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DOI

[10.3390/w13233327](https://doi.org/10.3390/w13233327)

Publication date

2021

Document Version

Final published version

Published in

Water

Citation (APA)

Raashid, M., Kazmi, M., Ikhlāq, A., Iqbal, T., Sulaiman, M., & Shakeel, A. (2021). Degradation of Aqueous CONFIDOR® Pesticide by Simultaneous TiO₂ Photocatalysis and Fe-Zeolite Catalytic Ozonation. *Water*, 13(23), Article 3327. <https://doi.org/10.3390/w13233327>

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Article

Degradation of Aqueous CONFIDOR[®] Pesticide by Simultaneous TiO₂ Photocatalysis and Fe-Zeolite Catalytic Ozonation

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Citation: Raashid, M.; Kazmi, M.; Ikhlq, A.; Iqbal, T.; Sulaiman, M.; Shakeel, A. Degradation of Aqueous CONFIDOR[®] Pesticide by Simultaneous TiO₂ Photocatalysis and Fe-Zeolite Catalytic Ozonation. *Water* **2021**, *13*, 3327. <https://doi.org/10.3390/w13233327>

Academic Editors: Minghao Sui and Tian Li

Received: 15 October 2021

Accepted: 22 November 2021

Published: 24 November 2021

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Abstract: Due to the importance of water for human survival and scarcity of freshwater resources, wastewater treatment has become very important recently. Some persistent pollutants, such as pesticides, are not removed even after multiple conventional wastewater treatment techniques. Advanced oxidation processes (AOPs) are one of the novel techniques that can be used to treat these persistent compounds. Photocatalytic ozonation is a promising AOP that combines photocatalysis and ozonation for synergistic effects and faster degradation of persistent pollutants. However, usually, only a photocatalyst is used while combining photocatalysis and ozonation. In this work, both a photocatalyst and ozonation catalyst have been simultaneously used for the degradation of commercially available CONFIDOR[®] pesticide, a Bayer product with Imidacloprid as the active ingredient. TiO₂ is employed as a photocatalyst, and Fe-coated Zeolite is employed as an ozonation catalyst. The results show that the reaction rate increases by 1.4 times if both catalysts are used as compared to the use of one photocatalyst only. Almost complete removal (>99%) of pollutant is achieved after 20 min with the simultaneous use of a catalyst when imidacloprid with an initial concentration of 100 mg/L is subjected to 250 W/m² UV of a wavelength of 253.7 nm and 100 mg/h ozone, where it takes 30 min if only one photocatalyst is used. The paper also explores the effect of initial concentration, UV intensity, catalyst dose and catalyst reuse while also briefly discussing the kinetics and mechanism.

Keywords: advanced oxidation processes; photocatalytic ozonation; Fe-coated zeolite; pesticide wastewater treatment

1. Introduction

Water is a necessity for human survival. As time passed, there was a dramatic increase in the populations that led to an increase in urbanization and population concentration in urban centres, discharging untreated wastewater in natural water streams, causing water pollution. When this polluted water, even if partially treated, is consumed by the household, especially in culinary uses and drinking water, it causes serious health problems [1]. Water pollution and the scarcity of freshwater have now been recognized as serious global problems, as these affect public health and the environment. No matter what model is used for prediction, future water scarcity and pollution is a recognized fate. That is why clean “water and sanitation” has been recognized by the United Nations as

a sustainable development goal, i.e., SDG No. 6, thus targeting the delivery of this goal to all of the human population by 2030 [2]. To make the water supplies safe for domestic consumption, a lot of physical and chemical processes are employed, such as coagulation, flocculation, sedimentation, filtration, disinfection and adsorption [3]. Nevertheless, due to industrialization, the discharge of industrial effluent increases pollutant concentration, making wastewater treatment difficult and affecting the health of humans, flora and fauna adversely. To overcome these modern challenges, various novel treatment technologies have been discovered by the researchers, such as membrane technologies, Fenton processes, advanced oxidation processes (AOPs), biological treatment and nanotechnologies [3]. As per the economic survey of Pakistan, agriculture is the largest economic sector of Pakistan, contributing 19.2% to the GDP (gross domestic product) and 38.5% to the labour force, while 65–70 percent of the population depends on agriculture for livelihood. The agricultural sector of Pakistan is characterized by poor agricultural practices and the unnecessary use of pesticides, thereby increasing the discharge of pesticides such as imidacloprid, which is one of the most widely used pesticides, to freshwater sources manifold [4].

