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Comparative analysis of the photocatalytic degradation of Malathion and Profenofos over Cu_2O, ZnO and TiO_2 nanostructures

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Abstract
Malathion and Profenofos are widely used organophosphate pesticides that can enter soil and water systems through agricultural activities, causing potential environmental and ecological concerns. Their persistence and complex chemical structures have increased the need for effective and environmentally sustainable degradation methods. Photocatalytic degradation using semiconductor nanomaterials has emerged as a promising approach for the removal of pesticide contaminants from environmental systems. This study provides a comparative assessment of the photocatalytic degradation of Malathion and Profenofos, with particular emphasis on Cu_2O, ZnO, and TiO_2 photocatalysts. The available literature on the properties, environmental significance, degradation behavior, and photocatalytic treatment of these pesticides is critically reviewed. The fundamental photocatalytic mechanism involving light-induced electron–hole generation and reactive oxygen species is discussed. The photocatalytic characteristics of Cu_2O, ZnO, and TiO_2 are comparatively examined to evaluate their potential for organophosphate pesticide degradation. Possible degradation pathways of Malathion and Profenofos are discussed based on reported studies, while existing limitations and research gaps are also identified. The comparative analysis provides useful insights into the role of semiconductor photocatalysts in the degradation of organophosphate pesticides and highlights the potential of Cu_2O, ZnO, and TiO_2 for future environmental remediation applications.

Keywords: Malathion, Profenofos, Organophosphate pesticides, Photocatalytic degradation, Cu_2O, ZnO, TiO_2

Introduction
Organophosphorus pesticides find wide use in agriculture due to their high efficacy against diverse insect pests. But frequent use of these chemicals results in the accumulation of residues in soil and water environments posing possible threats to environmental quality and non-target organisms. [1] Therefore, studies aimed at researching their persistence and transformations have become a topical issue to develop efficient degradation procedures.
Malathion is an essential organophosphate insecticide used widely in pest control. This compound as well as its degradation products receive much scientific interest due to their presence in environment. [2] In turn, Profenofos is one of the common organophosphate insecticides used to protect crops from pests. Environmental fate and possible impacts of Profenofos on ecosystems have prompted scientists to study approaches for degradation and elimination of this compound. [3]
Pesticide elimination is usually performed by traditional techniques such as adsorption, biodegradation and chemical oxidation. However, there are some drawbacks associated with these approaches that include incomplete degradation and production of secondary waste. Advanced oxidation procedure is one of the promising methods used for pesticide degradation, since semiconductor photocatalysts create active species in appropriate conditions. Reactive species react with organic compounds and initiate their decomposition into simple products. [4] Among semiconductor catalysts the following substances are studied actively to degrade organic pollutants: TiO_2 and ZnO. They have appropriate photocatalytic properties, stability and environmental applicability. [5] Nevertheless, the efficiency of photodegradation process depends on many factors like light absorption, charge separation, surface properties and interaction between pollutant and photocatalyst.
Another interesting feature of Cu_2O is that it has been considered as an excellent semiconductor photocatalyst due to its light-visible action and electronic properties. Thus, the use of this material in the photodegradation of contaminated environmental media has also attracted significant research attention. [6] The comparative study of the properties of Cu_2O, ZnO and TiO_2 can help understand better which photocatalysts are good choices to degrade organophosphate pesticides. Although there have been considerable advances in pesticide photodegradation, there has not been much literature on a comparative study of Malathion and Profenofos compared to Cu_2O, ZnO and TiO_2 nanoparticles. This work aims at making a comparative analysis of the degradation process, photocatalytic mechanism and probable degradation pathways of Malathion and Profenofos over these semiconductor materials.

Literature Review
The decomposition of Malathion was previously investigated by various researchers employing different chemical, biological, and advanced oxidation methods. The recent investigations were related to the decomposition of Malathion in photolytic conditions, and the results showed that the semiconductors-based systems could efficiently enhance the transformation of the pesticide using the generation of reactive oxygen species. [7] Other studies explored the impact of irradiation time, catalyst concentration, pH, and initial concentration of the pesticide on the decomposition process and found that the decomposition efficiency is highly dependent on the operating parameters. [8] The photocatalytic treatment was reported to lower the concentration of the Malathion via oxidation reactions, although the appearance and further

