


Research Article

Effect of Photoreactor Design on the Degradation of Thiamethoxam by Pure/Supported Titanium Dioxide

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Abstract

The environmental persistence of thiamethoxam (THX), a commonly used neonicotinoid insecticide, raises concerns about its long-term effects. This study explored the photocatalytic degradation of THX using pure and perlite supported TiO₂ photocatalysts in two distinct UV photoreactor configurations. Our investigation aimed to identify some optimal conditions for efficient THX removal while considering cost-effectiveness and sustainability for potential industrial applications. The results revealed that horizontal UV irradiation (System 1) significantly surpassed vertical irradiation (System 2) in both THX degradation rate and energy efficiency. This highlights the importance of photoreactor design for maximizing light utilization and mass transfer. While pure TiO₂ exhibited superior performance in both systems compared to perlite-supported TiO₂ (PST), the latter demonstrated an intriguing temperature dependence. PST achieved enhanced degradation at higher temperatures, suggesting its potential for industrial applications where waste heat is available. Furthermore, we discovered that low pH conditions substantially boosted THX degradation with PST, opening a promising avenue for optimizing industrial processes and minimizing chemical usage. This finding underscores the crucial role of operational parameters in tailoring photocatalytic performance. In conclusion, this study provided strong evidence for the effectiveness of TiO₂ photocatalysis in degrading THX, a persistent organic pollutant. We emphasized the impact of catalyst support, photoreactor design, and operational parameters, such as temperature and pH, on treatment efficiency. Notably, the enhanced performance of PST at higher temperatures and its responsiveness to low pH conditions suggest its potential for cost-effective and sustainable THX treatment in industrial settings. These findings pave the way for further research and development of optimized photocatalytic systems for mitigating environmental contamination by THX and other persistent organic pollutants.

Keywords

Photocatalyst, Degradation, Perlite, Perlite Supported TiO₂, TiO₂, Thiamethoxam

1. Introduction

The density use of pesticides in agricultural applications causes contamination of water and soil sources [1]. Amongst

neonicotinoids, thiamethoxam (THX) stands out as a systemic insecticide, offering potent activity against a vast array of

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insects [2]. Neonicotinoids, which are the most widely used pesticides globally, hold a significant 40% share in the insecticide market. These pesticides are registered in 120 countries, making them highly prevalent worldwide. In 2014, neonicotinoids accounted for over 25% of the global pesticide market, reaching a staggering value of more than US \$3 billion. Notably, the primary contributors to neonicotinoid sales in crop protection were thiamethoxam, imidacloprid, and clothianidin, collectively representing nearly 85% of total sales in 2012 [3]. Although thiamethoxam has a toxicological effect, it is widely used because of its low dose of efficacy, various application methods, and long half-life [4]. Decisions have been made in recent years to limit the use of thiamethoxam, which has been indexed to the limitation of bird migration and is responsible for up to 85% of the reduction in bee colonies [5]. Therefore, the use of thiamethoxam in Turkey from december 19, 2018 was forbidden for Pistachio, Pear, Pepper, Tomato (field), Apple, Hazelnut, Cucumber, Cabbage, Lettuce, Corn, Pomegranate, Cotton, Eggplant (field), Peach, Tobacco and Olives [6]. However, restrictive decisions taken in many countries are not sufficient to eradicate the pesticide effect from nature. Therefore, photocatalytic degradation is a frequently used method for pesticide removal [7]. While TiO_2 is widely recognized as a highly efficient photocatalyst in photocatalytic degradation processes, its application in water treatment necessitates expensive nanofiltration procedures post-usage. This problem can be prevented by immobilizing TiO_2 nanoparticles onto a support material. Immobilization

techniques are not limited to transparent materials like glass; they can also be applied to opaque materials such as activated charcoal, rocks, and metals [8].

This study breaks new ground by simultaneously investigating the influence of TiO_2 support (perlite) and photoreactor design on pesticide degradation. By comparing horizontal and vertical UV irradiation in two distinct setups, we not only elucidated the performance of pure vs. perlite-supported TiO_2 , but also identified optimal configurations for enhanced pesticide removal. These findings hold promise for developing cost-effective and scalable technologies to address the growing concern of pesticide pollution.

