



## Review Article

# A Critical Review of Photocatalytic Degradation of Organophosphorus Pesticide “Parathion” by Different Mixed Metal Oxides

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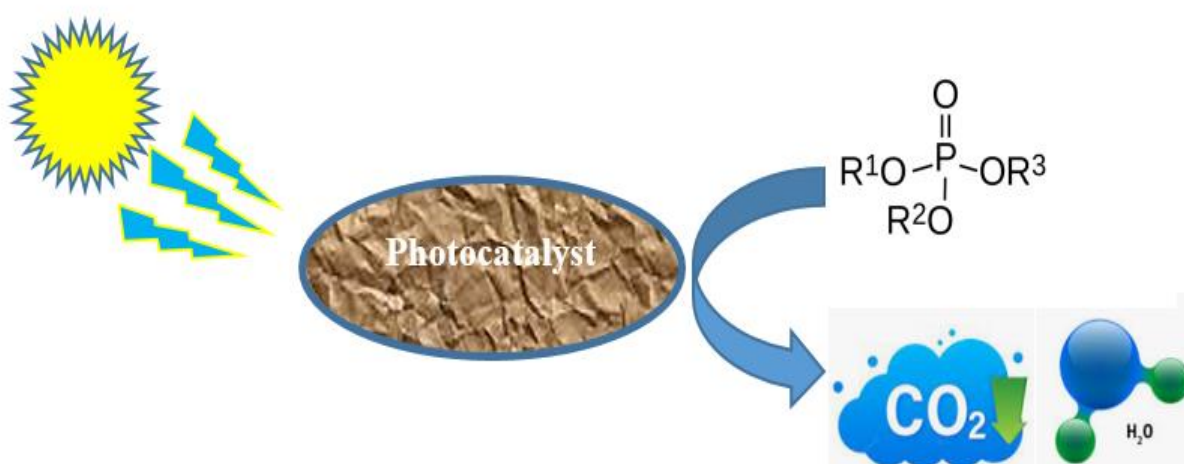
Parathion

Organophosphorus pesticide

## ABSTRACT

Pesticides are utilized to control pests; however, they are persistent and included in the top 10 toxic pollutants list. Despite toxicity, organophosphorus pesticides are the most widely used pesticide nowadays. Photocatalysis is an efficient way to degrade highly persistent pesticides. Features such as small size, high porosity, high surface area, and crystalline nature make metal oxides and mixed metal oxides efficient photocatalysts for the degradation of organo-phosphorus pesticide. In the current review, degradation of organo-phosphorus pesticide parathion by mixed metal oxides such as iron oxide, cerium oxide, titanium oxide, zinc oxide, zirconium oxide, and copper oxides are discussed in light of updated research data. Total use, toxicity, degradation methods, and Photocatalysis using different metal oxides are thoroughly discussed. The review provides complete details on the photocatalysis mechanism, advancements in Photocatalysis, and advanced strategies to increase the photocatalyst's and metaloxide-based photocatalysis's efficiency.

## GRAPHICAL ABSTRACT



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## Introduction

Nearly 9000 species of insects, 50,000 species of plant pathogen, and 8000 types of harmful weeds damage crops worldwide. [1,2] Fertilizers, pesticides, and plant growth stimulators are necessary to increase average crop yield. According to analysis, without pesticides, loss in crops will be exceeded up to 54-78%. To improve yield, farmers apply more pesticides than those validated by extension agents. If pesticides are used in excess, they are hazardous even at low concentrations. Pesticides are necessary because they help control pests and increase crop yield. However, their level of poisoning and safe limit must be known. Internationally, almost 3 billion kg of pesticides is used annually, costing ~40 billion USD [3]. As a result, their long-term use may lead to severe environmental and health issues. Though pesticides have been developed to control target organism toxicity, one of the major issues is that most of the time, they equally affect non-target species as well. A work led by Pimentel proved that only 0.3% of the total applied amount hit the aimed specie, whereas 99.7% affects surrounding species. A considerable amount of total pesticide never reached the target organism [4]. Pesticides are highly fat soluble, which is why they are highly dangerous for the target and non-target organisms. Some features of pesticides, such as high lipophilicity, bio-accumulation, extensive half-life, non-biodegradability, and long transport range, are responsible for poisoning the air, water, soil, and living organisms even after decades of application. According to the National Academy of Sciences, the chief cause of pesticides affecting infants or adults would be diet. According to the U.S. Pesticide Data Report, a noticeable amount of Malathion was present in 28% blueberries, 25% strawberries, and 19% celery samples. According to EPA, around 40 organophosphorus pesticides are registered for safe usage in the United States. Pesticide

occurrence in the diet is up to 30% [5]. Pesticides are considered as the most toxic and harmful chemicals invented by men. This study discusses the degradation of organo-phosphorus pesticide parathion methyl by different mixed metal oxides and their relative efficiency.

## Pesticides

Any substance designed and employed to prevent, destroy, kill, or control any kind of pest is called a pesticide [6]. Pesticides are persistent chemicals frequently used to increase yield production by controlling the pest. They are also called "PPP" plants protection product [7].

## Classification

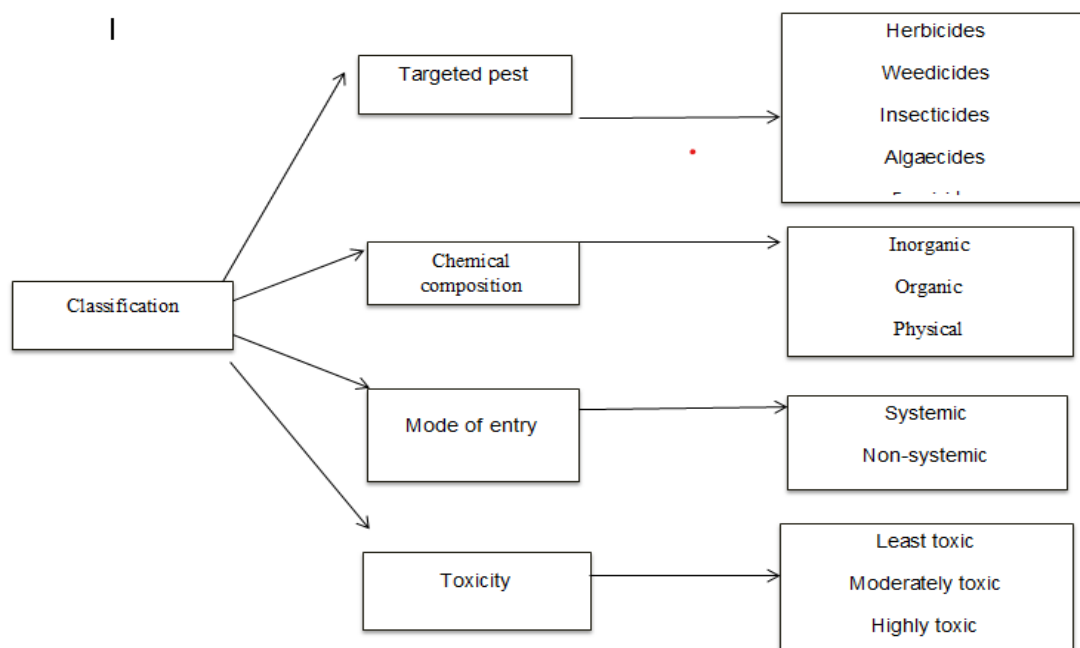
Pesticides can be classified in several ways; the general overall classification is given in Figure 1.

## Targeted pest

The first and simple classification of pesticides is based on targeted pests. This classification includes six major insecticides: herbicides, rodenticides, algacides, fungicides, and bactericides [8].

- a) Insecticides include organophosphates (TEPP, parathion, trimesters of phosphates and phosphoric acids), carbamates (aldicarb), organochlorines (dichlorodiphenyltrichloroethane, chlordane, Aldrin, dieldrin, lindane, endrin) and botanical insecticides (nicotine, rotenoids, and pyrethrum).
- b) Herbicides are used to destroy other invasive weeds by inhibiting of photosynthesis and oxidative stress. Based on their structure, they are grouped into chlorophenoxy compounds (e.g., 2,4-D, 2,4,5-T), dinitrophenols like 2-methyl-4,6-dinitrophenol (DNOC), bipyridyl compounds like paraquat, carbamate herbicides, substituted urea, triazines and amide herbicides like alanine derivatives.