decomposition of intermediate products was considered an important issue. [9]
The degradation of Profenofos was also studied by using the advanced oxidation and photocatalytic treatment techniques. The investigators showed that Profenofos could be decomposed in the irradiation conditions in presence of appropriate catalysts and reactive species. [10] Another study investigated the decomposition of Profenofos under various treatment conditions and demonstrated that the efficiency of the decomposition process is affected by catalyst characteristics and irradiation conditions. [11] Other researchers explored the transformation of Profenofos in the environment and found that such processes as hydrolysis, photochemical reactions, and biodegradation could be involved. [12] These studies revealed the necessity to develop the appropriate strategies for the treatment of the contaminated water and soil with Profenofos. The photocatalytic decomposition of the organophosphate pesticides attracted more and more interest among the researchers due to the generation of the electron-hole pairs under irradiation in the semiconductor-based catalysts. [13] It was reported that the formed reactive oxygen species, mainly hydroxyl and superoxide radicals, attack the pesticide molecules and facilitate their transformation into the smaller degradation products. [14]
From among the most commonly studied photocatalysts, TiO_2 and ZnO seemed to have potential in degrading organic pollutants due to their stability and good photocatalytic performance. [15] Similarly, Cu_2O was another visible light sensitive semiconductor and had shown potential in photocatalysis applications. [16] In general, past studies have shown that semiconductor photocatalysis was a useful method of breaking down pesticides; however, studies directly comparing Malathion and Profenofos on Cu_2O, ZnO and TiO_2 seemed to be comparatively rare. The lack of such study had formed the foundation of the current comparison of the pesticides and photocatalysts.

Fundamentals of Photocatalysis

Photocatalysis is an advanced oxidation process in which a semiconductor photocatalyst absorbs suitable light energy and generates electron–hole pairs. These charge carriers participate in surface redox reactions and contribute to the formation of reactive oxygen species (ROS), which can oxidize and degrade organic pollutants such as pesticides. The overall efficiency of photocatalysis depends on light absorption, charge separation, surface reactions, and the interaction between the photocatalyst and pollutant molecules.

1. Principle of Photocatalysis

When a semiconductor absorbs photons with energy equal to or greater than its band-gap energy, electrons are excited from the valence band (VB) to the conduction band (CB), generating electron–hole pairs.
Semiconductor + hν → $e^-(CB) + h^+(VB)$
The photogenerated electrons and holes migrate toward the surface of the photocatalyst, where they participate in reduction and oxidation reactions. Efficient charge separation is important for photocatalytic activity, whereas rapid electron–hole recombination reduces the availability of charge carriers and decreases the degradation efficiency.

2. Formation of Reactive Oxygen Species (ROS)

The photogenerated electrons and holes participate in surface redox reactions and generate reactive oxygen species (ROS). Conduction-band electrons can react with dissolved oxygen to produce superoxide radicals, while valence-band holes can react with water or hydroxyl species to generate hydroxyl radicals.

$$O_2 + e^- \rightarrow \bullet O_2^-$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+$$

The generated ■O_2^- and ■OH species are highly reactive and can attack pesticide molecules, initiating oxidation and chemical transformation.

Table 1: Major Reactive Species Involved in Photocatalytic Degradation

Reactive Species	Role
h^+	Oxidation of pesticide molecules
•OH	Strong oxidation and chemical bond cleavage
$\bullet O_2^-$	Oxidation and transformation of organic molecules
O_2	Electron acceptor and precursor of superoxide radicals

3. Photocatalytic Degradation Mechanism

The photocatalytic degradation of pesticides involves the interaction of pesticide molecules with the illuminated photocatalyst surface and their subsequent oxidation by the generated reactive species. Initially, pesticide molecules may adsorb onto the photocatalyst surface. The reactive species then attack susceptible functional groups and chemical bonds within the pesticide structure, resulting in structural transformation and the formation of intermediate products. These intermediates may undergo further oxidation and eventually form simpler products.
The overall transformation can be represented as:
Pesticide + ROS → Degradation intermediates → Simpler products → Mineralization
Under favorable conditions, further oxidation may lead to mineralization and the formation of relatively simple products such as CO_2, H_2O, and inorganic species.

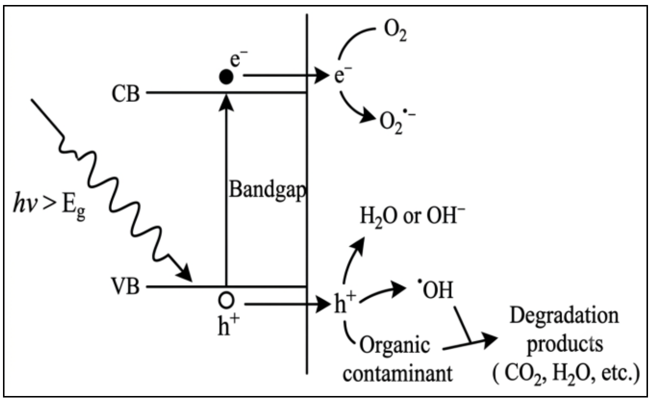

Fig 1: Schematic representation of semiconductor photocatalytic degradation of pesticides

4. Factors Affecting Photocatalytic Degradation

The efficiency of pesticide photodegradation is influenced by several factors, including light wavelength and intensity, photocatalyst type and dosage, initial pesticide concentration, pH, irradiation time, dissolved oxygen, and surface properties of the photocatalyst. These parameters influence pesticide adsorption, light utilization, charge-carrier behavior, ROS generation, and subsequent oxidation reactions. Therefore, proper control and optimization of these factors are important for achieving efficient photocatalytic degradation of Malathion and Profenofos.

