

PHOTOCATALYSIS OF SOME HERBICIDES IN WATER ENVIRONMENTAL MOLECULES

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Abstract

Research was conducted on the photocatalytic degradation of a few different herbicides belonging to distinct groups or categories. Bispyribac sodium (from the pyrimidinyloxybenzoic class), orthosulfamuron (from the sulfonylurea family), pendimethalin (from the dinitroaniline class), and fomesafen (from the diphenyl ether class) are the herbicides that have been looked into. Under the influence of direct sunshine, Milli-Q water, buffer solutions with pH 4, pH 7, and pH 9, as well as two distinct concentrations of herbicide residues, were subjected to an investigation into the photocatalytic breakdown of herbicide residues. The ZnO nanoparticles with diameters of less than 60 nm were chosen as the catalyst for the photocatalysis experiment. These nanoparticles were produced by a process involving triethanolamine and zinc acetate di hydrate. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Fourier Transformation Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), combined with Energy Dispersive X-ray analysis (EDX), and Dynamic Light Scattering (DLS) were used to characterise the nanoparticles that were obtained. The nanoparticles were found to have the form of needles, according to the findings. The nanoparticles were utilised for the application of photocatalytically breaking down pesticide residues in water using their properties.

keywords: *Photocatalysis, Herbicides, water*

INTRODUCTION

In an agroecosystem, the use of pesticides is widespread practise in order to reduce the number of pests and diseases that infest the crops and to raise the overall crop production. After they have been sprayed, these compounds have a good chance of leaching into the surrounding natural bodies through the soil. The primary purpose of herbicides is to suppress weeds, and once they have been applied to weeds, they can either become adsorbed into the soil surface, dissolve in the water that runs off of the weeds, or remain suspended as particles and be transported farther. The primary path that herbicides use to go from the location where they

were applied to many other locations is via the water run-off. The breakdown and mineralization of herbicide pollutants are considered to be the primary source of worry in the scientific community. According to research done the primary contributor to pesticide pollution is the excessive use of pesticides, as well as the by-products and intermediates that are created during the degradation process. A significant threat to public health is posed by the widespread use of crop protection chemicals in agricultural production, which can result in the contamination of surface water. In order to protect plants from weeds, pests, and fungus during agricultural production, pesticides are used extensively all over the world. However, the use of pesticides has been linked to a number of adverse health effects. According to Linder M. et al.'s research from 1995, organic compounds that are detected as pollutants in waste water need to be detoxified or decontaminated before being released into the environment. These organic chemicals might have originated from either home or industrial sources. The effect that pesticides have when they are employed in the field is dependent on their physical and chemical qualities such as adsorption, evaporation, leaching, persistence, and so on. The existence of residues of pesticides adds to the environmental water pollution. The buildup of residues in water reservoirs and other sources of water have directly affected not only the human population but also aquatic organisms. Groundwater is the most significant source of drinking water; nevertheless, the accumulation of residues has also had an effect on other sources of water. It has been demonstrated that even the presence of pesticides in minute levels may have a negative impact on the ecosystem.

Degradation by photocatalysis: the word photocatalysis refers to the combination of the processes of photochemistry and catalysis. "increase in the photoreaction in the presence of a catalyst" is how photocatalysis is technically described. Heterogeneous photocatalysis is the name given to the process when the photoreaction takes place on the surface of the catalyst. Photocatalysis is one of the most prominent techniques widely used in recent years by many researchers using semiconductor metal oxides as a photocatalyst to decontaminate the persistent organic compounds, pesticides contaminated water treatments, dye contaminated water treatments, drug contaminated water treatments, and to protect the ecosystem from the toxic contaminants. Photocatalysis is one of the most prominent techniques widely used in recent years by many researchers using semiconductor metal oxides as a photocatalyst. Researchers found that using nanoparticles with distinct physical and chemical characteristics as a catalyst in photocatalysis was more effective than using their traditional materials. This was determined by comparing the two sets of materials. It has been discovered that nanocatalysts are more effective in photocatalysis than traditional ones. This is likely because nanocatalysts have a larger surface area and a higher catalytic activity.

