

## Article

# Degradation of Sulfoxaflor Pesticide in Aqueous Solutions Utilizing Photocatalytic Ozonation with the Simultaneous Use of Titanium Dioxide and Iron Zeolite Catalysts

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**Abstract:** Water pollution is a globally recognized serious problem that is hindering human development and societal progress. One of the most feasible methods to eliminate this problem is wastewater treatment and reuse. Emerging micropollutants, such as pesticides, are notorious for not being removed using traditional treatment methods. Therefore, novel techniques such as advanced oxidation processes (AOPs) have been proposed, among which photocatalytic ozonation is arguably the best option. Sulfoxaflor belongs to a relatively newer class of compounds known as sulfoximines and has not been studied for degradation using photocatalytic ozonation. In this work, we explore the degradation of sulfoxaflor, specifically a Dow product containing sulfoxaflor as an active ingredient using various AOPs, particularly photocatalytic ozonation. Photocatalytic ozonation has shown a synergy of 2.23 times compared to photocatalysis and ozonation alone. Fe-zeolite can improve the treatment time as an ozonation catalyst, reducing the removal time from 22 min to 18 min while reducing the electrical energy per order and electrical energy per order (EEO) from 69.5 to 42.92 kWh m<sup>-3</sup> order<sup>-1</sup>. Catalysts have been characterized using scanning electron microscopy and point of zero charge. The effects of the initial concentration, UV intensity, catalyst dose, and catalyst reuse have been studied. Moreover, the rate constants have been determined using curve fitting, and the mechanism is proposed.

**Keywords:** advanced oxidation processes; photocatalytic ozonation; Fe zeolite; pesticide wastewater treatment; sulfoxaflor



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## 1. Introduction

Water is an essential resource that is considered vital for the survival of all life. It plays an integral role in the industry, economy, agriculture, and almost all walks of life; its contribution is important for the advancement of society [1]. The demand for water has increased over time with the increasing demands of the human population. A reduction in water demand and a decrease in water supply, especially freshwater resources, can cause water shortages and droughts [2]. Nowadays, the available water is contaminated with multiple pollutants, reducing the freshwater resources, causing many diseases, and threatening public health and quality of life [3–5]. Pollution is a complex problem because it involves point, nonpoint, and anthropogenic sources [6]. The treatment of wastewater

may be a viable alternative to provide reclaimed water for ensuring sustainable water use. Therefore, wastewater treatment and reuse can arguably be the best technique to tackle water shortages and provide treated water for several domestic uses [7].

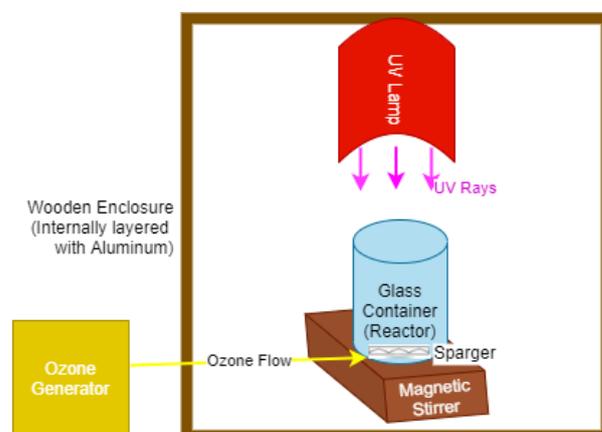
Recently, a growing list of water contaminants, i.e., emerging pollutants or micropollutants, has been identified, including household chemicals and other harmful substances such as fluoro-alkyl substances [8,9]. These substances have harmful and toxic effects on living organisms. Therefore, various techniques are used to remove these contaminants with miscellaneous results [10]. The toxic effects of the organic pollutants include irritation to skin, reactions when swallowed or ingested, increase in the water pollution, and even serious diseases such as cancer [11]. Pesticides are commonly employed chemicals in agriculture that eliminate unwanted organisms and increase crop production. Currently, there are 1378 listed pesticides in existence. These pesticides persist in the environment for long periods and are toxic to nontarget life [12]. Pesticides find their way into water bodies due to runoff and leaching and end up in food on the table. Almost 25 pesticides are frequently detected in surface water compared to groundwater [13]. Traditional wastewater treatment plants have not been commissioned to remove micropollutants, including pesticides. For example, one of the most widely used pesticides, imidacloprid, was found in the discharge of wastewater treatment plants with concentrations reaching 1 µg/L. The removal efficiencies of imidacloprid, acetamiprid, and clothianidin were only 10–20% [14]. Therefore, novel treatment methods are needed to handle the issue of micropollutants and pesticides. Advanced oxidation processes (AOPs) have been proposed to remove pesticides and micropollutants with promising results [15]. Photocatalysis, catalytic ozonation, and Fenton processes are some well-known AOPs. Photocatalysis generally uses heterogeneous catalysts, which are excited by photons emitted by a UV source. The reduction of mixing chemicals, cheap photocatalyst, and relatively lower energy costs make photocatalysis a very popular AOP [16]. Catalytic ozonation uses ozone, a powerful oxidant, which could be combined with a homogenous catalyst such as H<sub>2</sub>O<sub>2</sub>. In addition, metal ions, adsorbents, or heterogeneous catalysts can also be used [17]. The electro-Fenton process is an improved iteration of the traditional Fenton process, which involves H<sub>2</sub>O<sub>2</sub> and iron salts, with an aim to maximize the production of oxidative species [18]. AOPs require high energy inputs; therefore, electrical energy per order (EEO) has been introduced to determine the energy requirements of the AOPs, in which viable AOPs should have EEO of less than 100. EEO is defined as the energy in kilowatt hours (kWh) that is required to degrade a pollutant by 90% per m<sup>3</sup> of polluted water [19].