Comparative Photocatalytic Analysis of Malathion and Profenofos over Cu_2O, ZnO and TiO_2 Nanostructures

Cu_2O, ZnO and TiO_2 are important semiconductor photocatalysts for the degradation of organic pollutants. Their photocatalytic activity depends mainly on band gap, light absorption, charge separation, surface properties and reactive oxygen species (ROS). Recent studies have shown that doping and heterojunction formation can improve the photocatalytic performance of these materials.

1. Cu_2O as Photocatalyst

Cu_2O is a p-type semiconductor with a narrow band gap of about 2.0–2.2 eV, allowing visible-light absorption. However, charge recombination and photocorrosion can limit its stability. Hosseinzadeh (2023) [17] reported that a ZnO–Cu_2O heterojunction containing 40 wt% Cu_2O showed the best activity for paraoxon degradation, with a rate constant of 0.0201 min^{-1} under visible light. The enhanced activity was attributed to better visible-light absorption and reduced electron–hole recombination. [1]

2. ZnO as Photocatalyst

ZnO is an n-type semiconductor with a band gap of approximately 3.2–3.4 eV and mainly responds to UV light. It has good surface activity and can generate reactive species such as ■OH and O_2■$^-$. Its visible-light limitation can be reduced by coupling it with Cu_2O. The ZnO–Cu_2O heterojunction showed higher photocatalytic activity than pure ZnO. [1]

3. TiO_2 as Photocatalyst

TiO_2 is widely used because of its high stability, low toxicity and strong photocatalytic activity. Its band gap is about 3.0–3.2 eV, so its activity is mainly under UV light. Liu *et al*. (2019) [18] reported that Ce-doped TiO_2 increased Profenofos degradation from 34% to 53.3% after one day under field conditions. Increased ROS generation was associated with the enhanced degradation. [2]

4. Comparative Analysis of Cu_2O, ZnO and TiO_2

Cu_2O, ZnO and TiO_2 showed different photocatalytic characteristics due to their differences in band gap, light absorption and charge-carrier behaviour. Cu_2O had better visible-light absorption, whereas ZnO and TiO_2 mainly responded to UV light. TiO_2 showed better chemical stability, while the ZnO–Cu_2O heterojunction improved visible-light utilization and reduced electron–hole recombination. The reported experimental results are summarized in Table 2.

These results indicate that Cu_2O is promising for visible-light photocatalysis, ZnO provides good surface reactivity, and TiO_2 offers high stability and established photocatalytic performance.

5. Comparative Degradation of Malathion and Profenofos

Malathion and Profenofos contain phosphorus-containing functional groups that can interact with photocatalyst surfaces and reactive oxygen species (ROS). Their degradation therefore depends on molecular structure, surface interaction and photocatalyst properties. Direct photocatalytic data for Malathion and Profenofos over pure Cu_2O, ZnO and TiO_2 are still limited. However, reported studies provide useful comparative evidence.

Table 2: Comparative photocatalytic properties and reported results of Cu_2O, ZnO and TiO_2

Property	Cu_2O	ZnO	TiO_2
Semiconductor type	p-type	n-type	n-type
Band gap	~2.0–2.2 eV	~3.2–3.4 eV	~3.0–3.2 eV
Light response	Visible light	Mainly UV	Mainly UV
Major advantage	Better visible-light absorption	Good surface activity	High stability
Major limitation	Photocorrosion/recombination	Limited visible-light absorption	Limited visible-light absorption
Reported pesticide	Paraoxon	Paraoxon	Profenofos
Reported result	ZnO–Cu_2O (40 wt% Cu_2O): k = 0.0201 min^{-1} [17]	Activity improved in ZnO–Cu_2O heterojunction [17]	TiO_2/Ce increased Profenofos degradation to 53.3% after 1 day [18]

Table 3: Reported degradation results relevant to Malathion and Profenofos

Pesticide	Photocatalyst / Treatment	Reported result
Profenofos [18]	TiO_2/Ce	53.3% degradation after 1 day
Profenofos [18]	Natural degradation	34% degradation after 1 day
Malathion [19]	Bacterial consortium	7.37 → 2.25 area% in 96 h; 0% at 192 h
Profenofos [19]	Bacterial consortium	6.91 → 2.21 area% in 96 h; 0% at 192 h
Paraoxon [20]	ZnO/Cu_2O heterojunction	k = 0.0201 min^{-1}

Paraoxon is included as supporting evidence for organophosphate pesticide photocatalysis, not as a direct Malathion/Profenofos result.