The use of nanoparticles of zinc oxide and titanium dioxide as photocatalysts: Because of their one-of-a-kind qualities, ZnO nanoparticles have emerged as a leading efficient catalyst in green environmental management systems. These nanoparticles have a strong oxidising ability, a large free-exciton binding energy, and operate in the near-UV spectral region. When it comes to the interaction of materials with biological systems, the size and surface area of nanoparticles, as well as other physical characteristics, have a significant influence. When opposed to traditional materials, nanomaterials have a surface that is more reactive on its own since their size has been reduced, which results in an exponential rise in surface area relative to volume. zinc oxide nanoparticles have a broad band-gap semiconductor and a significant binding energy of 60 meV when the particles are at ambient temperature. According to Yu et al.'s research from 2009, the bandgap energies of a variety of nanoparticles were included in Table (I.1). ZnO's electrical, optical, and magnetic characteristics have the potential to be enhanced at the nanoscale. ZnO is compatible with all living species and is a material that is favourable to the environment; as a result, it does not pose any threats to humans or the environment. ZnO has demonstrated much greater activity in the mineralization of byproducts and the degradation of environmental contaminants. Since ZnO's band gap energy is also 3.2 eV, which is the same as that of TiO₂, its photocatalytic capacity is practically identical to that of TiO₂. When compared to ZnO nanoparticles, the utilisation of TiO₂ is wasteful in large-scale water treatment operations.

ZnO, on the other hand, has a cost that is significantly lower than TiO₂. When compared to other semiconducting metal oxide nanoparticles, ZnO nanoparticles have the capacity to absorb more light quanta and a wider range of the solar spectrum. This is the primary benefit of using ZnO nanoparticles. In a photocatalytic process, the pollutants and pesticides are broken down into water (H₂O) and carbon dioxide (CO₂) in the presence of ZnO nano particles and reactive oxidising species such as air or oxygen. ZnO's photocatalytic activity can be understood by considering the fact that when photons of a particular wave length are incident upon its surface, electrons are promoted from the valance band. These electrons then react with the hydroxylated surface to produce OH radicals, which are the most powerful oxidising species. This phenomenon can be used to explain the photocatalytic activity of ZnO. The following equation describes the amount of energy that must be supplied in order to move an electron from the valance band to the conduction band. This energy need is determined by the band gap energy of the photocatalyst.

Equation (1) $E_{bg} = 1240/\lambda_{min}$

In the absence of sufficient electron and hole scavengers, the stored energy is wasted within a few nanoseconds by recombination. This happens when there are no suitable electron and hole scavengers. It is possible for redox reaction to take place if an appropriate scavenger or a surface defect state is present to trap the electron. This will prevent the electrons from recombining, which will allow for the possibility of redox reaction.

Materials and Methods

Chemicals and Materials

The chemicals alachlor (99.2%), acetochlor (98.6%), and metolachlor (97.9%), as well as the byproducts of their breakdown, ethane sulfonic acid (ESA) and oxanilic acid (OA), were bought from HPC Standards GmbH in Cunnorsdorf, Germany. AEROXIDE® TiO₂ P25, a sample of commercial titanium dioxide with a specific surface area (BET) of 35–65 m²/g, was acquired from Evonik Industries AG in Hanau, Germany. We acquired some commercial titanium dioxide from Precheza a.s. in Perov, Czech Republic, and it came in the form of a sample called PRETIOX® TiO₂ AV-01. It had a specific surface area (BET) of 11–15 m²/g. See the product information for AEROXIDE® TiO₂ P25 and the product information for PRETIOX® TiO₂ AV-01 for further details about the commercial titanium dioxides that were utilised.

Results

Photocatalytic Degradation of Alachlor, Acetochlor, and Metolachlor

The chloroacetanilide herbicides alachlor, acetochlor, and metolachlor were subjected to photocatalytic degradation three times under each experimental condition. The results that were reported are the averages of the measurements that were carried out during this process. The fluctuations in the concentrations of alachlor, acetochlor, and metolachlor that were observed during the various experimental configurations of the photocatalysis process are illustrated in Figure 1.

