A Critical Review on the Photo Degradation of Diazinon, A Persistent Organic Pesticides

Fawad Ahmad*, Sana Nisar, Maira Mehmood, Zakiratullah
Department of Chemistry, University of Wah, Quaid Avenue, Wah Cantt (47040), Punjab, Pakistan
fawad.ahmad@uow.edu.pk; fawadnce@gmail.com

Summary: Broad production, utilization, and scrapping of pesticides worldwide increase the health concern of humans and animals, due to their bio-persistent and bio-accumulating nature. Among the present treatment methods, metaloxide based photocatalysis is the emerging technology for pesticide removal in aqueous medium, and has gained the interest of many researchers in the past years due to its feasibility, cost efficiency and higher degradation rate. This review briefly discusses the mechanism of metaloxide based photocatalytic degradation, reaction kinetics of pesticides degradation, optimization of operational parameters to enhance the degradation process, and different modifications such as binary, ternary or metal/non-metal dopped metaloxide photocatalysts to improve the effectiveness of degradation has also been analyzed. The effect of operational parameters like effect of catalyst dosage, pH, initial pesticide concentration, UV/sunlight, and irradiation time on the photocatalytic degradation of pesticide has been reviewed. The comparison of various photocatalysts for the degradation of diazinon from aqueous medium is summarized. However additional research is required to achieve fast and maximum degradation to keep the environment safe.

Keywords: Pesticides; Pollution; Photocatalysis; Photodegradation; Advance oxidation process; Toxicity; Diazinon.

Introduction:

The population of the world is growing so fast by every passing day and with it food demand is also increasing, so to improve the quality of food products for increasing population and to prevent crop diseases pesticides are required. Large numbers of pesticides are formulated by researchers in large quantity to meet the increasing world's food demand. These organic chemical compounds are used for protecting agriculture and forests against pests and also prevents plant diseases [1]. To repel, kill, prevent and lessen the damage caused by pests, pesticides are used. The pests can be insects, worms, birds, weeds, plant pathogens and microorganisms that destroy the plants, fields and spread different type of diseases [2]. 2.5×10^6 tons per year of pesticide is provided worldwide and its amount is increasing with every passing day as shown in Fig1. In Pakistan, the pesticides were used from centuries but from 1954, there is 254 metric tons usage of agrochemicals which is increased to 7000 tons/year by the mid of 1960's and then to 16,226 metric tons in 1977 [3]. From 1980-1990's large amount of pesticides are supplied to different areas of Punjab. Fig 2 shows the consumption of pesticides per year in Pakistan. Around 80 percent of the agrochemicals are sprayed on cotton fields while the rest are used for sugarcane, tobacco, maize, vegetables and fruits [3].
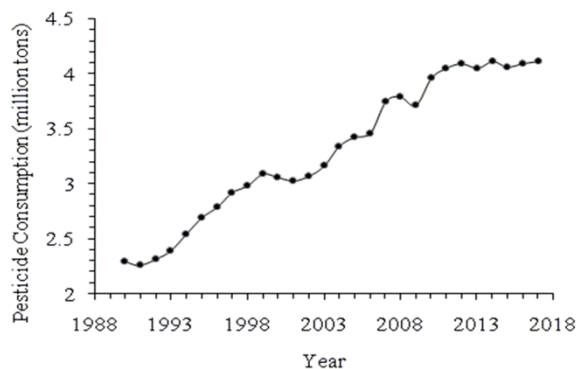

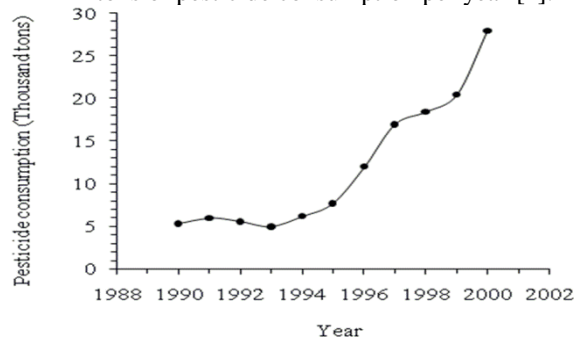Fig. 1: Total global pesticide use measure in million tons of pesticide consumption per year [4].

Fig. 2: Total pesticide use in Pakistan measured in thousand tons of pesticide consumption per year [4].

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*To whom all correspondence should be addressed.

Pesticides are fatal to pests as well as have harmful effects to the environment and consumers (affects tissues and organs causing acute or chronic diseases) but despite of its harmful effects its greater use is because of its other benefits such as improving food quality, prevent crop damage etc [1]. The harmful effects of pesticides are observed after 20 years of use [3]. During irrigation and heavy rainfall these organic chemicals are released into the water bodies and causes harmful effects to the aquatic life [1]. A report published in 1990 by EPA shows that 50% of the water pollution is caused by the chemicals used in agriculture [1]. Water resources are very important natural resources on earth and in 1980's small amount of pesticides were found in shallow water wells and surface water in Pakistan. Those areas of Punjab are affected more where there are cotton belts because of excessive use of pesticides. Recently in Pakistan a fish killing incident occurs at Rawal lake Islamabad, which supplies water for drinking to Rawalpindi (1.5×10^6 population), after filtration. In that incident, when researchers take the water samples from the lake, found that there were excessive pyrethroid pesticide, four times higher than the European Economic Union (EEC) standard for drinking water. The standard for pesticides in drinking water according to EEC is 0.5µg/L [3].

Pesticides also have adverse health effects e.g. can cause carcinogenesis, neurotoxicity, reproductive and developmental effects [5]. These organic chemicals also acts as a catalyst to the carcinogens [1]. 37000 cases of cancer are reported, three million people are poisoned and two lac died yearly in the developing countries due to the pesticides usage. Most of the banned pesticides by the developing countries due to their toxicity are still in use. In Pakistan the toxic effects of pesticides are even greater than being reported because of less data collection [3].

Pesticides

Out of twelve most toxic compounds on earth, nine of them are the pesticides and their derivatives [6]. These are the synthetically manufactured organic chemicals [7] used to prevent the damage caused by small insects to the plants. They have complex structure, and the intermediate formed from them are sometimes even more toxic than the parent pesticide [8] Some persistent pesticides don't degrade easily and enters into the environment through different routes and are fatal to humans, animals and aquatic life. Pesticides are non-biodegradable and have long lifetime in the environment. Due to fat soluble nature they retain inside the body of living organism and result in biomagnifications. Pesticides undergo different transformations into the environment through

hydrolysis, oxidation, photolysis, biotransformation, and photodegradation [9].

Contamination by pesticides

Contamination of surface/ground water

Water is essential for all living organisms, but is highly polluted due to human activities and some natural processes [10]. The amount of pesticides in water reaches to dozens of mg/L [11]. Water pollution by pesticides is caused by some natural sources like erosion, runoff etc. and also by some human activities [12]. The pesticide requirement increases because of the vigorous growth of plants that attracts the competitors. Pesticide pollutes the runoff, pond, cropland, ground, river, deep ground, and sea water [13]. The level of pesticide in ground and surface water can be determined by (i) Pesticide's soil mobility, (ii) Pesticide's carrying agent, (iii) Pesticide's level and presence [10]. Due to water pollution the aquatic food chain is also disturbed. The contamination is accumulated in fish's tissues and cause adverse effects on human health when these aquatic products are consumed by humans. The average concentration of all organochlorines found in individual sample of fish was about 0.03-0.180 ppm [14]. In Sindh and Punjab the areas near cotton fields are more affected. Pesticides enters into surface/ground water through different routes as shown in Fig 3 [9].
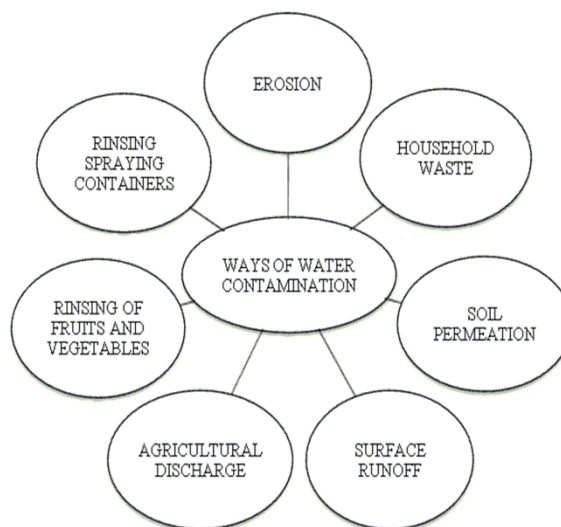

Fig. 3: Contamination of surface/ground water by pesticides [9]**.**

Contamination of soil

Soil is essential to humans and their health, and provides resource that can be used for food production. Transport of pesticides to food, air, plants and water occurs through soil and affects the aquatic life

and human beings. The contaminations (pesticides) move into animals and plant body to become a part of food chain through soil erosion, runoff, leaching, interflow and subsurface drainage etc [15]. The pesticides are persistent in the soil and can cause soil pollution due to slow rate of degradation [10]. Human activities like use of chlorinated chemicals, deforestation, domestic discharge and industrial discharge increase the soil erosion and leads to contamination [16]. Soil is a long- term storage space for pesticides [17]. The persistence of pesticides in soil depends upon soil humidity, temperature and microbial activity [18]. Microorganism cause degradation of pesticides and their intermediate products from soil and provide organic/inorganic materials to plants [10].

Contamination of air

According to EPA, quality of air affects the living organism and can be determined by the presence of contaminants, their concentration and persistence. Air humidity or radiations may degrade these pollutants or they can be settled down to earth surface. Volatile pesticide evaporates into air and can cause air pollution mostly from the tropical and subtropical regions [19]. During application of pesticides about 2% volatilized to the air. The size of the nozzle controls the droplet size and prevents evaporation [20]. Volatilization of pesticides depends upon the application method, diluents, wind speed, temperature, radiation and humidity. Pesticides can cause environmental pollution and also undergoes transformation in the environment like oxidation, photolysis and photodegradation etc [9]. The ultraviolet radiations from the sun have enough energy to break the chemical bonds of the pesticides by free radical reaction or photochemical reaction. Deposition of pesticides occurs due to the changing environmental condition [10]. Wet and dry deposition of pesticides causes there increased level in oceans, and marine water is the source of pesticides due to air exchange [21]. Recent studies showed the high concentration of thiophosphate insecticide in the air of arctic region [22]. Pesticides enter to the body through long exposure to contaminated air and causes health issues [10].