- c) Fungicides prevent fungus growth and include several structurally different chemicals like cap tan, folpet, pentachlorophenolzirarn, and nambam.
- d) Rodenticides are pesticides that kill rodents (rats, mice, squirell, chipmunks, beavers, porcupines). In this type, there are further two categories coagulant and anti-coagulants. Rodenticides include chlorphacinone, brometalin , diphacinone, zinc phosphide, and strychnine.
- e) Algaecides prevent and control the growth of algae in crops. Copper sulfates, copper chelates, and copper citrates are important algaecides.
- f) Bactericides kill bacteria's. An important example includes sodium di-acetate.



**Figure 1.** Classification of pesticides

#### Mode of entry

Based on the mode of entry, pesticides are of two type's systemic and non-systemic pesticides.

- a) Systemic pesticides are those pesticides that are taken and translocated to plant tissues. Systemic pest repellents are highly penetrating; they quickly enter and destroy intended entities through a uni-directional or multi-directional pathway. Penetration depends on physiological pH, vegetable and fruit matrix, and humidity. Significant examples include the carbofuran pesticide. Even these pesticides can be found in the tissues of the plant after ninety days.

- b) Non-systemic pesticides cannot enter the plant. These pesticides cannot penetrate plants, so they are less toxic than the above class.

#### Toxicity

Some pesticides are highly hazardous and classified as type 1, some are moderately hazardous and classified as type 2, and some are least hazardous and classified as type 3.

#### Chemical composition

Further, three categories are inorganic pesticides, organic pesticides, and biopesticides.

- Inorganic pesticides include Paris-green, sodium fluoride, sulfur, zinc, and copper.
- Organic pesticides include organophosphorus, organochlorine, organohalogen, triazines, substituted urea, phenol derivatives, carboxylic acid derivatives, and carbamate. 500 organic pesticides with 54,000 different formulations are in use.
- Biopesticides include Neem products, canola, oil, baking soda, and microorganism.

The four main pesticides are organochlorines, organophosphate, carbamates, and synthetic pyrethroids.

#### Organochlorine

Despite organochlorine pesticides being banned in 1960's [9] they are still used in some countries like North Korea, India, and Japan. Organochlorine is a synthetic pesticide and one of the most persistent organic pollutants. Being persistent and recalcitrant, they are banned, but still, they are used in developing countries. Some harmful effects are discussed in Table 1.

**Table 1.** Harmful effects of some organochlorine pesticides

Name	Harmful Effects	References
Dichlorodiphenyl-trichloroethane (DDT)	Lacrimation, anorexia, bradycardia, abdominal pain, hyperactivity, fretfulness, melancholy, and vomiting	USEPA 2000 Peterson & Talcot 2006
Lindane	Damage human liver, kidney, neural and immune system & induce birth defects, cancer, neurotoxicity, reproductive toxicity, and hepatotoxicity	Sahoo <i>et al.</i> , 2008 Bano and Bhatt 2010 Vijaya Padma <i>et al.</i> , 2011
Dialdrin	Neurotoxic, infertility, genotoxic, tumorigenic, anaemia	USEPA, 2003
Diazion	Hazy image, nervousness, psychiatric indications	Reigert & Roberts, 1999 Wagner, 1997 USEPA 2000

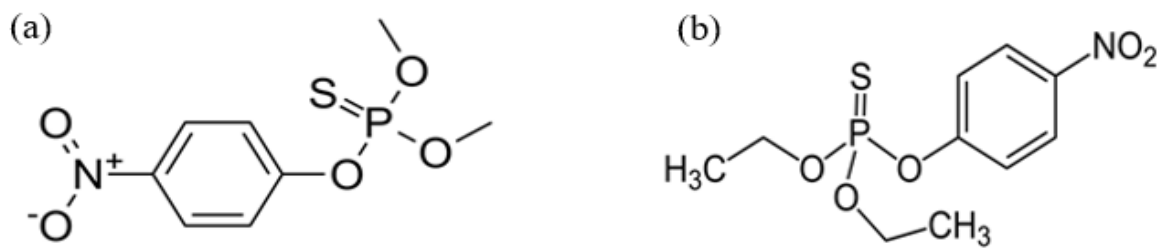
#### Organophosphorus

O.P.s have chiefly replaced organochlorine insecticides, having the additional benefit of being more rapidly biodegradable and less persistent. However, they are most toxic because they contain phosphoric acid. There are signs of histopathological and biochemical variations in the brain, kidney, liver, cardiovascular, blood, and uterus of O.P.s treated animals by induction of oxidative stress. Several teleosts change their behavior when treated with O.P.s and carbamates. The toxico-kinetics and toxico-dynamics of organophosphate depend not only on the path and degree of exposure but also on the agent's chemical nature. Around forty

organophosphate pesticides are listed with the E.P.A. in the U.S.

#### Parathion

Parathion comes under the category of organophosphate. It is one of the best-selling pesticides; however, unfortunately, it is 'extremely hazardous'. Parathion is an organophosphate pesticide with P=S bond. It is further classified according to the alkyl group attached as shown in Figure 2a and b. Features such as bio-accumulative and less solubility in groundwater and soil, its adsorption, souring, evaporation, and the abundance of intermediate can cause severe harm to our ecosystem.



**Figure 2.** (a) chemical structure of methyl parathion and (b) ethyl parathion

#### Carbamates

Carbamates pesticides (C.M.s) are the third primary class of pesticides used widely worldwide. These compounds are derived from carbamic acid. When these neurotoxic pesticides enter the water system, they affect the aquatic population badly. Now recent research goal is to efficiently remove organic toxins from the environment. Consequently, considerable efforts are devoted to achieving the goal. These pesticides have extremely high endocrine disrupting potency, so even their low concentration can be lethal. Because of the persistency and deadliness of these compounds, even at minute levels, there is increasing demand for the systems to sense, screen, and eliminate them without producing harmful byproducts.

#### Pyrethroids

The fourth class based on chemical composition is pyrethroid pesticides. Pyrethrins are their active element and are of two types: natural and synthetic pyrethroids.

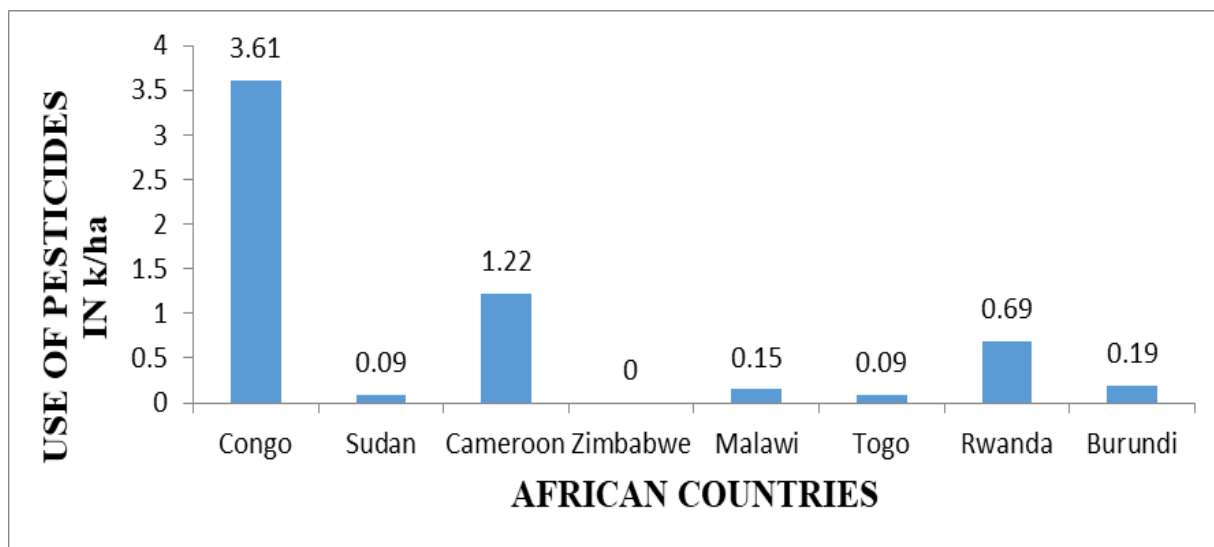
#### Use of pesticides

Consumption of pesticides is increasing by increasing the world population. However, overuse is not a scientific approach; it often leads to the growth of herbicide-resistant weeds, which may damage crops. In Australia, it is observed that wildflowers, for instance, *Avena*, *R. raphanistrum* and *Hordeum*, are herbicide resistant [16]. Excessive application should be avoided to solve the problem. Out of total pesticides most widely used pesticides are herbicides, followed by other types.