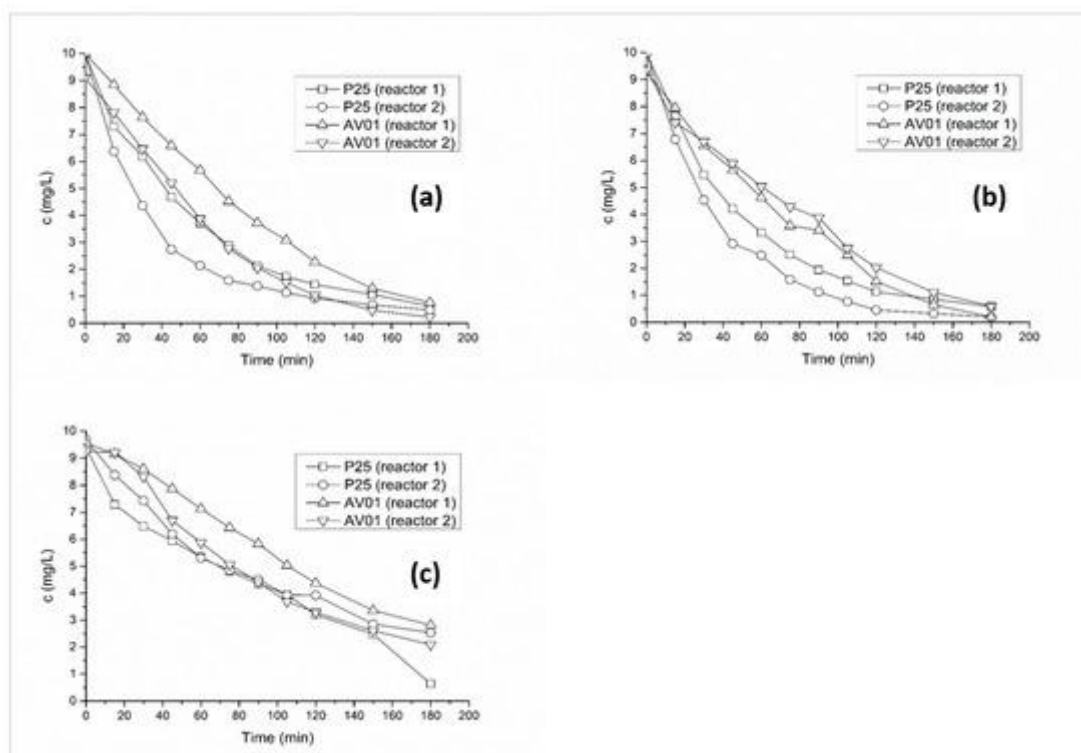


Figure 1. Changes in the concentration of the following herbicides were observed over the course of the various experimental configurations of the photocatalysis process: (a) alachlor, (b) metolachlor, and (c) acetochlor. Since there was a consistent error of less than 5% across all measurements, the error bars have been omitted from the graphs representing the data. As a direct consequence of this, the error bars are tiny in comparison to the dimensions of the plot's markers. Including error lines would result in the graphs being more difficult to understand.

The combination of the AV-01 photocatalyst and reactor R2 resulted in the greatest amount of alachlor being removed (97.5%). On the other hand, the combination of photocatalyst AV-01 and reactor R1 demonstrated a removal level of 92.4%, which is equivalent to the lowest efficiency for the degradation of alachlor. In about 180 minutes, the removal rates of 93.9% and 95.1%, respectively, were achieved by combining photocatalyst P25 with reactors R1 and R2. Reactor R1 had a reduced rate of deterioration across the board for both photocatalysts.

The combination of photocatalyst P25 and reactor R1 resulted in a removal efficiency of 93.1% for acetochlor, which was the maximum possible value. In contrast, the amount of acetochlor that was removed by using other photocatalysis experimental setups was significantly smaller. After 180 minutes of photocatalytic reaction, the amounts of acetochlor removal that were reached were 73.8%, 70.6%, and 77.4%, respectively, when the procedure was carried out using P25/reactor R2, AV-01/reactor R1, and AV-01/reactor R2, respectively. The findings that were obtained for alachlor are compatible with the findings that were obtained for the

photocatalyst AV-01, which demonstrated a slower degradation profile. On the other hand, it was found that the degradation profile of the photocatalyst P25 in reactors R1 and R2 did not exhibit any significant deviations from one another.

The combination of photocatalyst P25 and reactor R2 resulted in a removal of metolachlor that was 98.2% more effective than any other method. The combination of photocatalyst P25 with reactor R1 and photocatalyst AV-01 with reactor R2 resulted in removal levels of 95.0% and 93.7%, respectively, after 180 minutes. However, a nearly equal level of removal (97.9%) was obtained with photocatalyst AV-01 and reactor R1. When compared to acetochlor, the results obtained for the degradation profile were in the other direction. For photocatalyst P25 in reactors R1 and R2, no significant variations in the degradation profile were identified; however, for photocatalyst P25 in reactor R1, a slower degradation profile was seen.