Contamination of food

People are becoming more concerned as different technologies are utilized to assess the trace amount of pesticides in food [23]. In developed countries precise analysis has been performed to determine the toxicity level of pesticides in food [10]. In Canada, researchers introduced pesticide free production of crops with no use of pesticides from sowing to harvesting, and the soil is also not treated with any type of pesticide with exception to some fertilizers [24]. In the developing countries about 80% (according to FAO) of the yield comes from the already cultivated land, which increases the chances of exposure of food to the pesticides. Pesticides in plants come from polluted water and soil, plants by absorbing nutrients from the soil transport them to the various parts of plant body through water [10]. In Pakistan, pesticide residues are investigated in fruits, cottonseeds, vegetables, milk, feed [25] etc. In Pakistan, 105 food items are investigated to have high level of pesticide residues. The maximum residual limit (MRL) of pesticides in food is 0.01mg/Kg [10]. Fig 4 shows various stages of pesticide entry into the environment.
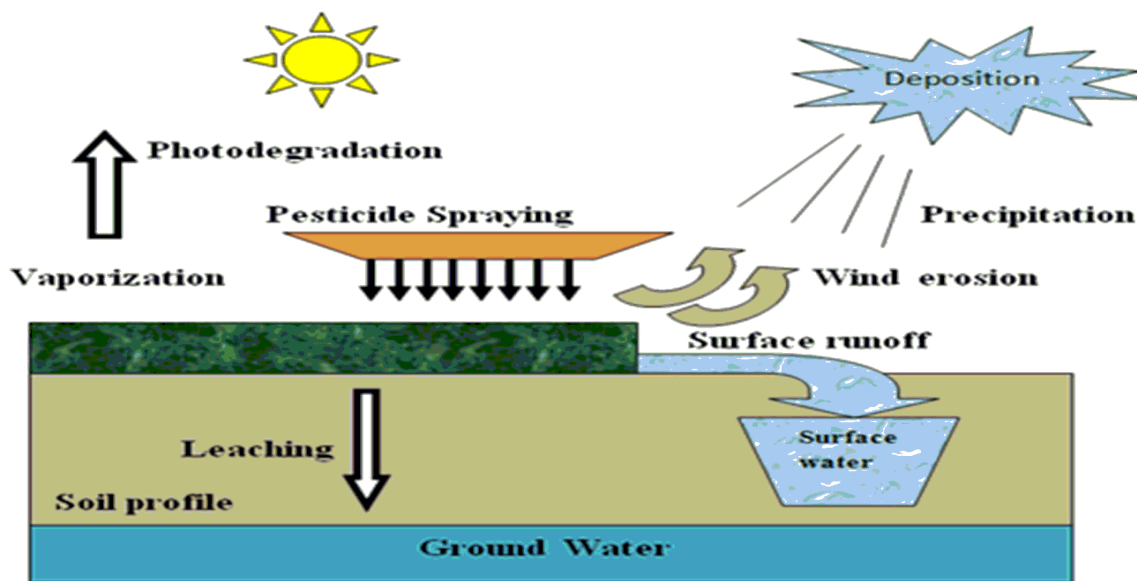

Fig. 4: Stages of pesticide entry into the environment [1, 9].

Classification of pesticides

On the basis of modes of entry, type of pests, biodegradability and chemical composition etc. pesticides are classified into following different categories.

On the basis of mode of entry

The mode of interaction of pesticides with pests are through body contact, respiratory tract, and digestive tract. The systemic insecticides absorbed by plant tissues and transported via the circulatory system to kill the organism. Example includes 2,4-D and N-(phosphonomethyl) [2]. Contact pesticide kills the pest by entering through epidermis and kills the targeted insect through poisoning. Example includes paraquat and diquatdibromide [2]. Some pesticides work by entering into the pest's mouth and damaging the digestive track e.g. Malathion. Fumigants produce toxic vapors which enter through the respiratory tract of the pest and damage it. It is usually used for protecting fruits and vegetables. Repellents don't kill but makes the site or food unattractive for the pests [2].

On the basis of targeted pests

On the basis of types of pests kill, pesticides are classified as herbicides, rodenticides, fungicides [2] etc. as shown in Fig 5.
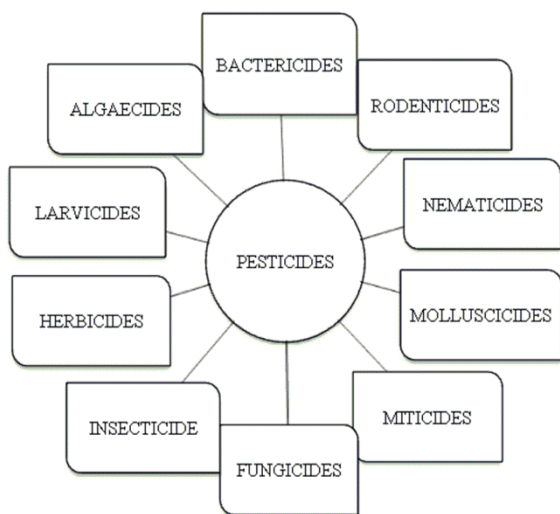

Fig. 5: Classification of pesticides on the basis of target pests [1, 2].

On the basis of range of pests kill

Pesticides are also classified into selective and non-selective on the basis of range of pests it kills. Selective pesticide kills the specific pests whereas the non-selective kills all the pests which comes in contact [2].

On the basis of physical state

Physical state can classify the pesticides as liquid (oil solutions mixed with emulsifiers), powders (finely ground), granules (active compounds mixed with clay to form particles upto 80 mesh), baits (mixed with the food for pests), and dust etc [2].

On the basis of biodegradability

On the basis of biodegradability pesticides are classified into two types; biodegradable which can be degraded by microbes into harmless compounds and persistent which take long time in the environment to break [26].

On the basis of toxicity

World Health Organization (WHO) categorized pesticides into four classes based on toxicity. Experiments were performed by WHO on rats and other animals and give them pesticide dose dermally and orally, and then introduce median lethal dose. Pesticides are categorized as extremely poisonous, highly poisonous, moderately poisonous, slightly poisonous, and less poisonous [27].

On the basis of chemical structure

Chemical structure can classify the pesticides into the following types e.g. organophosphate (malathion, diazinon etc), organochlorines (DDT,BHC etc), carbamates (carbaryl, bendiocarb etc), pyrethrins, pyrethroids etc [2] are shown in Fig 6. The first pesticide synthesized were organochlorines which were used as insecticides and have harmful effects on the environment. E.g. are DDT, aldrin and chlordane etc. In most of the developing countries DDT is banned due to its hazardous environmental effects. Organophosphate pesticides are derived from phosphoric acid; it works by preventing the transmission of nerve signals and causing death. Carbamates are derived from carbamic acid, works like organophosphorus pesticides and can be easily degraded [2].
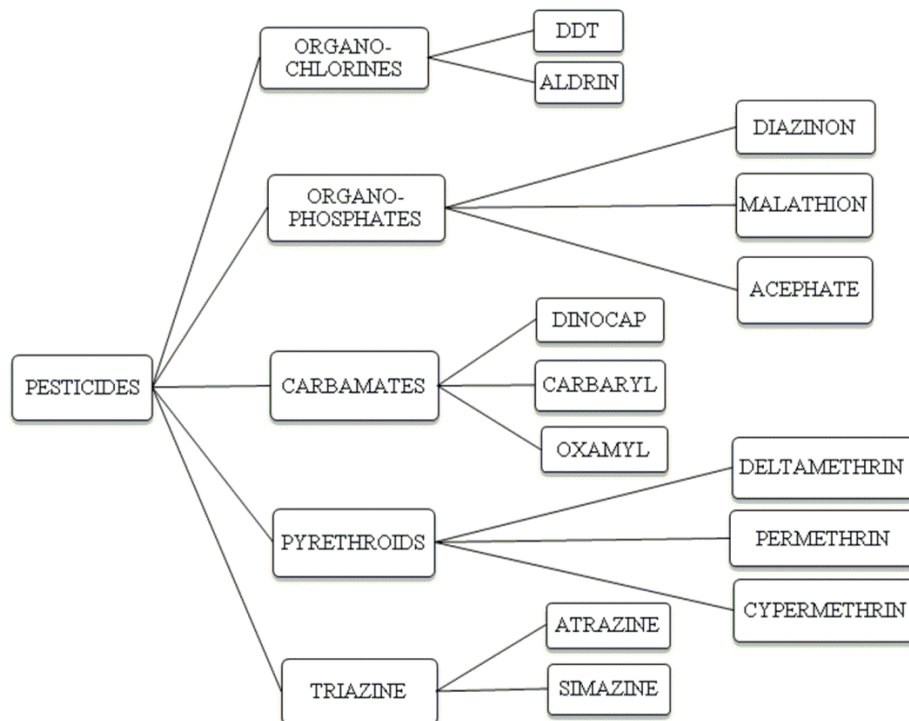
Fig. 6:　Classification of pesticides on the basis of chemical composition [2].

Organochlorine pesticides

Organochlorine insecticides remain in the environment for longer time and intoxicate human health and environment, thus many countries banned organochlorine based insecticides. They enter into the body of organism by absorption through skin, inhaling its vapors, ingesting contaminated food or water and due to their solubility and polarity they retain into the body of the organism. Due to their persistent nature they are banned by some developed countries [28]. Exposure to organochlorines leads to vomiting, headache, dizziness, nausea, dermatitis, irritability, sweating, anxiety, spasm, weakness and even lead to death. Their intermediates are even more toxic than the parent organochlorine compounds [29]. Examples are DDT, aldrin, toxaphene and chlordane etc [26] are shown in Fig 7.

