increasingly geared to environmentally friendly management systems, aimed at reducing the damages produced by agrochemicals to humans and the environment [1].

High intensity agricultural models are characterized by a massive use of pesticides and herbicides contaminating water and soil [2–4]. In 2018, the worldwide quantities of applied pesticides corresponded to 4112.3 metric tons, and in Italy alone to 54.1 metric tons [5]. Animal waste from farms, sediments, organic debris, pesticides, and fertilizers have long proven to be the major causes of ground and surface water pollution [6,7].

Soil and water bodies risk contamination every time pesticides are manipulated [8]. Pesticide drift, percolation, drainage, runoff, and leaching greatly depend on their cor-

rect management, both before and after the treatment, including the correct use of the application equipment, i.e., the pneumatic sprayers [9–11]. A known source of point source pollution is represented by incorrect practices in the disposal of spray remnants and tank rinsing water. Directive 2009/128/EC [12] regulates the disposal of agro-wastewater containing pesticides; however, it is quite common for, after the application, the spray remnants in the barrel of the spray-tank to be deposited on the ground or even discarded directly into water bodies, often without any dilution. These point sources of pollution from leftover mixture and cleaning water disposal are a matter of concern since pesticide residues may persist for a very long time; some compounds can be still detected many years after their ban [13,14].

Several solutions have been studied and proposed to remove or inactivate pesticides in water. Most are plants based on water evaporation produced by solar radiation and wind (Heliosec®, Syngenta Agro sas, Guyancourt, France) or by infrared radiation and heat (Osmofilm®, Panteck- France sarl, Montesson France) [15]. Quicker evaporation can be obtained by using electrical resistance, filtering the vapors through activated carbon filters (Evapofit®, Staphytr, Inchy-en-Artois, France) [15]. Otherwise, a chemical pretreatment of coagulation–flocculation can be used to produce decantation of the active ingredient as solid material (Sentinel®, Alba environnement sas, Cluny, France) [15]. Various systems are based on biomass beds, based on microbial degradation (using fungi, bacteria, actinomycetes, and viruses) into less toxic forms [1,9,16]. However, all these solutions require a place and/or a plant where they can be carried out.

More effective treatment systems are required, and the most recent and effective water treatment technologies are based on advanced oxidation processes (AOPs), a set of innovative techniques including UV-based techniques, ultrasound, electron beams, γ rays, and plasma methods, which remove organic contaminants by mineralization [17]. The UV treatments are the easier and less expensive ones, optimized by the addition of a photocatalyst or a radical mediator, such as H_2O_2, which promotes the radical-mediated degradation of the molecules [18–20], according to the main steps illustrated in Scheme 1.

$$H_2O_2 + h\nu \rightarrow 2\,HO^\bullet$$

$$HO^\bullet + R \rightarrow ROH\bullet \qquad \textbf{(a)}$$

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \qquad \textbf{(b)}$$

$$HO^\bullet + R \rightarrow OH^- + R^{\bullet+} \qquad \textbf{(c)}$$
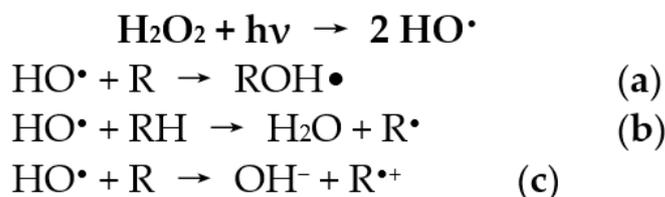
Scheme 1. UV irradiation in the presence of H_2O_2 produces the hydroxyl radicals responsible for the fragmentation of the organic molecules via (**a**) radical addition to double bonds, (**b**) hydrogen abstraction, and (**c**) electron transfer to the molecule.

Exactly like other organic pollutants, agrochemicals can be degraded by light irradiation, especially by UV light. A huge number of studies on the photochemistry of these pollutants have been carried out, determining the photodegradation kinetics, the degradation pathways, and the optimal conditions such as the addition of oxidants and/or catalysts able to enhance the process for the most recalcitrant compounds [21–31].

Our research group is involved in the practical application of AOPs for the remediation of polluted waters to reduce environmental dispersion and restore water quality for further reuse [32–34]. Deeply convinced that the best compliance to ecofriendly management of agro-wastewater can be obtained offering simple, flexible, cost-effective, and time-saving solutions, we designed and built up a small, portable device, a photoreactor effective enough in degrading the active ingredients, which is cheap, extremely easy to use in situ, and not time-consuming concerning the abovementioned solutions. We employed UV irradiation in the presence of hydrogen peroxide to reduce the concentration of the agrochemicals, selecting three pesticides that are widely used in our region, each one representing a different family of agrochemicals: insecticides, herbicides, and fungicides.

Terbuthylazine (TBA), used worldwide as a pre-emergence herbicide in corn farming, shows persistence, toxicity, and endocrine disruption effects on wildlife and humans [35]. Imidacloprid insecticide (IMI), today among the top ten agrochemicals worldwide [36], has been ascribed chronic toxicity to multiple aquatic taxa [37], and negative effects on pollinators [38,39]. Azoxystrobin fungicide (AZO), used since 1996, is very toxic for aquatic organisms and can lead to long-term adverse effects [40]. We tested our degradation prototype on the same solutions used on the farm for treatment. We employed the commercial formulation (CFs) of the compounds, which could behave differently with respect to the pure active ingredients because of the presence of the excipients [41], calculating an average residual volume of solution diluted with a suitable volume of water usually employed to rinse the tank. Since a degradation procedure aims to eliminate the pollutants' negative impact on the environment, the success of the procedure is usually witnessed by the reduction or disappearance of their biotoxicity. We evaluated the biotoxicity of irradiated and non-irradiated solutions by applying two ISO standard biological tests for water quality assessment, based on *Vibrio fischeri* light emission inhibition and *Pseudokirchneriella subcapitata* (now *Raphidocelis subcapitata*) algal growth inhibition, respectively [42,43].

2. Materials and Methods

The commercial formulations of the tested agrochemicals were: TrekP® (ADAMA AGAN, Ltd., Ashdod, Israel) for the herbicide Terbuthylazine, Confidor® (Bayer AG, Leverkusen, Germany) for the insecticide Imidacloprid, and Ortiva® (Syngenta Italia, Milano, Italy) for the fungicide Azoxystrobin. The chemical structure of the active ingredients is reported in Figure 1.
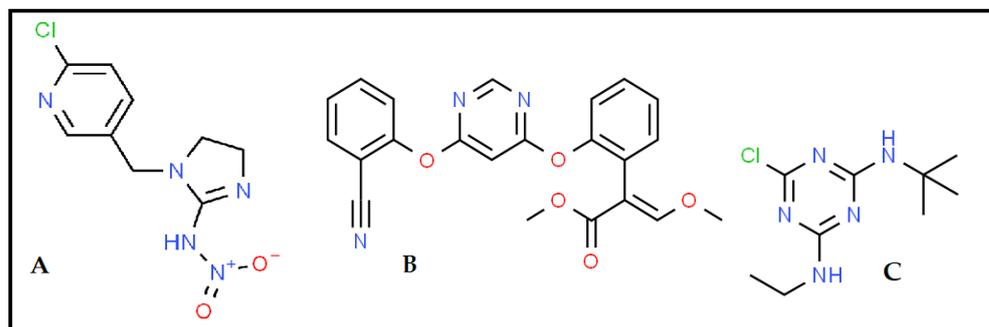

Figure 1. The chemical structure of the compounds under study: (**A**) imidacloprid, (**B**) azoxystrobin, and (**C**) Terbuthylazine.