Toxicity Evaluation

Toxicity of Single Chloroacetanilide Herbicides

An experiment with a growth inhibition test was carried out with the purpose of determining whether or not the chloroacetanilide herbicides alachlor, acetochlor, and metolachlor were hazardous to the freshwater alga *Chlorella kessleri*. After 72 hours of exposure, there was a correlation between the concentration of herbicides in the exposure medium and the growth inhibition that was observed. Figure 2 displays the estimated dose–response curves that indicate the progression of the harmful impact of alachlor, acetochlor, and metolachlor on *Chlorella kessleri*. These chemicals were used in the study. Figures S1–S3 of the Supplementary Material provide the estimated dose–response curves for each and every herbicide. These curves may be found in the Supplementary Material. Table 1 provides a summary of the predicted values of the EC50 after 72 hours, along with confidence ranges for 95%. Testing for toxicity revealed that *Chlorella kessleri* was most susceptible to alachlor (14.07 g/L), followed by acetochlor (19.13 g/L), and finally metolachlor, which resulted in toxicity that was an order of magnitude lower (115.10 g/L). The results of our study were published in the journal *Environmental Toxicology and Chemistry*. According to the findings of our study, each herbicide posed a significant threat to the freshwater alga *Chlorella kessleri*.

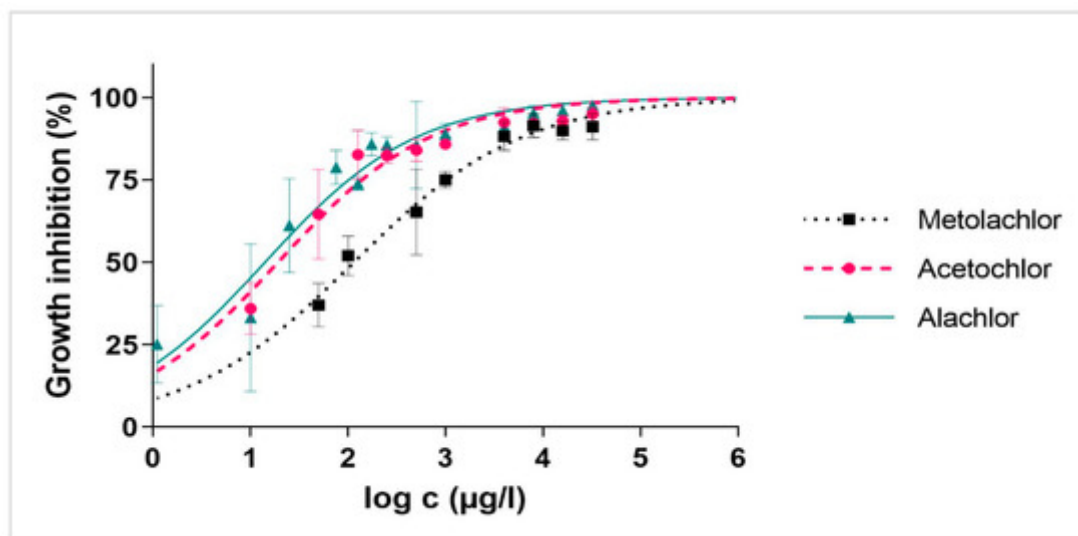


Figure 2. After exposure for a period of 72 hours, an estimation of dose–response curves was performed to describe the toxicity of chloroacetanilide herbicides to *Chlorella kessleri*.

Table 1. When *Chlorella kessleri* was treated to chloroacetanilide herbicides for 72 hours, the following are the estimated values in micrograms per litre for the EC50: included are confidence ranges for 95% of the results.

Chloroacetanilide Herbicide	Metolachlor	Acetochlor	Alachlor
72 h EC ₅₀ (µg/L)	115.10 (86.19–148.50)	19.13 (13.25–25.71)	14.07 (9.59–19.66)

EC50—concentration inducing 50% effect growth inhibition.

An experiment called a growth inhibition test was used to determine the level of toxicity that mixes of herbicides and the products of their photocatalytic breakdown had after being exposed to light for 0 to 180 minutes. Figure 3 illustrates the dependences of the inhibition at various stages throughout the photocatalysis in comparison with the average efficacy of the photocatalysis and the concentration of herbicides used in the experiments. The graphs were constructed using the average findings obtained from each distinct photocatalysis modification, which can be found published in the supplementary material (see Figures S4–S6).