Organophosphate pesticides

The commonly used pesticides for agricultural purpose alternative to organochlorines (because of their toxicity) are the organophosphorus pesticides (OPs) [30]. Organophosphorus compounds are derived from phosphorus compounds in which the hydrogen atoms are replaced by organic groups. OPs are included among those pesticides which are used more than one third of the total pesticide worldwide. There are approximately 250 organophosphorus compounds prepared all over the world, among which 140 are the pesticides and the rest are used in industries for different purposes. They are less persistent in the environment but are toxic to living organisms [31]. Organophosphate pesticides are resistant to natural decomposition in environment and have high dissolution due to which can easily move to the other places and penetrate deep into the soil and can cause reproductive toxicity [30]. In late 1970's the organochlorine compounds are replaced by organophosphorus compounds because of their less persistence in the environment [31]. Advanced oxidation processes (AOPs) are used for the photocatalytic degradation of organophosphate (OPs) pesticides using hydroxyl radicals (OH•) and convert them into non-hazardous compounds [30].

Classification of organophosphate pesticides

Organophosphate pesticides are classified as phosphates, thiophosphates, dithiophosphates, phosphonates, and phosphoramides on the basis of their structure [30].

Phosphates

In phosphates, a phosphorus atom is attached to four oxygen atoms [30]. Examples are;

Chlorfenvinphos, Dichlorvos, Mevinphos, Monocrotophos, Tetrachlorvinphos etc. are shown in Fig 8.

(i) Chlorfenvinphos (CVP)

A colorless matter, sold as amber liquid [32]. Degradation of chlorfenvinphos using titanium dioxide, or photo-fenton or using both under sunlight is studied [33]. The degradation of chlorfenvinphos occurs by oxidation through highly reactive hydroxyl radicals and follows first and zero-order kinetic [30].

(ii) Dichlorvos (DDVP)

Dichlorvos is used to control parasites and as a repellent against small insects in the form of aerosol spray. It is carcinogenic and highly toxic placed in class I by EPA. Pt/TiO_2 and H_2O_2 is studied for the photocatalytic degradation of dichlorvos. The dichlorvos oxidation by TiO_2-mediated photocatalyst under sunlight irradiations show pseudo first-order kinetics [34].

Dithiophosphates

Dithiophosphate contains phosphorus sulphur double bond and phosphorus sulphur single bond. Examples are malathion, phorate, terbufos, azinphos-methyl and dimethoate etc. are shown in Fig 9.
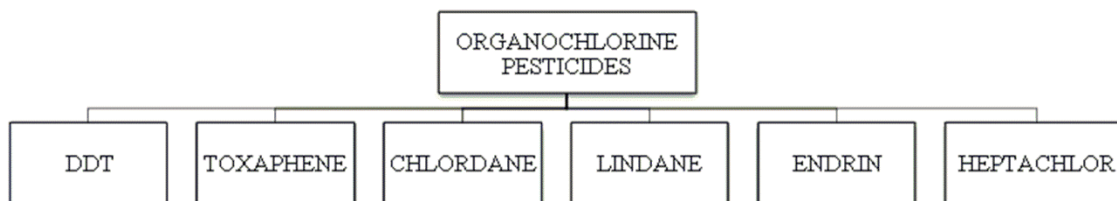

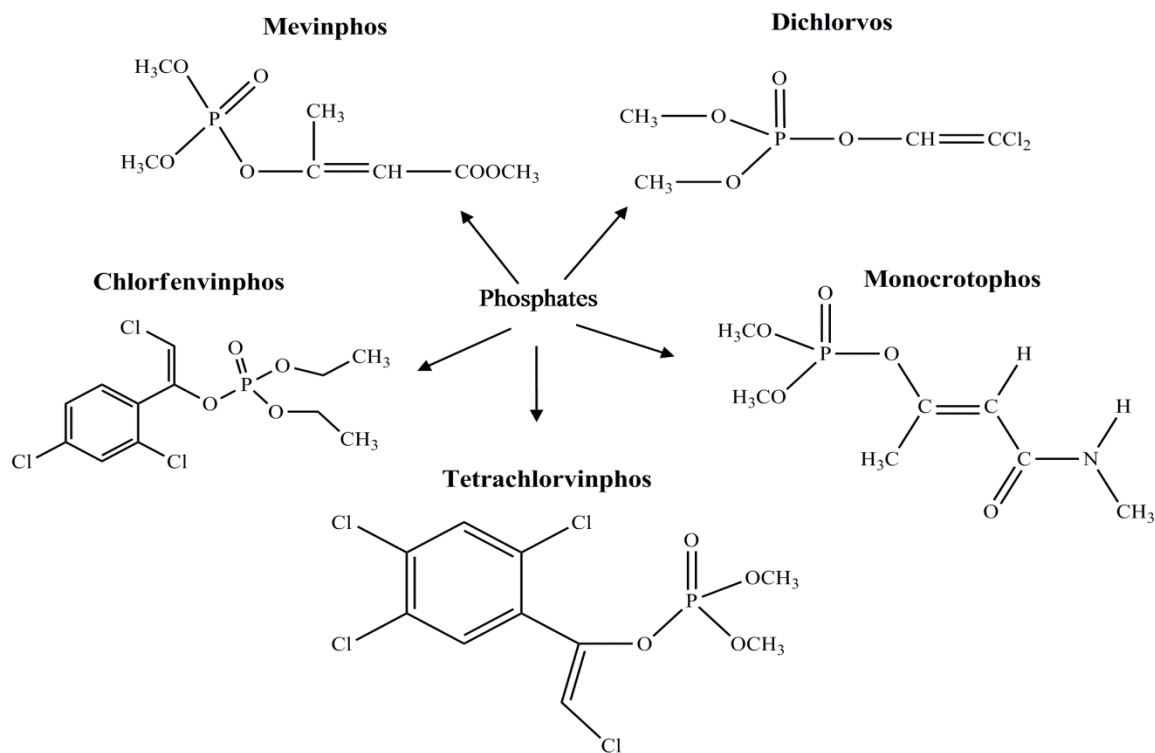Fig. 7: Example of organochlorine pesticides [9].

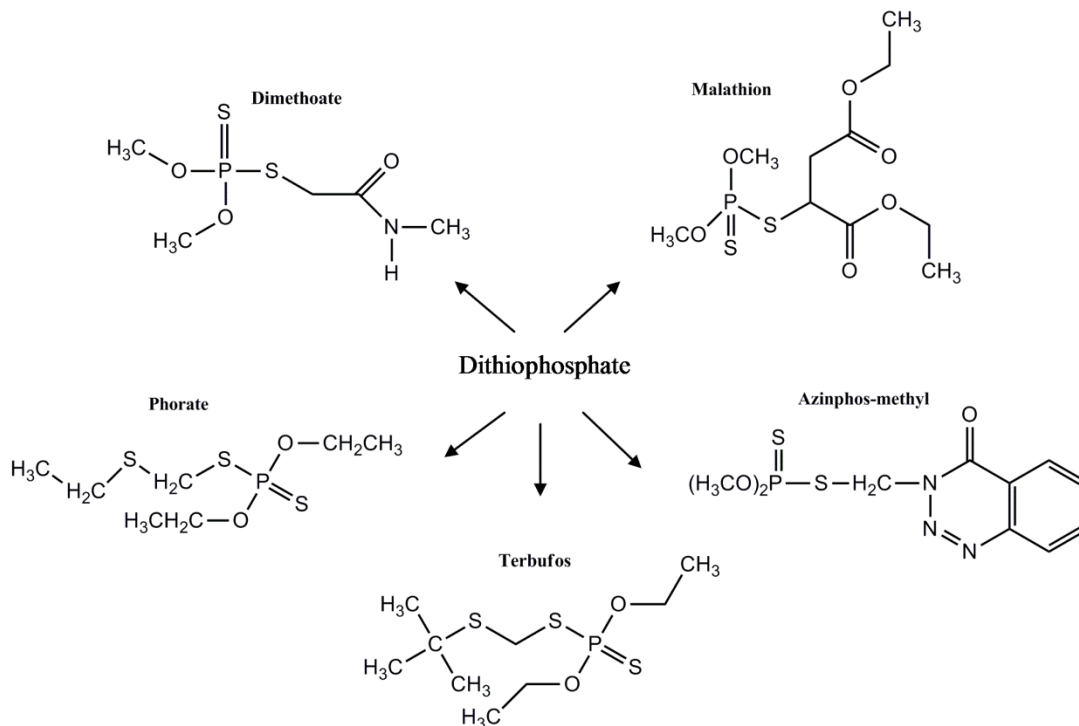Fig. 8: Chemical structure of organophosphate pesticides [30].

Fig. 9:   Chemical structure of dithiophosphate pesticide [30].

(i) Malathion

This pesticide is used for pests on vegetables, fruits, and also used for flies, mosquitoes and head lice. It is slightly toxic compound and placed in class III by EPA [30].

(ii) Azinphos-Methyl

Azinphos-methyl is used as a miticide and nematicide, kills pests by contact or stomach poison and is used for vegetables, fruit trees, nuts, tobacco and ornamental plants [30].

(iii) Phorate

Cotton, corn, coffee, pine trees and some ornamental plants are sprayed with this pesticide. It is highly toxic to humans and placed in class I by EPA [30].

Phosphonates

Phosphonates contains phosphorus carbon (P—C) bond and P=O or P=S bond. Example is trichlorfon etc. [30].

(i) Trichlorfon

Ticks, cockroaches, bedbugs, flies, mosquitoes, and leaf-hoppers are controlled using trichlorfon. Trichlorfonis moderately toxic and placed in class II by EPA [30].

Phosphoramides

Phosphoramides contains phosphorus nitrogen linkage P—NHR or P—NH$_2$. Examples are methamidophos, acephate, and fenamiphos etc. [30].

(i) Acephate

P—O, P—S, and P—N linkage is present in acephate. Different ornamental plants, fruit trees, vegetables and field crops are sprayed with this pesticide [30].

(ii) Fenamiphos

Highly toxic compound placed in class I by EPA, and used against roundworms and sprayed on different fruit trees like banana, pineapple, citrus, tobacco and crops [30].