2. Materials and Methods

2.1. Materials

All experimental chemicals were analytical grade. Evonik (Germany) provided the photocatalyst, P25 titanium dioxide (TiO_2), whose key properties are summarized in Table 1. Expanded perlite, obtained from TAŞPER Perlite (Turkey), supported the photocatalyst. Thiamethoxam (Sigma-Aldrich, >99% purity) was used directly, dissolved in distilled water at the required concentration.

Table 1. Properties of Degussa P25 [9, 10].

Mean diameter(nm)	Specific surface area (m^2/g)	Anatase/rutile ratio (w:w)	Density (g/cm^3)
21	50	80:20	4

2.2. Synthesis of Perlite Supported TiO_2

Perlite supported TiO_2 was prepared according to our previous study [11]. Perlite grains were sieved to 1-2 mm. Then the perlite grains were washed and dried. Then, 6 grams perlites were weighted. Weighted perlite was mixed with TiO_2 (2.4 gram), HNO_3 (pH=3.30, 5mL), and absolute ethanol (50 mL). After that, the mixture was subjected to an ultrasonic bath for 5 minutes. After ultrasonic bath, it was mixed with 100 rpm for 1 hour. End of the mixing the samples were taken into the drying-oven for 12 hours.

After 12 hours, perlite supported TiO_2 (PST) was heated to 450 °C for 1 hour in a muffle furnace. Then, it was washed and dried at 120 °C for 4 hours, respectively. Finally, PST was obtained for photocatalytic degradation experiments.

2.3. Photoreactor Configurations

In this study, two different setups based on the different directions of light were used (horizontal and vertical). All effects were observed in these systems separately.

2.3.1. System 1 (SY1)

System 1- Thiamethoxam degradation process setup is shown in Figure 1 The reactor was wrapped in aluminum foil, effectively preventing the escape of UV light and minimizing the infiltration of visible light. UV light (62W, 365 nm) is given as the horizontal direction through the reaction solution.

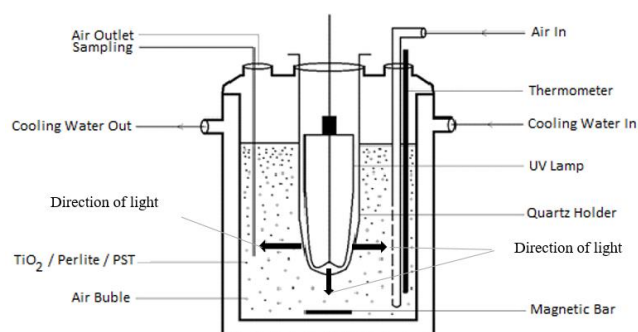


Figure 1. System 1 Setup.

2.3.2. System 2 (SY2)

System 2-Thiamethoxam degradation process is shown in Figure 2. The reactor was covered with aluminum foil and black light proof boxes to prevent passing the UV (365 nm) light out and visible light inside of the reactor. The reaction solution was irradiated with 6 W, 365 nm UV light, delivered vertically.

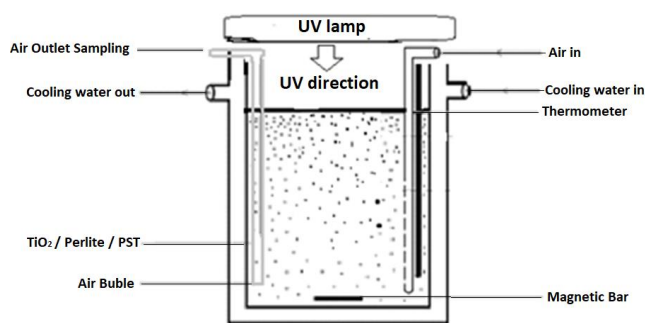


Figure 2. System 2 Setup.