Imidacloprid is the oldest neonicotinoid pesticide and the most widely used pesticide in the world that, together with clothianidin, accounts for 85% of pesticide usage in the world. Moreover, samples of surface waters in eight countries indicate such neonicotinoid pesticides, thereby suggesting that neonicotinoid pesticides are not treated by traditional wastewater treatment methods [5]. Therefore, clothianidin pesticides belong to the class of persistent organic compounds and AOPs, a new class of wastewater treatment methods, which are quite effective in removing persistent organic compounds, seem to be a viable option for the treatment of such pesticides. Various authors have reported the successful use of AOPs for the treatment of persistent pollutants, citing the advantages such as the virtually complete degradation of persistent pollutants, acceptable energy usage, ease of concept and economic feasibility under controlled conditions [6–8]. Photocatalysis is one of the most popular AOPs that involves the application of a light radiation source (ultraviolet or visible) to activate a photocatalyst such as TiO_2 , and it has been successfully used for the degradation of persistent pesticides in wastewater [9–11]. On the other hand, many recent works utilize other AOPs, i.e., ozonation, along with Fenton ozonation catalysts such as Fe-coated particles [12–14]. Therefore, it can be inferred that combined, ozonation and photocatalysis will lead to even more increased degradation of persistent pollutants such as pesticides. Indeed, several authors have successfully shown the combined approach the works best for persistent pesticides [15,16]. There is also an instance where only the ozonation catalyst was used while treating pesticide wastewater, and the photocatalyst was ignored [17]. Research works where both photocatalyst and ozonation catalysts have been simultaneously used are rare, although some instances can be found in the literature [18,19]. Although it is not very clear whether Fe ions act as ozonation catalysts, in a recent study, Fe-coated zeolites have recently been explicitly identified to act as ozonation catalysts [20].

This being said, no such work can be found in the literature for imidacloprid to the best of our knowledge. Moreover, we also observed that most of the published works obtain analytical grade pure pesticides for treatment, whereas the treatment of actual commercially available pesticides is very limited. Therefore, the current work is the first-ever attempt to simultaneously use TiO_2 for photocatalysis and Fe-coated zeolites for ozonation in a single setup to treat wastewater based on actual commercially available imidacloprid-based pesticide CONFIDOR[®] by Bayer with imidacloprid as the active ingredient.

2. Materials and Methods

CONFIDOR[®] Pesticide was purchased from a Bayer authorized dealer. All chemicals, such as ACN, Fe Salts and Zeolite, P25 TiO_2 were procured in analytical grades from the local laboratory supplier Dawn Scientific Company. A 100 mL glass container, covered with quartz glass plate placed directly under a Quanzhiyan Electronic Co. UV lamp and on a Quanbu magnetic stirrer, was used as a reactor in which inlet for ozone from a Sterhen ozone generator and ozone traps were provided. All equipment was enclosed in a

wooden shielding box covered with aluminium foil to avoid UV loss. The schematic of the experimental setup is shown in Figure 1.

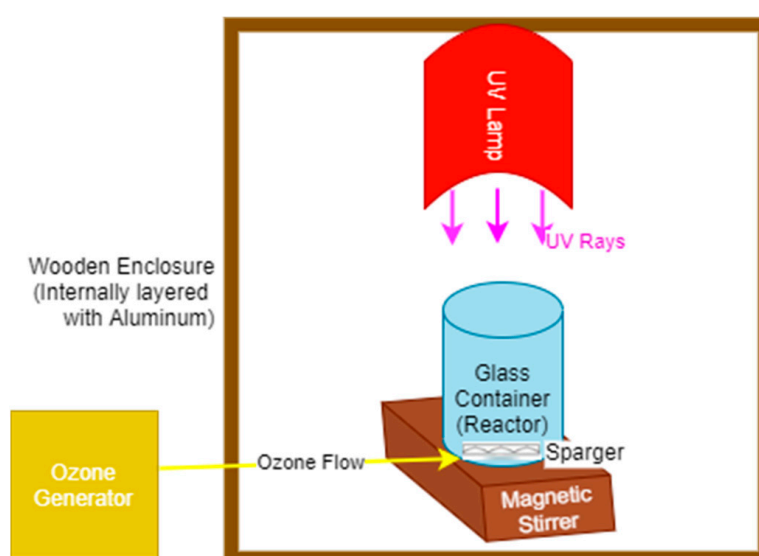


Figure 1. Experimental setup for photocatalytic ozonation.

Both the 4Å zeolite along with its properties are listed in Table 1 [12], and process loading, i.e., Fe-coating on zeolite [13], has been previously described in the literature.