Thiophosphates

In thiophosphates a phosphorus atom is attached to a sulphur atom by double bond. Examples are diazinon, chlorpyrifos, fenitrothion, parathion-methyl and triazophos etc. [30] are shown in Fig 10.
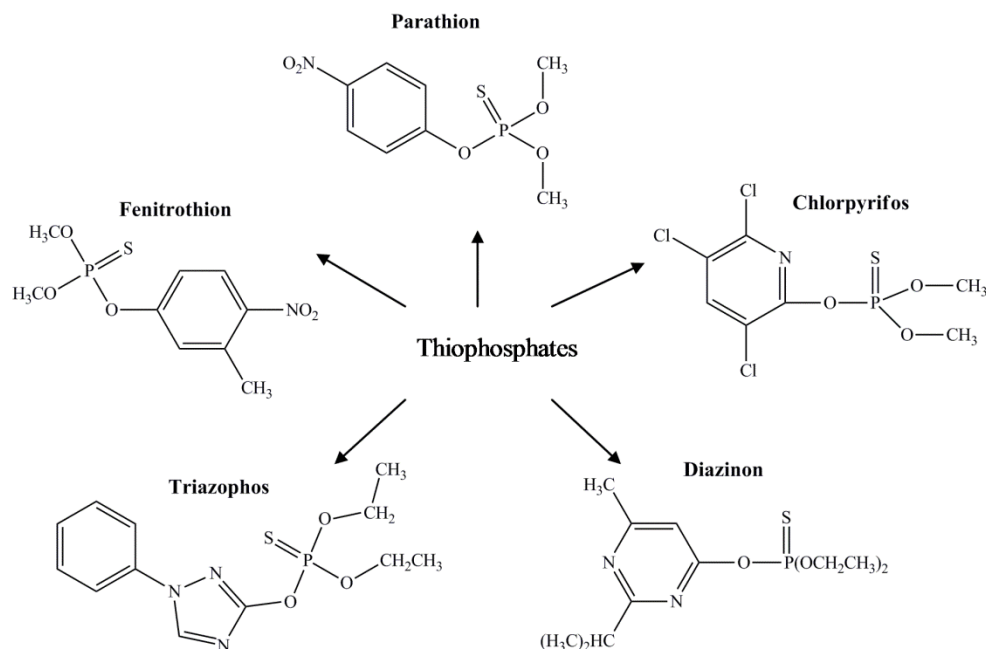
Fig. 10: Chemical structure of Thiophosphate pesticides [30].

(i) Chlorpyrifos

An insecticide used for various crops, but it is mixed with oily liquid due to its partial miscibility with water and then sprayed on crops. It is placed into moderately poisonous class by EPA [30].

(ii) Parathion-Methyl

This pesticide is mostly used for cotton fields, is a fumigant and miticide. It is placed into highly toxic class by EPA. The degradation of parathion-methyl by TiO_2/SiO_2 beads at 650°C is studied [30].

Carbamates

The structure of carbamates is similar to organophosphorus compounds, but their origin is different. They are derived from carbamic acid, whereas the organophosphorus compounds are derived from phosphoric acid. They affect the nervous system of the pest, and sometimes used as contact, fumigant or stomach poison [27]. Carbamates, just like organophosphorus pesticides also manipulate the nervous system and cause dysfunctioning of an enzyme that directs the neurotransmitter. Carbofuran, aldicarb, and ziram are those carbamates pesticides that affect the endocrine activity [35], mitochondrial function, cellular metabolism and also effects reproductive issues. It is genotoxic and cytotoxic to ovarian cells and in T lymphocytes cause apoptosis and also cause necrosis and apoptosis to immune cells. Carbamate pesticides also results in neurobehavioral issues and increases the chance of dementia [26, 36, 37]. Examples of carbamates pesticides are shown in Fig 11.

Pyrethroid

It is a naturally existing pesticide, present in a flower named as chrysanthemums. Pyrethroids are synthesized in such a way to have greater environmental stability. Pyrethroids have surfactants in them called pyrethrins (I-IV), among them the most active are pyrethrins I and II. Their decomposition takes place under intense light and so they are non-persistent [26, 29]. They have less toxicity towards birds and mammals but are more toxic to fish and insects. Among the other pesticides, pyrethroids are considered to be safe for their use in food [27]. Fig 12. show some common examples of pyrethroid pesticides.

Experimental

Degradation of pesticide

Conventional treatment technologies

Different technologies were used for the degradation of pesticide contaminated water and soil, but choosing any one most suitable among them is hard. Many processes were introduced from years and are currently use for the removal of toxic

pollutants. The conventional method includes surface adsorption [30], membrane filtration [38], air stripping, and biological degradation [10]. In coagulation the pollutant is transferred from one phase to another instead of degradation [39]. Methods like ion exchange resins, reverse osmosis, filtration, and adsorption are used these days, but the membranes can be deformed and difficult to handle [10]. Biological degradation is environment friendly but is time consuming and really ineffective [40]. Filtration and sedimentation produce toxic secondary products for the ecosystem. All these methods are effective but have some drawbacks like time, cost, ineffectiveness, and applicability [10].

Physical method for pesticide remediation

Different physical methods are used as a remediation for pesticides e.g. adsorption, settling, membrane, filtration, and air stripping as shown in Fig 13. These methods are rapid but there will be no degradation of pesticides [10]. Different material used for the removal of pesticides includes;

(i) Clays

Natural clay is negatively charged, hydrophilic, and is modified to improve the retention of pesticides on its surface. Clay is modified to improve its sorption capacity for polar and non-polar pollutants [41, 42]. The adsorption depends upon pesticide amount, quantity of adsorbent (clay), pH, time of contact of pesticide with adsorbent, and temperature. But the drawback is that it is difficult to separate out the adsorbent from the water [26, 43].

(ii) Charcoal

Activated charcoal has high ability to adsorb organic contaminant on its surface due to its porosity and surface area. Contaminants adsorption also depends upon the surface chemistry, structure, and adsorbate nature [44]. Charcoal can be in the form of granular active carbon, black electrode, powdered form, fiber and carbon. Due to cost effectiveness the powdered active form is best for the treatment of drinking water [26, 45, 46].

(iii) Polymeric membranes

Polymeric membranes are used for water purification because it adsorbs the impurities at its surface. The advantages are low energy, low cost and regeneration of adsorbents. Examples are cyclodextrins, dendrimers, and hyper cross-linked polymers [26, 47, 48].

Chemical method for pesticide remediation

Oxidation, reduction, hydrolysis, catalysis, photo-fenton, ozonation and coagulation are some chemical ways for the degradation of pesticides as shown in Fig 14. These methods are complex and highly expensive with the formation of toxic byproducts [10].

Thermal method for pesticide remediation

Thermal method of degradation of pesticide includes combustion that is highly expensive and unsuitable for recalcitrant compounds with no by-product formed [10].
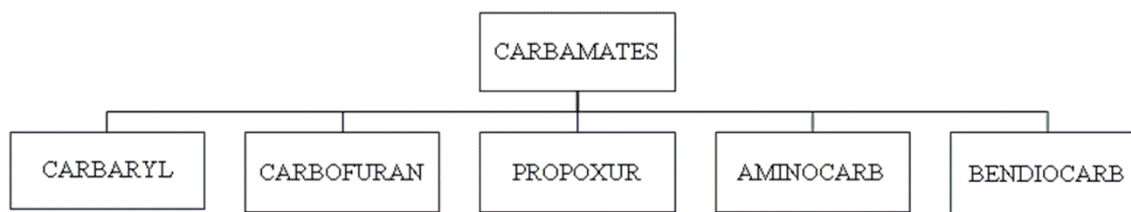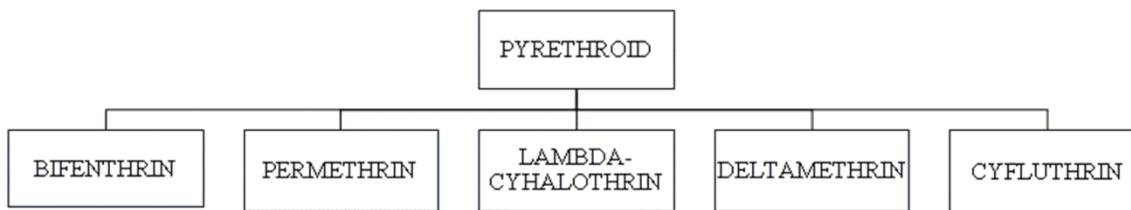
Fig. 11: Example of carbamate pesticides [27].

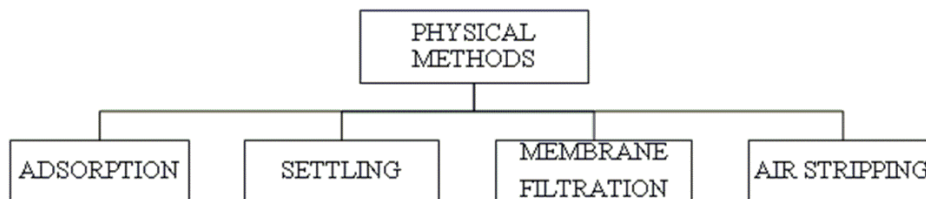Fig. 12: Examples of pyrethroid pesticides [27].

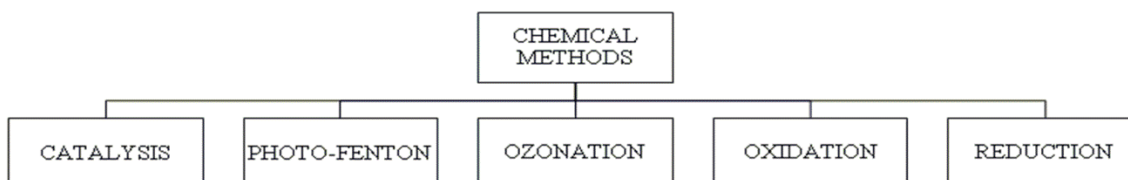Fig. 13: Physical method for pesticide remediation [10].

Fig. 14: Chemical method for pesticide remediation [10].

Biological method for pesticide remediation

Degradation using microbes is less effective and very slow. The pesticides are degraded and toxic by-products are formed by biological method [10].