Photocatalytic ozonation is one of the best AOPs and has the advantages of a single reactor system, synergy between the two processes, and reduced residence times. It has often been observed that the use of photocatalytic ozonation results in better degradation of refractory organic compounds compared with other pollutants. Therefore, those pollutants that were not degraded by traditional treatment methods can be subjected to AOPs, particularly photocatalytic ozonation, for enhanced removal to achieve the aim of environmental betterment. The synergy between ozonation and photocatalysis is the major effect responsible for the better performance of photocatalytic ozonation as compared with other AOPs, whereby synergies ranging from 1.2 to 7.5 times have been reported in literature [20]. Usually, photocatalytic ozonation only employs a photolysis catalyst, traditionally titanium dioxide (TiO<sub>2</sub>) [21]. Although many new catalysts for photocatalysis are being discovered, TiO<sub>2</sub> remains the photocatalyst of choice due to its advantages of excellent catalysis properties, stability, low cost, easy availability, and its nontoxic nature [22]. TiO<sub>2</sub> has found new and novel uses in catalysis, especially with its nanoparticle form, and currently finds applications in the fields of water and wastewater treatment, carbon dioxide reduction, water splitting, handling air pollution, food industry, and disinfection and microorganism removal [23]. Almost every work conducted on photocatalytic ozonation solely utilizes a photocatalyst and usually ignores the ozonation catalysis. In case the rate of photocatalytic ozonation is required to be enhanced further, the introduction of an ozonation catalyst can do the job. Iron (Fe) ions immobilized on inert solids such as ash or zeolite have

been recently identified as ozonation catalysts. The role of Fe ions has not been explicitly established yet. However, some recent studies have suggested that Fe ions act as excellent ozonation catalysts by doing experiments of bicarbonate quenching [24]. Sulfoxaflor belongs to sulfoximines, a relatively new class of pesticides that act on the nicotine receptors of the unwanted insects and are therefore confused with the traditional neonicotinoids. These act on sap-feeding insects and are useful where traditional alternatives fail [25]. The use of several neonicotinoid insecticides has been recently banned in most of the advanced countries of the world due to their toxicity to living organisms such as bees. Sulfoxaflor is found to be less toxic than the banned neonicotinoids but is more toxic than the neonicotinoids still in use. In addition, the toxicity of sulfoxaflor was found to be of concern at only intermediate and higher levels of doses, and not for the recommended dosage amounts [26]. Sulfoxaflor has also exhibited toxic side effects of behavioral changes, orientation loss, and memory loss [27]. After a thorough literature survey, it was found that no work currently exists that studies the photocatalytic ozonation of sulfoxaflor. It has also been observed that most of the studies of pesticides in literature take pure analytical-grade substances as reactant materials, and commercially available pesticides are relatively less studied. In this work, a first-ever attempt has been made to study the degradation of sulfoxaflor by photocatalytic ozonation in a single experimental setup. Sulfoxaflor is commercially available as TRANSFORM<sup>®</sup> manufactured by Dow or Corteva belonging to sulfoximines, a newer group of pesticides. TiO<sub>2</sub> has been used as a photocatalyst, and Fe-zeolite has been added to improve the reaction rate as an ozonation catalyst. This work aims to determine whether photocatalytic ozonation using simultaneous ozonation of ultraviolet (UV) photocatalysis is the best option for the degradation of sulfoxaflor. Moreover, the effect of adding Fe-zeolite as an ozonation catalyst was examined.

## 2. Materials and Methods

Sulfoxaflor pesticide was ordered from the local authorized distributor of Dow and Corteva products in 50% purity as a wettable granule (WG) formulation. All the required chemicals, including acetonitrile, Fe salts, zeolite, and P25 TiO<sub>2</sub>, were procured in analytical grades and purchased from Dawn Scientific Company. The AOP reactor consists of a 100-mL glass container with a quartz glass lid placed on its top. The reactor is illuminated directly under a UV lamp (Quanzhiyan Electronic Co., Fujian, China) and placed on top of a magnetic stirrer (Quanbu). An inlet line for ozone was provided by the Sterhen ozone generator, and ozone traps were installed at the outlets. The experimental setup was placed in a wooden shielded box that was internally layered with aluminum to prevent UV loss. Figure 1 shows the schematic diagram of this apparatus.



**Figure 1.** Experimental setup for the advanced oxidation processes.

The photocatalyst was characterized by SEM imagery, particle size, and point of zero charge. Table 1 presents the other important properties of both catalysts, namely TiO<sub>2</sub> and

Fe-zeolite, such as particle size in  $\mu\text{m}$ , pore size in  $\text{\AA}$ , dry composition, thermal stability temperature in  $^{\circ}\text{C}$ , and specific surface area in  $\text{m}^2/\text{g}$ , as provided by the supplier. The points of zero charge have been experimentally determined to have the values of  $6.6 \pm 0.2$  and  $6.5 \pm 0.2$  for titanium dioxide and zeolite, respectively.

**Table 1.** Properties of catalysts used.

	Titanium Dioxide	Zeolite
Particle size ( $\mu\text{m}$ )	0.5	0.40
Pore size ( $\text{\AA}$ )	86	10
Surface area ( $\text{m}^2/\text{g}$ )	54	61.3

The variation with an initial concentration was observed at three values, i.e., 100 mg/L, 200 mg/L, and 300 mg/L. In addition, three different catalyst loadings, i.e., 0.5 g/L, 1 g/L, and 1.5 g/L, were used. All experimental runs were performed for 30 min, which was considered sufficient for method comparison, as results later showed that the best setup performed virtually complete degradation (>99%) in 18 min.