These results indicate that TiO_2-based photocatalysis has demonstrated direct activity toward Profenofos, while Cu_2O–ZnO heterojunctions show promising visible-light photocatalytic performance toward organophosphate pesticides. [1, 3] Direct comparative experiments on Malathion and Profenofos using Cu_2O, ZnO and TiO_2 are therefore needed.

Degradation Pathways of Malathion and Profenofos

The photocatalytic degradation of Malathion and Profenofos over Cu_2O, ZnO and TiO_2 involves light absorption followed by the generation of electron–hole pairs. These charge carriers produce reactive oxygen species (ROS), mainly ■OH and O_2■$^-$. The generated ROS attack the pesticide molecules and cause cleavage of susceptible bonds and functional groups. The resulting intermediate compounds undergo further oxidation and degradation, leading to smaller and less harmful products.

For Malathion, degradation may involve attack on its phosphorus-, sulfur- and ester-containing groups. For Profenofos, the phosphorus-containing groups and other susceptible bonds can undergo oxidative cleavage. The degradation pathway therefore depends on the molecular structure of the pesticide as well as the surface and electronic properties of the photocatalyst.

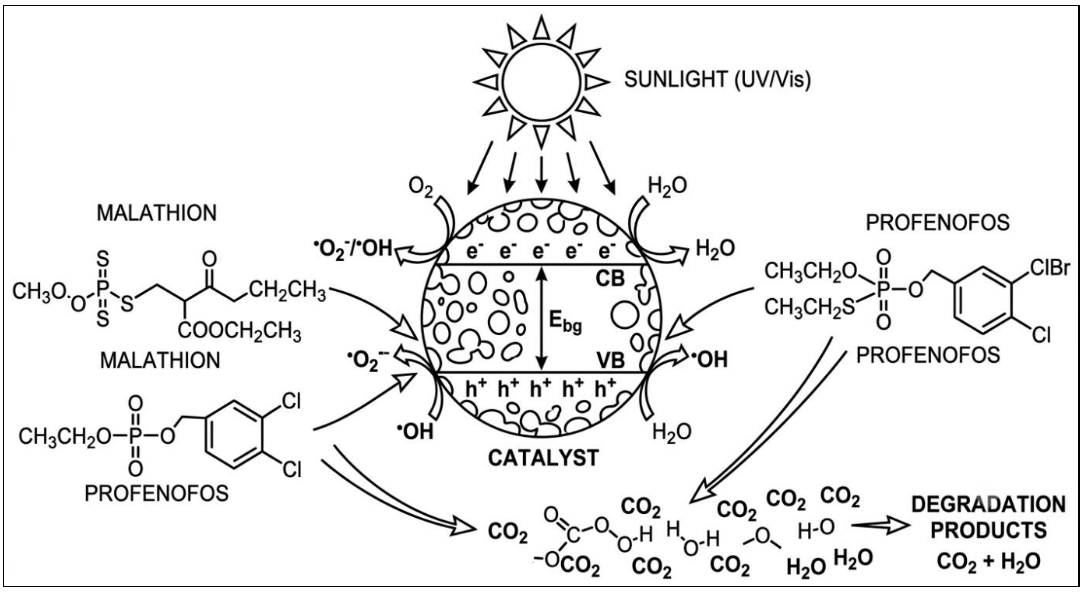

Fig 4: Photocatalytic Degradation Pathways of Malathion and Profenofos

Conclusions

Malathion and Profenofos are important organophosphate pesticides that can persist in environmental systems and require effective degradation methods. Cu_2O, ZnO and TiO_2 are promising semiconductor photocatalysts because of their ability to generate electron–hole pairs and reactive oxygen species under light irradiation. Cu_2O offers better visible-light absorption, while ZnO and TiO_2 provide good surface activity, stability and oxidation potential. Reported studies have demonstrated enhanced degradation of Profenofos using modified TiO_2 and improved photocatalytic activity of Cu_2O/ZnO-based systems for related organophosphate pesticides. However, direct comparative experimental data for Malathion and Profenofos over Cu_2O, ZnO and TiO_2 are still limited. Therefore, comparative experimental and computational studies are required to understand their degradation pathways, surface interactions and photocatalytic efficiency.

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