Advanced oxidation process (AOPs) is introduced to overcome the limitations of conventional treatment methods to completely degrade the pesticides into less hazardous products [49].

Advanced oxidation processes (AOPs)

Degradation of pesticides by conventional treatment methods are costly, time taking and also produces secondary pollutants, so advanced oxidation processes is used, which produces reactive hydroxyl species (OH$^\bullet$) to degrade pesticides [50]. The oxidation potential of OH$^\bullet$ is 2.8eV, highest after fluorine [51]. At the surface of the photocatalyst, these highly reactive radicals reacts with the pesticides by initiating different reactions and results in the degradation of pesticides. There are two types of AOPs discussed below [9].

(i) Homogeneous advanced oxidation processes (AOPs)

The targeted pesticide absorbs the photon and the bond is cleaved or rearranged to form new stable product, but this mechanism is shown by those compounds which absorbs photons in solar spectrum [5]. H_2O_2, O_3, and Fenton reagent alone or with light is used for degradation process [30]. The energy used can be UV rays, electrical energy, microwave irradiation and sonolysis. It can further be categorized like photo-fenton, and UV/H_2O_2 etc. [9, 52].

(ii) Heterogeneous advanced oxidation processes (AOPs)

Heterogeneous means two phases, one is the photocatalyst in the solid form and the other is the aqueous solution of pesticides. Photocatalysts are used to degrade the pesticides into biodegradable products, and then mineralize to CO_2 and H_2O [53]. The holes and electrons generated leads to chain of redox reactions which degrade the pesticide at the surface of the photocatalyst [9]. Semiconductor catalysts are used in heterogeneous process such as ZnO, TiO_2, ZnS etc. [54, 55].

Results & discussion

Photocatalysis

Photocatalysis means using catalyst to accelerate a photoreaction [56]. In photoreaction, photon of light (sunlight or artificial) whose energy is equivalent to or higher than the band gap energy of catalyst generates the e$^-$+h$^+$ pair at the catalyst surface and produce OH$^\bullet$ (hydroxide) radicals and other highly reactive radicals, which degrade the poisonous organic pollutants [57]. The catalyst activity is based on its ability to produce e$^-$+h$^+$ pairs. The advantages of photocatalysis are that, in other advance oxidation processes hydrogen peroxide and ozone are used as an oxidizing agent, which are quite expensive; where as in photocatalysis atmospheric oxygen is used as an oxidant. But using hydrogen peroxide and ozone the photocatalytic activity is enhanced [58]. This method is non-toxic and economical, but there are also some disadvantages related to photocatalysis such as CdS and PbS are highly toxic catalysts, sometime toxic intermediates are formed, regeneration of catalyst, and

recombination of electron hole pair which can be reduced by dopping metaloxide nanoparticles. The lifetime of electron-hole pair is femtosecond that is enough to carry out a redox reaction [59].

Fig 15. represents the principle of photocatalysis that includes the generation of electron hole pairs when the UV light is illuminated at the catalyst surface and the reactive hydroxyl (OH$^{•}$) and other radicals are formed which degrade the non-biodegradable contaminants into less hazardous forms such as H_2O, CO_2 and other compounds [53]. The highest occupied is the valence band containing holes, whereas the lowest unoccupied is the conduction band containing electrons, both are distanced by energy bandgap [60]. When the photon falls at the surface of semiconductor photocatalyst the electron excites from the valence energy band (VB) to the conduction energy band (CB) and results in the generation of e$^-$+h$^+$ pair. In the conduction band, electrons react with the O_2 (oxygen) to form $O_2^{-•}$ (superoxide anion radicals) [61].

The valence band hole generates the hydroxide radical which degrades the toxic organic pollutants into CO_2, H_2O, and other minerals. Both the oxygen reduction and the oxidation of pollutants takes place simultaneously [9].

Mechanism of photocatalysis

Heterogeneous photocatalysis occurs in the following steps [62, 63];

1. Transfer of pollutants at the surface of photocatalyst.
2. Adsorption of the toxic contaminants.
3. Reaction of the toxic pollutant in the adsorbed phase.
4. Product desorption.
5. Product diffusion from the surface.

The process of photocatalysis starts with the generation of electron-hole pair as oxidizing and reducing agent.
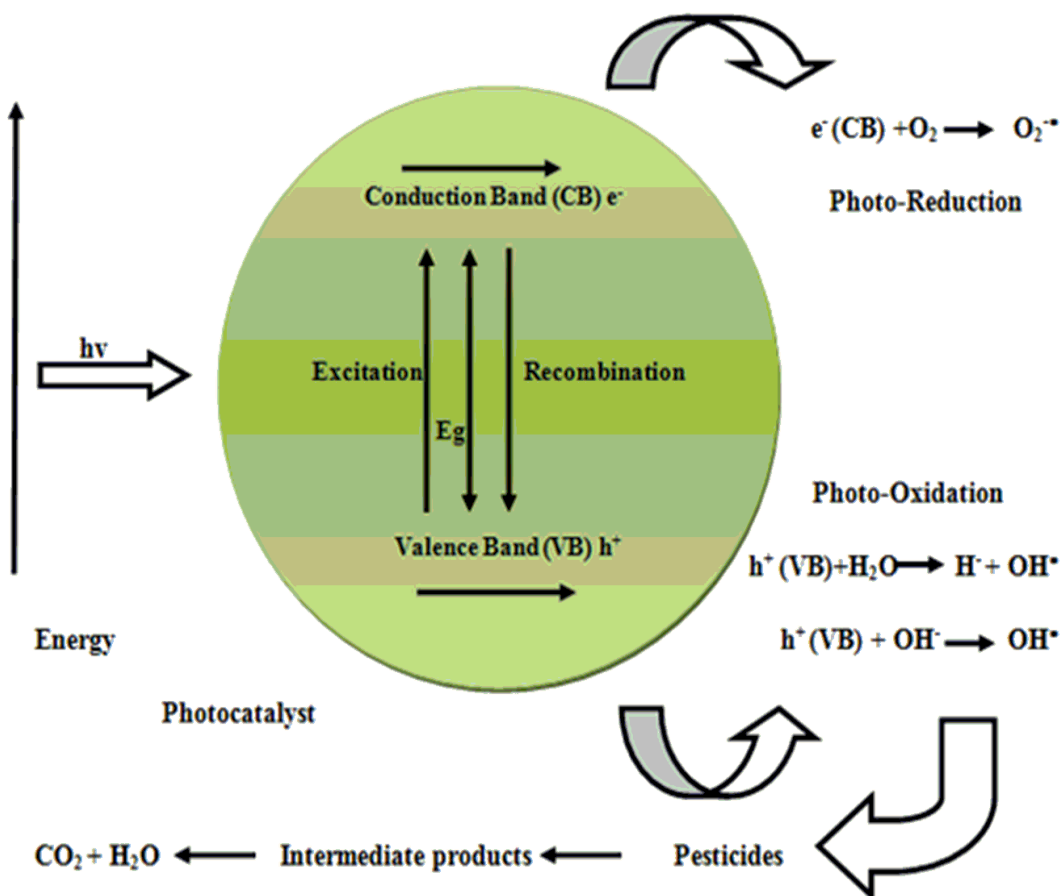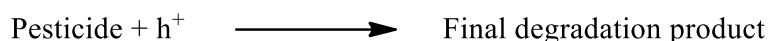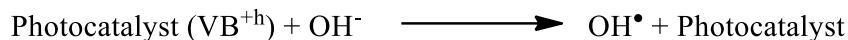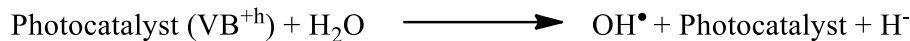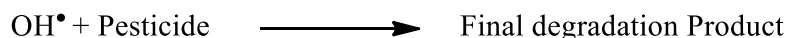

Fig. 15: Mechanism of degradation of pesticides at the surface of photocatalyst [30].

Photocatalyst + hν $\longrightarrow$ Photocatalyst (CB^{-e} + VB^{+h})

Oxidation:

Photocatalyst (VB^{+h}) + H$_2$O $\longrightarrow$ OH$^\bullet$ + Photocatalyst + H$^-$

Photocatalyst (VB^{+h}) + OH$^-$ $\longrightarrow$ OH$^\bullet$ + Photocatalyst

Pesticide + h$^+$ $\longrightarrow$ Final degradation product

Reduction:

Photocatalyst (CB^{-e}) + O$_2$ $\longrightarrow$ O$_2^{-\bullet}$ + Photocatalyst

O$_2^{-\bullet}$ + H$^+$ $\longrightarrow$ HO$_2^\bullet$

Photocatalyst (CB^{-e}) + H$^+$ + HO$_2^\bullet$ $\longrightarrow$ Photocatalyst + H$_2$O$_2$

OH$^\bullet$ + Pesticide $\longrightarrow$ Final degradation Product
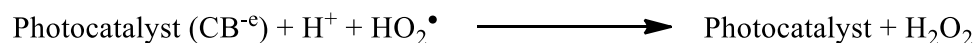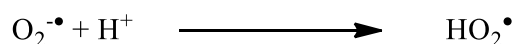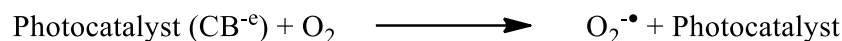
Kinetics of photocatalytic degradation

The reaction kinetics and the photocatalytic mechanism depends on pH, dose and type of the catalyst, quantity of pesticide, amount of formed intermediates, temperature, and the quantity of dissolved oxygen [64]. The kinetics of heterogeneous photocatalysis can be explained by L-H (Langmuir-Hinshelwood) model [65]. According to this model the rate of heterogeneous photocatalytic reaction depends on the fraction of surface area cover by the pesticide.

r (rate of oxidation of pesticide) = dC/dt = kKC/(1+KC)
C = Pesticide concentration in ppm.
r = Pesticide oxidation rate in ppm/min.
t = irradiation time.
k = rate constant in ppm/min.
K = Langmuir adsorption coefficient of the pesticide at the catalyst surface in ppm [9].