Table 1. Properties of Fe-zeolite Catalyst.

Pore Size (Å)	Composition (Dry)	Thermal Decomposition (°C)	Surface Area (m ² /g)	Point of Zero Charge (pH _{pzc})
4	2Na ₂ O-Al ₂ O ₃ -1.75SiO ₂ -6H ₂ O	700	91.3	6.2 ± 0.3

The initial concentration of the samples varied between 100 and 400 mg/L, and the catalyst loading varied from 0.5 g/L to 1.5 g/L. Each run was performed for 30 min as sufficient degradation (>99%) was observed from 10 to 20 min for most of the cases. In addition to the start and end of experimentation, samples for analysis were also withdrawn after 5 min, 10 min and 20 min in case of all runs. All the samples, pre- and post-treatment, were analyzed for imidacloprid using a Shimadzu HPLC, the, Detector SPD-20A as per the method obtained by the Provincial Pesticide Reference Laboratory. The method specified the detector wavelength of 252 nm, oven temperature of 40 °C using a mixture of 60% ACN and 40% water as mobile phase in a C18 column. The initially set flow rate of the mobile phase was 1.2 mL/min, though this is adjustable so that imidacloprid is detected at around 2 min mark. All the samples were filtered from 0.2 µm filtration assembly before HPLC analysis and thereafter compared with the standard curve developed, which was of linear nature, and LOD and LOQ were calculated using statistical regression analysis and were found to be 0.0014 and 0.0043 mg/L, respectively, using the lower end data values. The main purpose of this work was to explore the benefit of simultaneous ozonation catalysts and photocatalysts. Therefore, the wavelength of the UV lamp was fixed at 253.7 nm, so it comes under the UVC classification. The lamp could be operated at three input powers of 9 W, 18 W and 27 W. A 15 W ozone generator was used to provide ozone at a flow rate of 100 mg/h with a sparger outlet. A magnetic stirrer was used with an rpm fixed at 1000 rpm, as this was the highest rpm possible without the risk of overflow and foaming. All the applicable AOPs were applied one by one for comparison. However, some additional parameter study was done, including the variation of initial concentration, catalyst dose and catalyst reuse. The data obtained from experimentation are available. All experiments

were performed at room temperature in a temperature-controlled room and neutral pH. All operations were done in an empty room for safety purposes.

3. Results

3.1. Degradation Studies

The degradation of the CONFIDOR[®] active ingredient, imidacloprid, using (i) ozone alone, (ii) UV+ Ozone with the photocatalyst and (iii) UV+ Ozone with both the photocatalyst and ozonation catalyst has been studied here. As seen in Figure 2a, imidacloprid, the active ingredient of CONFIDOR[®], degrades quite well over time. Even ozone or UV (with TiO₂) alone show the degradation of imidacloprid over time. However, improved removal was achieved through photocatalytic ozonation due to synergy. Almost 99% degradation was achieved in just 20 min, whereas if Fe-zeolite catalyst was not used and TiO₂ was used as catalyst, it took 30 min to achieve 99% degradation. All degradation studies were performed at an initial concentration of 100 mg/L of imidacloprid and 250 W/m² UVC intensity, except for ozonation alone. The photocatalyst dose of 1 g/L was used and 20% Fe-zeolite was added when both catalysts were utilized, as these were the optimum values found. All experiments were conducted in triplicate, with the average values being used for producing graphs. The percentage removal values were rounded off to three decimal places for further calculations. Moreover, the degradation efficiency of employed AOPs was significantly different at shorter intervals of time, as can be seen in Figure 2b.