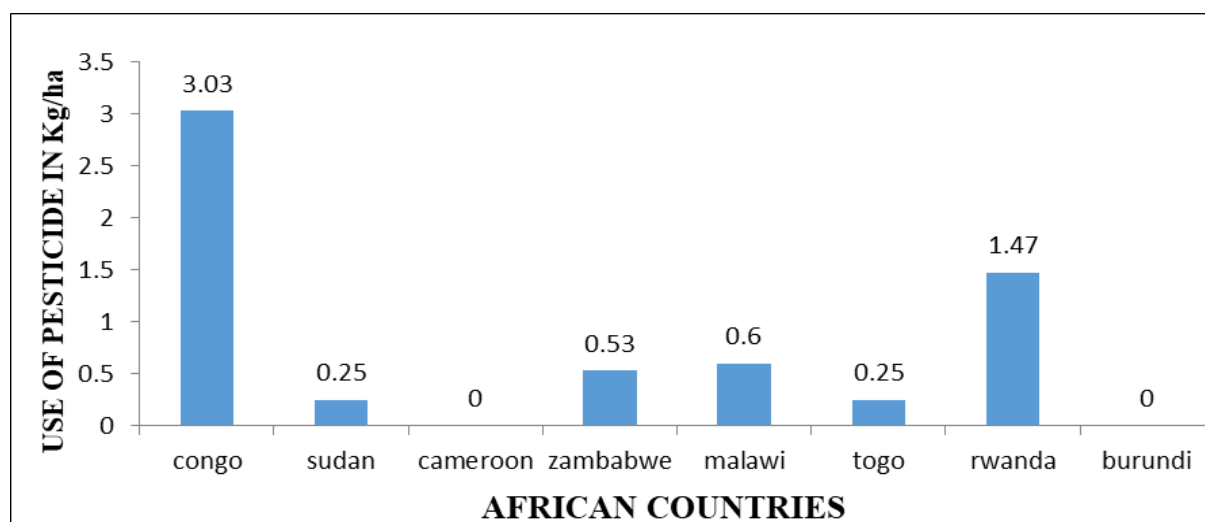
The highest pesticide-consuming countries are China, America, Argentina, Thailand, Brazil, Italy, France, Canada, Japan, and India.

#### Use of pesticide in Africa

In comparison among African countries Congo having highest use of pesticide followed by Sudan, Zimbabwe, Malawi, Togo, Rwanda, and Burundi, as shown in Figure 3. In Africa, most of the farmers use Malathion even though it is moderately hazardous, according to WHO.



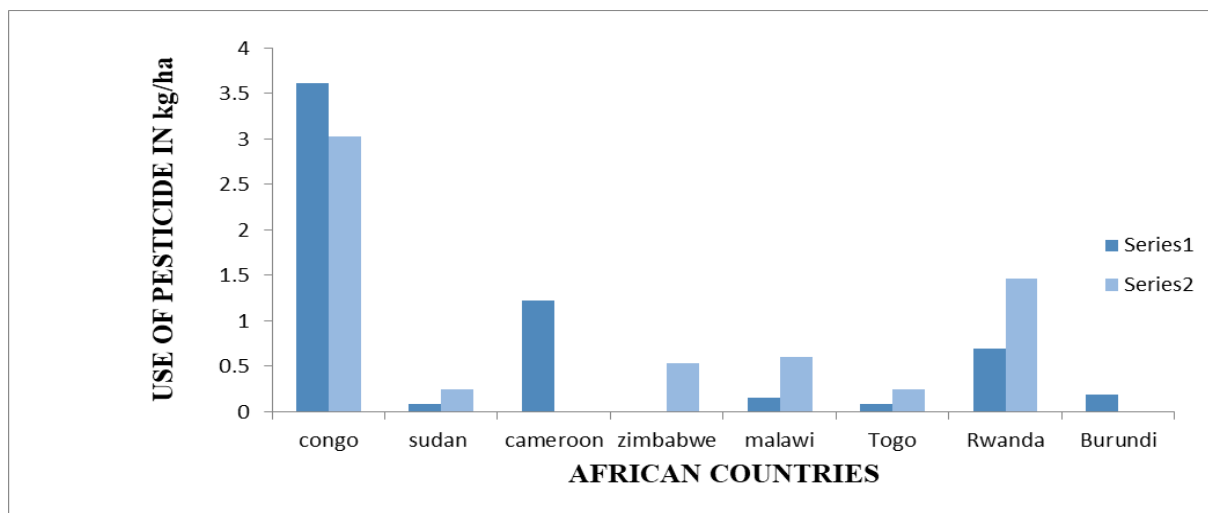
**Figure 3.** Use of pesticides in Africa in 2010



**Figure 4.** Amount of Pesticides used in Africa in 2014

According to Figure 4, the minor use of pesticides is in Zimbabwe, followed by Togo and Sudan (0.09 kg/ha), followed by Malawi (0.15), followed by Burundi (0.19 kg/ha), followed by Rwanda (0.69 kg/ha). The highest value is reported for Cameroon (1.22 kg/ha). A similar

study was conducted in 2014, with slightly different results. Figure 5 is again the same study but in 2014. According to this data, the highest consumption occurs in Congo, and Cameroon and Burundi are the minimum pesticide-pesticide-consuming countries.



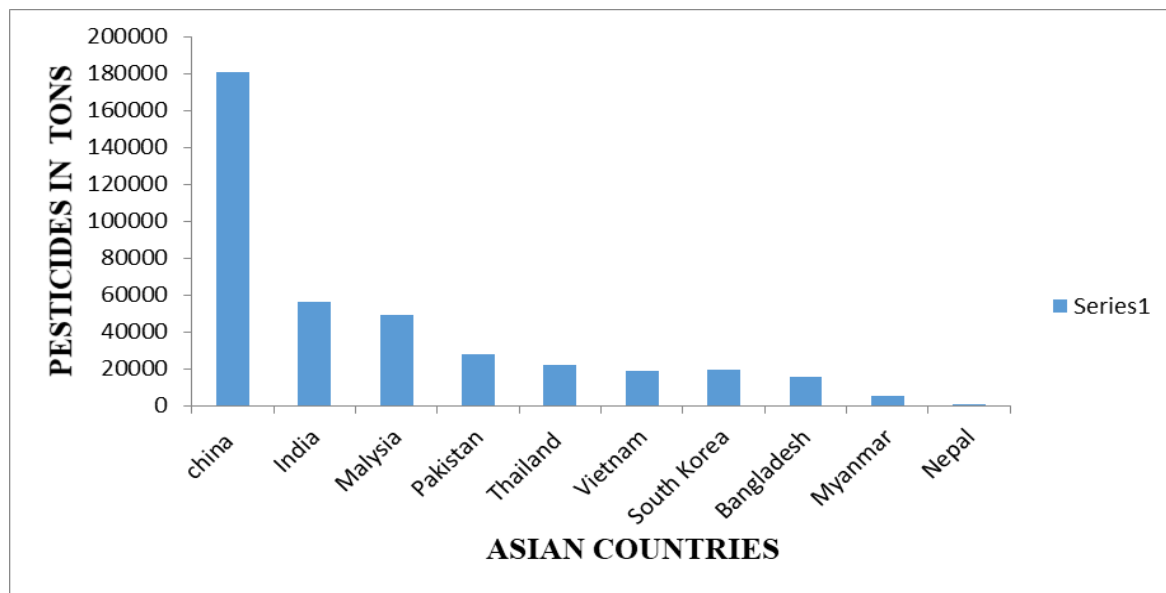
**Figure 5.** Comparison of total use of pesticides in different countries of Africa in 2010 vs. 2014

Figure 5 reveals that the total use of pesticides dropped in Congo while a clear increase is observed in other countries from 2010–2014.