The pseudo-first order kinetics is followed by the organic compounds at low substrate concentration during photocatalytic degradation [66]. The substrate concentration and the time is related as;

In C/C$_o$= K (obs)t

C$_o$= Initial pollutant concentration in solution.
C = Residual pollutant concentration.
K$_{obs}$= Reaction rate constant at reaction time.

The rate determining step is the reaction of hydroxide radical with the pollutant at the surface of the catalyst [67].

Operational variables affecting photocatalytic pesticide degeneration

The outcome of initial concentration on pesticide degeneration

Literature studies show that the effectiveness of pesticide degradation is affected by its concentration. The rate of pesticide degeneration is improved with the increase in its amount, but upto an optimum level. If the pesticide concentration is lower, the hydroxyl radicals formed during photocatalysis attack the pesticides and the remaining OH$^\bullet$ radicals combine together and H$_2$O$_2$ is formed, but if the amount of pesticide is high the rate of recombination decreases and the rate of degeneration of pesticide molecule increases. At very high quantity of pesticide the rate of degeneration decreases because the competition for the reaction between hydroxyl radicals and pesticide molecules increases. Thus the optimized concentration of pesticide is considered. The rate of degradation of diazinon decreases from 51.3-10.8%, when its concentration is increased from 7.82-65.19μM [68].

The outcome of catalyst dosage on pesticide degeneration

Increase in photocatalyst concentration, increases the catalyst surface area so light penetrated easily and large amount of photons are absorbed at

the catalyst surface and more reactive hydroxyl radicals are formed and thus the rate of degradation of pesticide increases [69]. A very high concentration of photocatalyst decreases the effectiveness of degradation, due to higher cloudiness, which prevents the light perforation into the active sites [70]. Also, the accumulation of excess of catalyst deactivates the active surfaces [71]. So optimum amount of photocatalyst is preferred for effective degradation of pesticides.

The outcome of pH on pesticide degeneration

Literature review shows that the solutions pH is another significant factor that decides the rate of decomposition of poisonous contaminants. The rate of generation of reactive hydroxyl radicals during photocatalytic degradation is controlled by solutions pH and thus affects the overall rate of degeneration. In acidic environment, the rate of generation of $OH^{•}$ increases because their rate of recombination to form H_2O_2 decreases. Whereas at higher pH of the solution the hydroxyl radicals recombine to form H_2O_2, as a result degradation reaction ceases. At neutral and basic medium the reactivity of hydroxyl radicals decreases as compared to the acidic medium. The nature of the organic pollutant i-e ionic or molecular also affects the pH of pesticide degradation. Thus the pKa value of the toxic pollutant determines the pH of the degradation. Those pollutants having no ionizable groups at their surface show less degradation variance in observed pH range. The degradation of pesticide chlorpyrifos increased by increasing the pH from 5-7, whereas decreases after pH 7. Similarly dichlorvos show maximum rate of degradation at pH 3, due to the generation of greater $OH^{•}$ in acidic medium [68].

The outcome of oxidizing species on pesticide degeneration

H_2O_2 is a source of generation of additional hydroxyl radicals ($OH^{•}$) to enhance that rate of degradation of toxic organic pollutants. Higher degradation is achieved by combining UV light and H_2O_2 as compare to both the methods operated separately due to increase in the generation of reactive $OH^{•}$ by the decomposition of H_2O_2. Higher rate of degradation is achieved at optimum concentration of hydrogen peroxide, whereas at higher concentration the additional H_2O_2 prevent the generation of reactive $OH^{•}$. The optimum concentration of H_2O_2 depends upon the working circumstances. The rate of degradation of a pesticide methyl parathion increased by adding hydrogen peroxide in 10:1 ratio of H_2O_2 to pesticide, whereas the decrease in the rate of degradation is observed at 20:1 ratio of H_2O_2 to pesticide [68].

The outcome of irradiation time on pesticide degeneration

The rate of degeneration of pesticide also depends upon irradiation time. With increase in time the rate of degradation increases because at longer time, contact between the catalyst and the photon increases, and greater reactive radicals are produced [72]. Also, pesticide molecules and reactive radicals reacts completely at longer irradiation time [73].

Nano-based approach for pesticide degradation

Contamination of water by pesticides has attracted the scientist's attention towards this problem due to excessive pollution. Nanomaterials due to their small size and good activity are used as a remediation for environmental pollutants including pesticides [74]. Metaloxide nanocomposites, bimetallic nanoparticles, metal nanoparticles and adsorbents have been used as a remediation for pesticides [75, 76]. Metaloxide nanoparticles are efficient photocatalyst towards the degradation of different types of pollutants [77]. For remediation of pesticides and other organic pollutants, nanomaterials as photocatalyst are successful advanced oxidation technology; Photocatalytic technology is successful for degrading the hazardous contaminants such as pesticides, dyes, pharmaceuticals from waste water [78]. Nano-based photocatalyst degrade the pollutants into non-toxic intermediates. Several nano-based materials like metals, metaloxide and nanocomposites are used as a photocatalyst to generate electron-hole pair for redox process. In heterogeneous catalysis, nano-based semiconductors are mostly investigated because of their capacity to degrade pollutants in gaseous or aqueous medium [79]. Semiconductor nanomaterials also have wide applications in electronic devices, photocatalysis and solar cells [80]. The catalytic properties of semiconductors are due to their band gap, charge transport, light absorption, electronic structure, and long life of electron-hole pair [81]. Semiconductors are economical, less toxic (except PbS and CdS etc.) and have high surface to volume ratio etc [10].

Metaloxide semiconductors

TiO_2, Fe_2O_3, CdS, ZnS, WO_3, and ZnO are used as a semiconductor photocatalyst for pesticides degradation but TiO_2 and ZnO are used commonly.

(i) Titania (TiO$_2$)

The most effective photocatalyst is TiO$_2$ [82] because it is easily synthesized, has high activity, chemical stability, less cost, and non-toxicity, but its disadvantage is not activated by visible light but by ultraviolet (UV) light. The molecular structure of titanium dioxide is very stable and it is biocompatible. It has four forms that are anatase, TiO$_2$, rutile and brookite. Anatase has tetragonal structure with bipyramidal habit and under UV irradiation used as a photocatalyst. TiO$_2$ has monoclinic crystalline structure and is used as a paint pigments, in solar cells, electrochemical electrodes, capacitors etc. Rutile has tetragonal structure with prismatic habit and is used in paints as white pigment. Brookite has orthorhombic crystal structure. TiO$_2$ is the effectively used photocatalyst for the pesticide degradation because its photocatalytic reaction takes place at room temperature and it can be easily loaded on the supports such as activated carbons, stainless steel, glass, sand, fibers and can be reused. The photogenerated electrons reduce to form superoxides from dioxygens. Metal or non-metal dopping improves the photocatalytic activity of TiO$_2$ [83, 84]. The most commonly used photocatalyst for degrading dyes, pesticides and other toxic organic pollutants is TiO$_2$ but due to some drawbacks ZnO is introduced.

(ii) Zinc oxide (ZnO)

ZnO is not a threat to the environment nor to the human health. The energy gap of zinc oxide (ZnO) is 3.2eV [85] almost equivalent to TiO$_2$ and also shows similar photocatalytic activity to that of TiO$_2$. A wide bandgap is shown by ZnO and absorbs higher solar radiations. The surface of catalyst acts as a lewis base and acid and adsorbs the toxic organic pollutants at its surface. The drawbacks of ZnO are photocorrosion and large bandgap which result in low photocatalytic efficiency of ZnO [9]. Sol gel method is used to synthesize zinc oxide using poly vinyl alcohol (PVA) as surfactant and annealing at 500°C. It can also be synthesized without surfactant by precipitation method using zinc acetate dehydrates. ZnO nanoparticles can be synthesize using zinc nitrate hexahydrate by hydrothermal method [86].

Dopped metal oxide semiconductor

By dopping, the absorption of light by semiconductor is shifted towards the visible region of electromagnetic spectrum and can also increase the life span of electron hole pair [87]. Dopping introduce new energy levels to the energy gap between conduction energy band and valence energy band and decreases the energy band and also minimize the recombination rate of e⁻+h⁺ pair. If metal is used as a dopant than it attracts the electron from the conduction energy band and reduces the recombination rate of e⁻+h⁺ pair. Photocatalytic activity of TiO$_2$ can be improved by metal dopping such as Pt, Pd, Ag, V and Mo etc. and codopping metal and nonmetals like N, S, F and C [9]. Dopping can be positive-type and negative-type. In negative-type dopping the dopant donate the electrons or negative charge to the conduction band of semiconductor or in positive-type dopping the dopant as acceptor can accept electrons from the surrounding atoms leaving a hole or positive charge in semiconductor valence band [9].

Metaloxide Nanocomposites (NCs)

Two or more pure materials having different mechanical, electrical, magnetic, optical, and chemical properties combine to give a new material with improved properties. In the last two decades, the entire synthesis of nanomaterials was focused on single material. Since 2009, to improve the magnetic, electrical, optical and chemical properties nanomaterials are synthesized by using two or more materials [88]. Due to the quantum yield and photoluminescence properties [89] of inorganic hetero-nanoparticles they are mostly used as a photocatalyst and in solar cells [90]. Due to the enhanced chemical and electronic properties, metal oxide nanoparticles such as ZnO, TiO$_2$, CuO, Fe$_2$O$_3$, NiO, and Al$_2$O$_3$ have become popular [91]. Lifetime of electron-hole pair enhance the photocatalytic activity. In binary nanocomposites the electron moves from the conduction energy band (CB) of one metal oxide to the other under irradiation of light, whereas the hole transfers from the valence energy band (VB) of the other to the first, as a result the lifetime of e⁻+h⁺ pair increases [88].