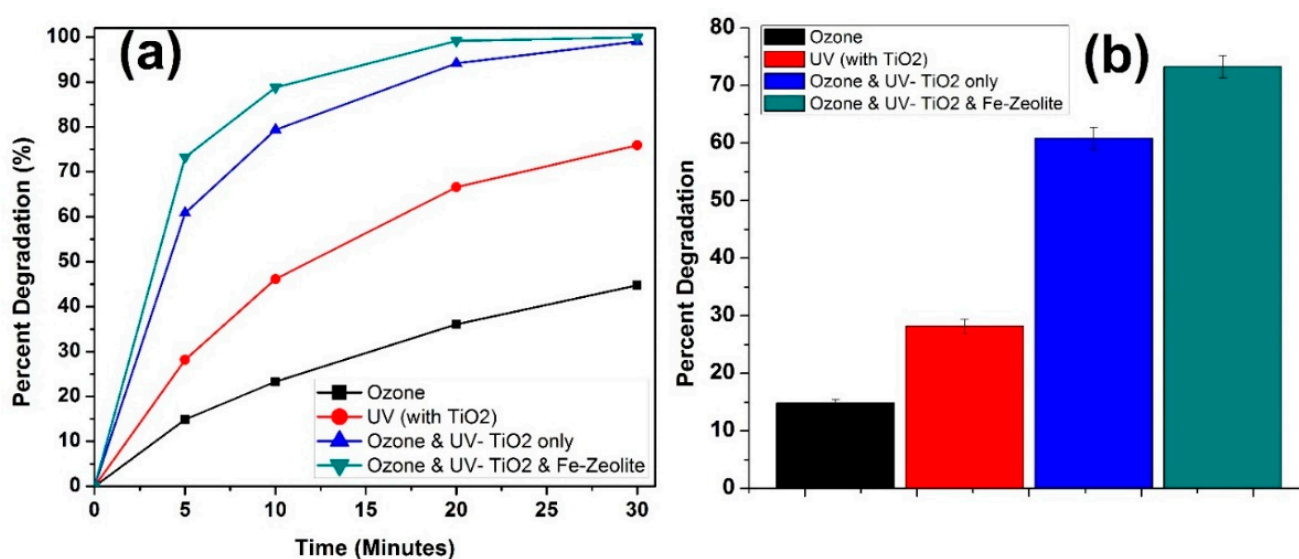


Figure 2. (a) Comparison of various AOPs for degradation of imidacloprid as a function of time, (b) percent degradation of Imidacloprid for different AOPs at a time interval of 5 min.

3.2. Effect of Initial Concentration

The degradation of the pesticide was tested at four values of initial concentrations of imidacloprid, i.e., 100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L for the combined photocatalytic ozonation process, with catalyst dose of 1 g/L with 20% Fe-zeolite while illuminated under 250 W/m² intense UVC. Figure 3 shows that almost complete removal of imidacloprid at 100 mg/L took around 20 min, whereas the time was increased to almost 30 min for 200 mg/L and imidacloprid was still present in greater quantities after 30 min in case of 300 mg/L and 400 mg/L increased initial concentrations. Therefore, the degradation of imidacloprid is decreased by increasing the initial concentration. These findings are consistent with other photocatalytic studies of imidacloprid [15,21]. Additionally, similar observations were recorded when both ozonation catalyst and photocatalyst were simultaneously used for the degradation of formaldehyde [19].

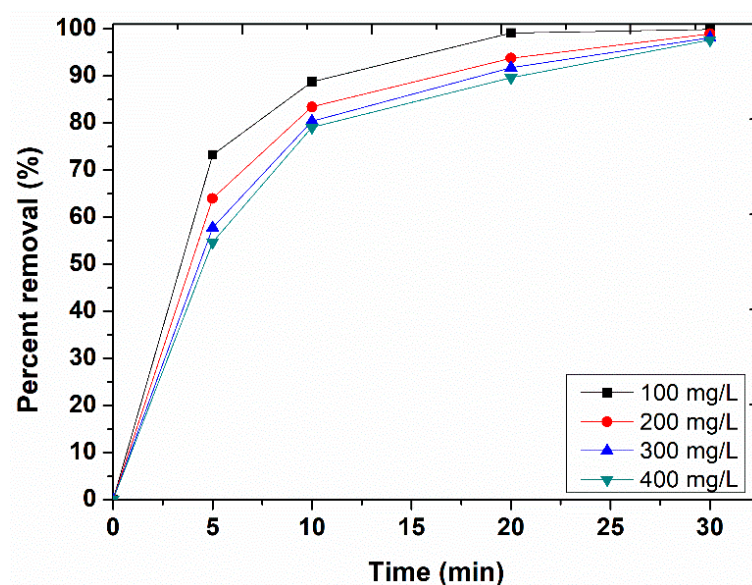


Figure 3. Effect of initial concentrations of imidacloprid on its degradation percentage by using combined photocatalytic ozonation process.

3.3. Variation of UV Intensity

The 253.7 nm UV lamp could be operated at three intensities, i.e., 125 W/m², 250 W/m² and 375 W/m², corresponding to input powers of 9 W, 18 W and 27 W, respectively. From Figure 4, it can be observed that 250 W/m² intense UV sufficiently improves the 100 mg/L initial concentrated pesticide degradation for the combined photocatalytic ozonation process with a catalyst dose of 1 g/L with 20% Fe-zeolite.