2.4. Photocatalytic Degradation of Thiamethoxam

Photocatalytic degradation of Thiamethoxam was evaluated by pure TiO_2 and PST composites. A pyrex glass reactor of 1 L equipped with UV lamp (365nm) was used for thiamethoxam degradation experiments (Figure 1). The photoreactor was covered with aluminum foil to block the transition of external light to the inside of reactor and to prevent any light leakage from the UV source to the outside. Temperature of the reaction media was kept constant at 20 °C by recycling cooling water. Air flow (18 L/h) was fed to the reactor and the flow rate was controlled by a flowmeter. Air was distributed through the suspension by the aid of holes in the air tubing placed at the bottom of the reactor to provide a homogeneous distribution of air. The mixture was maintained in darkness while stirring continuously for 30 minutes to complete the adsorption-desorption equilibrium, and then the air flow and UV source was turned on. A portion of the samples were collected from the reactor periodically and filtrated to determine thiamethoxam concentration. To quan-

tify thiamethoxam, its absorbance was measured at 252 nm with an Analytic Jena Specord 200 Plus UV Spectrometer. Experimental studies were carried out in SY1 and SY2 in both with 4 g of PST samples in 500 mL thiamethoxam solution (1.46 ppm) and the mixture was stirred at 270 rpm using a magnetic stirrer. The same procedure was performed with 1.15 g of pure TiO_2 (Degussa P-25) to compare with PST samples. To ensure consistency with our previous findings [12], which demonstrated that 4.00 g of PST contains approximately 2.85 g of perlite and 1.15 g of pure TiO_2 , the mass of each material was selected for this study.

2.5. Kinetic Investigation of THX Degradation

After determining THX concentration, $\ln(C_0/C)$ versus time graphs were drawn by using Langmuir-Hinselwood model;

$$r_R = \frac{-dC_R}{dt} = \frac{k_r K C_R}{1 + K C_R} \quad (1)$$

r_R = rate of reaction; C_R = solute concentration; t = reaction time; k_r = reaction rate constant; K = adsorption constant.

As the THX concentration was small in this investigation, the $K C_R$ term was considered insignificant, leading to a pseudo-first-order behavior for the observed reaction rate. Integrating the relevant equation with the boundary condition $C_R = C_{RO}$ at $t = 0$ provides.

$$-\ln \frac{C_R}{C_{RO}} = k_{app} t \quad (2)$$

k_{app} (min^{-1}) = The pseudo-first-order rate constant; C_{RO} = Initial concentration; t = time

2.6. Electric Energy per Order (EE/O) for System 1 and System 2

As stated in section 2.3, the power of UV lamps of each system are different, System 1 works at 6x2 W, System 2 works at 6 W. To ensure consistency and enable direct comparison, we calculated the EE/O values for all experiments using Equation 3. This equation considers the power consumption of the UV lamp (P), the volume of the reaction solution (V), duration of irradiation (t), and both initial (C_0) and final (C) THX concentrations, guaranteeing evaluation at specific degradation levels and identical time intervals:

$$EE/O(kWh/m^3) = \frac{P * t * 1000}{V * 60 * \log \frac{C_0}{C}} \quad (3)$$

Equation 3 is indirectly related to Langmuir-Hinshelwood (L-H) model first-order kinetics (Equation 2).

Thus, this equation can be obtained as below [13];

$$EE/O(kWh/m^3) = \frac{P * 38.38}{V * k_{app}} \quad (4)$$

Equation 4 was used for the determination of model electrical energy per order for the idealized batch reactor.

3. Results and Discussion

3.1. Characterization of Perlite Supported TiO₂

Crystal structure of TiO₂ has an important role for its photocatalytic activity. Even rutile is the most stable TiO₂ crystal, because of the higher Fermi level of anatase phase, anatase has higher photocatalytic activity than rutile [11]. XRD pattern of PST can be seen in Figure 3. XRD pattern showed that anatase is the main crystalline phase for TiO₂ and PST samples. According to SEM images of the samples, there is no significant modification after coating of TiO₂ on perlite and calcination (Figure 4).