The H_2O_2 solution (30%) Perhydrol®, used as a catalyst in the AOP experiments, was supplied by Merck Life Science (Milano, Italy). The LCK-385 test-in-cuvette kit for the total organic compound determination was supplied by Hach Lange (Milano, Italy). Lyophilized aliquots of the luminescent bacteria *V. fischeri* were prepared from fresh cultures at our laboratory starting from an original batch supplied by the Pasteur Institute (Paris, France). The 96-wells "Black Cliniplate" microplates were supplied by Thermo Scientific (Vantaa, Finland) and the luminometer was the Victor Light 1420 model from Perkin-Elmer, USA. The Istituto Zooprofilattico Sperimentale of Abruzzo and Molise "G. Caporale" (Teramo, Italy) supplied the freshwater microalga *P. subcapitata* culture. Inorganic salts and nutrient broth components for the bioluminescent bacteria and algal growth were obtained from Sigma-Aldrich. Tap water was chosen as the solvent of the agrochemicals.

A DR5000 spectrophotometer (Hach Lange, Milano, Italy) was employed to evaluate the active ingredients concentration and the total organic compounds (TOC) content.

The photoreactor prototype was assembled at the Proambiente laboratories by using materials currently employed in AOP experiments (UV lamps and stainless steel components).

2.1. The Photodegradation Treatment

The experiments were planned according to the hypothesis that the residual volume of agrochemical solution in a spray tank after the treatment was about 5 L. Agrochemical solutions were prepared at concentrations very close to the recommended ones employed on fields. Accordingly, we decided to dissolve 6.25 mL of each pesticide suspension in 5 L of tap water, and then this volume was brought to 50 L, simulating the water volume used during the rinsing operation of an 800 L tank. Before starting the degradation process, 50 mL of H_2O_2 30% solution was added, obtaining a 10 mM final concentration.

Small specimens of the solution under treatment (5–10 mL) were collected before the start and after 2, 3, 4, 5, 6, 7, and 8 h after the beginning of the irradiation. The lamps were always switched on during the treatment time.

The degradation process was evaluated by following the decrease of the active ingredients' concentration by measuring their absorbance (ABS) at the maximum wavelength for each compound: 242 nm for TBA and AZO and 270 nm for IMI. The mineralization process was followed by spectrophotometrically measuring the TOC value determined by the Hach Lange test kit. The test was performed according to the manufacturer's instructions. Shortly thereafter, the sample was added to the cuvette containing the digestion reagents. After 5 min in the TOC-X5 shaker (Hach Lange, Milano, Italy), a second cuvette containing the revealing reagent was screwed on the digestion cuvette, which was placed in a thermostat for two hours. After cooling at room temperature, the revealing cuvette was read by the spectrophotometer. All experimental results were obtained in at least triplicate and the data were expressed as means $\pm$ SD.

2.2. The Toxicity Assays

2.2.1. Bioluminescence Inhibition Assay

Lyophilized aliquots of *V. fischeri* containing NaCl 3% *w/v* were reconstituted with 1 mL of distilled water and re-suspended in 10–30 mL of the nutrient broth (NaCl 15 g, peptone 2.5 g, yeast extract 1.5 g, glycerol 1.5 mL, HEPES 0.01 M in 500 mL, pH 7). NaCl was added to the treated and untreated solutions to the 3% *w/v*. 200 μL of the bacteria suspension and 100 μL of each sample was dispensed into the microplate wells. The controls consisted of 200 μL of bacteria plus 100 μL of a 3% NaCl solution in tap water. The emitted light was recorded at fixed intervals in the range 0–48 h. A minimum of 5 replicates and a maximum of 12 were tested for each sample and the light emission values, reported as relative luminescence units (RLU), were expressed as means $\pm$ SD.

The bioluminescence inhibition percentage (*I*%) was used to express the toxicity of the samples and calculated according to:

$$I\% = \frac{L_{blank} - L_{sample}}{L_{blank}} \times 100 \qquad (1)$$

where *L* is the intensity of the light emitted by the sample or by the control (blank).

2.2.2. Algal Growth Inhibition Assay

The starter culture of *P. subcapitata* was prepared by inoculating in Erlenmeyer flasks 1 mL of microalgae suspension per 100 mL of the Jaworski's culture medium ($Ca(NO_3)_2 \cdot 4H_2O$ 20 g L^{-1}; KH_2PO_4 12.4 g L^{-1}; $MgSO_4 \cdot 7H_2O$ 50 g L^{-1}; $NaHCO_3$ 15.9 g L^{-1}; EDTAFeNa and EDTANa$_2$ both at 2.25 g L^{-1}; H_3BO_3 2.48 g L^{-1}; $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ 1 g L^{-1}; $MnCl_2 \cdot 4H_2O$ 1.4 g L^{-1}, cyanocobalamin, biotin, and thiamine, each one 0.04 g L^{-1}, $NaNO_3$ 80 g L^{-1}; $NaH_2PO_4 \cdot 2H_2O$ 36 g L^{-1}).

The flasks were stopped by a porous cotton plug and illuminated by a white lamp/red lamp Osram daylight 2 × 36 W plus an Osram Gro-Lux lamp 36 W (8 h light/16 h dark) at room temperature of 20 °C.

To perform the tests, smaller flasks were filled with equal volumes of the treated or untreated samples, added with the suitable amount of Jaworski's medium salts and the algal diluted suspension (approximately 10^5 cells mL^{-1}). The small flasks were kept in the

same conditions as the starter culture. Controls were prepared by adding one volume of the Jaworski's salts mixture to one volume of algae suspension. We evaluated the algal density by measuring the ABS at 545.6 nm, an indirect method for cell counting also suggested in the ISO 8692/2004 [44]. Aliquots of carefully hand-shaken samples or controls were measured without dilution, in triplicate, and then the aliquots were poured back into the flask.

3. Results

3.1. The Portable Photoreactor Prototype

The prototype was assembled at the Proambiente laboratories based on the idea of developing a device effective enough to produce significant detoxification of quite large water solution volumes during a reasonable time period (hours) that is robust and easy to be used anywhere a power supply is available. These characteristics of the system, together with the reduced production costs and the simple procedure, should encourage its regular use any time agro-wastewater has to be managed.

To design the irradiating unit (or portable reactor) illustrated in Figure 2, we considered the average capacity of the spray tanks to be about 800 L, the average volume of residual solution to be 5 L, and the washing volume for this tank to be about 50 L (data obtained from personal communication with Italian spray machine sellers and users). The simplest solution, taking into account that the unit had to be easily transportable, was to prepare a stainless steel, cylindrical container (Ø 300 cm, high 1.007 cm) capable of holding up to 70 L of liquid. The UV lamps were selected, among those commercially available, according to the dimensions of the container. We employed four immersion, 20 W, low-pressure mercury UV lamps emitting a monochromatic light at λ = 254 nm. The lamps were mounted on a circular support to obtain a uniform distribution of the irradiated light inside the sample volume. The support was completed by adding the electric contacts and was placed inside the system case, whose upper part was hermetically closed by a circular cover blocked by a flange to prevent the escape of UV radiation. In addition, the container was equipped with a circular glass window to check the proper functioning of the lamps and with a drain cock to allow for sampling during the irradiation and emptying at the end of the treatment.