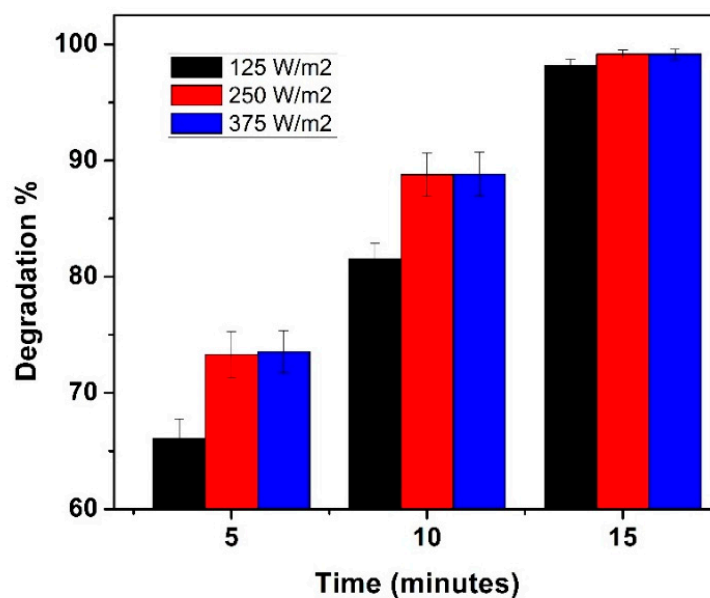


Figure 4. Comparison of pesticide degradation at different UV intensities by using combined photocatalytic ozonation process.

3.4. Effect of Catalyst Dose and Fe-Zeolite Percentage

To check the effect of the catalyst dose, a total of six combinations were studied for 20 min each with varying amounts of catalyst and percentages of Fe-zeolite, setting the initial concentration of imidacloprid at 100 mg/L and using photocatalytic ozonation while placed under the UVC source with a light intensity of 250 W/m². As evident from

Figure 5a, the optimum results were observed for the catalyst dose of 1 g/L spiked with 20% Fe-zeolite. Although all the tests were conducted for 30 min, the graph shown is for 20 min only, because after 20 min, the graphs become similar, unless zoomed to a high level. The reason being, as explained in the kinetics, is that all reactions follow pseudo-first order kinetics. Therefore, the rate of all reactions is fast at the beginning and slows down at later stages. In fact, the difference between various catalyst doses and Fe-zeolite would be more pronounced if seen at even shorter time intervals. Figure 5b shows the same comparison made at 10 min, where the advantages of the optimum catalyst dosage are more pronounced.

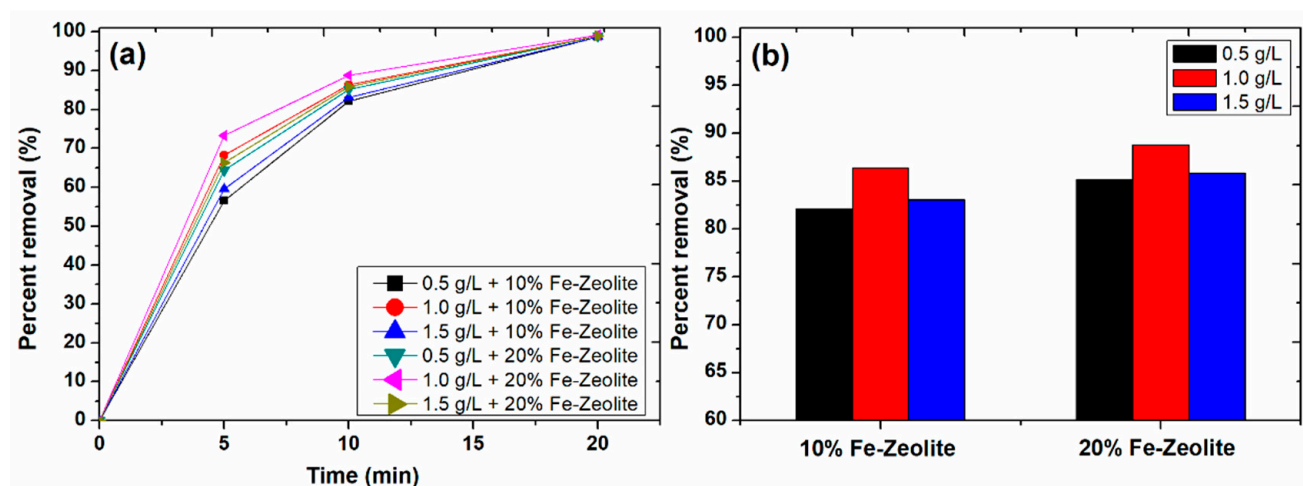


Figure 5. (a) Effect of catalyst dose and Fe-zeolite percentage on degradation of imidacloprid as a function of time, (b) percent degradation of imidacloprid using different catalyst doses and Fe-zeolite percentages at a time interval of 10 min.