#### *Use of pesticides in Asia*

Asia is a highly populated continent with almost 4.56 billion population, so to fulfill the demand of a large population, this region is consuming the most significant amount of pesticides. India

produces 56120 tons of pesticides annually. Similarly, Pakistan uses 27885 tons of pesticides on an annual basis. Bangladesh is a major rice-producing country, so to prevent the crops from pest attacks, Bangladesh used 15833 tons of pesticide in 2017. In Bangladesh, most pesticides are in the granular form and sometimes in the form of powder or liquid. Nepal uses 454 tons of pesticides annually. China is the world's highest pesticide producer, consumer, and exporter [11].



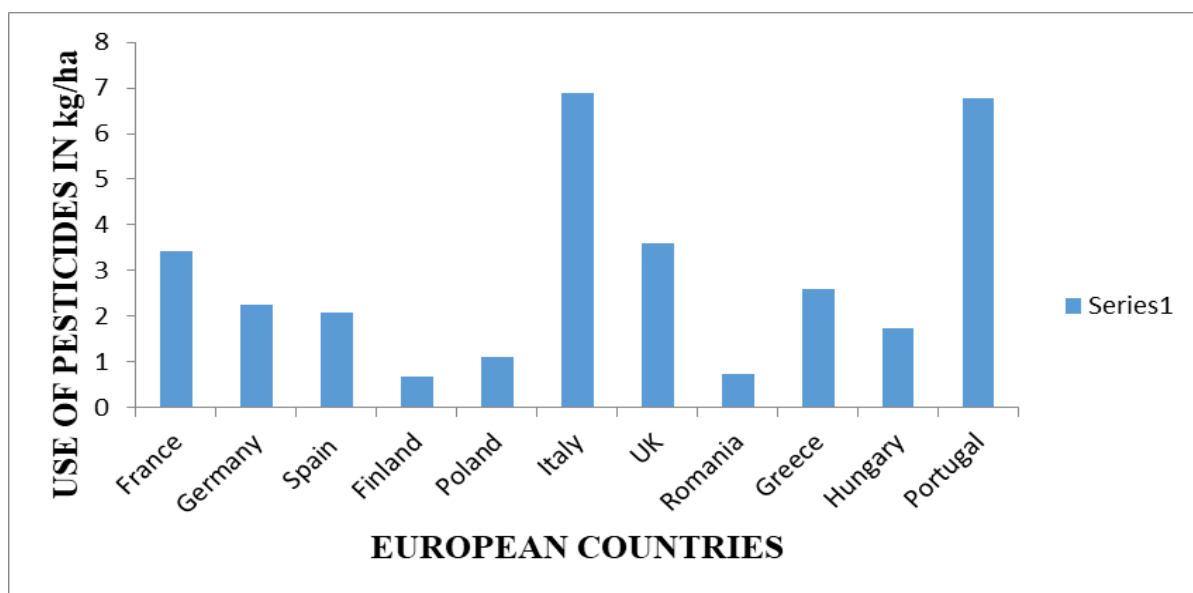
**Figure 6.** Annual use of pesticides in different Asian countries



According to Figure 6, China contributes more than all other countries in Asia, followed by India and Malaysia.

#### *Use of pesticide in Europe*

The total population of Europe is 746.4 million, and it is the third most populated continent. To control the pest attack, approximately 400'000 tons of pesticides are used by Europe each year.



**Figure 7.** Use of pesticides in 2012 in Europe

#### *Use of pesticides in north and south America*

Five hundred million kg of pesticides are used in America annually with an average cost of 1 billion or more. Atwood and Paisley-Jones find out that America accounts for about 18% of the total world usage of pesticides. Among all classes of pesticides, U.S. uses herbicides almost 60%. Around 90% is used by the agricultural sector and the rest by the nonagricultural sector. Mexico is the third big market in America for agrochemicals. Mexico is also in 6<sup>th</sup> number for the use of DDT (Dichlorodiphenyl-trichloroethane) [12]. During the past decade, several studies have been conducted in Latin America to reveal the toxic nature of pesticides. In Mexico, an analysis conducted on 30 people exposed to pesticides proved higher genotoxicity compared to the unexposed group when tested by S.C.E. and M.N. [13] Excessive use of

agricultural chemicals is reported in America, with the majority of glyphosate-based chemicals [14]. In Brazil, half a million tons of pesticides were reported in 2013. Similarly, Argentina consumes 236 million kg/year. Like North America's major pesticide is herbicide 64%. However, the demand for pesticides is still increasing in South America.

#### *Sources of pesticides*

##### *Point sources*

Any spill of pesticide during spraying, transport, and filling. They initially enter the environment through point sources and then further dispersed [15].

### *Nonpoint sources*

Most pesticides are highly stable substances and possess long-range transport, so they can travel and contaminate areas far away from their original point source. Nonpoint source contamination starts with rains and precipitation [16].

### *Pesticide pollution*

Pesticide pollution is a global issue that needs to be openly addressed to sustain the environment. Pesticides equally affects air, water, and soil. It is estimated that 0.2 Million tons of pesticides percolate below the roots each year worldwide. [17] South America, and Asia, mainly Brazil, Japan, Chile, China, Malaysia, and Argentina, are highly pesticide-polluted countries. Misuse and overuse of pesticide is the main reason for pesticide pollution.

### *Soil pollution*

Four major pesticides entering the soil are leaching, volatilization, diffusion, and runoff. Sandy texture, high precipitation, low organic matter, and low temperatures are key factors. Penetration is also influenced by the polarity of the pesticide [18]. Permeability of soil and the dose of pesticide applied are also very crucial. When considering pesticide pollution, soil taxonomy, composition, texture, and profile are essential. When pesticides are applied to soil, particular binding develops between pesticide and soil depending on several factors such as organic matter, texture, temperature, humidity, pH, cation exchange capacity, and composition. In other words, applied pesticides' persistency and degradation rate directly depend on the abovementioned factors. However, among all the factors, the major contributing factor is organic matter. While discussing soil pollution, leaching and solubility also have considerable effects.

### *Water pollution*

Drainage, rainwater, bacterial action, maximum soil temperature, application amount, and pesticides' solubility, movement, and half-life are vital factors. Despite all these efforts, their concentration in water is not according to the safe limit. The concentration of pesticides in different water sources ranges between 0.1 and 107 mg/L.

### *Air pollution*

As most of the time, pesticides are directly sprayed onto the crop; that is the way they are the major source of air pollution. A higher level of organophosphate pesticide has been found in the urine of children living in agricultural areas.

### *Toxicity of O.P.P.'s*

O.P.P.s affects the working of enzymes, i.e., acetylcholinesterase, subsequently causing breathing issues, cardiac functioning, and critical effects on neuromuscular functions. Parathion poisoning can be a reason for renal injury. These are known to inhibit the action of acetylcholinesterase. O.P.P.s interrupt growth stimulation by stopping the action of several enzymes and permeability, which is vital for the development of plants. They are the reason for initiating dermatitis irritation, tumor, sickness, and biliousness in individuals and minor to seriously lethal for fishes and other vertebrates [19]. Out of the total cases, 86% cases were of O.P.P.s poisoning. The survey is conducted in the pesticide manufacturing unit, and the result showed chromosomal aberration in workers. Similarly, another survey is conducted on 1000 cotton field workers, and a decrease in male fertility is observed in female workers' abortion rate is high compared to normal females. It is found that 75% of the honey in the world has traces of insecticides.