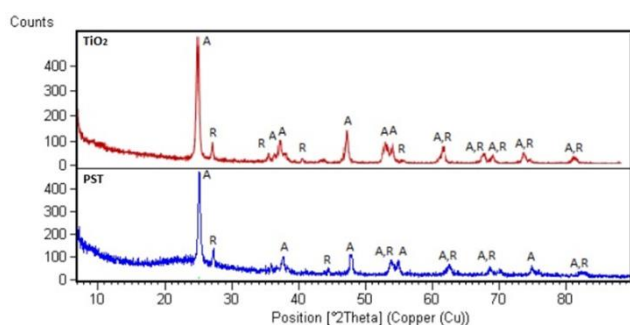


Figure 3. XRD patterns of PST [11].



Figure 4. SEM images of TiO₂ (5000X), perlite (1000X), and PST (5000X) samples [11].

3.2. Photocatalytic Degradation of THX

Photocatalytic degradation of THX was studied with pure thiamethoxam and perlite supported TiO₂ in long wavelength (365nm). Effect of temperature, pH, and process design was investigated.

3.2.1. Effect of Photoreactor Design on Degradation Efficiency

The design of photocatalytic reactors takes into account three fundamental concepts: specific rate, modeling of the distribution of irradiation, and the transport phenomena on macroscopic and microscopic scales [14]. Moreover, the design of the reactor has to take into account the high

degradation rate, the reduction of energy, and investment cost [14]. For SY1, the light sources are multidirectional while for SY2, the UV lights are just coming from the top of the reactor. Degradation efficiency results obtained from (SY1 and SY2) using pure TiO₂ and also for PST can be seen in Figures 5 and 6, respectively. As can be seen, the degradation percentage of THX hardly changed to richly 70% after one hour (60 minutes) for both systems. However, after 1 hour, the degradation efficiencies are higher in the case of SY1 for both photocatalysts. Then SY1 system showed better photocatalytic degradation efficiency than SY2. With increasing time, the gap widened further to give after 220 minutes to give 98% degradation for system 1 and only 60% for system 2. This can be interpreted with UV light direction. The main difference between both reactors lies in the distribution of the irradiation. In System 2, UV light can not reach to all particles in the solution homogeneously due to the vertical direction of the light. Floating perlite can block the UV light through to the solution. The result clearly demonstrated that SY1 has the best photocatalytic performance under our experimental conditions.

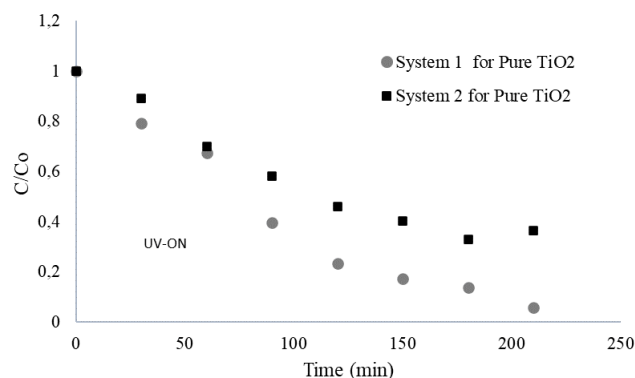


Figure 5. THX Degradation efficiency of Pure TiO₂ in SY1 and SY2.

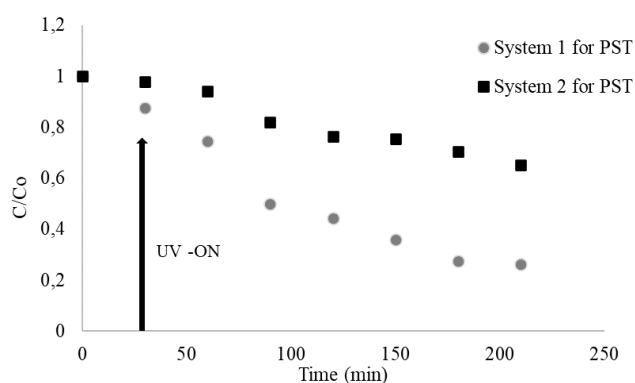


Figure 6. Degradation efficiency of PST in SY1 and SY2.