3.5. Catalyst Reuse

To check the reuse of the catalyst, the TiO_2 and Fe-zeolite catalysts were washed, heated and dried based on an already established technique [22]. The initial concentration was taken as 100 mg/L, whereas the percentage of degradation was calculated after 20 min for each cycle while utilizing 250 W/m² UVC. *Prima facie*, satisfactory performance is observed (see Figure 6).

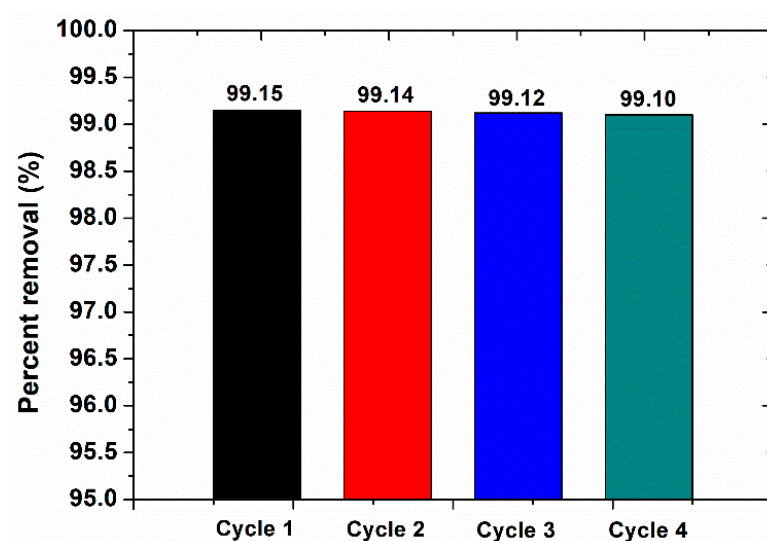


Figure 6. Catalyst reuse performance in the combined process with TiO_2 and Fe-zeolite catalyst after 20 min and 4 wash–dry reuse cycles.

4. Discussion

The reason that the quickest results were obtained for ozonation and photocatalysis (Figure 2a) is that both ozone and UV radiation attack imidacloprid molecules and degrade them at a faster speed as compared with any other technique. Therefore, a synergy exists between ozonation and photocatalysis for the treatment of imidacloprid. The degradation findings are consistent and corroborate other findings in the literature [15,21]. However, the simultaneous use of TiO₂ as a photocatalyst and Fe-zeolite as an ozonation catalyst results in even greater removal of imidacloprid, suggesting that this may be the best advanced oxidation process yet. Moreover, the performance is enhanced by simultaneous use of TiO₂ as a photocatalyst and Fe-zeolite as an ozonation catalyst, and the results are consistent with the findings for the degradation of formaldehyde and flumioxazin [18,19]. However, our work deals with imidacloprid, and it shows similar behaviour, albeit qualitatively only. The difference is more pronounced at shorter time intervals, as depicted in Figure 2b. Figure 2b compares the efficiencies of the employed AOPs at 5 min interval and depicts that the best results, i.e., an additional 20.5% benefit over the second-best technique, was obtained for the photocatalytic ozonation in presence of both TiO₂ and Fe-zeolite catalysts.

The degradation of imidacloprid is decreased by increasing its initial concentration (Figure 3), as an increased number of molecules of the pollutant take a longer time to degrade. These findings are consistent with other photocatalytic studies of imidacloprid [15,21]. Additionally, similar observations were recorded when both ozonation catalyst and photocatalyst were simultaneously used for the degradation of formaldehyde, as more pollutant removal understandably takes longer [19]. It should be noted that even higher concentrations will be degraded if the treatment time is increased. While studying the effect of UV intensity, it was seen that an increase in UV intensity leads to greater pollutant degradation (Figure 4) due to the production of more photons, as previously found as well [10]. It should also be noted that the difference between 125 W/m² and 250 W/m² is more pronounced at smaller time intervals. As time passes and degradation reactions approach completion, the gap reduces. When a higher intensity of 375 W/m² was applied, no visible progress (<1%) was observed. This suggests that the use of higher UV intensity leads to an increase in the degradation of imidacloprid but only to a certain limit. No effect of a further increase in UV intensity is explained by the fact that all the catalyst sites and available surface area are being fully utilized, so additional UV intensity does not help. The phenomenon of degradation increased with an increase in photocatalyst dosage to a certain limit (Figure 5), and thereafter the decline in performance was due to the scarcity of active particle sites and scattering of irradiation, which is also verified by literature [23]. It is also seen that increase in the amount of Fe- increases the degradation efficiency, as is consistent with literature findings for formaldehyde; however, the cited studies only explored the addition of Fe up to 5% [19]. As evident from Figure 6, even after four cycles, there was hardly any activity loss, which was measured at 0.05%, and a satisfactory degradation was observed even after four cycles for the combination of TiO₂ and Fe-zeolite.

