Review Article: Pesticides' Taxonomy, Functioning, Their Associated Risks to Human and Environment, and Degradation Technologies

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ABSTRACT

Pesticides are helping to meet up the demand for population growth in today's agriculture. They are also being utilized for numerous issues including domestic pests control, home gardening, and disease vectors. Though, they are extremely poisonous in nature. They also cast false impact on surroundings. When used for the agricultural purpose, their toxic residues are continually left behind, and thus forming a major origin of pollution. The unwanted risky chemical groups are contaminating natural assets at a shocking rate. Agricultural pesticides left behinds are among the most harmful contaminants to the soil and water. Removing them from wastewaters is critical as they have bioaccumulation potential, toxicity, and a high persistence. Pesticides have long been used to improve manufacturing efficiency and extend the shelf-life of food goods. Their residues should be removed from food products and waters to limit human pesticide exposure. To remove pesticides, various processes are usually employed which include the adsorption process, membrane processes, and improved oxidation reactions, while microorganisms degrade them naturally i.e. bioremediation/biodegradation. Many organic and inorganic materials have been fabricated for rapid and complete degradation of pesticides. Semiconductor materials contribute to the pesticide oxidation and reduction because they have a proclivity for producing radicals through the charge separation. This review focuses on the pesticides' taxonomy, functioning, their associated risks to human and environment, and degradation methods involving the current discoveries and progress in the utilization of several approaches for their probable removal from wastewater. The advanced oxidation, adsorption, bioremediation, photocatalysis, semiconductor materials, phytoremediation, and membrane technologies are some of these processes discussed in this investigation. In the upcoming researches, it will be required to generate the novel concepts in the current farming that will reduce the need of toxic pesticides and enable manufacturing of selective to target and less persistent pesticides.

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Content

1. Introduction

A chemical substance in any state that adds into atmosphere and causes its excellence to lower to such a point that atmosphere may not function properly is called as pollutant [1-2]. The environmental pollution is caused by pollutants produced from nature, and then alter by human actions both directly/indirectly [3]. Human activities that include the constant use of chemicals that are not suitable to environment causes pollution of environment components thus causes the environmental deterioration, and hence poses the potential risk to the living things [4]. Air pollution is mainly caused by fossil fuel burning, industrial productions, volatile gases leaking from interior decorations, and vehicle traffic [5]. These gases are poisonous and acidic in nature and causes the ecosystem damage [6]. They affect human health and climate [7]. Also they cause respiratory and cardiovascular diseases, corrosion of construction material, and poles melting. Water pollution is often caused by the industrial effluents, fertilizers, and pesticides applied to the agricultural lands or from sewage [8]. These all leads to fresh water scarcity, plant eutrophication, aquatic system pollution, and hazards to human health [9]. In soil, the excess of toxic substances changes the soil health, and thus effects crop, sinks [10], and mammalian health [11]. Soil pollution is usually caused by the industrial waste, agrochemicals, and heavy metals [12].

Agrochemicals include pesticides. These pesticides are widely used in agriculture. Around 80% to 90% of agrochemicals that are practical to crops strike the unintentional targets and can also move from the treated region to any other sites and sully environment. Farmers often lack technical handling of pesticides and their safety aspects. However, they have only the conventional understanding of pesticides [13]. Rapid urbanization and overpopulation leads to increase food production. Therefore, pesticides intake has increased [14].

Pesticide residues cause’s harmful effects to human health such as birth defects, infertility, damages in central nervous system and immune systems, disorders of endocrine, gene mutations, and include causes of cancer [15-17]. Conversely, certain pests controlled by pesticides change their status, become resistant or resurgent. Soil, a significant common asset supporting the endurance and improvement of individuals, is an essential asset for vegetation on earth. Soil is the greatest sink to the natural contaminations [18]. Also, farmland soil is a vital piece of horticultural biological system. Subsequently, the harvests nature and food handling is firmly connected with nature of soil that is consequently identified with human well-being [19]. Soils are the most fundamental piece in biological systems, might be sullied by organic and inorganic contaminations including pesticide [20]. The conventional farming is the main issue that causes environmental pollution because it involves the use of fertilizers, herbicides, and pesticides to produce various products or to protect plants. However, the inaccurate dosage and inefficient application causes mistake in agrochemical usage [21]. The excessive usage of nitrogen containing fertilizers causes increase in the amount of pest and disease (due to the imbalance of nutrients) [22]. Due to fertilizers and domestic waste disposal directly to the plants causes increase in amount of phosphor in soil and ground water which act as a major barrier of nutrients. A small amount of phosphate and nitrogen will help sustain life of water plants such as algae. Soil pollution causes the ground water pollution as both are in inseparable area. Polluting substances from soil get dissolved into groundwater. Pesticide residue can become a part of food chain and causes harmful effects to the living organisms that consume them. Contamination can also occur due to the hazardous material that moves through the flow of water, spread by wind or through organisms being exposed to the agrochemicals [22].