Electric Energy per Order calculation

Due to making an accurate comparison, the electric power per order values were calculated by using Equation 3, the

obtained results are given in Figure 7.

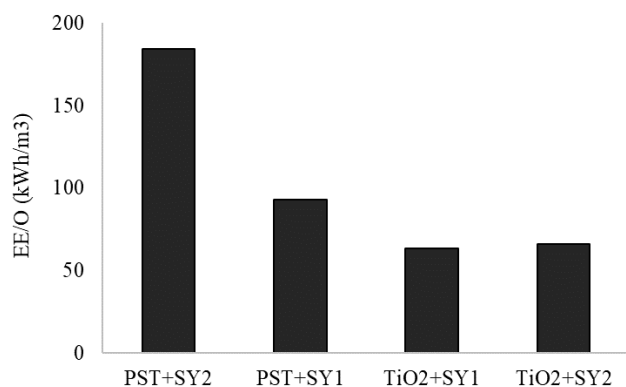


Figure 7. EE/O values obtained from SY1 and SY2.

As can be seen in Figure 7, the consumption of electrical energy of System 1 is less than System 2 in the case of using PST. Considering the observed performance, it's plausible that the floating perlite in SY2 blocked light from reaching the solution effectively. This implies that System 1's photoreactor design allows for more efficient light exposure and utilization for THX degradation with PST. Interestingly, when pure TiO₂ is used, both photoreactors perform similarly, suggesting that design factors might be less influential in that scenario.

3.2.2. Effect of Supported Material on THX Degradation Efficiency

To observe the effect of supported material on photocatalytic degradation, it was studied with perlite supported TiO₂ and pure TiO₂ for each system (SY1 and SY2).

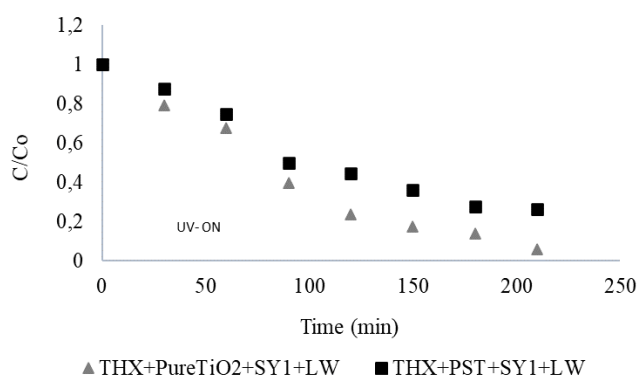


Figure 8. Effect of Perlite on photocatalytic degradation efficiency for System I.

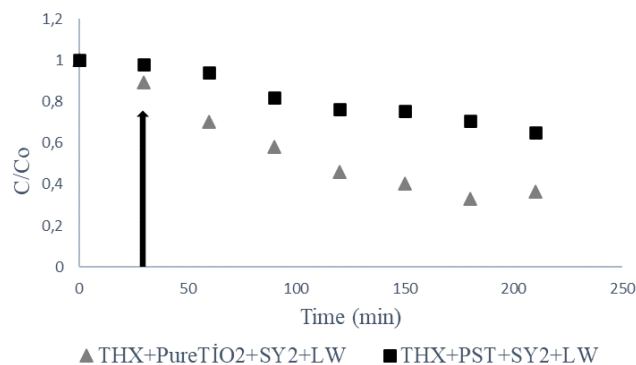


Figure 9. Effect of Perlite on photocatalytic degradation efficiency for System 2.

As we can see in Figures 8 and 9, when the degradation efficiencies for each system separately are compared, it was observed that the degradation efficiency is less in the perlite supported photocatalysts (SY1 and SY2). The contrasting performance of the two systems can be attributed to the differing light paths experienced by the THX molecules. In System 1 (horizontal irradiation), UV light directly interacts with the solution throughout the reaction vessel. Conversely, in System 2 (vertical irradiation), the perlite layer acts as a partial shield, deflecting and weakening the light before it reaches the THX molecules at the bottom. This reduced light exposure translates to lower photodegradation efficiency.