In order to explore the kinetics, the plot of $-\ln C/C_0$ vs. time is given in Figure 7, which shows the straight lines for all techniques used with reasonable values of R².

The straight line in Figure 7 shows that the use of ozonation and simultaneous UV and ozonation, whether with the photocatalyst only or both the photocatalyst and ozonation catalyst, which all show pseudo first-order kinetics, which corroborates the works of other researchers [21,24]. The curve-fitting technique for an exponential curve was applied to identify the kinetic parameters in the equation of type:

$$\frac{C}{C_0} = e^{-\frac{t}{\tau}}$$

where t and τ are in minutes

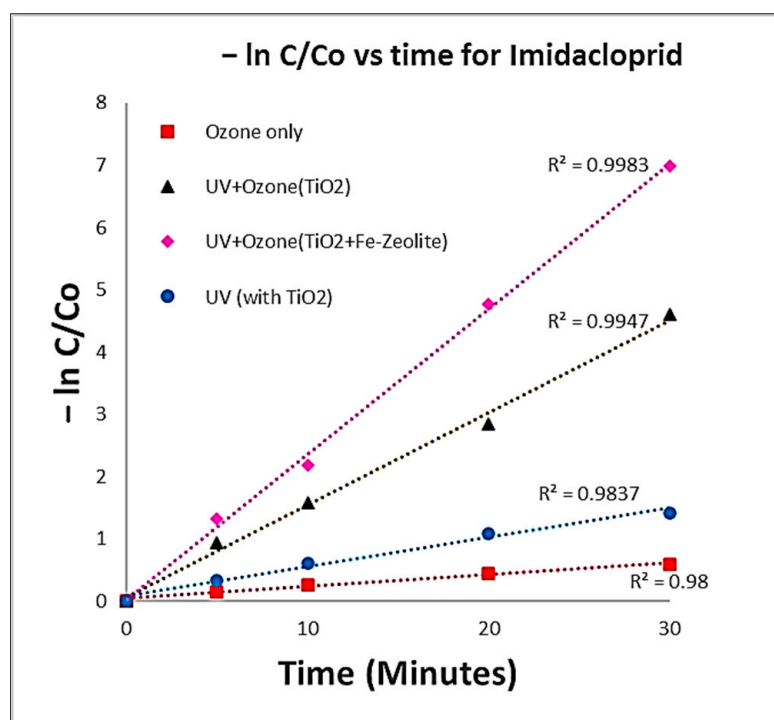
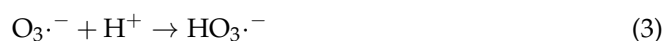


Figure 7. Kinetics of imidacloprid degradation by various AOPs. The dotted line represents the model fitting.

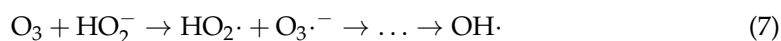
The intercept was set as 1, as it is the initial value of C/C_0 . $(1/\tau)$ was found to be 0.021 and 0.051 when only ozone and UV (with TiO_2) were used, respectively. $(1/\tau)$ increased to 0.151 when UV and Ozone were simultaneously employed in presence of TiO_2 . However, when Fe-zeolite was added as well, the value of $(1/\tau)$ elevated to 0.234. The increasing value of $(1/\tau)$ to 0.151 suggests that the photocatalytic ozonation is the better treatment method, as compared to either ozone or UV alone. However, the highest value of 0.234 was achieved with the combined use of the photocatalyst as well as the ozonation catalyst. This value of $(1/\tau)$ is almost 1.5 times greater, suggesting that this may be the fastest way to achieve degradation of persistent pollutants in a tertiary treatment setup, which is consistent with the findings for the degradation of formaldehyde [19].