The samples for concentration analysis were withdrawn at 0, 5, 10, 20, and 30 min. High-performance liquid chromatography (HPLC) (Shimadzu, Kyoto, Japan) was used to analyze the concentration of sulfoxaflor on all the withdrawn samples. The analysis was performed as per the Provincial Pesticide Reference Laboratory method. For the obtained method, the specified parameters include 260-nm detector wavelength, room column temperature, and 35% methanol aqueous solution as a mobile phase with the addition of formic acid to maintain the pH. The flow rate was set at 1.4 mL/min for the mobile phase, enabling the detection of sulfoxaflor at around the 6-min mark. Before injection in the HPLC, all samples were filtered through a 0.2- $\mu\text{m}$  filtration assembly. The standard calibration curve for sulfoxaflor was linear, with a limit of detection and a limit of quantitation values of 0.023 mg/L and 0.070 mg/L, respectively, as calculated by statistical regression analysis.

The UV lamps used had a wavelength of 253.7 nm, which is under UVC classification. Three lamp powers, i.e., 9 W, 18 W, and 27 W, were available to study the effect of UV intensity. The power requirement for the ozone generator was 15 W, along with a sparger output providing 100 mg/h of ozone flow rate. The magnetic stirrer on which the reactor was placed was set at 1000 rpm, as stirring above it sometimes caused foaming and content spilling. All experiments were performed at room temperature and neutral pH inside a temperature-controlled empty room to ensure no outside interference and complete safety.

### 3. Results

#### 3.1. Degradation Studies

Four different degradation studies were performed to visualize the removal of sulfoxaflor, i.e., the active ingredient of TRANSFORM<sup>®</sup>, from wastewater. The pesticide in discussion was degraded by (i) ozone solely; (ii) UV, with  $\text{TiO}_2$  as the photocatalyst; (iii) ozone + UV, i.e., photocatalytic ozonation with  $\text{TiO}_2$  as the photocatalyst; and (iv) ozone + UV, i.e., photocatalytic ozonation with  $\text{TiO}_2$  as the photocatalyst and Fe-zeolite as the ozonation catalyst. Figure 2 shows the SEM image of  $\text{TiO}_2$ . Scanning electron microscopy (SEM) is a technique used to obtain enhanced structural images of a material using an electron beam instead of an ordinary light source, and the final SEM image is obtained through several complex interactions [28]. The analysis of shape, size, and surface is very critical to understand the catalyst activity and properties [29]. For obtaining an image through SEM, the magnification selected was 30,000 times and the electron acceleration energy was 30 kV. As shown in Figure 3a, all AOPs successfully degrade sulfoxaflor over time. However, photocatalytic ozonation shows better removal percentages than ozonation and photocatalysis alone, possibly because of synergy. Almost 99% degradation is observed at 22 min, which decreases to 18 min if Fe-zeolite is added.

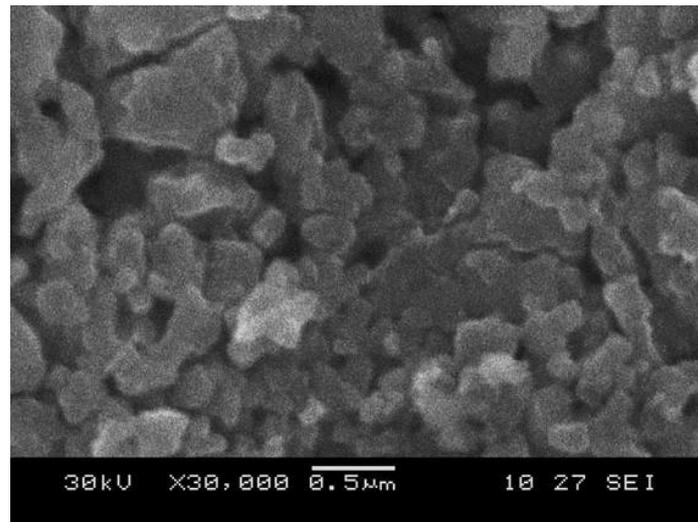


Figure 2. SEM image of photocatalyst  $\text{TiO}_2$ .