3.2.3. Effect of pH on Degradation Efficiency

To observe the effect of pH on photocatalytic degradation, one experiment was carried out with fixed solution pH at 4, while the other experiment was carried out without any fixing at its own pH value as 5.43. Looking closely at Figure 10, which represents the results of this study, we can state that pH does not have a big effect on photocatalytic degradation. Even so, a decreasing in efficiency was observed because of the degradation of THX reaches the optimum value at pH=4 [14].

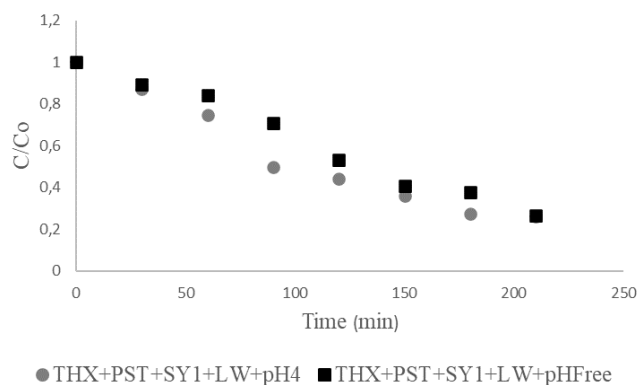


Figure 10. Effect of pH on photocatalytic degradation efficiency.

3.2.4. Effect of Temperature

Understanding the intricate relationship between temperature and photocatalytic efficiency is crucial for process optimization. Therefore, we implemented a three-pronged approach: controlled isothermal conditions at 20 °C and 30 °C to elucidate the fundamental impact of temperature, and a non-isothermal experiment (Figure 11) to mimic real-world scenarios with fluctuating temperatures and assess potential dynamic effects.

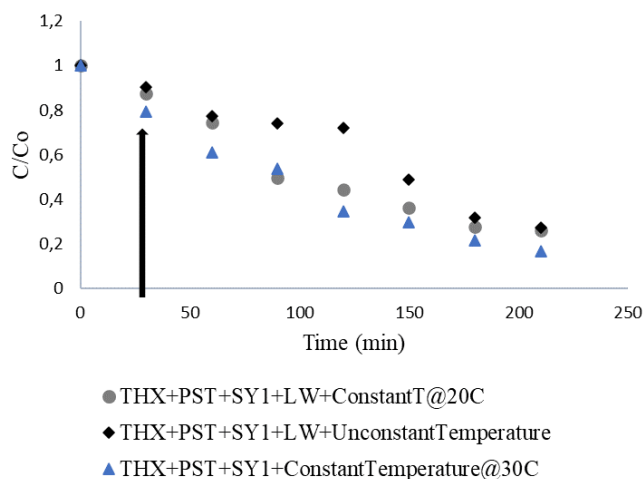


Figure 11. Effect of temperature on photocatalytic degradation efficiency.

Comparing system-specific efficiencies revealed that higher temperatures positively impacted photocatalytic degradation with perlite-supported TiO₂ in System 1. This aligns with literature reports, citing an optimal temperature of 36.2 °C for THX degradation using similar catalysts [15].

3.2.5. Effect of UV Wavelength on Degradation Efficiency

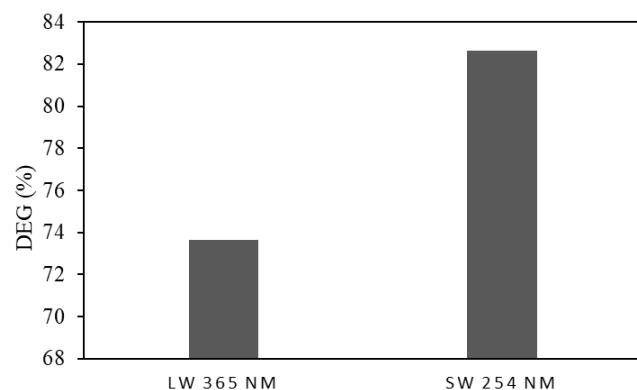


Figure 12. Degradation efficiency obtained by using a different wavelength UV lamp.