To proceed with the photodegradation, the washing water must be transferred inside the prototype. The filling of the prototype with the agrochemical solutions can occur at the spray-tank side using an immersion pump, connected on one side to a tube, capped by a filter, and placed inside the solution into the barrel of the spray-tank. On the other side, it is connected to a tube with an automatic stop dispenser to avoid overfilling the container (Figure 3).

3.2. The Photodegradation and Mineralization Profiles

Of the samples withdrawn from the pesticide solution under treatment, we determined a decrease in both the active ingredient concentration and the degree of mineralization, expressed by the reduction in the ABS and in the TOC value, respectively.

The amount of hydrogen peroxide added to the solutions (50 mL of H_2O_2 at 30% solution) was selected according to our previous experience at the lab scale [33] and the literature data [21]. The pH values of the three solutions after hydrogen peroxide addition were in the range 7.4–7.6, and they were not modified, because this photodegradation procedure was intended for use at farms where a pH adjustment would be an unusual and unlikely operation. Furthermore, those values were suitable for performing the biotoxicity assays both before and after treatment.
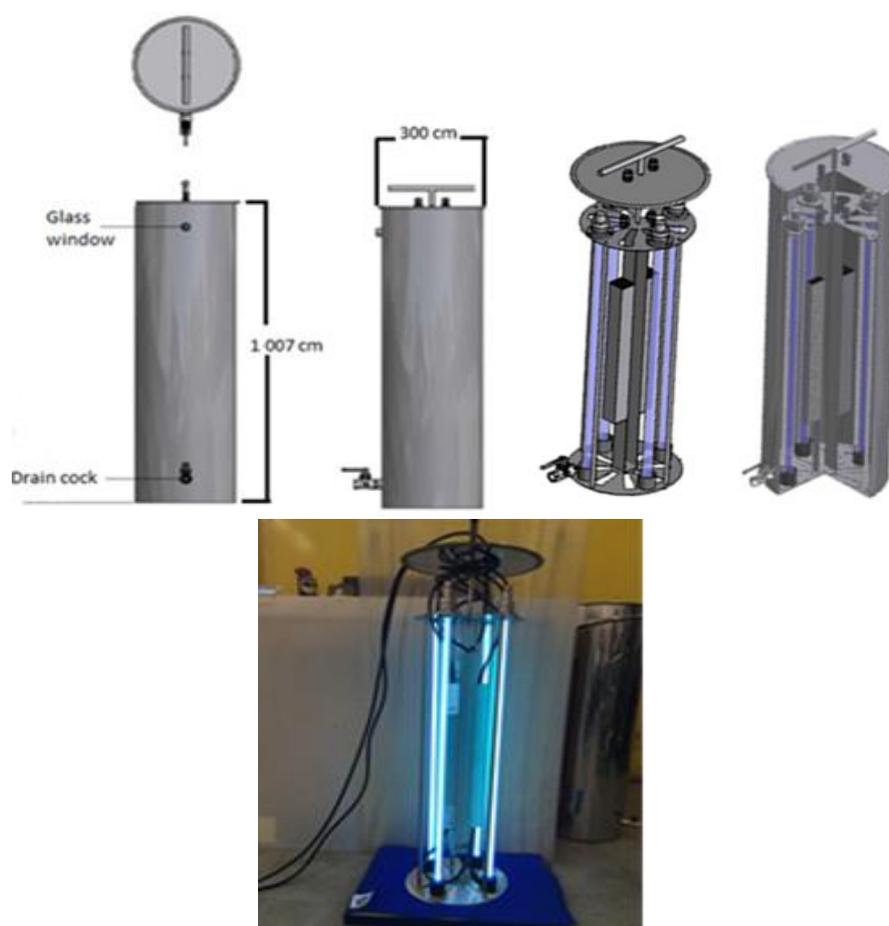
Figure 2. The portable photolytic cell. From left to right: external aspect and dimensions of the system case, scheme of the UV lamps support, the support inside the case system. Below, a photo of the completed lamps' support.
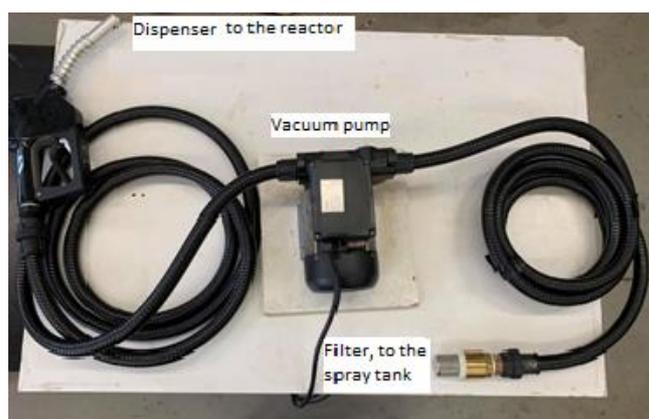

Figure 3. The vacuum pump system employed to quickly and safely transfer the pesticide solution from the spray-tank, or any other container, to the photodegradation unit.

It was out of the scope of this work to follow the photodegradation mechanism by determining the kind and amount of the photoproducts, first of all because our main aim was to develop a more effective device by adapting the UV–H_2O_2 AOP to the out-of-lab conditions encountered at farm locations. On the other hand, several studies on the photochemistry of the selected compounds were already available in the literature, as mentioned in the Introduction.

In Figure 4, for each pesticide, the data obtained for the absorbance and the TOC parameters were reported in a double-axis graph in order to compare the trends of the two processes. Two hours was the first sampling interval chosen to evaluate the degradation. At that time, only the reduction in concentration of TBA and IMI and a modest IMI mineralization were measurable. Indeed, the AOPs proceed through complex pathways, starting with the fragmentation of the parental organic molecules, followed by various transformations leading, in optimal conditions, to the production of CO_2 and carbonates. The disappearance of the parent compound and the reduction of the organic molecule content can follow completely different kinetics.
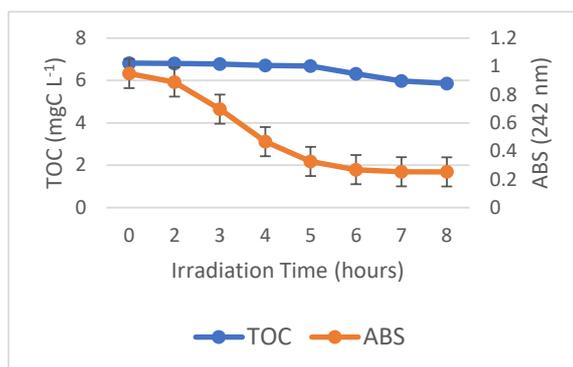
(**a**)
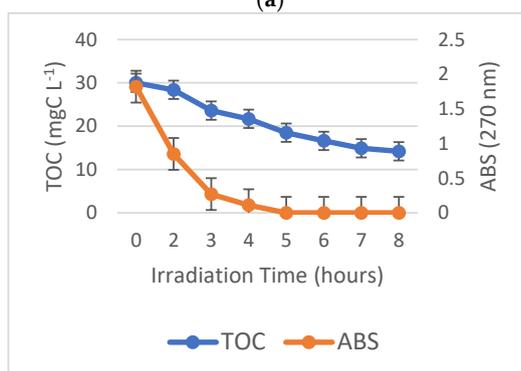
(**b**)
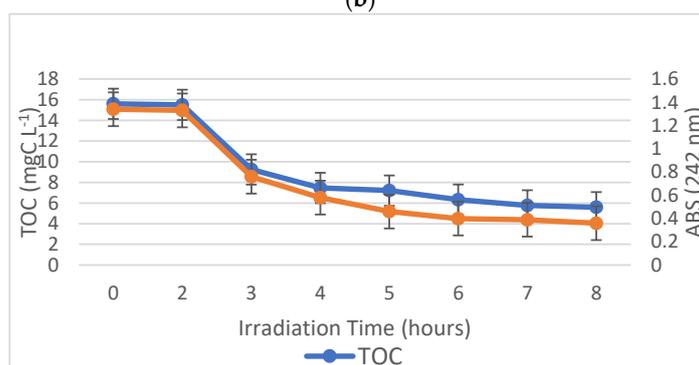
(**c**)

Figure 4. The changes in both the active ingredient concentration and in the TOC content over time with respect to the untreated solutions (irradiation time 0). (**a**) TBA, (**b**) IMI, (**c**) AZO.