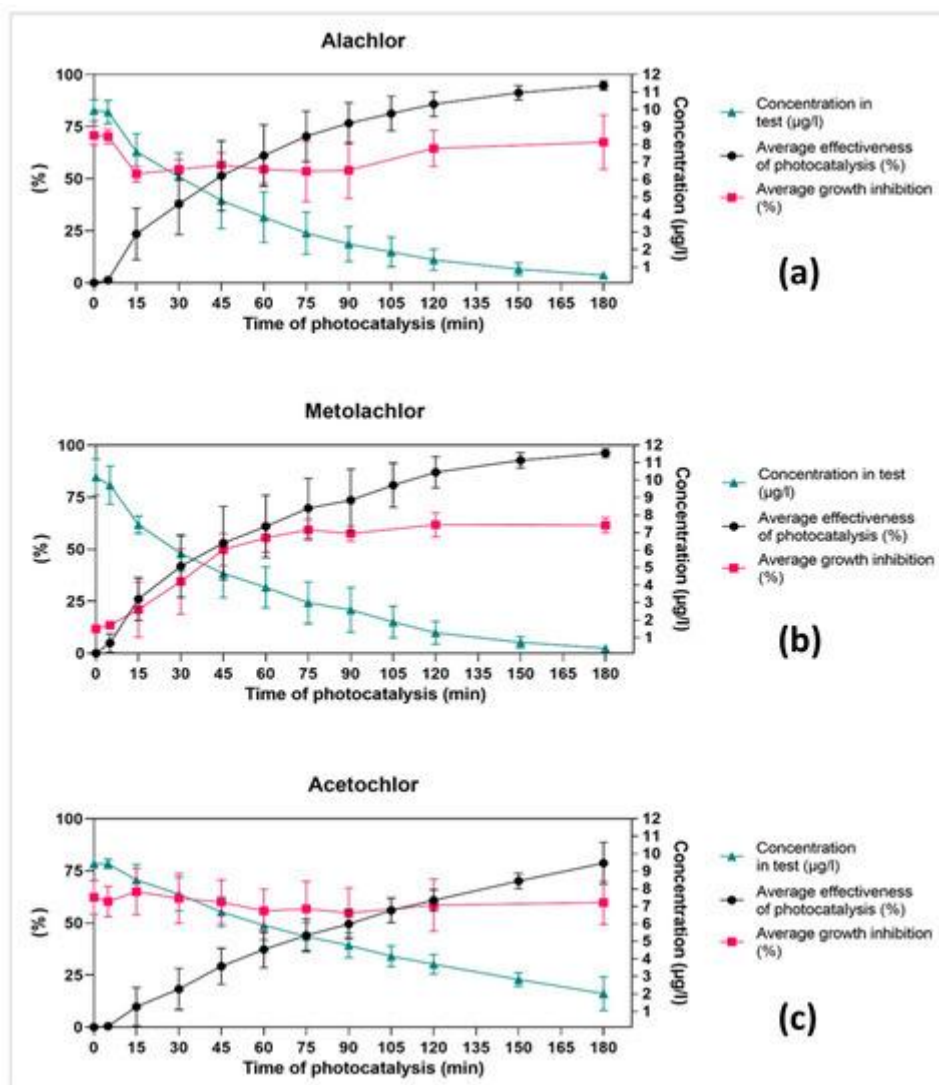


Figure 3. The average growth inhibition (%) of *Chlorella kessleri* exposed to a mixture of herbicides and their photocatalytic degradation products collected at different photocatalysis times (a point at 5 min represents the time of photocatalyst contact with herbicides, but without irradiation) in comparison with the average photocatalysis effectiveness and herbicide concentration in tests (right axis): (a) alachlor, (b) metolachlor, (c) acetochlor.

In this experiment, we anticipated a decline in toxicity in proportion to the amount of herbicide present in the exposure medium. At the beginning of the photocatalysis process, the concentrations of herbicides were at the level that corresponds to the EC50 for alachlor and acetochlor, and they corresponded to the EC25 for metolachlor. After 72 hours, there was no correlation between the growth inhibition and any of the herbicide concentrations found in the exposure conditions (Figure 3). The toxicity of combinations of herbicides and the products of their photocatalytic degradation rose (in the case of metolachlor and acetochlor), remained the

same (in the case of alachlor), or somewhat dropped and subsequently increased (in the case of alachlor). This was the case even though the concentrations of all herbicides fell during photocatalysis. The herbicide concentration or toxicity was unaffected by the catalyst even in the absence of irradiation (5 minutes). As can be seen in Figure 4, after 60 minutes of photocatalysis, each of the three herbicides had essentially the same level of toxicity. After 180 minutes of photocatalysis, the alachlor product combination that is the most dangerous to humans remained. It is conceivable that the experimental design of photocatalysis resulted in the production of chemicals other than the observed ethane sulfonic acids and oxanilic acids. These compounds impact the growth of algae more than primary herbicides.