To understand the impact of UV wavelength on THX photodegradation efficiency with PST, experiments were conducted under optimal conditions using both a long-wavelength (LW, 365 nm) and a short-wavelength (SW, 254 nm) UV lamp (Figure 12). Notably, SW light achieved an 83% THX removal after 180 minutes, compared to 74% with LW light, demonstrating a slightly higher degradation capacity. However, it's crucial to remember that SW radiation poses significant safety concerns due to its harmful and carcinogenic nature, requiring stricter handling procedures.

3.3. Kinetic Modelling of THX Degradation

Linear plots of $-\ln(C/C_0)$ versus irradiation time indicated that the photocatalytic degradation of THX at the experimental conditions followed pseudo-first-order Langmuir–Hinshelwood kinetics (Figures 13, 14). Pseudo first order rate constants, $k(\text{min}^{-1})$, calculated from the slope of linear plots and obtained R^2 values were given in Table 2.

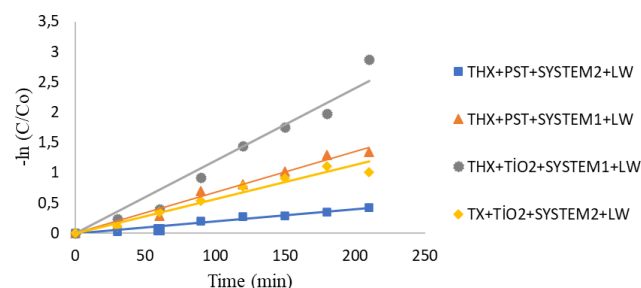


Figure 13. THX degradation kinetic modelling for each system.

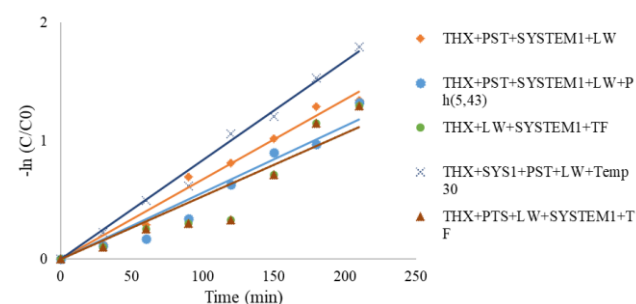


Figure 14. THX degradation kinetic modelling for different pH and Temperature.

Table 2. Pseudo first order rate constants (k_{app}) and R^2 .

	$k_{app}(\text{min}^{-1})$	R^2
THX+PST+SY1+LW	0.0067	0.9804
THX+PST+SY2+LW	0.0025	0.9625
THX+PureTiO ₂ +SY1+LW	0.012	0.9559
THX+PureTiO ₂ +SY2+LW	0.0057	0.9536

	$k_{app}(\text{min}^{-1})$	R^2
THX+PST+SY1+LW+FreeT	0.0053	0.8715
THX+PST+SY1+LW+pH (5.43)	0.0056	0.9468
THX+PST+SY1+LW+HighT	0.0084	0.9909

When the data are compared based on system, it can be seen that k_{app} values are higher in System 1. It can be concluded that THX degradation is faster in System 1 than in System2. Comparing the supported material effects, it can be seen that the k_{app} values are higher with Pure TiO_2 . Thus, the degradation rate of PT is higher than PST.

When the temperature effect is observed, it is shown that the unconstant (not arranged temperature) system has a lower k_{app} value. Thus, working with arranged temperature in the jacketed reactor resulted in higher degradation rate. THX degradation rate is maximum at 30°C . In addition, as expected, the k_{app} value is higher for pH at 4.

3.4. Total Organic Carbon (TOC) Analysis

This study employed Total Organic Carbon (TOC) analysis, a popular technique for assessing mineralization, to quantify the level of organic molecules or contaminants present in the water sample. TOC analysis boasts high specificity towards organic compounds and, ideally, captures all covalently bonded carbon present in the water. Because of its efficiency compared to SY2, the SY1 photoreactor was used in this experiment. Analyzing the TOC data in Figure 15 for THX demonstrates a substantial decrease from 12.21 mg/L to 1.76 mg/L after 270 minutes of degradation, corresponding to an 85.58% removal of organic carbon. This high level of organic carbon removal mirrors the observed THX degradation percentage of approximately 87%, indicating that the majority of the degraded THX likely mineralized completely within the photoreactor.