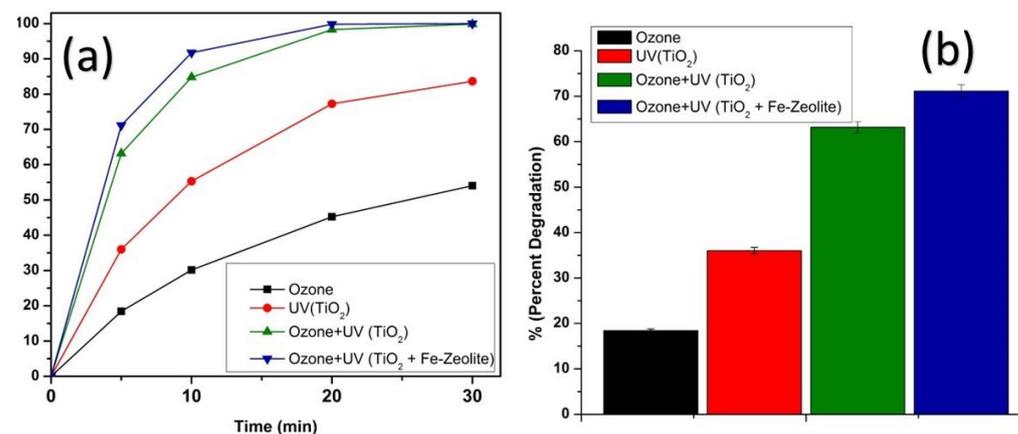
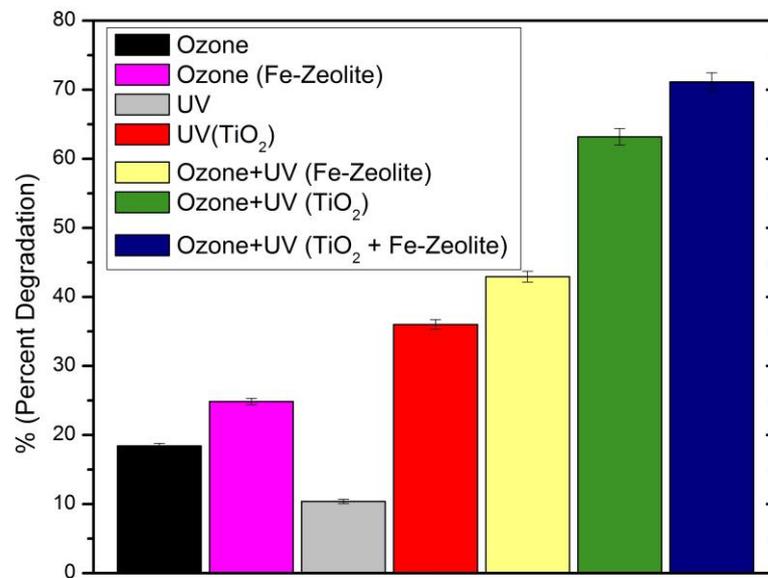


Figure 3. (a) Degradation results obtained from various AOPs for the degradation of sulfoxaflor. (b) Degradation of sulfoxaflor after 5 min.

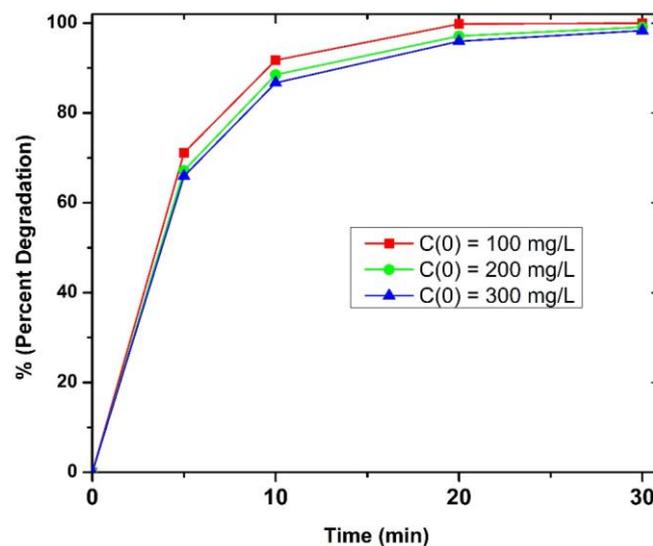
The most optimum operating conditions, determined later, were used to compare these AOPs. The initial concentration of sulfoxaflor used was 100 mg/L using an 18W UV lamp and with a catalyst dose of 1 g/L. Fe-zeolite was added as 20% when both catalysts were used. All experiments were conducted in triplicate, excluding the outliers, and the final values were averaged. As shown in Figure 3b, the faster degradation of combined processes can be better observed at shorter time intervals, where all processes are compared at shorter time intervals, i.e., 5 min, by column graphs along with the corresponding error bars. For further insight, Figure 4 includes three more AOPs, i.e., ozone only with Fe-zeolite, UV only without photocatalyst, and combined photocatalytic process with only Fe-zeolite, thus taking the total to seven AOPs. The literature survey indicated that these combinations are usually not covered, and rightly so, because these are not the best alternatives available. For example, the combined process of photocatalytic ozonation with  $\text{TiO}_2$  only or with  $\text{TiO}_2$  + Fe-zeolite results in much better performance as compared with photocatalytic ozonation with Fe-zeolite only.



**Figure 4.** Comparison of seven AOPs for the degradation of sulfoxaflor after 5 min.

### 3.2. Initial Concentration

Three initial concentrations, i.e., 100 mg/L, 200 mg/L, and 300 mg/L, of sulfoxaflor, the active ingredient of TRASNFORM, were used for comparison. A combined process of photocatalytic ozonation was employed with a photocatalyst dose of 1 g/L of TiO<sub>2</sub> under 18W UVC power, and 20% Fe-zeolite was added. As shown in Figure 5, sulfoxaflor is almost completely degraded (>99%) in 18 min with an initial concentration of 100 mg/L. However, this time increases when the initial concentration is increased and reaches 25 min in the case of 300 mg/L initial concentration.



**Figure 5.** The effect of initial concentration on the degradation of sulfoxaflor by photocatalytic ozonation.

### 3.3. UV Intensity

The 253.7-nm UV lamps were operated at three powers, i.e., 9 W, 18 W, and 27 W, for photocatalytic ozonation corresponding to three intensities, i.e., 125 W/m<sup>2</sup>, 250 W/m<sup>2</sup>, and 375 W/m<sup>2</sup>, respectively, at an initial concentration of 100 mg/L with 1 g/L TiO<sub>2</sub> and 20% Fe-zeolite. As shown in Figure 6, an increase of UV intensity from 125 W/m<sup>2</sup> to 250 W/m<sup>2</sup> substantially improves the degradation percentage; however, when the UV intensity increases to 375 W/m<sup>2</sup>, the further improvement is only slight, and it is not

worth spending the additional electric power. Therefore, it can be inferred that the best degradation in this scenario is provided by the 18 W UV lamp with 100 mg/L of initial concentration and a catalyst loading of 1 g/L with 20% Fe-zeolite.