Concerning the selected pesticides, these differences were particularly evident for the compound TBA. This molecule, or better its degradation derivatives, resulted in being the most recalcitrant. TBA was degraded at 80% after about 6 h, but the TOC value of the solution was quite unaffected after 8 h of treatment (Figure 4a).

A similar, and definitely less pronounced, discrepancy between the two processes was observed for the insecticide IMI; the parental molecule completely disappeared after 5 h of treatment, while to halve the TOC value, 7 h of irradiation was required (Figure 4b).

On the opposite, the two phenomena showed the same trend in the case of AZO. The disappearance of the active ingredient was strictly followed by the reduction of the TOC value, both halved after 3 h of treatment. After this time, the two curves slightly diverged, probably because of the formation of resistant photoproducts (Figure 4c).

The prototype was able to remove about 80% (mean value) of the active ingredients in an acceptable time (8 h), which can correspond, for example, to an overnight treatment. The mineralization rate was significantly lower, the mean value being about 44%, but it was known that to obtain the disappearance of any organic compound is a rather more difficult task.

3.3. The Toxicity Assays

In order to evaluate in depth the efficiency of remediation technologies such as AOP treatments, the determination of the pollutant degradation and of the mineralization rate must be coupled to various biological methodologies in order to determine the actual changes in toxicity of the treated materials. Toxicity assessment is usually performed by using a set of tests based on simple organisms living in the environment of interest. We applied two of the most used assays to assess the water quality, the bioluminescent bacteria *Vibrio fisheri*, and the freshwater microalga *Pseudokirchneriella subcapitata*, representing the basic level of heterotrophic and autotrophic organisms.

3.3.1. The Bacterial Bioluminescence Inhibition Test

In Figure 5a–c, we reported, separately for the three compounds, the intensities of the bacterial light emission from the controls (blank), the solutions treated for 2 h, and those at the end of the treatment (8 h).
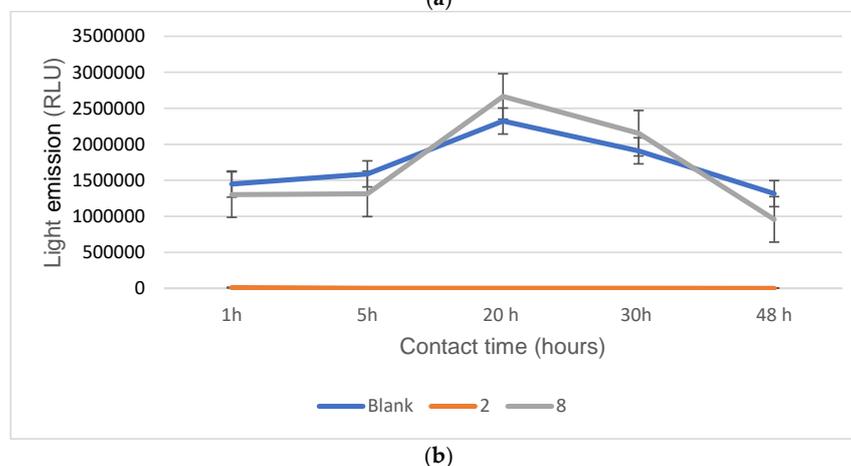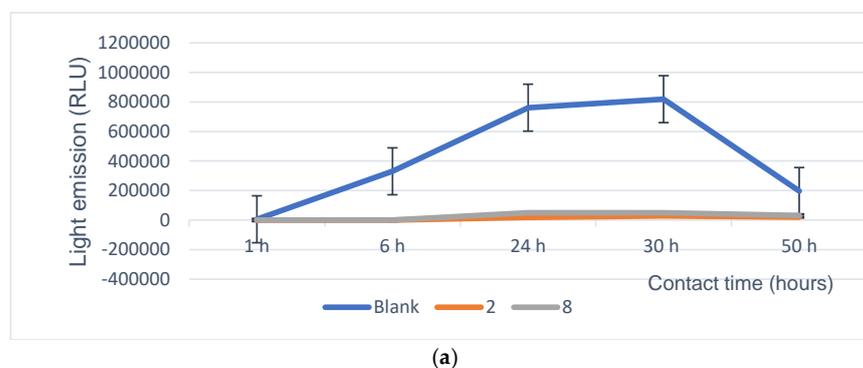

(**a**)
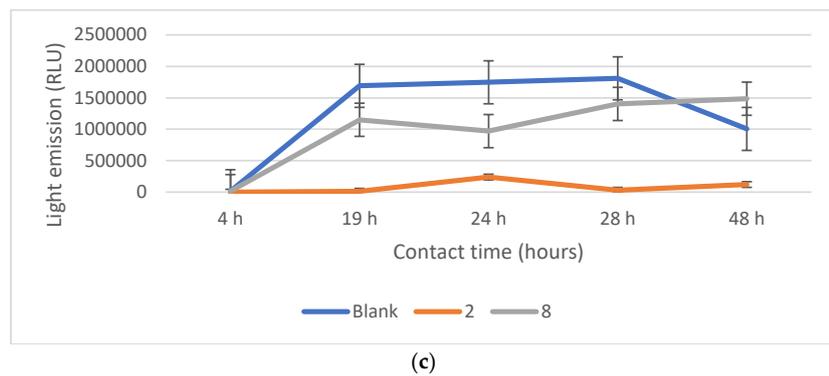

(**b**)

Figure 5. *Cont.*

(c)

Figure 5. Light emission from bacteria in contact with the untreated solutions (blank) and the solutions after 2 h and 8 h of irradiation. (**a**) TBA, (**b**) IMI, (**c**) AZO.

Both solutions of TBA, at 2 and 8 h, reduced the light emission to zero, confirming that the important decrease in the active ingredient concentration was ineffective in reducing the toxicity of this compound, a characteristic probably completely retained by its photoproducts.

On the contrary, the sample of IMI collected after 2 h of treatment still completely inhibited the light emission, confirming the solution toxicity, but the sample at the end of the treatment showed no inhibition. The light intensity was practically overlapped with that of the control. The incomplete mineralization of the solution did not represent a problem of residual toxicity from the degradation products.

A similar behavior was observed by comparing the control's emission with those of the first and last treated samples of the AZO solution. Again, the sample after 2 h of treatment deeply inhibited the light emission, whereas at the end of the treatment it was possible to observe a reduced, albeit still detectable, toxic effect.