Water is the main source of life on earth, and it is highly contaminated with pesticide and industrial pollutants [23]. Water is abundant, but its abundance is limited by certain factors: (i) 97% of total water is sea water also 2/3 of 3% remaining is immobilized, (ii) water is not equally distributed and land is also unequally populated, and (iii) water got polluted due to human activities and causes pollution in water bodies when discharged [24]. Therefore, solution of water scarcity is a major concern. Therefore, water treatment is highly needed to diminish the hazards on human health and environment. **Figure 1** displays the pesticides consumption worldwide in the last nine years [25].

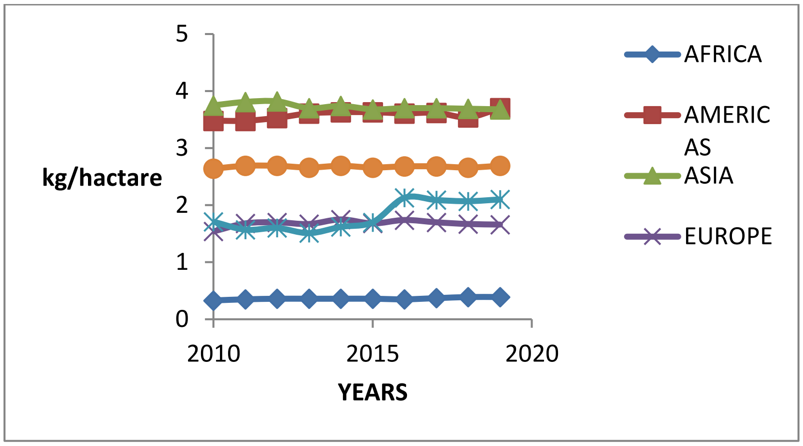

Figure 1. Worldwide utilization of pesticides in the last 9 years

2. Pesticides Taxonomy

The pesticides taxonomy is according to chemical nature, target organism, and origin [26]. Pesticides are usually grouped according to their chemical formulation in major families that include Organochlorine (OC) (**Figure 2**), Organophosphates (OP) (**Figure 3**), Carbamates (**Figure 4**), Carbanilates and Pyrethroids (**Figure 5**), Acylanalides, Benzonitriles, Benzoic acid derivatives, Dipyrids, Phthalimides (**Figure 6**), Triazines, Acetamides, Toluidines, Phenoxy alkanoates, and Benzonitriles. Pesticides are also categorized upon their target organism: they may be insecticide, herbicide (**Figure 7**), rodenticide, fumigants, fungicide, or insect repellent [27]. Pesticides may be naturally occurring or prepared in industries. They include the types of pesticides indicated in **Figures 2**, **3**, **4**, **5**, **6**, and **7**.

Organochlorine (OC) pesticides are highly toxic and are cancer causing, [28] estrogenic, and resistant to biodegradation [26, 21]. They also