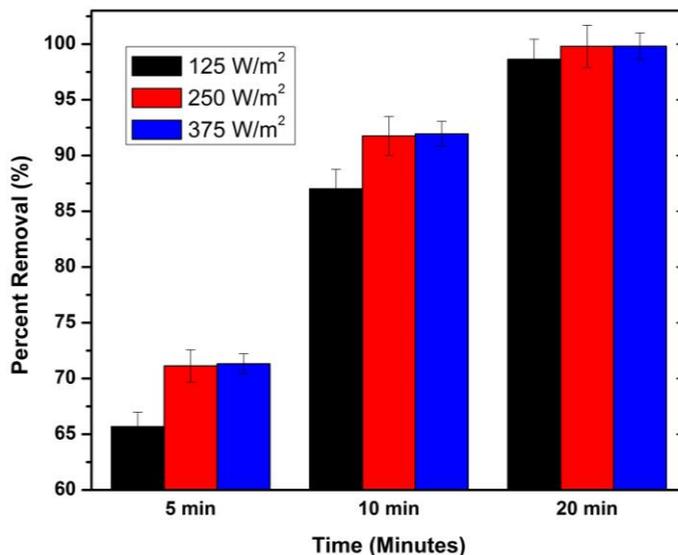


Figure 6. The effect of UV intensity on the degradation of sulfoxaflo.

### 3.4. Catalyst Dose and Fe-Zeolite Percentage

Six combinations of photocatalyst and ozonation catalyst were implemented to study the effect on removal percentages. The combinations were (i) 0.5 g TiO + 10% Fe-zeolite, (ii) 1 g TiO<sub>2</sub> + 10% Fe-zeolite, (iii) 1.5 g TiO<sub>2</sub> + 10% Fe-zeolite, (iv) 0.5 g TiO<sub>2</sub> + 20% Fe-zeolite, (v) 1 g TiO<sub>2</sub> + 20% Fe-zeolite, and (vi) 1.5 g TiO<sub>2</sub> + 20% Fe-zeolite, all while using 100 mg/L initial concentration of sulfoxaflo and 18W of UV lamp power. As shown in Figure 7a, removal improves as the catalyst dose increases from 0.5 g/L to 1 g/L, but further increasing the catalyst dose to 1.5 g/L slightly decreases the degradation. The best degradation is obtained for a catalyst dose of 1 g/L spiked with 20% Fe-zeolite. The graph was drawn for 20 min, as it is sufficient to compare the effects. After 20 min, the graphs essentially become the same unless zoomed to a higher level, as these processes follow pseudo-first-order kinetics. Therefore, the optimization for catalyst doses will be more easily observable at shorter intervals, e.g., 10 min, as illustrated in Figure 7b.

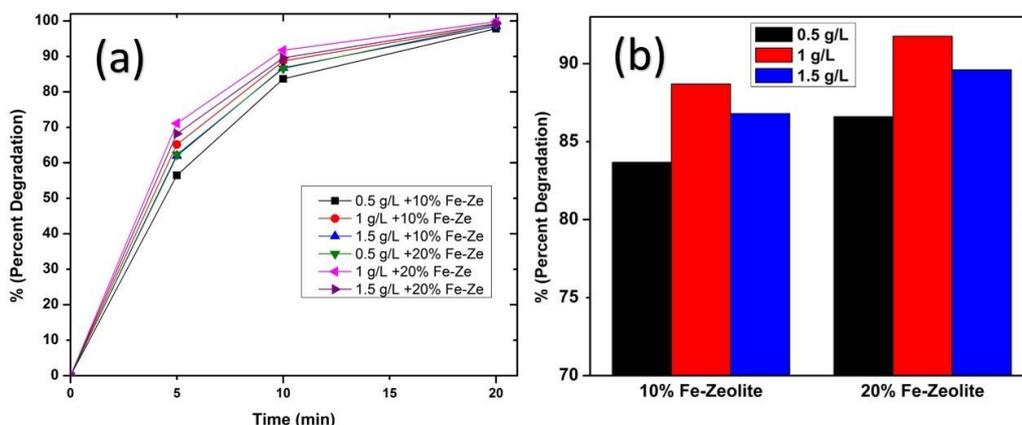


Figure 7. (a) The effect of catalyst dosage and Fe-zeolite doping on the degradation of sulfoxaflo. (b) Percent removal of sulfoxaflo using photocatalyst and Fe-zeolite percentages after 10 min.

### 3.5. Catalyst Reuse

After a run, the photocatalyst  $\text{TiO}_2$  and ozonation catalyst Fe-zeolite were thoroughly washed. The sample was heated and dried as per the widely available technique [30]. The combined photocatalytic ozonation process was employed with an optimum concentration of 100 mg/L, 18 W of UV, and 1 g/L of  $\text{TiO}_2$  with 20% Fe-zeolite. The catalyst reuse has been explored. Figure 8 shows the results. Even after five cycles, the performance remains satisfactory, with hardly an activity loss of <0.75%.