The mechanism of photocatalytic ozonation has been sufficiently discussed in detail in the literature, though it is still considered to be proposed instead of definitive. The synergy observed in photocatalytic ozonation processed is owed to three factors. (1) Firstly, during photocatalytic ozonation, ozone generates $\text{OH}\cdot$ radicals on the surface of TiO_2 in a series of steps via ozonide radical, as shown in Equations (1)–(4). The use of ozone helps since ozone is a more powerful oxidizer and scavenger as compared with oxygen [25].



(2) Secondly, $\text{OH}\cdot$ radicals are be formed through ozone photolysis as well. Additionally, ozone can also react with superoxide ion radicals to form $\text{OH}\cdot$ Radicals, as shown in Equations (5)–(7) [26].

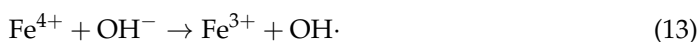
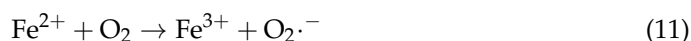




(3) Thirdly, because of the more efficient trapping of photogenerated electrons by ozone, the recombination rate of electrons and holes is minimized. In addition, superoxide radicals, resulting from the trapping of the photo-generated electrons by oxygen, can also react with ozone. These phenomena have been shown in Equations (8) and (9) [27].



Moreover, when TiO_2 is doped with Fe, this improves the trapping of electrons to inhibit electron-hole recombination during irradiation, as per Equations (10)–(13). The high performance demonstrated when adding Fe could be the result of the fact that Fe^{3+} ions can act as electron- and hole-trapping sites, thereby inhibiting the recombination of the photogenerated charge carriers and prolonging their lifetimes [28].



Finally, zeolites provide additional benefit of adsorption, albeit neither the effect nor the use of Fe itself is perceived to be very beneficial, since the very rationale of the AOPs is that these are not significantly removed by traditional means.

5. Conclusions

Pesticides are one of the most persistent pollutants that are not removed by conventional wastewater means; however, their use is necessary for improved agriculture. AOPs shows promises to remove such persistent pollutants from wastewater. Imidacloprid, one of the most widely used pesticides in the world, has been successfully treated while applying advanced oxidation processes and is commercially available in various formulations, such as CONFIDOR® by Bayer. All advanced oxidation processes employed, i.e., ozone, photocatalytic ozonation with photocatalyst only and photocatalytic ozonation with a photocatalyst as well as Fe-zeolite can remove imidacloprid. However, the quickest method is photocatalytic ozonation with a photocatalyst as well as Fe-zeolite. Most researchers do not use an ozonation catalyst when combining photocatalysis and ozonation and only use photocatalyst. This work shows that the simultaneous use of photocatalyst and ozonation catalysts results in even quicker pollutant treatment. Under the optimal conditions of 100 mg/L initial concentration of imidacloprid, 250 W/m² intensity of UV 253.7 nm and a catalyst dose of 1 g/L with 20% Fe-zeolite, imidacloprid is virtually completely removed (>99%) within 20 min of operation. Furthermore, all AOPs showed pseudo first-order reaction kinetics. It has also been observed that the degradation of pesticide increases with UV intensity and catalyst dose but only up to a certain limit, whereas increasing the initial concentration of the pesticide has a detrimental effect on the degradation percentage. Catalysts do not lose any significant activity when tested, even after four cycles. Although the setup of AOP initially costs more than traditional wastewater methods, the benefits of the treatment of persistent pollutants surely outweigh the costs and therefore, will help to achieve the United Nations' Sustainable Development Goal of Clean Water and Sanitation. Additionally, it would be ideal to evaluate the by-products of such treatment processes and evaluate their toxicity as well. It has been concluded that the photocatalytic ozonation process, while using both a photocatalyst and ozonation catalyst, showed promise in the degradation of persistent pollutants in wastewaters and therefore, combined with the process of combined catalyst use, warrants more attention.

Author Contributions: Conceptualization, M.R., M.K., A.I. and T.I.; methodology and investigation, M.R. and M.S.; data curation, M.R., M.K. and A.I.; writing—original draft preparation, M.R.; writing—review and editing, M.K., A.I., A.S., M.S. and T.I.; supervision, M.K. and A.I.; funding acquisition, M.R., M.K., A.S. and T.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the University of Engineering and Technology Lahore.

Institutional Review Board Statement: Not Applicable.

Informed Consent Statement: Not Applicable.

Data Availability Statement: All data can be made available on demand.

Acknowledgments: The authors acknowledge the support of Ali Afzal, Provincial Pesticide Reference Laboratory, Kala Shah Kaku, Punjab Pakistan and Department of Chemical, Polymer and Composite Materials Engineering, University of Engineering and Technology Lahore.

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

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