### *Properties of toxic pesticides*

- a) Low water solubility
- b) More fat solubility
- c) Lipophilic
- d) Bioaccumulation [20]
- e) Persistence
- f) Carcinogenic nature
- g) Stability

Pesticides, which are significantly persistent and low biodegradable, are highly toxic and lethal since they persist when they enter the food chain [21]. As pesticides easily enter groundwater, lakes, stream, soil, and rivers, removing them is crucial to protect the ecosystem from their harmful and toxic effects. Specific conventional methods are used to degrade harmful pesticides, and now more advanced processes are also in practice and proven efficient. As most organo- chlorine pesticides have a long half-life and less degradation, they are banned now. That is the way effective pesticides that are used nowadays are organophosphates. O.P.P.s belonging to classes a and b are the center of discussion for researchers because they are highly used pesticides nowadays, but they are risky for human health, and so great concern is to degrade them; different useful techniques are discussed here.

### **Degradation Methods for O.P.P.s**

#### *Biological treatment*

Biological treatment can be of two types either aerobic or anaerobic. Biological techniques have lower total costs and are more eco-friendly.

#### *Membrane bioreactors*

Membrane bioreactors demand high energy and costly aeration, but they are effective for removing pesticide [22]. It is a combination of

membrane filtration techniques & biological treatment.

#### *Activated sludge*

The activated sludge technique is another biological treatment. The herbicide glyphosate was treated using activated sludge, and the herbicide was removed in 18 h [23].

#### *Microbial degradation*

Pesticides are directly applied to crops and are degraded naturally by soil-dwelling microorganisms. Microorganisms excrete some special enzymes and play an interesting role in the natural degradation of recalcitrant pollutants. Still, as pesticides are highly toxic, sometimes this natural process fails.

#### *Bio sorption*

According to a study, snail mucus and silk settled somewhere on sediments and are taken as bio sorbents to degrade atrazine and parathion. Similarly, modified clay and organomontmorillonite have been used to remove four herbicides. The montmorillonite was modified through an ion-exchange reaction [24]. Likewise, tire rubber is used to adsorb atrazine [25]. Sorption and desorption of herbicides are observed through natural soil.

#### *Physical treatment*

Filtration is a physical technique to remove the pesticide from water, and the type of membrane depends on the targeted pesticides. Membranes with an average size between  $10^{-2}$  and  $10^{-3}$   $\mu\text{m}$  are ideal for removing bacteria's and organic molecules.  $\text{ZrO}_2$  nanoparticle membrane was fabricated to treat water contaminated with pesticide & the removal efficiency of carbofuran by a membrane was approximately 82% [26].

## Chemical treatment

### Adsorption

The adsorption process is one of the most used processes. The most recent approach to this technique is to replace costly sorbents with low-cost and readily available sorbents. In this regard, researchers are now more focused on using natural waste biomaterial for sorption, and many studies offer efficient results. Bio sorbents can be either employed directly or with certain other modifications. In addition to these processes, sometimes a combination of two or more two processes are also used. Successful experimental trials include banana peels, yeast, coconut fibers, sludge, date pits, and seaweeds [27]. Living and dead materials can be used as a biosorbents [28]. Further, many inorganic materials, such as silica, clay, and graphene, can be used. Different adsorption routes are:

- a) Biomass
- b) Clay, zeolites, and silica materials
- c) Agricultural waste
- d) Polymers
- e) Activated carbon
- f) Nanomaterial adsorbents
- g) Composites

The main key point about adsorption is the number of active sites & porosity of sorbent material [29]. When more active sites are available, more interaction occurs between sorbent and target specie. And it ultimately leads to more efficient degradation. The major drawback of the process is that contaminants are not entirely mineralized, which is why scientists are now heading towards an eco-friendly approach [30].

### Advanced oxidation process (AOPS)

In Advanced oxidation processes consist (A.O.P.s), oxidizing agents are used in a reaction to start oxidation reduction series of reactions and hence degradation [31]. Advanced oxidation

processes are simple to substitute for conventional treatment methods. These techniques have one additional benefit: they are eco-friendly and generate harmless products. However, it requires a unique understanding of the chemistry of each target substance that will be degraded. Further types of A.O.P.s are :

- a) Ozone treatment
- b) Ultraviolet treatment
- c) Electrochemical oxidation
- d) Catalytic oxidation
- e) Photocatalytic oxidation

Persulphate is an efficient and strong oxidant as seventeen pesticides are degraded with the help of persulphate, resulting in nearly 97% degradation [32]. Similarly, 4 mg/L atrazine is removed with persulphate, resulting in 90% removal efficiency [33]. Peroxymonosulfate (P.M.S.) is a strong oxidizing agent that generates hydroxyl & sulfate radicals in the solution.

### Ozone treatment

As recent demand is for pure organic food, ozone has proven to be an effective technique due to its disinfectant nature [34]. Oxidation can be carried out with ozone [35]. Ozone treatment is more advantageous because it is more economical and does not need sophisticated & complicated instruments as in the case of  $H_2O_2$ . [36]. Moreover, a great advantage is its wide range; it can degrade various harmful pollutants, including pesticides and organic contaminants, and does not generate harmful secondary intermediates [37].

### Ultraviolet treatment

Degradation of diazinon is observed by ultraviolet treatment [38]. U.V. light is used to degrade fenitrothion, and significant results are obtained. U.V. degrades Carbaryl, and synergistic effects are obtained [39]. In another study, degradation for carbaryl is observed for two different frequencies at 130 kHz and 32 kHz, and

more good degradation results are observed for 130 kHz. It is also observed that the photochemical process is better than sonochemical degradation because of the additional effect of U.V. light. More recent approach is coupling U.V. light with hydroxyl radicals/ozone. Pesticide vydine is degraded using U.V. light in 254 nm to 350 nm, and 95% degradation is observed [40].

#### *Electrochemical oxidation*

Electrochemical oxidation is another way to degrade pesticides. Organochlorine pesticides are removed from lindane pesticides by electrochemical oxidation. Harmful pesticide is converted to non-poisonous carboxylic acid [41]. Acetamiprid is degraded up to 40% in 3 h with the help of electrochemical oxidation [42]. Photon and the electrochemical process can be combined for more efficient results. The reason for greater efficiency is a higher rate of production of free radicals [43]. Electrochemical degradation of methyl parathion is carried out by using Pt/Ti as an anode and stainless steel as a cathode. Considerable degradation is observed, and several intermediates were detected [44]. Pretilachlor is an herbicide, and it is hazardous and bio-refractory. Pretilachlor is degraded by Sb-doped Ti/SnO<sub>2</sub> with very efficient results; approximately 98% degradation is achieved in 60 min [45]. Different techniques can also be merged with electrochemical oxidation to improve degradation efficiencies, such as electrocoagulation, electro-oxidation, or electro-Fenton [46].

#### *Catalytic oxidation*

Catalyst for degradation is a successful route because of these advantages. They are non-corrosive and eco-friendly. Pesticide decamba is degraded with the help of Ce doped TiO<sub>2</sub> catalyst [49]. Catalyst can be single metal atoms, metal oxides, mixed metal oxides, bimetallic/trimetallic

compounds, and nanocomposites. However, the literature review showed that doped metal oxides & composites are better than single metal oxides for several reasons, such as appropriate band gap and lower electron-hole pair recombination rate.

#### *Photocatalysis*

Photo-catalysis is "Reaction in the presence of a light and a catalyst." Fujishma and Honda used titanium dioxide in 1972 in the water-splitting reaction. To tackle the worldwide problem of environmental pollution, the most practical tool is Photocatalysis [47]. A significant amount of electric energy is saved by using U.V. light. Since then, semiconductor photocatalysis has gained much attention, and a clear indication is the growing number of publications. There used in varied applications extending from the environment to the energy sector. For instance, water splitting and degrading toxic pesticides, and harmful organic pollutants are evidence of their efficient nature and potential.