In Figure 6 we reported, for a direct comparison among the three compounds, the mean values of the chronic toxicity, i.e., the % of light emission inhibition produced by all the irradiated solutions and the untreated samples with respect to the control after 24 h of contact with the bacteria. In this way, it was easier to highlight the effects of the H_2O_2–UV treatment on the light emission inhibition over time.
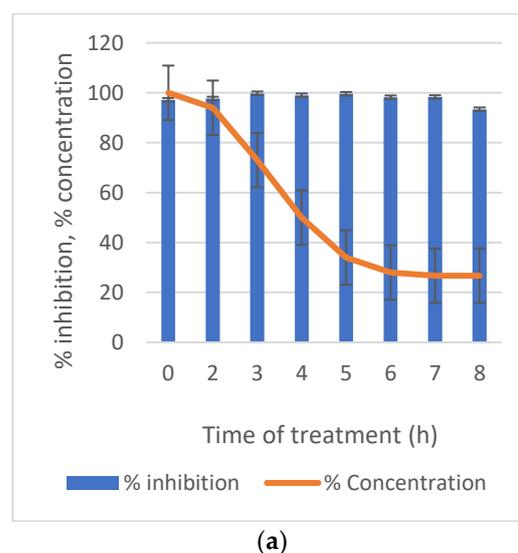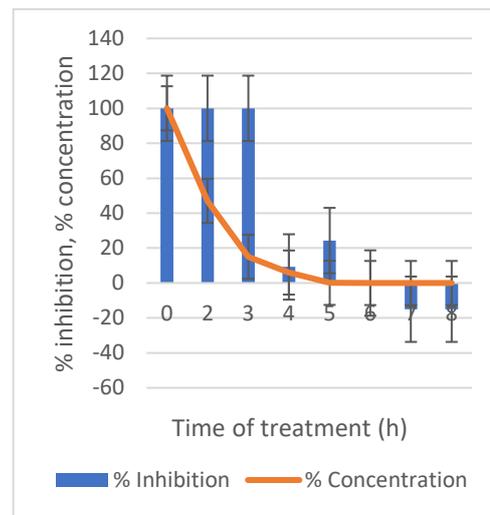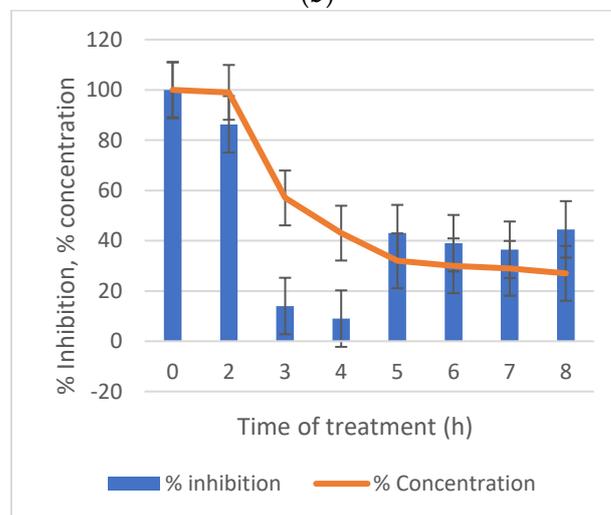

(a)

Figure 6. *Cont.*

(b)

(c)

Figure 6. The inhibition of light emission produced by the eight solutions of each compound, including the untreated solutions (time of treatment = 0). (**a**) TBA, (**b**) IMI, (**c**) AZO.

Apart from TBA, for which inhibition never decreased significantly, interesting behaviors can be observed. After 4 h of treatment, a sudden reduction in IMI toxicity from 100% to 6% occurred. The negative inhibition values produced by the last three samples indicate that the photoproducts slightly stimulate the wellness of the bacteria, most probably acting as a supplementary carbon source. A significant drop in AZO toxicity occurred after 3 h of treatment (from 83% at 2 h to 14%). Surprisingly, AZO solutions treated for a longer time (5–8 h) partially recovered their toxicity (39%). This result confirmed the partial toxicity represented in Figure 5c, and we can hypothesize that the photoproducts obtained at those times were more toxic than the previous ones.

3.3.2. The Algal Growth Inhibition Assay

The effects of the pesticide solutions on the microalgae growth rate appeared, as expected, different from those on bacteria and, in some cases, more complicated to interpret. The sensitivity of these organisms is surely lower than that of bioluminescent bacteria, and all solutions, treated or not, took the same, quite long, time to influence their growth (Figure 7). At the start of the experiment and still after 4 days of contact, the optical density in the samples (defined as the absorbance at 545.6 nm) and the controls were very similar. Stopping the experiment at 72 h, as frequently done, these compounds could

be declared nontoxic. However, after 6 days of contact, the controls continued to grow, whereas all the samples of IMI and TBA (Figure 7a,c) produced a variable drop in the microalgae population. The effect of the various IMI samples was practically the same, i.e., concentration independent. On the contrary, the effects of the herbicide were more specific and dependent on its concentration, and this effect was more evident after 4 days of contact. It was not possible to define a clear toxic effect of AZO solutions at all times, since the counts of samples and controls were in the same range even after 6 days from the beginning, indicating this fungicide as a not harmful compound to these organisms.
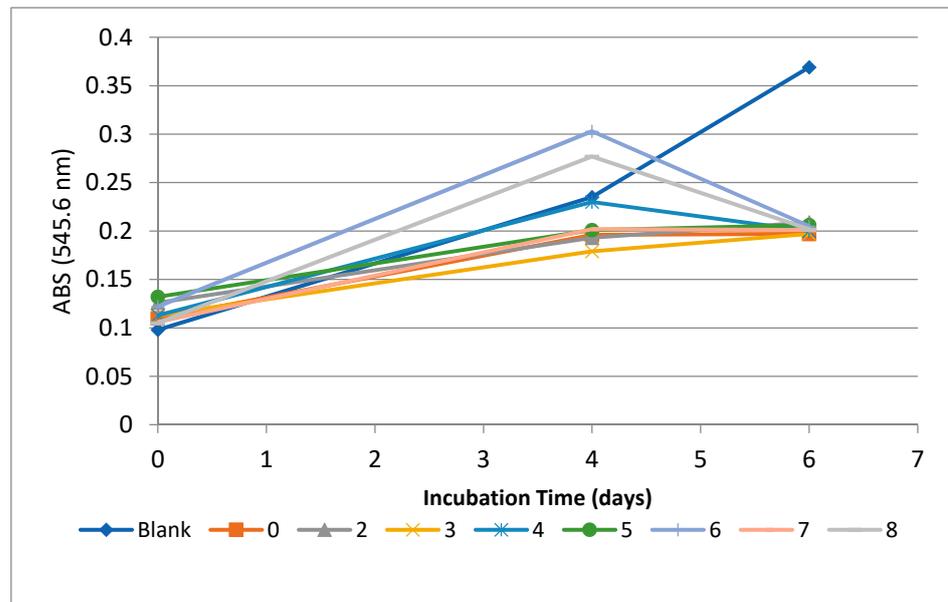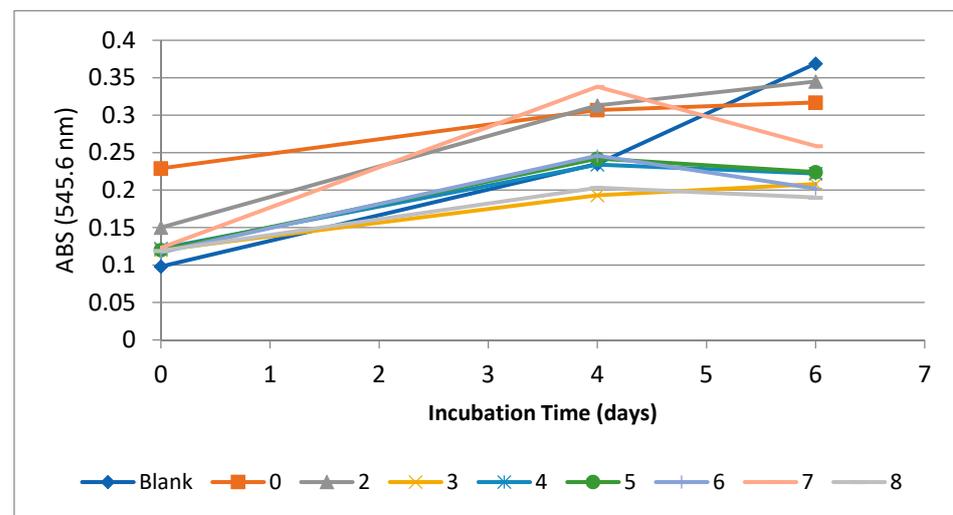