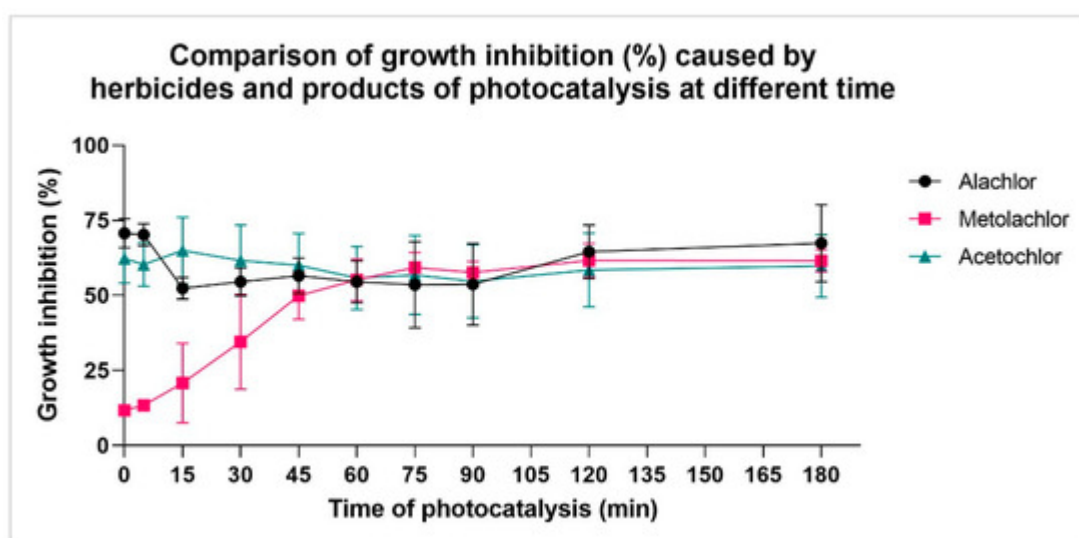


Figure 4. The average percentage of growth inhibition caused in *Chlorella kessleri* when it was subjected to a combination of herbicides and the products of their photocatalytic breakdown collected at various times during the photocatalysis process.

Discussion

Heterogeneous photocatalysis with TiO₂/UV is one of the most promising approaches for fighting environmental pollution with extremely stable organic molecules. This method uses photocatalysis. Because of its great photocatalytic stability, chemical inertness, low cost, and safety for both humans and the environment, titanium dioxide is regarded to be very near to a perfect semiconductor for use in photocatalysis. During the process of photocatalysis, TiO₂ itself does not alter in any way, in contrast to other semiconductors like ZnO, CdS, and GaP, which can dissolve and generate poisonous by-products during this stage of the reaction. As a consequence of this, the photocatalyst may be regenerated for continued usage with no appreciable reduction in the amount of catalytic activity it possesses. Studies on recyclability

revealed that photocatalysts based on TiO₂ may be effectively reused in a number of different photocatalysis cycles.

The fact that heterogeneous photocatalysis did not require any consumable chemicals led to a significant reduction in the amount of material used and made the process considerably easier to carry out. Furthermore, because the contamination is highly attracted to the surface of the photocatalyst, the degradation process will continue even at extremely low concentrations of the contaminant. This is because the photocatalyst acts as a magnet for the contaminant. As a consequence of these benefits, the resulting technology has a cheap cost, is kind to the environment, and has a high treatment efficiency.

Direct photolysis has been demonstrated to be an effective method for the degradation of chloroacetanilide herbicides. When compared to direct photolysis, the decay rate of alachlor was dramatically accelerated when it was subjected to photocatalysis using TiO₂, as was observed. This is most likely owing, in a significant part, to the presence of a photocatalytic route that is parallel to, or extra to, the one that is used for direct photolysis.