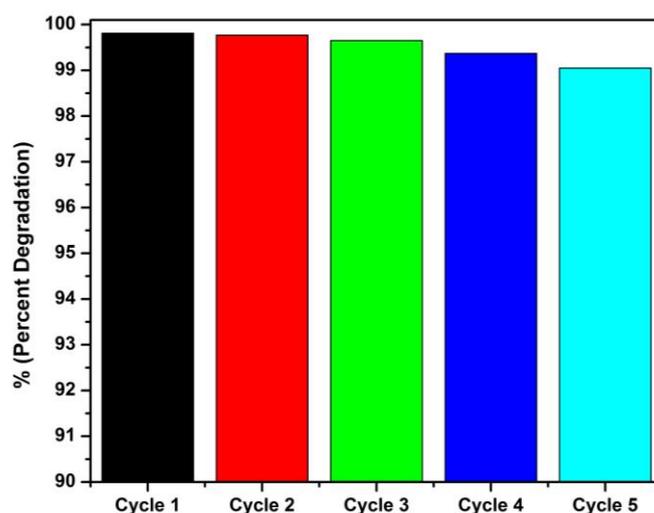


Figure 8. Activity % after catalyst reuse.

## 4. Discussion

The best results in degradation studies were obtained when photocatalytic ozonation was used, as evident from Figure 3a. This behavior is portrayed because photocatalytic ozonation is a synergistic process compared to ozonation and photolysis alone, therefore showing better results. Combined UV and ozone better attack the sulfoxaflor molecules and degrade them faster than other AOPs. The results agreed with various other studies in the literature for photocatalytic ozonation [31,32].

These findings are also consistent with the literature for removal of formaldehyde, flumioxazin, and imidacloprid [33–35]. Here, the degradation of sulfoxaflor was studied, showing a similar degradation behavior to formaldehyde, imidacloprid, and flumioxazin. Figure 3a shows the degradation of sulfoxaflor, with the difference between various processes more easily observed at shorter time intervals of 5 min, as depicted in Figure 3b. The use of combined catalysts provided an improvement of 19% as compared to the use of the photocatalyst alone, which is the traditional way for photocatalytic ozonation.

As shown in Figure 5, increasing the initial concentration of the pesticide will increase its treatment time, which is understandable since more molecules will take additional time to degrade in a provided setup. Although the first-order reactions are independent of concentration, the experimental setup limitations, the availability of UV to photocatalyst, and transport problems limit the degradation rate, as shown by various other works [36,37]. It should be noted that eventually, given enough time, even higher concentrations of the pollutants will also be degraded. The increased treatment times could be explained by a greater absorbance of the reacting pesticide molecules on the photocatalyst surface, therefore reducing the availability of the photocatalyst particles to UV radiation. Similar observations were made when the photocatalyst and ozonation catalysts were used for the photocatalytic ozonation of formaldehyde and imidacloprid [33,35].

As shown in Figure 6, increasing the UV intensity from 125  $\text{W}/\text{m}^2$  to 250  $\text{W}/\text{m}^2$  initially improved the degradation percentages, as more irradiation energy leads to more pollutant's removal due to the production of more photons. The difference in results

between various UV intensities was more clearly observed at shorter time intervals due to the first-order nature of the reaction and because reactions approach completion over time. However, no major progress was observed when the UV intensity increased to  $375 \text{ W/m}^2$ . Therefore, it is deduced that with higher UV intensities, there will be a positive effect on the degradation of sulfoxaflor, but only until a limit. Further increasing UV will not show noticeable improvements because all catalyst sites and available surface areas will already be fully utilized [38].

An increase in the degradation phenomenon can be detected in Figure 7a, as the photocatalyst dosage was increased from an initial value of  $0.5 \text{ g/L}$  to  $1.0 \text{ g/L}$ . It was followed by a decline in removal when the  $\text{TiO}_2$  catalyst amount was further increased to  $1.5 \text{ g/L}$ . This could be attributed to the scarcity of active particle sites, UV deprivation, and radiation scattering [39]. As shown in Figure 7b, observing the same processes at shorter intervals will provide more insight into this behavior, where these effects will be more pronounced. Adding Fe-zeolite will increase the degradation rates by up to 5%, as observed for formaldehyde [33]. Both these effects of UV intensity and catalyst dose are qualitatively similar, as observed for imidacloprid in a combined photocatalyst and ozonation catalyst study [35]. With a loss of only 0.75% after five cycles, the reuse performance is quite satisfactory [24].

The kinetics of the AOPs has been studied by plotting  $-\ln C/C_0$  versus time in Figure 9. All techniques yield a straight line with acceptable values of  $R^2$ . The straight lines in Figure 9 indicate that all AOPs studied, i.e., ozonation, photocatalysis, and photocatalytic ozonation, follow pseudo-first-order kinetics, although with different rates of reactions and different rate constants [37,40]. To determine the rate constants, in Figure 10, curve fitting has been applied to a type of Equation (1):

$$\frac{C}{C_0} = e^{-\frac{t}{\tau}} \quad (1)$$

where  $t$  is the time and  $\tau$  is the retention time, which are both expressed in minutes.