(**a**)
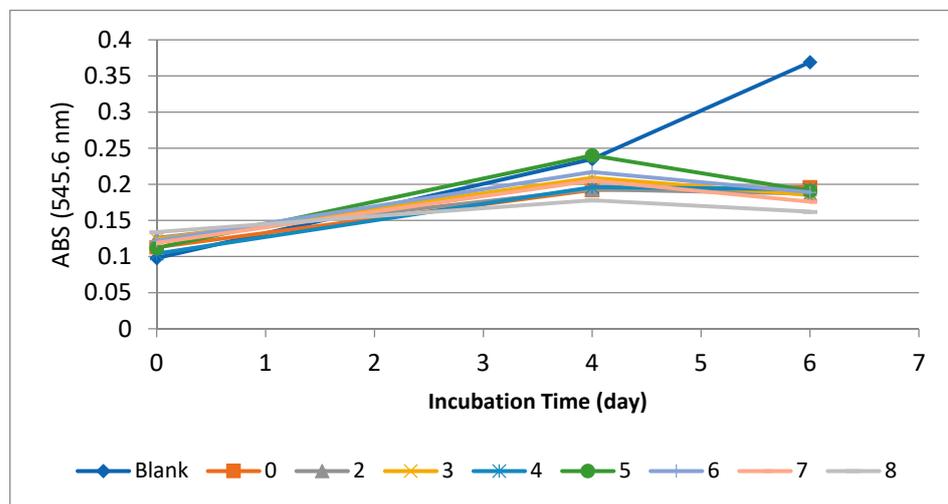
(**b**)

Figure 7. *Cont.*

(**c**)

Figure 7. The absorbance values were recorded for the microalgae populations in contact with the various solutions (0–8) and for the control (blank) immediately after the preparation of the samples–algae mixture (incubation time = 0) and after 4 and 6 days. (**a**) TBA, (**b**) IMI, (**c**) AZO.

4. Discussions

Nowadays, the general awareness about the incalculable damages produced by agro-chemicals on all living beings imposes that we take reasonable precautions to ensure that the storage, handling, and disposal of these products do not endanger further human health or the environment. Nevertheless, each crop requires various treatments, and a direct consequence of any phytosanitary treatment is, among others, the generation of a pesticide containing a volume of agro-wastewater from the remnants and rinsing of the treatment machinery. In most cases, the fate of unused tank mixes is to be simply disposed of on the soil of treated fields or at the farm area, since the several developed alternatives to correctly treat these waste results are expensive and time (and space)-consuming, or the threat posed by this action is not completely understood. Efficient, more applicable, and flexible methods are in demand.

To promote the degradation of pollutants by the oxidation of the organic compound is a powerful solution actually applied mainly to the treatment of wastewaters. Among the various possibilities offered by the advanced oxidation processes, we selected one of the most used in its simpler and possibly cheaper formulation, the UV promoted oxidation supported by the addition of hydrogen peroxide as the hydroxyl radicals' source, in a portable, flexible format.

We assembled a photodegradation cell able to contain and treat most parts of the remnant volumes from spraying activities or leftover pesticide waste. The use of this device is elementary; it must simply be filled and connected to the electric power. Its size make it easily transportable and the costs are really reduced. The cost of purchasing it is in the range of €3000–4000 and the maintenance costs concern the substitution of the exhausted UV lamp, in addition to the electric power consumption. Such costs can be supported by any farm, even one of reduced dimensions, and this device can become a small but effective facility, located exactly where the wastewater detoxification is required.

By using the commercial formulation of pesticides with different degrees of suscep-tibility to mineralization, the tap water to prepare the solutions, and the concentrations usually present in the spray-tank washing volumes, we exactly simulated the scenario occurring at farms and planned a suitable treatment time, long enough to be effective but no too long so as to be practically unacceptable.

The chemical determination of the pollutants' degradation and of the mineralization rate was coupled to biological evaluations aimed at determining if the degradation actually

resulted in a reduction of the toxic effects on the environment, confirming the effectiveness and usefulness of the device.

The disappearance of the active ingredient can have completely different kinetics with respect to the reduction of the organic matter content, that being the sensitivity of the parental compound and of its derivatives to oxidative degradation, as well as their toxicity, which are often completely independent [32–34].

The degradation of the selected compounds began immediately, except for the fungicide, whose concentration was reduced later than 2 h, but mineralization was not appreciable before 3 h. After 8 h, the degradation of the active ingredients was very satisfying. Overall, for the test, the mineralization rate was significantly lower and at 8 h, less than 50% mineralization had been attained, as an average value. In particular, the photoproducts of TBA are known to be recalcitrant to mineralization [45,46], and this compound was selected just to simulate the worst working conditions. Additionally, the results obtained for the imidacloprid were in agreement with the literature data reporting the formation of several photoproducts during the degradation process of IMI, mainly the well-known 6-chloronicotinic acid, which slows down the mineralization process [25,47].

Nevertheless, these results can be considered extremely positive, and they already seem to offer useful indications for the correct use of the device as such. Indeed, the photoproducts are often more prone to bio- or phytodegradation than their parent compounds, for which fragmentation promotes the different inherent water remediation processes.

It was known that photocatalytic or even more powerful techniques must be applied to obtain exhaustive mineralization processes, but these also increase, in parallel, the costs and/or the skills required to carry out these procedures. Moreover, the complete mineralization of organic pollutants is not always necessary. It is not rare that degradation intermediates show higher biotoxicity than the parental compound [47], suggesting that avoiding the presence of these compounds in the environment (blocking them before they reach soil or water) is the only solution. For example, the toxicity of the fungicide collapses after three hours of treatment, corresponding to a drastic increase in both the degradation and mineralization of the parent compound. However, after four hours, toxicity partially resumes and no longer subsides until the test is complete. It is interesting to note that in precisely the vicinity of the fourth hour and, above all, of the fifth hour, the degradation and mineralization curves of the compound diverge, albeit slightly. It could not be excluded that, from that moment on, a toxic product reluctant to mineralization was formed. The use of the device for AOPs for 3–4 h seems to be preferable both to shorter and longer times (within the limits of what has been tested in this work).

On the other hand, Imidacloprid shown still the 100% toxicity at 3 h, changed to less the 10% after 4 h of treatment. Nevertheless, the IMI concentration was not so different among 3 and 4 h and in both cases very low. It is possible to imagine that the photoproduct(s) retaining the toxic effect underwent definitive degradation only at 4 h, whereas the organic content was still high (low mineralization rate). Additionally, in this case seems that the optimal effect of the device takes place in 4 h.