According to the findings of our research, photocatalytic degradation of chloroacetanilide herbicides in water by the use of TiO₂/UV looks to be a successful technique. The effectiveness of photocatalytic degradations varied, despite the fact that our approach was successful in eliminating all of the chosen herbicides. When viewed from this angle, the results that were obtained with metolachlor and alachlor were the most favourable. It has been reported in the past that a batch reactor containing P25 at a concentration of 90 mg/l and UV-A may be used for the photocatalytic degradation of an aqueous solution containing 5 mg/l of metolachlor. After an irradiation time of sixty minutes, there was an 88% increase in the removal efficiency. It was reported that employing TiO₂ nanoparticles as a photocatalyst to remove alachlor at UV-C wavelengths resulted in the highest possible removal efficiency of 98.44%. It has been claimed that a photocatalytically aided ozone procedure with commercial P25 and synthesised TiO₂ as photocatalysts may remove even one hundred percent of the chemical metolachlor.

On the other hand, the degradation of acetochlor was typically less effective, and the percentage efficiency of removing acetochlor at the conclusion of the experiment (180 min) was, on average, 20% lower compared to the removal of alachlor and metolachlor. This conclusion may be reached by considering the various rates of breakdown that occur throughout the process of photocatalysis. over the first 90 minutes of the irradiation time, the rate of degradation of alachlor and metolachlor was much higher than it was over the following 90 minutes, when the rate of degradation steadily declined. On the other hand, the rate of acetochlor degradation remained constant throughout the duration of the irrigation process. The relationship between the amount of material removed and the amount of time exposed to irradiation was almost

linear. This phenomena occurred regardless of the experimental configuration that was being employed. In light of this fact, extending the amount of time spent undergoing irradiation may lead to an increase in the amount of acetochlor that is successfully removed.

The most often documented metabolites emerging from the breakdown or mineralization of chloroacetanilide herbicides are ethane sulfonic acid and oxanilic acid. Both of these acids are sulfonic acids. Additionally, ethane sulfonic acid is the most prevalent transformation product of chloroacetanilide herbicides that may be discovered in soil. Even though the quantities of these compounds in irradiated samples were monitored by the HPLC-MS-MS method, which allowed for the monitoring of concentration levels in nanograms per litre, none of the compounds were found because their concentrations were below the limit of detection. This is because the method allowed for the monitoring of concentration levels in nanograms per litre. According to these findings, ethane sulfonic acid and oxanilic acid were not the primary compounds that resulted from the breakdown of chloroacetanilide herbicides over the course of this research.

The current investigation made use of two different types of TiO₂ that are currently on the market as photocatalysts. P25 is a well-characterized material with high photocatalytic activity. It consists of the anatase and rutile phase (80:20 or 70:30), and it is the material that is considered to be the gold standard in the field of photocatalytic processes. It was discovered that P25 has stronger photocatalytic activity compared to the other TiO₂ photocatalysts that are available for purchase on the market. This is because P25 TiO₂ has a structure that is a mixture of many types. It was discovered that the rutile phase does not exist as an overlayer on the surface of the anatase particle, but rather that it exists independently from the anatase particles. It has been previously reported that P25 can be used as a photocatalyst for the photocatalytic degradation of both alachlor and metolachlor. On the other hand, AV-01 is an anatase form of titanium dioxide. This type of titanium dioxide is most commonly seen in paints, but it may also be utilised for the colouring of rubber mixes or for direct injection into paper pulp. In the current investigation, a commercial TiO₂ AV-01 was used for the first time as a photocatalyst for the first time. This particular material was chosen in light of the general consensus that the anatase phase of TiO₂ possesses the highest degree of photoactivity. Because of this, we reasoned that it was possible for AV-01 to function as a photocatalyst. Because the degradation of chloroacetanilide herbicides that was carried out with AV-01 and P25 was comparable, and no significant changes were identified between the two, this hypothesis was proven to be correct. In addition, much like P25, AV-01 is a non-hazardous compound that can be purchased in stores and is quite affordable. The growth inhibition test with *Chlorella kessleri* provided conclusive evidence that neither AV-01 nor P25 are hazardous to the organism. The inclusion of photocatalysts into the primary reaction solution did not result in an increase in the level of

toxicity that was detected, as there was not a discernible shift in the proportion of growth that was inhibited.

In addition to this, the influence of the reactor on the deterioration was investigated. It was hypothesised that increasing the amount of irradiated surface area in reactor R2 would result in improved degradation efficiencies. This would be due to an increase in the amount of photons coming into contact with the photocatalyst. Although reactor R2 had a better degradation efficiency compared to reactor R1 in the majority of the trials that were carried out, in other instances, the degradation profile was the same in both reactors. This was the case in some of the cases. During the process of photocatalysis, the inhomogeneity of the reaction solution can be to blame for this. Because reactor R2 had a rectangle cross-section rather than reactor R1's square cross-section, it is possible that the catalyst was not evenly distributed throughout the reactor. As a direct consequence of this, the number of reaction sites may be constrained.