#### *Photocatalytic degradation*

Recently, nanoparticles such as TiO<sub>2</sub> are excellent adsorbents and efficient photo catalysts for degrading more or less whole OCs O.C.s and other toxic pesticides. Notably, such methodologies are economical, fast, and efficient. Advance Oxidation Process (A.O.P.s) may decontaminate organic pesticides in water. These reactions produce very reactive chemical species, destroying even the most persistent and toxic molecules into less harmful biodegradable compounds. The mechanism of Photocatalysis is the generation of free radicals. In turn, these reactive species oxidize organic molecules into carbon dioxide and inorganic smaller ions. Photocatalysis is promising technology that can deal with persistent contaminants. Photo-degradation of organic pollutants proves as a possible answer for extensive water

contamination. Hazardous pollutant remains for years in soil and water after their application. Carey *et al.* in 1976 used TiO<sub>2</sub> photocatalyst. Photocatalytic technologies have recently been used to eliminate harmful toxins by simple, economical, efficient, and facile routes.

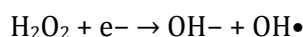
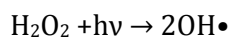
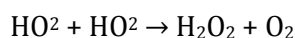
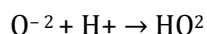
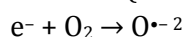
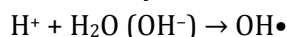
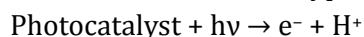
#### Types of catalysis

The basic two types of catalysis are homogeneous and heterogeneous catalysis.

- a) Homogeneous catalysis has the same phase of reactant and catalyst.
- b) Heterogeneous catalysis has a different phase of reactant and catalyst. Heterogeneous catalysis is preferred over homogenous catalysis because, in homogenous catalysis, separation at the end of the reaction is complex and complicated.

#### Principle of photo catalysis

The principle of Photocatalysis is the reduction and oxidation by simply absorbing radiation of appropriate wavelength and frequency. Photocatalyst excites the electron that goes to the conduction band, enabling a series of oxidation-reduction reactions and hence the generation of reactive species known as free radicals. The materials with narrow bandgap are the best be used as a photocatalyst so that electrons can easily excite to conduction band by absorbing Visible light [48]. The basic mechanism involves the absorption of radiation by a semiconductor photocatalyst and successive generations of free radicals that help in the degradation of persistent organic pollutants in simple, more minor, and nontoxic intermediate byproducts.



The most exciting features of this process rendering it advantageous are:

- The process can be carried out at room temperature and without overpressure.
- Oxidation of the target pesticide into CO<sub>2</sub> and other inorganic species is complete.
- The oxygen needed for the reaction can be directly supplied from the atmosphere.
- The catalyst is economical, nontoxic, harmless, and can be reused.
- The catalyst can be easily supported on various types of inert support such as glass, fibers, stainless steel, inorganic materials, sand, and activated carbons, permitting reuse
- The light source for photo-exciting the catalyst can be provided by the Sun.
- The photocatalyst is low-cost.

#### Photochemical sources

##### U.V. driven photo catalysis

Typical range of U.V. is 100-400 nm. Photocatalytic degradation using a transition metal oxide/U.V. system has been reported. But more focus now a day is on designing visible light-driven photo catalysts because visible light is easy to provide, and hence the process is economical.

##### Visible light driven photo catalysis

About five percent of U.V. radiations touch the upper exterior of the earth. This U.V. energy is insufficient for the complete photocatalytic breakdown of persistent chemicals [50]. Besides this, U.V. is expensive and risky. Nonetheless, visible light is a significant portion of the spectrum. Subsequently, visible-light-driven photocatalyst is required. Patel *et al.* observed that TiO<sub>2</sub> is a more efficient photocatalyst than the single doped TiO<sub>2</sub> due to more visible light sensitivity and likely lessening recombination frequency [51].

*Gamma radiation assisted photocatalysis*

Gamma radiation can be used as a photochemical source for the excitation of the electron. Shaoqing examined gamma radiation as a photochemical source for catalytic degradation of p- nitro phenol (PNP).

*Microwave-assisted photocatalysis*

Ju *et al.* explored the breakdown of Malachite green by  $\text{TiO}_2$  under the microwave. Results indicated that Malchite was disintegrated just in 3 min with a proficiency of 85% [52].

*Factors affecting photocatalytic activity*

Series of the experiment usually performed to determine catalytic activity and efficiency. The photocatalytic activity depends upon.

*Number of active sites**Electron hole recombination rate**Time, Temperature, Dose, pH, Concentration**Light intensity and wavelength**Number of active sites*

The number of active sites, depends on the crystallinity and surface area. Catalysts with the high surface area and smaller size show more significant photocatalytic activity. Among all the factors, crystallinity and surface area which B.E.T. analysis is generally performed to find out the surface area [53]. Especially, the high crystallinity of a catalyst encourages the transfer and electron and hole charge separation. In the presence of visible light, the electrons in the valence band absorb the energy and are excited or transferred to the conduction band, generating holes. Highly crystalline photo catalyst quickly transfer electrons to the surface, stimulating the separation, and improving the activity [54]. In one study, different

morphologies of ZnO such as rice-like, rod-like, cone-like, flower-like, and disk-like were prepared to examine its effect on Photocatalysis, rod-like ZnO particles showed the most efficient results, followed by rice-like and disk-like ZnO particles. This is due to more surface area of rod-like particles. TiFe mixed oxides have a surface area of  $460 \text{ m}^2/\text{g}$  and show degradation efficiency up to 70%.

Table 2 explains how active sites directly affect the degradation efficiency. Surface area is mentioned in the first column, and corresponding active sites and percent degradation are in the second and third columns. As surface area increases, active sites increase, and ultimately, degradation efficiency increases. Maximum degradation is 92%, achieved at a maximum surface area of  $109 \text{ m}^2/\text{g}$ . The most crucial factors controlling photocatalytic efficiency are crystallinity and surface area [55].

*Electron hole pair recombination rate*

When photocatalysts are irradiated with light, the electron jumps to the conduction band, promoting oxidation-reduction reaction [56]. Photo-generated electrons and holes upon excitation govern photocatalytic reactions. Hence, the chemistry of photo carriers must be known to understand the entire process. Trapping of electrons reduces the possibility of recombining with holes and thus elongates the lifetime of holes [57]. To achieve this, doping a catalyst with appropriate metal or nonmetal is one of the successful and facile techniques with good results.

*pH, Concentration, Dose, Time & Temperature effect*

Each catalyst works best at a specific temperature, time pH, and concentration called optimum conditions. Because of point zero charges, adsorption is different at various pH. The efficiency & oxidation rate of a photocatalyst

is governed by several parameters like pollutant level, photo catalyst amount, pH, reaction temperature, light intensity, irradiation time, inorganic ions, and oxidants.

**Table 2.** Relationship between active sites and percent degradation

S.A. m <sup>2</sup> /g	Active Sites	Percent degradation
53	33	11.1
56	34	11.9
62	34.8	53.8
45	25.2	20.3
38	23.6	19.4
34	21.1	19
56	35.7	56.2
60	37.5	56.8
80	35.2	64.2
54	33.13	63.9
33	31	63.6
66	34.8	80.6
109	41.6	92
70	30.6	83
55	26.1	56.6

### pH

The degradation of pesticides strictly depends on pH values (Table 3). At low pH, holes are the primary oxidation species, while at neutral or high pH levels, OH is the main specie. In an alkaline solution, OH radicals can be quickly produced. Thus, the logical process should become more efficient [58]. But in an alkaline solution, there are Columbia repulsions among the negatively charged surface of photocatalyst & hydroxide anions. This can stop the formation of OH, thus lessen the photooxidation. It is also reported that in low pH values, particles tend to agglomerate, thus decreasing the surface area and, in turn, the photocatalytic activity [59].

According to Baran *et al.*, when the solution's pH is decreased from pH 8.0 to pH 4.5, absorption increases almost more than six times. So acidic basic properties affects photocatalytic efficiency [60]. An essential thing to be considered is the pH of the reaction. It directly disturbs the efficiency of catalysts. Some pesticides are best degraded at lower pH, some at higher, and some at neutral. It all depends on the nature of the pesticide and P.Z.C. Value. So the critical point here for the researchers is that the nature of the pesticide must be considered first before experimenting. The results from several studies indicated that light intensity and soil also affect the photodegradation of pesticides. Still, the most critical parameter is pH.