The assessment of the post-treatment toxicity by the highly sensitive *Vibrio fisheri* test revealed that in only one case, the TBA, did treated and untreated solutions show the same inhibition effect. The difficulties encountered in removing this compound, or better, its derivatives, surely represent a serious, but fortunately not so frequent, obstacle in wastewater remediation.

A detectable impact of the agrochemical solutions on the freshwater microalgae population was observed only after a rather long contact period (144 h). It must be underlined that, for the most part, this kind of assay collects data for shorter periods (72–96 h). In this case, our samples should be considered as not harmful to these organisms.

In conclusion, it is possible to affirm that the overall performance of this first version of the photodegradation portable cell was positive, even though the pollutants' concentration/pH/H_2O_2 ratios were not the optimal ones, which can be employed in laboratory studies to maximize the degradation yields.

Further improvements of the prototype are under study, such as the application of an accessory to mix the solution during the treatment and to enhance the homogeneity of the UV rays' absorbance in the whole volume.

The results obtained from the current studies must be confirmed on a wider selection of agrochemicals and on a mixture of different compounds and organic pollutants to ascertain the effectiveness and feasibility of this device in various conditions and indicate the possibility for scaling it for different applications. The use of the studied device could also improve crop management in terms of bioeconomy, thanks to the increased possibility of recovering contaminated washing water for other agronomic uses [48].

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References

1. De Wilde, T.; Spanoghe, P.; Debae, C.; Ryckeboer, J.; Springael, D.; Jaeken, P. Overview of on-farm bioremediation systems to reduce the occurrence of point source contamination. *Pest Manag. Sci.* **2007**, *63*, 111–128. [CrossRef]
2. Boyd, A.; Ridout, C.; O'Sullivan, D.M.; Leach, J.E.; Leung, H. Plant–pathogen interactions: Disease resistance in modern agriculture. *Trends Genet.* **2013**, *29*, 233–240. [CrossRef]
3. Duru, M.; Therond, O.; Martin, G.; Martin-Clouaire, R.; Magne, M.A.; Justes, E.; Journet, E.P.; Aubertot, J.N.; Savary, S.; Bergez, J.E.; et al. How to implement biodiversity-based agriculture to enhance ecosystem services: A review. *Agron. Sustain. Dev.* **2015**, *35*, 1259–1281. [CrossRef]
4. Sakadevan, K.; Nguyen, M.-L. Chapter Four-Livestock Production and Its Impact on Nutrient Pollution and Greenhouse Gas Emission. *Adv. Agron.* **2017**, *141*, 147–184.
5. FAO. World Food and Agriculture—Statistical Pocketbook 2020. Rome. Available online: https://doi.org/10.4060/cb1521en (accessed on 16 March 2021).
6. Viessman, W., Jr.; Hammer, M.J. *Water Supply and Pollution Control*, 6th ed.; Addison Wesley Longman Inc: Boston, CA, USA, 1998; pp. 876–885.
7. Breach, R.A. UK experiences in developing a catchment scale, risk based, approach to mitigating all routes for pesticide loss to water. In *Proceeding of the International Advances in Pesticide Application, Robinson College, Cambridge, UK, 9–11 January 2008*; Alexander, L.S., Carpenter, P.I., Cooper, S.E., Glass, C.R., Gummer Andersen, P., Magri, B., Robinson, T.H., Stock, D., Taylor, W.A., Thornhill, E.W., Eds.; Association of Applied Biologists: Wellesbourne, UK, 2008; pp. 353–356.
8. Shen, C.; Yang, X.; Wang, Y.; Zhou, J.; Chen, C. Complexation of capsaicin with β-cyclodextrins to improve pesticide formulations: Effect on aqueous solubility, dissolution rate, stability and soil adsorption. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *72*, 263–274. [CrossRef]
9. Briggs, J.A.; Riley, M.B.; Whitwell, T. Quantification and remediation of pesticides in runoff water from containerized plant production. *J. Environ. Qual.* **1998**, *27*, 814–820. [CrossRef]
10. Vischetti, C.; Capri, E.; Trevisan, M.; Casucci, C.; Perucci, P. Biomassbed: A biological system to reduce pesticide point contamination at farm level. *Chemosphere* **2004**, *55*, 823–828. [CrossRef]
11. Grella, M.; Miranda-Fuentes, A.; Marucco, P.; Balsari, P. Field assessment of a newly-designed pneumatic spout to contain spray drift in vineyards: Evaluation of canopy distribution and off-target losses. *Pest Manag. Sci.* **2020**, *76*, 4173–4191. [CrossRef]
12. Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides (Text with EEA relevance). *OJ L 24.11.* **2009**, *309*, 71–86. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32009L0128 (accessed on 16 March 2021).
13. Vischetti, C.; Monaci, E.; Coppola, L.; Marinozzi, M.; Casucci, C. Evaluation of BiomassBed system in bio-cleaning water contaminated by fungicides applied in vineyard. *Int. J. Environ. Anal. Chem.* **2012**, *92*, 949–962. [CrossRef]

14. Özkara, A.; Akyıl, D.; Konuk, M. Pesticides, environmental pollution, and health. In *Environmental Health Risk-Hazardous Factors to Living Species*; Larramendy, M.L., Soloneski, S., Eds.; IntechOpen: London, UK, 2016. [CrossRef]

15. Jouy, L.; Moquet, M.; Yème, P.-V. Rinçage et lavage du pulvérisateur: Au champ ou à la ferme, bien gérer ses effluents phytosanitaires. *Perspect. Agric.* **2009**, *354*, 34–42.

16. Fait, G.; Nicelli, M.; Fragoulis, G.; Trevisan, M.; Capri, E. Reduction of point contamination sources of pesticide from a vineyard farm. *Environ. Sci. Technol.* **2007**, *41*, 3302–3308. [CrossRef] [PubMed]

17. Vagi, M.C.; Petsas, A.S. Recent advances on the removal of priority organochlorine and organophosphorous biorecalcitrant pesticides defined by Directive 2013/39/EU from environmental matrices by using advanced oxidation processes: An overview (2007–2018). *J. Environ. Chem. Eng.* **2020**, *8*, 102940. [CrossRef]

18. Acero, J.L.; Real, F.J.; Benitez, F.J.; Matamoros, E. Degradation of neonicotinoids by UV irradiation: Kinetics and effect of real water constituents. *Sep. Purif. Technol.* **2019**, *211*, 218–226. [CrossRef]

19. Zheng, Q.; Wang, L.; Chen, B.; Chen, Y.; Ma, Y. Understanding and modeling the formation and trasformation of hydrogen peroxide in water irradiated by 254 nm ultraviolet (UV) and 185 nm vacuum UV (VUV): Effects of pH and oxygen. *Chemosphere* **2020**, *244*, 125483. [CrossRef] [PubMed]

20. Reddy, P.V.L.; Kim, K.-H. A review of photochemical approaches for the treatment of a wide range of pesticides. *J. Hazard. Mater.* **2015**, *285*, 325–335. [CrossRef]

21. Rozas, O.; Vidal, C.; Baeza, C.; Jardim, W.F.; Rossner, A.; Mansilla, H.D. Organic micropollutants (OMPs) in natural waters: Oxidation by UV/H2O2 treatment and toxicity assessment. *Water Res.* **2016**, *98*, 109–118. [CrossRef]