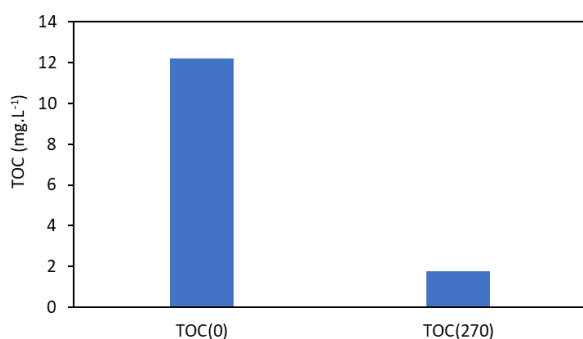


Figure 15. TOC analysis results for THX degradation.

3.5. Assessment of Organic Matter Reduction

To quantify the organic matter removal efficiency, Chem-

ical Oxygen Demand (COD) analysis was performed after THX degradation in SY1 (Figure 16). The COD of the THX solution (COD-THX) gradually decreased over time, reaching approximately 3 mg.L^{-1} after 270 minutes, indicating a reduction of 70% compared to the initial value of around 10 mg.L^{-1} . This suggests that after 270 minutes of irradiation, approximately 3 mg.L^{-1} of oxygen would be required to completely oxidize the remaining organic matter in the solution.

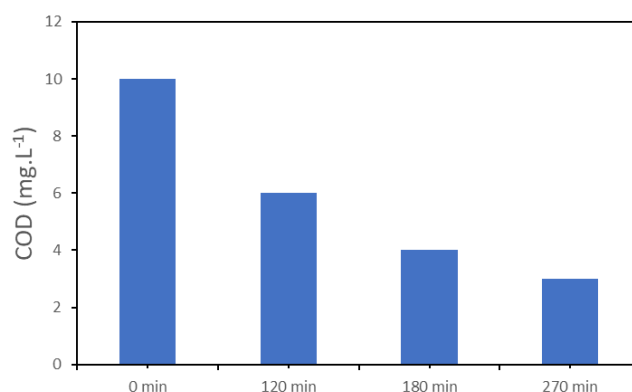


Figure 16. Variation of COD during the process.

4. Conclusions

TiO_2 /perlite composites were prepared by coating TiO_2 with perlite. Although almost all thiamethoxam was degraded by pure TiO_2 (Degussa P25) under 365 nm, 2x6W or 6W UV irradiation during 180 min, perlite supported TiO_2 showed lower capacity (about 35% in SY2, 74% in SY1) because of retarder effect of perlite to the light and air diffusion through TiO_2 photocatalyst embedded inside of perlite pores. The intimate contact between the three parameters which are UV light, the pollutant THX, and the TiO_2 photocatalyst supported or not in SY1 greatly favored its efficiency compared to SY2. Although perlite supported TiO_2 has lower degradation yield than TiO_2 , they can be easily separated from the mixture by taking advantage of the flotation method.

As a conclusion, perlite supported TiO_2 can be used industrially for pesticide degradation. However, the chosen photoreactor design should allow the UV light to pass through both the solution and the photocatalyst surface simultaneously. Perlite-supported TiO_2 offers a cost-effective approach for THX degradation in large-scale settings. Utilizing photoreactors like System 1 at low pH and without the need for cooling systems presents a practical and economical solution for industrial applications.

Abbreviations

COD	Chemical Oxygen Demand
EE/O	Electric Energy per Order

LW	Long-Wavelength (LW, 365 nm)
PST	Perlite Supported TiO ₂
PT	Pure TiO ₂
SW	Short-Wavelength (SW, 254 nm)
SY1	System 1
SY2	System 2
THX	Thiamethoxam
TOC	Total Organic Carbon

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Conflicts of Interest

The authors declare no conflicts of interest.

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