Binary Nanocomposite

Intermetallic oxides are the hot discussion and research topic among the researchers because of its high activity and variety of application. Some semiconductors don't absorb higher solar radiations because there energy gap energy lies within the UV region. It is no need to synthesize a new material which can absorbs maximum sunlight in the visible region, because the structural and electronic properties of semiconductor metal oxides are enhanced by synthesizing mixed metal oxide nanocomposites [92]. Metal-oxygen-metal or metal-metal interaction improves the properties of

composite material such as charge parting efficiency, enhance charge carrier life time and charge carrier is also increased. For photocatalysis, two metal oxides containing composite is formed such as TiO_2-WO_3, CuO-ZnO, ZnO-Ce_3O_4, ZnO-NiO and ZnO-MgO. As compare to single metal oxide the binary metal oxide composite has enhanced charge separation efficiency. NiO is a positive-type semiconductor compound with energy gap 3.5-4 eV, ZnO is negative-type semiconductor compound with energy gap of 3.37eV, and CuO is positive-type semiconductor compound with a low energy gap 1.2 eV, cheaper and nontoxic [93], all these metal oxides have applications in photocatalysis, batteries, and gas sensing etc. Fe_2O_3 is positive-type semiconductor compound with energy gap 2.2 eV and have excellent magnetic properties, CdO is negative-type semiconductor compound with energy gap 2.5 eV [92]. Composites with mixed metal oxides are formed by using these metal oxides. When an negative-type and positive-type semiconductors are mixed together p-n junction is formed and it results in improving the properties of material [86]. As compare to single phase metal oxides, binary and ternary metal oxides are proved to be more useful for photocatalytic and other applications [94].

Ternary Nanocomposite

The coupling of more than two photocatalytic compounds improves the photocatalytic efficacy because of more efficient separation of e^-+h^+ pair. Composites like Sm_2WO_6/ZnO/GO [95], ZnO-WO_3-$ZnWO_3$, Ga_2O_3/ZnO/WO_3, and CaO-CoO-SiO_2 etc. are also reported in different research works and prove to have higher efficiency towards degradation of organic pollutants [94]. The tungstate compounds are drawing researchers because of their unique structure and tremendous potential for commercial uses such as catalyst etc. Furthermore, Graphene oxide (GO), a carbon based material also have novel structure, large surface area and excellent charge transfer capacity. It has been regarded as a promising platform to make nanocomposites that boost the photocatalytic efficiency [95]. Sm_2WO_6/ZnO/GO nanocomposite have very effective degradation of a textile dye methylene blue and a pollutant ciprofloxacin under UV light irradiation. Ga_2O_3 is a semiconductor with a large band gap that is commonly employed in high temperature electrical devices, photodetectors and gas sensors etc. It is well known photocatalyst that can significantly boost photocatalytic efficiency due to its morphological flexibility. Ga_2O_3/ZnO/WO_3 composite show improved degradation of rhodamine B dye due to high redox capacity of Ga_2O_3 [96].

Among various methods used for the preparation of mixed metaloxide composites, co-precipitation method is cheaper, easier, efficient, and requires low temperature [92].

Comparison of different catalysts for the degradation of diazinon

Diazinon

Molecular formula $C_{12}H_{21}N_2O_3PS$
Chemical Name:
O, O diethylO-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate

Diazinon was first used as an insect repellent in 1952 for crops like fruit trees, tobacco, palm, corn, sugar cane, rice and horticultural plants. It is categorized in class II (moderately hazardous) by EPA [50]. It is non-polar, having vapour pressure 0.00014 mmHg at 20°C. It don't volatilize from soil and water and its henry's law constant is 0.0000014atmm^{3}mol^{-1} [97] as represented in Table–I. Diazinon is non-systemic, digestible, and contact pesticide [98]. It has low persistence in the environment, but is highly toxic e.g. cytotoxic, neurotoxic, cardiotoxic [99] and genotoxic. It inhibits acetylcholinesterase and affect the nervous system [99]. AOPs is used for the degradation of diazinon using light and semiconductor catalyst as a source of OH$^•$ and O$_2^•$ radicals. The photocatalytic degeneration of diazinon by ZnO nanocrystals under ultraviolet light is studied and with respect to diazinon concentration follows pseudo first order kinetics [50].

Table–I: Characteristics of diazinon.

λ_{max} (nm)	274
Density g per ml at 20°C	1.11
Molecular weight (g/mol)	304.3
Vapour pressure (mmHg at 20°C)	0.00014
Henry's law constant (atmm^{3}mol^{-1})	0.0000014
WHO class	II

Toxicity of diazinon

The main issue of using diazinon as a pesticide includes surface water contamination and it affects the aquatic life and kills birds. The amount of diazinon is increasing in sewerage and urban waterways. The toxicity of diazinon is due to the reason that it inhibits the enzyme acetylcholinesterase. It overstimulate nicotinic and muscarinic receptors [50, 100]. Due to the exposure to diazinon human health and environment is at risk and the European environmental committees have investigated its applications. Due to its toxicity to humans and animals, EPA prohibits the indoor use of

diazinon. It also affects the human nervous system. The standard of drinking water for diazinon is 0.001mg/L set by EPA [100]. The fatal dose of diazinon for aquatic organisms and humans is 350 ppt and 90-444 ppm [97]. Due to its continuous use, diazinon residues are found in food crops, soil and waterways. Therefore, to protect human health treatment of contaminated water systems are required [50].

Different studies show the degradation of diazinon using different semiconductor photocatalyst. ZnO powder was synthesized and used as a photocatalyst to degrade diazinon under UV-C light, and in 80min 80% activity is achieved. Diazinon is also degraded using TiO_2-ZnO binary metaloxide photocatalyst under UV-C light, and the degradation efficiency is increased at neutral pH and by adding H_2O_2. Platinized TiO_2 is also used to degrade diazinon and 88% activity was observed under UV light after 30h [101].

Comparison of removal efficiency of diazinon by various photocatalysts

The degeneration efficiency of diazinon by various photocatalyst is compared by maintaining the exact reaction conditions. Initial amount of diazinon was 20mg/L, concentration of catalyst 0.5g/L and pH maintained at 7. The degeneration efficiency of pesticide diazinon under ultraviolet light alone was 57.98%, TiO_2-alone 17.66%, ZnO alone 20.89%, UV-TiO_2 74%, UV/ ZnO-TiO_2 87.26%, UV-ZnO 78%, and ZnO-TiO_2 28.21% using parameters from Table-II is shown in Fig 16. This comparison shows that the % degeneration of diazinon in the present of binary composite ZnO-TiO_2 is greater as compare to ZnO alone and TiO_2 alone. 87.26% degeneration of diazinon was observed by illuminated ZnO-TiO_2 photocatalyst. The greater degradation of diazinon by binary composite is due to the transfer of electron from the conduction energy band of zinc oxide to the conduction energy band of titania and hole from the valence energy band of titania to the valence energy band of zinc oxide. This increases the life time of electron-hole pair, that's why has improved photocatalytic degradation as compare to zinc oxide alone and titania alone [102].

Table–II: Comparison of different photocatalysts for diazinon degradation.

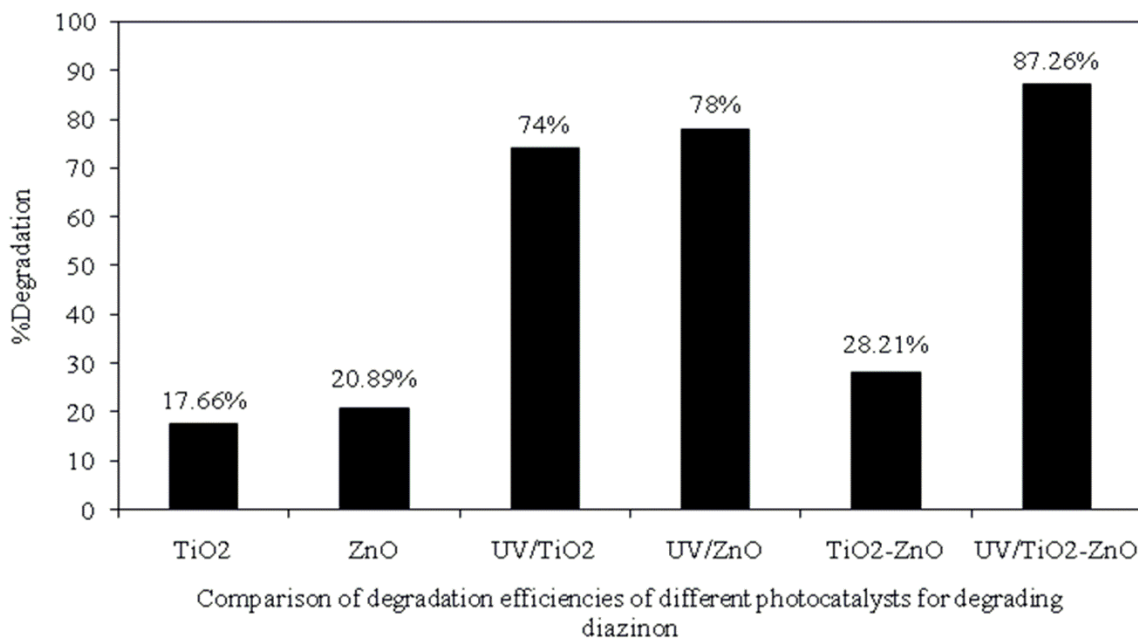| Photocatalysts	pH	Catalyst Dose	Diazinon concentration (ppm)	Time (min)	% Removal	Reference
Nano-TiO_2	6	2×10^{-4}ppm	40	120	99.64	[103]
C, N-TiO_2	5	12mg	18	30	86.93	[104]
US/UV/ Fe-TiO_2	5.5	4×10^{-4}ppm	30	100	85	[105]
TiO_2/Fe_2O_3	-	1×10^{-4}ppm	10	45	88.93	[101]
ZnO-TiO_2	7	5×10^{-4}ppm	20	120	28.21	[102]
UV/TiO_2-ZnO	7	5×10^{-4}ppm	20	120	87.26	[102]
UV/H_2O_2/TiO_2-ZnO	7	5×10^{-4}ppm	20	120	100	[102]