22. Fenoll, J.; Garrido, I.; Flores, P.; Hellín, P.; Vela, N.; Navarro, G.; García-García, J.; Navarro, S. Implementation of a new modular facility to detoxify agro-wastewater polluted with neonicotinoid insecticides in farms by solar photocatalysis. *Energy* **2019**, *175*, 722–729. [CrossRef]

23. Díez, A.M.; Sanromán, M.A.; Pazos, M. New approaches on the agrochemical degradation by UV oxidation processes. *Chem. Eng. J.* **2019**, *376*, 120026. [CrossRef]

24. Vela, N.; Fenoll, J.; Garrido, I.; Pérez-Lucas, G.; Flores, P.; Hellín, P.; Navarro, S. Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse. *Sci. Tot. Env.* **2019**, *660*, 923–930. [CrossRef]

25. Kitsiou, V.; Filippidis, N.; Matzavinos, D.; Poulios, I. Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in acqueous solutions. *Appl. Catal. B Environ.* **2009**, *86*, 27–35. [CrossRef]

26. Sanlaville, Y.; Guittonneau, S.; Mansour, M.; Feicht, E.A.; Meallier, P.; Kettrup, A. Photosensitized degradation of terbuthylazine in water. *Chemosphere* **1996**, *33*, 353–362. [CrossRef]

27. Wamhoff, H.; Schneider, V. Photodegradation of imidacloprid. *J. Agric. Food Chem.* **1999**, *47*, 1730–1734. [CrossRef]

28. Lányi, K.; Dinya, Z. Photodegradation study for assessing the environmental fate of some triazine-, urea-, and thiolcarbamate-type herbicides. *Microchem. J.* **2005**, *80*, 79–87. [CrossRef]

29. Kurwadkar, S.; Evans, A.; DeWinne, D.; White, P.; Mitchell, F. Modeling photodegradation kinetics of three systemic neonicotinoids-dinotefuran, imidacloprid, and thiamethoxam-in aqueous and soil environment. *Environ. Toxicol. Chem.* **2016**, *35*, 1718–1726. [CrossRef]

30. Boudina, A.; Emmelin, C.; Baaliouamer, A.; Païssé, O.; Chovelon, J.M. Photochemical transformation of azoxystrobin in aqueous solutions. *Chemosphere* **2007**, *68*, 1280–1288. [CrossRef]

31. Katagi, T. Direct photolysis-mechanism of pesticides in water. *J. Pestic. Sci.* **2018**, *43*, 57–72. [CrossRef] [PubMed]

32. Emmi, S.S.; Caminati, S.; Castro, C.; Esposito, B.; Saracino, M.; Sconziano, S. Comparison between Ionizing and Non-Ionizing Radiation Technologies for Wastewater Remediation. Proceeding of the 1st Research Coordination Meeting on "Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters Containing Organic Pollutants", Vienna, Austria, 2–6 May 2011; pp. 82–91. Available online: http://www-naweb.iaea.org/napc/iachem/working_materials/RC-1188-1_report_complete.pdf (accessed on 16 March 2021).

33. Emmi, S.S.; Caminati, S.; Esposito, B.; Saracino, M. About the OH yield in the radiolysis of an aqueous/H_2O_2 system. Its optimisation for water treatment. *Radiat. Phys. Chem.* **2012**, *81*, 1430–1433. [CrossRef]

34. Esposito, B.R.; Capobianco, M.L.; Martelli, A.; Navacchia, M.L.; Pretali, L.; Saracino, M.; Zanelli, A.; Emmi, S.S. Advanced water remediation from ofloxacin by ionizing radiation. *Radiat. Phys. Chem.* **2017**, *141*, 118–124. [CrossRef]

35. Tasca, A.; Puccini, M.; Clematis, D.; Panizza, M. Electrochemical removal of Terbuthylazine: Boron-doped diamond anode coupled with solid polymer electrolyte. *Environ. Pollut.* **2019**, *251*, 285–291. [CrossRef]

36. Simon-Delso, N.; Amaral-Rogers, V.; Belzunces, L.P.; Bonmatin, J.M.; Chagnon, M.; Downs, C.; Furlan, L.; Gibbons, D.W.; Giorio, C.; Girolami, V.; et al. Systemic insecticides (neonicotinoids and fipronil): Trends, uses, mode of action and metabolites. *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 5–34. [CrossRef] [PubMed]

37. Morrissey, C.A.; Mineau, P.; Devries, J.H.; Sánchez-Bayo, F.; Liess, M.; Cavallaro, M.C.; Liber, K. Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review. *Environ. Int.* **2015**, *74*, 291–303. [CrossRef]

38. Bryden, J.; Gill, R.J.; Mitton, R.A.A.; Raine, N.E.; Jansen, V.A.A. Chronic sublethal stress causes bee colony failure. *Ecol. Lett.* **2013**, *16*, 1463–1469. [CrossRef] [PubMed]

39. Sanchez-Bayo, F.; Goulson, D.; Pennacchio, F.; Nazzi, F.; Goka, K.; Desneux, N. Are bee diseases linked to pesticides?—A brief review. *Environ. Int.* **2016**, *89–99*, 7–11. [CrossRef]

40. Hocinat, A.; Boudemagh, A. Biodegradation of commercial Ortiva fungicide by isolated actinomycetes from the acti-vated sludge. *Desalination Water Treat.* **2015**, *57*, 6091–6097. [CrossRef]

41. Banić, N.D.; Šojić, D.V.; Krstić, J.B.; Abramović, B.F. Photodegradation of neonicotinoid active ingredients and their commercial formulations in water by different advanced oxidation processes. *Water Air Soil Pollut.* **2014**, *225*, 1954. [CrossRef]

42. ISO 11348-3:2007. Water Quality—Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio Fischeri (Luminescent Bacteria Test). Available online: https://www.iso.org/standard/40518.html (accessed on 16 March 2021).

43. ISO 14442:2006. Water Quality—Guidelines for Algal Growth Inhibition Tests with Poorly Soluble Materials, Volatile Compounds, Metals, and Wastewater. Available online: https://www.iso.org/standard/34814.html (accessed on 16 March 2021).

44. ISO 8692:2004. Water quality–Freshwater Algal Growth Inhibition Test with Unicellular Green Algae. (Revised by ISO 8692:2012). Available online: https://www.iso.org/standard/29924.html (accessed on 16 March 2021).

45. Lányi, K.; Dinya, Z. Photodegradation study of some triazine–type herbicides. *Microchem. J.* **2003**, *75*, 1–14. [CrossRef]

46. Navarro, S.; Vela, N.; Giménez, M.J.; Navarro, G. Persistence of four s-triazine herbicides in river, sea and groundwater samples exposed to sunlight and darkness under laboratory conditions. *Sci. Total Env.* **2004**, *329*, 87–97. [CrossRef]

47. Žabar, R.; Dolenc, D.; Jerman, T.; Franko, M.; Trebe, P. Photolytic and photocatalytic degradation of 6-chloronicotinic acid. *Chemosphere* **2011**, *85*, 861–868. [CrossRef]

48. Han, B.; Kim, J.K.; Kim, Y.; Zommer, N. Treatment of wastewater for reuse with mobile electron beam plant. In Proceedings of the 1st Research Coordination Meeting on "Radiation Treatment of Wastewater for Reuse with Particular Focus on Wastewaters containing Organic Pollutants", Vienna, Austria, 2–6 May 2011; Available online: http://www-naweb.iaea.org/napc/iachem/working_materials/RC-1188-1_report_complete.pdf (accessed on 16 March 2021).