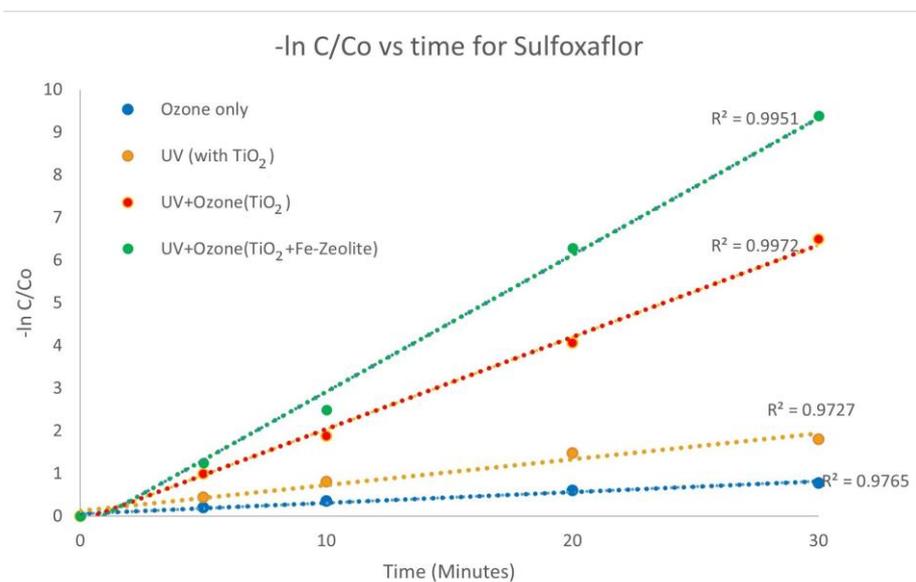
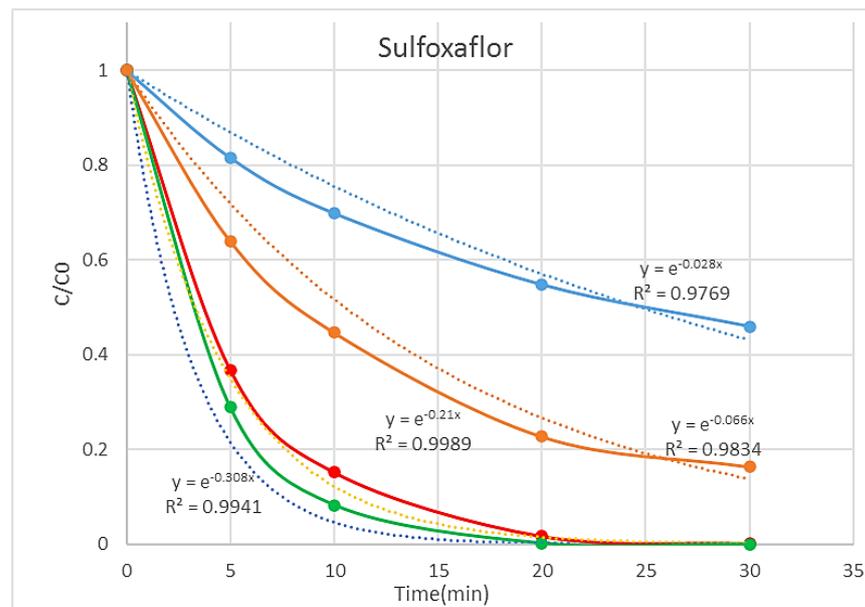


Figure 9. Fitting of rate constants to  $-\ln C/C(0)$  graphs.



**Figure 10.** The determination of rate constants of sulfoxaflor for various AOPs.

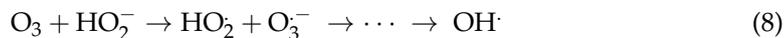
To find out the values of kinetic parameters, the intercept value in Figure 10 was fixed at 1, which is the initial value of  $C/C_0$ . When ozone was solely used, the value of  $(1/\tau)$  was  $0.028 \text{ min}^{-1}$ . Instead, using the photocatalysis provided  $(1/\tau)$  of  $0.066 \text{ min}^{-1}$  showed that photocatalysis with UV and  $\text{TiO}_2$  degraded sulfoxaflor at a faster rate. However, when the two processes were combined using  $\text{TiO}_2$ , the value of  $(1/\tau)$  climbed to  $0.21 \text{ min}^{-1}$ . Therefore, a synergy of 2.23 times was observed, showing that the combined photocatalytic process gives better results compared with ozonation alone or photocatalysis alone. With doping of Fe-zeolite, this figure further rose to  $0.34 \text{ min}^{-1}$ , showing a synergy of 3.62 times, which is 1.62 times greater than using photocatalysis only. This suggests that combining a photocatalyst and ozonation catalyst is the fastest and most viable method to degrade the persistent pollutants, such as pesticides, in a tertiary treatment setup. Similar conclusions are observed in the literature for formaldehyde and imidacloprid [33,35].

The mechanism of photocatalytic ozonation is still not definite and is only proposed usually. A literature survey revealed that photocatalytic ozonation degrades the reactant molecule in several ways. Three factors in photocatalytic ozonation are responsible for a synergistic behavior. (A) First,  $\text{OH}^\cdot$  radicals are generated by ozone on the surface of  $\text{TiO}_2$  in a series of steps with an ozonide radical as a pathway, as depicted by Equations (2)–(5). Ozone is a more powerful oxidizer and a better scavenger than oxygen and is much more useful [41].



(B) Second,  $\text{OH}^\cdot$  radicals are also generated with the help of ozone photolysis. Ozone can then react with superoxide ion radicals to produce more  $\text{OH}^\cdot$  radicals. These steps are shown by Equations (6)–(8) [42].





(C) Lastly, ozone efficiently traps photogenerated electrons, reducing the recombination rate of electrons with the holes. Additionally, oxygen also traps the photogenerated electrons, leading to the production of superoxide radicals. These superoxide radicals then may react with ozone. Equations (9) and (10) show this phenomenon [43].