**Table 3.** Relationship of pH with a degradation rate of the pesticide parathion

pH	Percent Degradation	Target Pesticide
4	68%	parathion
6	78%	parathion
8	90%	parathion
10	83%	parathion

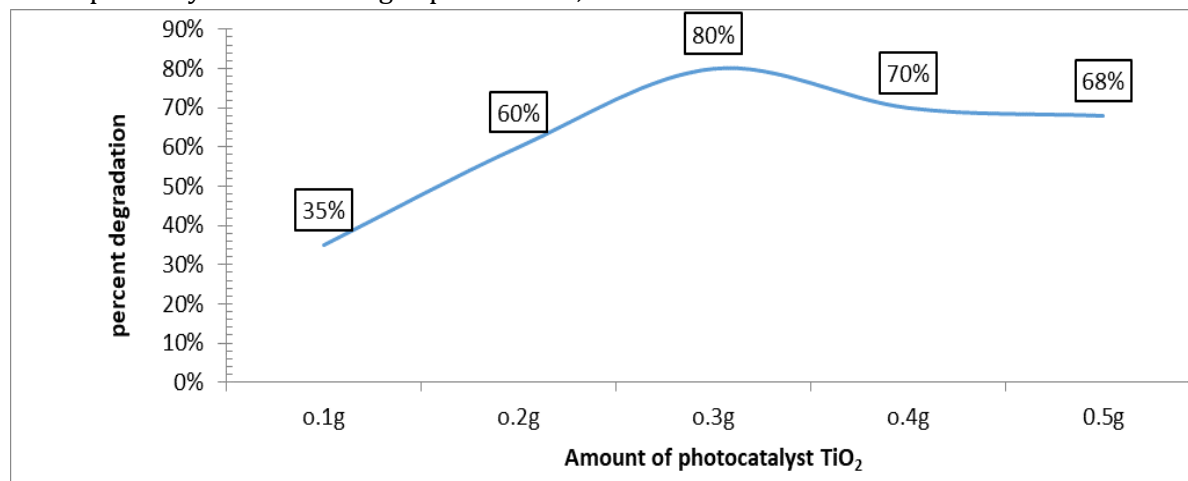
### Catalyst concentration

Generally, when the amount of a catalyst increases, active sites increase; therefore, 'OH radicals increase, which takes part in the



reaction. Therefore, a linear increase in the photocatalytic performance should be observed. But when the amount of catalyst is increased further, a decline in the activity or efficiency is observed probably due to less light penetration,

ultimately leading to the less generation of hydroxyl radicals due to less production of charge carriers, and hence directly reduces the degradation rate.



**Figure 8.** Effect of TiO<sub>2</sub> concentration on the degradation of insecticide imidacloprid [61]

According to Figure 8, maximum degradation for the TiO<sub>2</sub> catalyst is observed at 0.3 g. When catalyst concentration is increased gradually from 0.1 to 0.3 g, degradation efficiency also increases until it reaches the maximum point, 80% at 0.3 g, but after 0.3 g, further, increase in concentration results in a decrease in degradation efficiency. The optimum concentration of each catalyst is different.

#### Dose

An essential factor while determining the degradation efficiency is the amount of the catalyst used to destroy a particular amount of the targeted pest. In other words, degradation efficiency is strictly related to the amount of photocatalyst used. As mentioned in Table 4, titania, Iron mixed oxides are prepared by the

simple precipitation method and showed degradation efficiency < 70%, while the dose used is 1 mg pesticide per 50 mg of sorbent [62]. Similarly, Cerium iron oxide is prepared by the same route and used in the same amount showing 100% degradation [65]. 1 mg of ZnO/CuO prepared by sono co-precipitation method is used to degrade 20 mg of parathion, and the result showed 78% degradation. TiO<sub>2</sub>/CeO<sub>3</sub> oxide is used to degrade parathion, and the amount used is 1 mg/50 mg of pesticide [65].

Table 5 summarizes that when the same photocatalyst is used for the same target material but in different amounts, it results in different degradation efficiency, indicating one optimum value where the maximum of the target pesticide can be degraded, keeping other parameters constant.

**Table 4.** Relationship between dose and percent degradation

Catalyst	Dose	Percent Degradation	Target Pesticide
TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	1 mg/50 mg	<70%	parathion
CeO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	1 mg/50 mg	100%	parathion
ZnO/CuO	1 mg/20 mg	78%	parathion

**Table 5.** Degradation of Parathion by ZnO/CuO in different dosages

Photocatalyst	Dose	Percent Degradation	Targeted Pesticide
ZnO/CuO	0.5 g/20 mg	60.16%	parathion
ZnO/CuO	1 g/20 mg	78%	parathion
ZnO/CuO	1.5 g/20 mg	78%	parathion

### Temperature

Temperature effect the activity of photocatalyst and hence its degradation capability. Here the term temperature is, the temperature during synthesis as well as temperature during the degradation experiment. Annealing, in general is used to increase the crystallinity of the material [66]. The synthesis temperature refers to the photocatalyst's annealing and calcination temperature. During the preparation of TiO<sub>2</sub>/CeO<sub>2</sub>, the un-annealed sample shows better results than annealed one, probably due to a considerable decrease introduced Ce<sup>+3</sup>/Ti<sup>+4</sup> states, which have more active sites.

### Time

The kinetic study tells the optimum time for the catalyst, and each catalyst works best at a particular time. Similarly, when irradiated by a light source, each catalyst shows maximum activity at a particular time [67].

### Light intensity

Photocatalytic properties of the material is directly affected by the wavelength and intensity of light used [69,71].

## Advancement in Photocatalysis

### Metal oxides

Metal oxides have been demonstrated as the best catalyst to improve the performance of materials used in their combination [68]. The first and very initial photo catalysts used were

simple semiconductors because of their light adsorption properties, charge transfer, lifetime of excited state, and electronic structure [72]. A wide range of materials such as ZnO, TiO<sub>2</sub>, CdS, WO<sub>3</sub>, Cu<sub>2</sub>O, ZnS, CdS etc are used as a photo catalyst because of their stability, narrow band gap, effective response to solar radiation, and dual electronic structure (occupied V.B. & unoccupied C.B.) [73]. Much effort have been devoted to fabricate visible light-driven photo catalyst .Up till now almost 150 semiconductor materials are used as a photocatalysts [74]. The most common use photocatalysts are wurtzite phase of ZnO and the anatase phase of TiO<sub>2</sub> due to their appropriate electronic structure. The new attractive properties of single metal oxides can be achieved by combining them with other metal oxides and organic frameworks. Different strategies to increase visible light absorption of wide-bandgap metal oxide photocatalysts are:

### Doping

One of the main issue is the band gap of metal oxide as some metal oxides have a more significant band gap, to make them visible light has driven doping is usually done. Doping increases the thickness of sample material under consideration [72]. It alter the electronic structure also, and hence band gap of the metal oxides comes under visible light range. Doping with nonmetals and transition metals is a recent study area for most researchers. Doping with metal cations, nonmetal anions, and nonmetal molecules can enormously enhance a photocatalyst's adsorption by influencing a

semiconductor's electronic structure. The chemical state of the dopant and the location are strongly influencing the effectiveness of the doping procedure. Some wide band gap semiconductors are not visible light driven to adjust their band gap. They are doped with nonmetals like carbon, nitrogen, and sulfur.

#### *Intermetallic compounds*

Any material offering altered electronic or structural properties is interesting for heterogeneous catalysis. While intermetallic compounds fulfill this condition, they offer three advantages:

- Stability is caused by chemical bonding, which can prevent segregation or decomposition in a reactive atmosphere.
- A wide range of chemical potential of the involved (transition) metals.
- Peculiar combinations of electronic and crystal structure.

Very recently, supported bi-metallic compounds were introduced as catalytic materials by Wasserscheid *et al.* [75].