Fig. 16: Comparison of different photocatalysts for degrading diazinon [102].
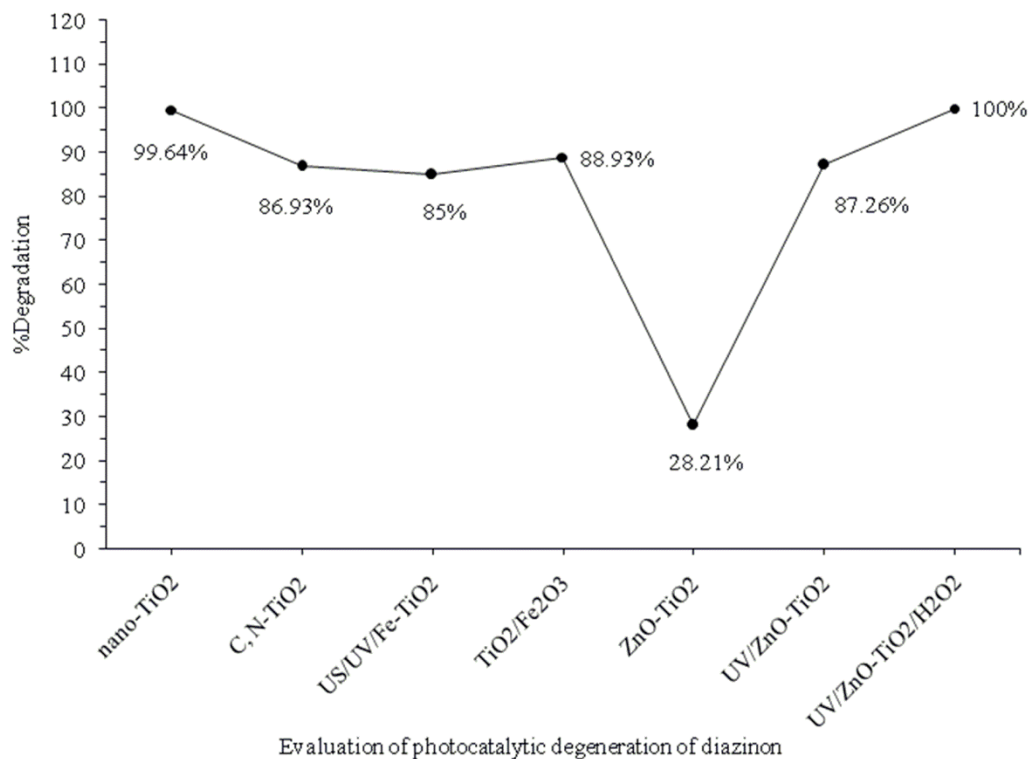
Fig. 17: Evaluation of photocatalytic degeneration of diazinon by various photocatalysts [102].

The degeneration of diazinon by nano-titania was studied with irradiation time 120min, at different pH values 4, 6, 7, 8, and 10. At pH 6 there was maximum degradation achieved. The pH_{pzc} of TiO_2 was reported 6.3-6.9. When the pH_{pzc} is less than pH the TiO_2 surface becomes negatively charged and if pH is less than pH_{pzc} the surface becomes positively charged, and if pH is equals to pH_{pzc} the surface becomes neutral. Diazinon has pKa value 2.6 and above pH 2.6 its surface becomes negative, whereas at pH below 6.5 the titania surface becomes positive. At this condition diazinon is attracted and adsorbed at nano-titania surface. After optimizing pH the concentration of nano-TiO_2 is varied from 0.2-0.6g/L. The photocatalytic degeneration improved with increase in catalyst dose due to enhancement in surface area and active sites. When the concentration of catalyst is very high then turbidity prevents the ultraviolet light penetration and the rate of the reaction slow down. Thus 0.2g/L is the optimum dose of catalyst for the degradation. The initial amount of diazinon is varied from 12-450mg/L. With increase in concentration of diazinon the degradation decreases because the intermediates formed are adsorb at the surface of the photocatalyst and deactivates its active sites. 99.64% removal of

diazinon was observed with nano-TiO_2 at pH 6 with catalyst dose 0.2g/L [103] as shown in Fig 17.

Comparison of removal efficiency of parathion by various photocatalysts

The highest degradation efficiency was less than 70% because parathion methyl was not degraded on surface of pure oxides. Mixed metal oxides possess high surface area and chemical stability, with reasonable cost of production and less toxicity. Ce_2O_3/Fe_2O_3 composite decompose dangerous organophosphorus pesticide parathion and the degree of conversion approaches to 100%. It is also noticed that cerium oxides prepared through wet synthetic route do not exhibit degradation efficiency towards hazardous pollutants. ZnO/CuO nano photocatalyst were prepared by sono-precipitation method and degraded the parathion 100% after 60 min of sono-photoirradiation in the optimal experimental conditions.

To determine the optimal amount of CuO in the composite oxides a series of experiments are performed with different ratio of ZnO/CuO. About 88.42%, 100%, 86%, and 72.58% of the parathion 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 e^-+h^+ pair separation. A decrease was observed in the photocatalytic activity at a higher percentage of CuO (20% and 30%), because of decrease in the specific surface area [106, 107].

Degradation pathway of diazinon

Mass spectrometry investigations were carried out to study the degradation mechanism of diazinon on the basis of species formed. Diazinon with the molecular mass of 304 loses two methyl group in the first step, yielding a molecule with a molecular mass of 276. The removal of methyl and ethyl group from pyrimidine bonded to oxygen forms a compound with a molecular mass 205, followed by the removal of phosphorothioate group with the formation of a compound with a molecular mass 96, and at last the 1, 3-dioxan-2-ol is converted into carbondioxide and water [108].

Stability and reuse of photocatalyst

Mixed metaloxide photocatalysts are highly stable and reusable, because they are easy to recycle. The recycling and reuse of photocatalyst is important because it lowers the overall cost of waste management, so efficient engineering is essential for developing photocatalyst that can be readily reused and recycled. Mixed metaloxide photocatalyst degrade the pollutants at its surface into eco-friendly products [109].
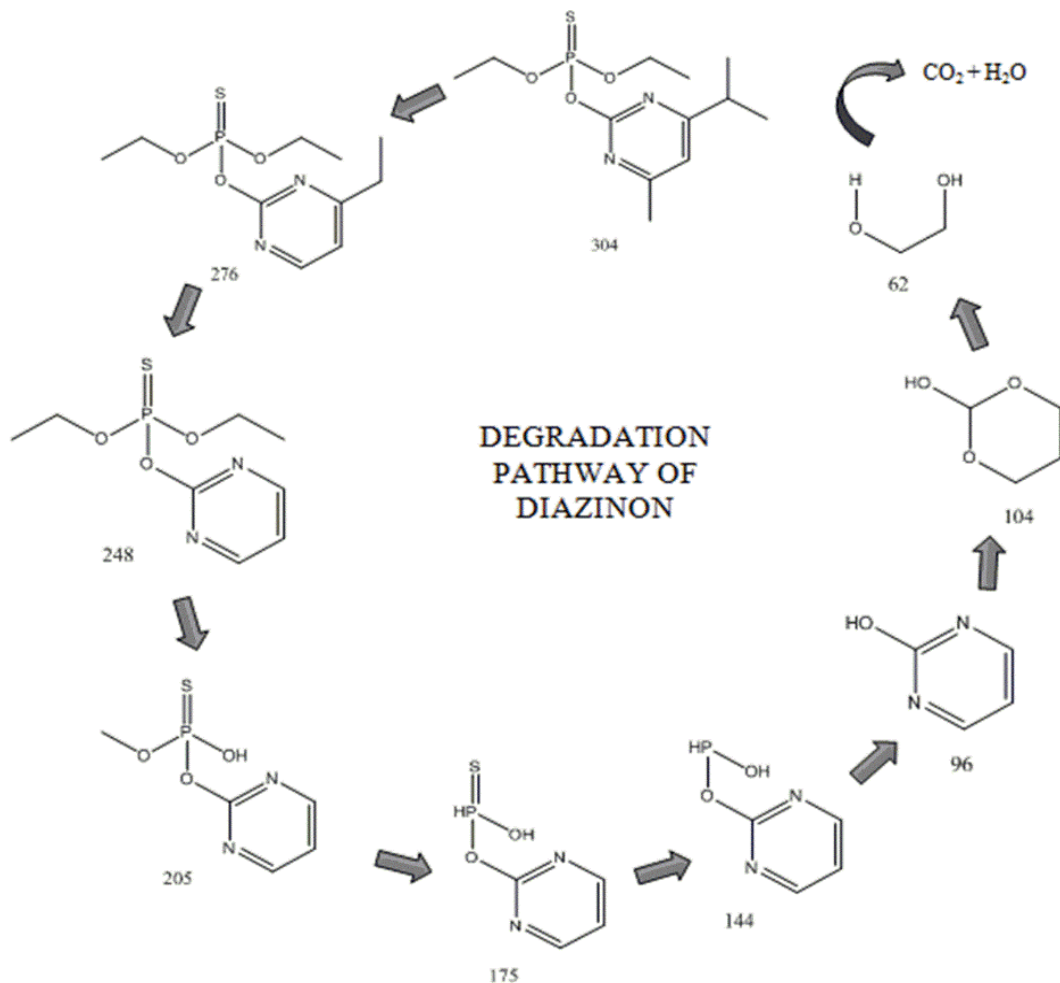

Fig. 18: Proposed pathway for the degradation of diazinon [108].

Conclusion

Aquatic pollution caused by pesticides is the biggest problem that requires effective solutions. To sort out this issue various initiatives have been taken. For the removal of pesticides by photocatalytic degradation various nanoparticles, binary and ternary nanocomposites have been widely explored. Photocatalytic degradation involves the excitation of molecules by absorbing the solar radiations and resulting in the formation of highly reactive peroxide and oxide radicals that oxidizes the functional groups present in a pesticide molecule. Instead of transforming the pesticides into other intermediates, photocatalytic degradation mineralizes them into water, carbondioxide and other less hazardous products. From literature review it is observed that binary and ternary nanocomposites act as potential photocatalysts as compare to other semiconductor based photocatalysts. Degradation efficiencies of different photocatalysts are compared for diazinon at the same reaction conditions. Photocatalytic degradation is also effected by pH, irradiation time, concentration of pesticides and catalyst dosage. Wide research has been performed for the pesticide degeneration however to evaluate the detrimental effects of agrochemicals on environment further research is required.

Conflict of interest

The authors declare no conflict of interest in the present study.

Acknowledgements

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