Moreover, electron trapping is improved with the doping of Fe ions, inhibiting electron-hole recombination when UV is irradiating, as per Equations (11)–(14). This is because the  $\text{Fe}^{3+}$  ions can act as electron- and hole-trapping sites, stopping the charged particles produced under UV light from recombining. This prolongs their lifetimes and results in a better overall performance [44].



The positive holes  $h^+$  formed by the above mechanisms can then directly react with the reacting substrates, as shown in Equation (15), due to their high oxidative potentials. Besides conventional mechanisms, the organic compounds may be degraded by other mechanisms such as Type I, Type II, Type III, and z-mechanism, some of which are covered in the preceding equations [45].



As seen in the abovementioned equations, different oxygen reactive species, including the ozonide radicals  $\text{O}_3^-$ ,  $\text{HO}_2^-$ , and  $\text{O}_2^-$ , can be identified to be present during ozonation. In addition, the combination of hydrogen and oxygen results in the generation of the famous hydroxyl free radical  $\text{OH}^\cdot$  and  $\text{HO}_3^-$ . Similarly, reactive species identified in photocatalysis are  $\text{O}_3^-$ ,  $\text{OH}^\cdot$ , and  $\text{HO}_3^-$ . Additionally, photocatalysis may sometimes generate organic peroxides and nitric peroxides [46]. For ozonation, literature reports the occurrence of the same oxygen reactive species as mentioned above, with  $\text{O}_2^-$  and  $\text{OH}^\cdot$  being more prevalent [47]. After explaining the kinetics and mechanism, Equation (16) can be used to finally determine the *EEO* values for pseudo-first-order kinetics for all techniques for sulfoxaflo [48].

$$EEO = \frac{38.4 \times P_{el}}{V \times k_{app}} \quad (16)$$

where  $P_{el}$  is electric power in kW,  $V$  is volume of the reactor in L, and  $k_{app}$  is the rate constant for the pseudo-first-order kinetics in  $\text{min}^{-1}$ .

Table 2 summarizes the calculated *EEO* values using the already determined rate constants. The required power to operate the experimental setup has also been mentioned.

**Table 2.** EEO values and rate constants for various AOPs.

Process	$P_{el}$ (kW)	Rate Constants ( $\text{min}^{-1}$ )	EEO ( $\text{kWh m}^{-3} \text{ order}^{-1}$ )
O <sub>3</sub>	0.020	0.028	274.3
UV + TiO <sub>2</sub>	0.023	0.066	133.8
O <sub>3</sub> + UV + TiO <sub>2</sub> (TiO <sub>2</sub> only)	0.038	0.21	69.5
O <sub>3</sub> + UV + TiO <sub>2</sub> + Fe-Zeolite	0.038	0.34	42.9

As presented in Table 2, the EEO values are within the upper limit of 100 for photocatalytic ozonation. Photocatalytic ozonation without Fe-zeolite and photocatalytic ozonation with Fe-zeolite are both viable as far as EEO is concerned. Since no EEO studies are available for sulfoxaflo, the EEO values are compared with some other compounds, which are found to reach as high as 38.4 and 71.27  $\text{kWh m}^{-3} \text{ order}^{-1}$  for methyl orange and nitrophenol, respectively [19,48]. It should be noted that pesticides, especially the novel ones, are usually more resistant to degradation; their EEOs are understandably high, though still within the range.

## 5. Conclusions

In this study, different AOPs, including ozonation, photocatalysis, and photocatalytic ozonation, were used to successfully degrade a commercially available sulfoxaflo confection. All the AOPs studied during the experiments were able to degrade sulfoxaflo. However, the only process that could completely remove sulfoxaflo during the observation was photocatalytic ozonation (>99%; within 22 min). Fe-zeolite was added as an ozonation catalyst to further improve the removal rates, and the treatment time was reduced to 18 min. The corresponding rate constants were  $0.028 \text{ min}^{-1}$ ,  $0.066 \text{ min}^{-1}$ ,  $0.21 \text{ min}^{-1}$ , and  $0.34 \text{ min}^{-1}$  for ozonation alone, UV alone (with TiO<sub>2</sub>), photocatalytic ozonation (with TiO<sub>2</sub>), and photocatalytic ozonation (with TiO<sub>2</sub> + Fe-zeolite), respectively. Thus, a synergy of 2.23–3.62 times was observed for the combined process. Therefore, although all the AOPs studied can degrade sulfoxaflo, the highest removal rates will be achieved in the case of a combined process owing to the synergy effect.

Through operational optimization, it was observed that the optimum degradation was achieved when considering the lowest initial concentration of sulfoxaflo (100 mg/L), a medium UV intensity obtained by an 18 W lamp power, and a medium catalyst dose of 1 g/L enhanced by the addition of 20% Fe-zeolite. All the kinetic parameters were obtained by linear curve fitting on natural log plots, and the mechanism was proposed from a literature survey. The EEO values were within the acceptable limit of 100  $\text{kWh m}^{-3} \text{ order}^{-1}$  for photocatalytic ozonation of AOPs. Therefore, photocatalytic ozonation is a successful method to degrade pesticides. However, it still has the limitations of high energy requirements, high operational costs, and the potential formation of unwanted byproducts. Moreover, the conversion of laboratory setups and pilot plants to industrial setups and their incorporation into existing wastewater treatment plants are unexplored areas. Therefore, studies on economics, scaling, and byproducts warrant further attention because AOPs in general and photocatalytic ozonation in particular have the potential to simultaneously mitigate water scarcity and water pollution, which are the two major problems facing the world.

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