#### *Mixed metal oxides*

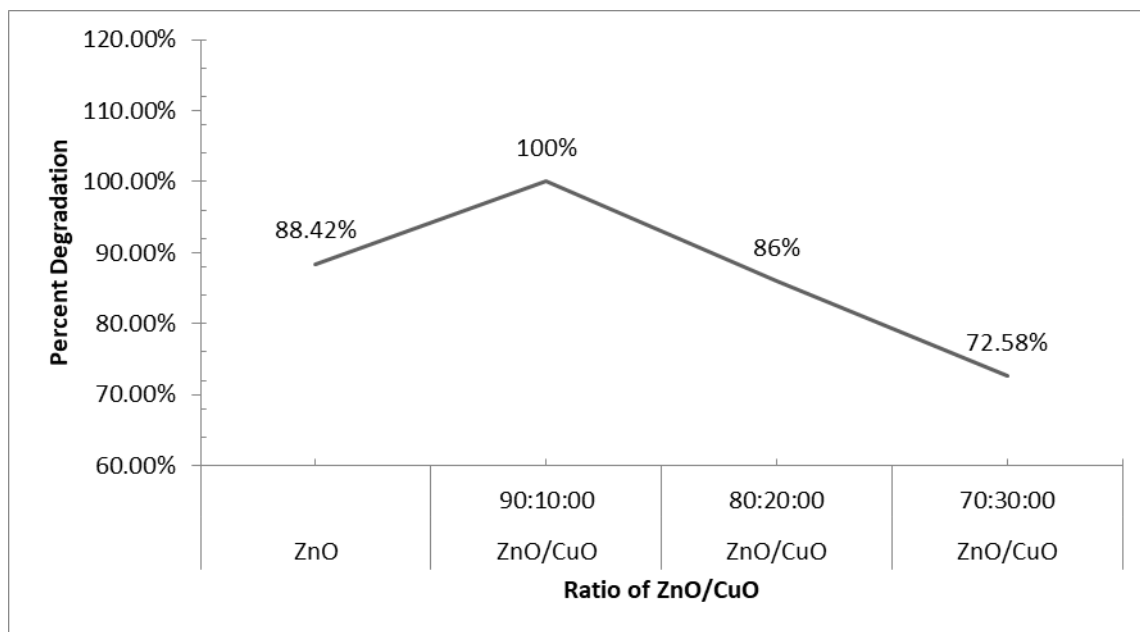
Because of specific issues like fast electron-hole pair recombination and less efficiency of single metal oxides, researchers are now more convinced that mixed metal oxides like TiCe, TiZr, Fe<sub>2</sub>O<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, ZnO/CuO are more efficient photocatalysts [67,71].

#### **Degradation Efficiency of Mixed Metal Oxides:**

The highest degradation efficiency was <70%; contrary, parathion methyl was not degraded on

the surface of pure oxides [59]. This prepared material is an example of mixed oxide possessing high surface area and chemical stability, with a reasonable cost of production and no toxicity. Janos *et al.* synthesized Ce<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> composite by a simple co-precipitation method to decompose dangerous organophosphorus pesticide parathion, and the degree of conversion approach 100%. It is also noticed that cerium oxides prepared through a wet synthetic route do not exhibit degradation efficiency towards hazardous OPP'S. Aghaei *et al.* synthesized ZnO/CuO nano photocatalyst by sono-precipitation method. The parathion was completely entirely (100% removal) degraded after 60 min of sono-photoirradiation in the optimal experimental conditions. The detailed study of the degradation of pesticides is published by Andreas *et al.*, by TiO<sub>2</sub> & U.V. light [63].

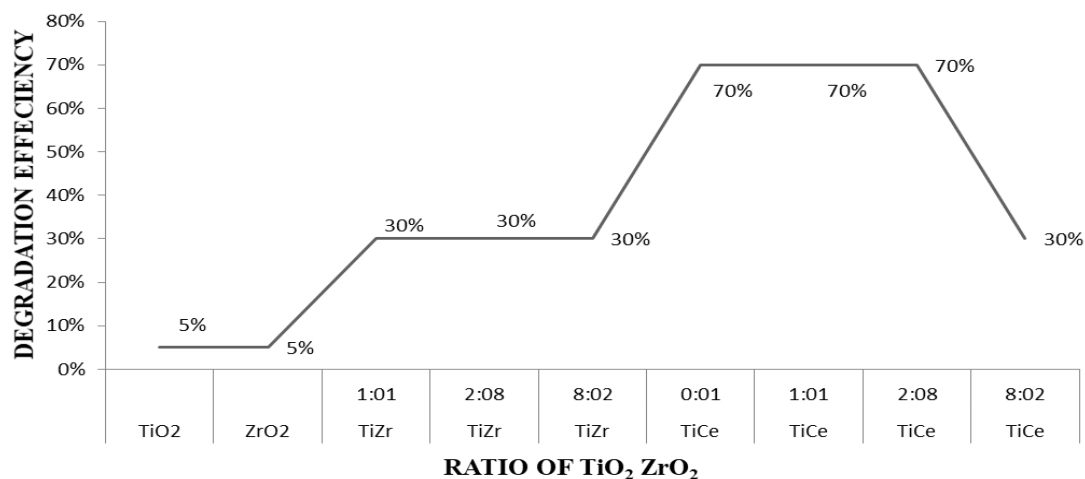
To determine the optimal amount of CuO in the composite oxides, a series of experiments are performed with different ratios of ZnO/CuO. As Figure 9 shows, 88.42%, 100%, 86%, and 72.58% of the target pollutant was photo-degraded by pure ZnO, ZnO/CuO (90:10), ZnO/CuO (80:20), and ZnO/ CuO (70:30), respectively. When the ZnO/CuO molar ratio was increased from 100:0 to 90:10, the efficiency of photocatalytic reaction under solar light irradiation increased. This is due to the reduction of the bandgap energy (<3.2 eV) by coupling the ZnO/CuO that was activated in the visible light region, which results in electron-hole pair separation. A decrease was observed in the photocatalytic activity at a higher percentage of CuO (20% and 30%), because of decreasing the B.E.T. specific surface area.



**Figure 9.** The ratio of ZnO/CuO and relative degradation efficiency

Similarly, the result indicated that the ZnO/TiO<sub>2</sub> presented improved photocatalytic efficiency compared to single metal oxide and was even more significant than P25 TiO<sub>2</sub>. An explanation is given based on the very well bonded Zinc oxide Titanium oxide heterostructure, which encourages less recombination of the photo-generated electrons and holes and cuts the recombination process. Kurán prepared Titania-Zirconium and Titania-Cerium Oxides and

concluded that the most efficient sorbents were TiCe (2:8), TiCe (1:1), TiCe (0:1) (50-70 %) followed by TiZr (1:1), TiCe (8:2), TiZr (8:2), TiZr (2:8) (20-30%) and TiO<sub>2</sub>, ZrO<sub>2</sub> (less than 5 %) as clearly illustrated in Figure 10 . Combining titanium oxide and cerium oxide enhanced the intake efficiency of U.V. light to yield more electron and hole trap points and stop the electron-hole recombination.



**Figure 10.** Ratio of TiO<sub>2</sub> and ZrO<sub>2</sub> and relative degradation efficiency

Recently, one group of researchers has proved that precipitation using urea is a suitable way to prepare TiO<sub>2</sub>/CeO<sub>2</sub> composite for degradation of Parathion methyl. Mai *et al.* tested Fe<sub>2</sub>O<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> nanoparticles to degrade parathion. The pesticide solution has a pH of around 6.7. More than 90% of this substance was degraded after 15 min.

## Conclusion

Pesticides are used to improve crop yield, but because of the persistency and non-biodegradability of a pesticide, various physical, chemical, and biological methods are used to degrade pesticides. Among chemical methods most widely used method nowadays is photocatalytic degradation. Different methods are used to improve the efficiency of a photocatalyst. Advancement in photocatalysis includes doping of photocatalysts with metal and nonmetals, intermetallic compounds, and composites. Parathion is degraded by various mixed metal oxides Ti/Ce Ti/Zr Fe<sub>2</sub>O<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> and ZnO/CuO with maximum degradation efficiencies reported as 70%, 30%, < 70%, 100% and 100 %. Mixed metal oxides are more efficient photocatalysts as compared to single metal oxides.

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## Disclosure statement

The authors reported no potential conflict of interest.

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