Regarding the fact that herbicides are known to be hazardous to creatures other than the ones they are intended to kill, the scientific literature has a number of research on the herbicides' effects on aquatic organisms, including microalgae. In experiments with algae, the three toxicological characteristics that are most frequently investigated are growth rate, abundance, and biomass. There have been very few contemporary research conducted that attempt to investigate the mechanism of action.

When it comes to the EC50 values that can be discovered in the scientific literature, the values are given in the form of micrograms of herbicides per litre and can range anywhere from a single unit to hundreds of units depending on the type of alga and herbicide that was tested. It is common knowledge that algae and higher aquatic plants are more susceptible to herbicides than other aquatic organisms (like daphnids, for example), with EC50 values that are even three orders of magnitude lower. For instance, in a research involving the green alga *Raphidocelis subcapitata*, the 72-hour EC50 values for the chemicals metolachlor and acetochlor were determined to be 46 g/L and 3 g/L, respectively. These values are quite comparable to the ones we observed. In addition to this, the scientists found that the toxicity of metolachlor was significantly higher than that of acetochlor by an order of magnitude. In a different investigation, the toxicity of metolachlor was examined on *Raphidocelis subcapitata*, and the EC50 value after 48 hours of exposure was calculated to be 159 g/L. After 72 hours of exposure, the value reduced to 98 g/L. In a separate investigation with *Chlorella vulgaris*, the estimated 96-hour EC50 values for alachlor and metolachlor were 26 and 84 micrograms per litre, respectively. The values that we have experimentally identified are, as a result, consistent with those that can be found in the relevant literature.

The literature that is currently accessible has a very limited amount of information on the toxicity of pesticide degradation products. It is not very usual for these products to be evaluated, despite the fact that they are frequently found in aquatic environments and that sometimes their concentrations are even greater than those of the parent substances. In general, the toxicity of degradation products may be lower or comparable to that of the parent chemical; nevertheless, an increase in toxicity was seen in one third of the studies that were available. Several investigations, including our own, have discovered evidence of an increasing level of toxicity in the products of degradation. On the freshwater microalgae *Pseudokirchneriella subcapitata*, for instance, products of UV irradiation via simulated wastewater treatment of water containing alachlor, metolachlor, and acetochlor were evaluated. According to the findings of this research, the toxicity of the breakdown products of all three herbicides was significantly higher than that of the herbicides themselves. Another study came to a similar conclusion, reporting an increase in the toxicity of metolachlor to the marine luminescent bacterium *Vibrio fischeri* when the researchers used TiO₂ as photocatalysts. *Vibrio fischeri* was utilised in additional studies that were available to evaluate the toxicity profile of the herbicide clopyralid before and after its photocatalytic breakdown using TiO₂. These experiments were conducted using the herbicide clopyralid. The scientists found that the early stages of degradation resulted in an increasing level of toxicity, which they ascribe to the gradual production of intermediates that were more toxic than the parent molecule or to synergistic effects among the transformation products. On the other hand, as the duration spent in photocatalysis increased, the toxicity finally reduced.

Conclusions

The photocatalytic destruction of chloroacetanilide herbicides using TiO₂/UV-A is the primary focus of the present research. These herbicides include alachlor, acetochlor, and metolachlor. The findings indicate that a photocatalytic process mediated by titania is an effective method for the elimination of chloroacetanilide herbicides from an aqueous solution. As photocatalysts, two different commercial TiO₂ materials were used: P25, which is considered to be the industry standard for photocatalytic applications, and AV-01, which is being reported as a photocatalyst for the very first time. On the other hand, it was demonstrated beyond a reasonable doubt that the anatase titanium dioxide AV-01 had photocatalytic activity and may be utilised effectively in the role of a photocatalyst. Even though the greatest removal efficiency for alachlor, acetochlor, and metolachlor was 97.5%, 93.1%, and 98.2% respectively, this was not sufficient to reduce the toxicity of the compounds. First, the findings of our study demonstrated that the

freshwater alga *Chlorella kessleri* is extremely sensitive to all of the herbicides that were studied. In addition, the toxicity of the resultant herbicide mixes and the photocatalytic degradation products of the herbicides rose or stayed the same as that of the herbicide solutions used initially.

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