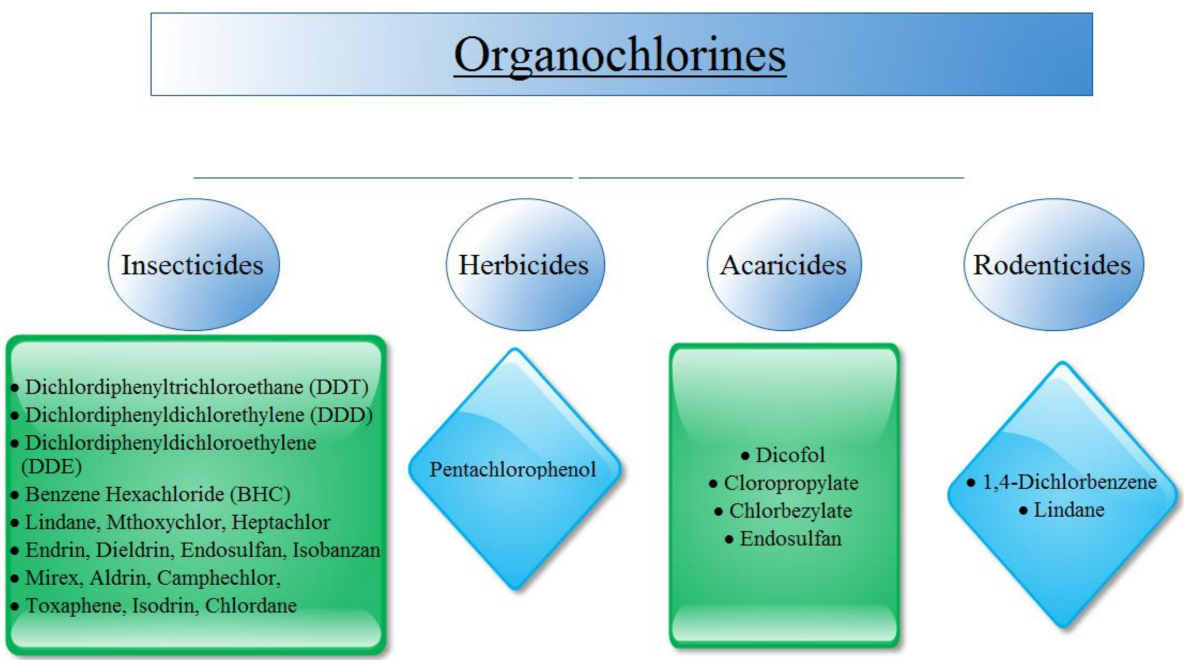

Figure 2. Organochlorine pesticides

cause bio-accumulation [29]. OCs are chlorinated hydrocarbons used in agriculture and mosquito control [30]. They have 10 to 30 years half-life. They are soluble in lipids, stores inside the animal fatty tissue, and then passed down the food chain, harmful for many species, and prolonged relentless. Many countries of different continents have banned OC pesticides, but they are present in environment due to their high perseverance [31]. German chemists developed organophosphorous pesticides (OPPs), during World War (II). Organic solvents and water are solvents for OPPs. They are less persistent than chlorinated hydrocarbons in infiltrating and reaching groundwater, and some of them harm the NS. Plants absorb them, transfers them to leaves and stems, where they are fed to leaf-eating insects. OPPs are used as an alternative to the OC pesticides for controlling insects in fruits, vegetables, and grains around the globe. OPPs and carbamates are still used due to their relative low cost, low persistence, and wide applicability. They act by inhibiting acetylcholinesterase enzyme, and thus disturb the central nervous system of human and insects. Nearly 80% of hospitalization related to pesticides toxicity in humans is due to the OPPs exposure [32]. The use of OPPs became a major issue in the field of environmental chemistry. The OPPs residues in soil not only effect non-target organisms [33], but also disturb equilibrium in ecology of pesticide degrading microorganisms [13,34]. Their residue could be found on supplies and water bodies due to the broad use and high resistance to degradation. Moreover, their transformation byproduct can be a major shock on human health. Toxicity, bioaccumulation, and long-term effects are the factors of pesticides effecting environment. OPPs are found to be dangerous on human life owing to their mutagenic, teratogenic, and carcinogenic effects. Several diseases are linked with OPPs such as Lymphoma and Parkinson's disease. OPPs have a harmful effect on nervous system as they have insecticidal and nematicidal actions credited to anti-acetylcholinesterase. OPPs represent a large portion of world insect-killer utilization. OPPs reduce fertility in human being by decreasing the testosterones level. They are also responsible for behavioral problems in children and involved in immune problems in human and animals [35]. Intelligent quotients (IQ) of children are damaged by an organophosphate insecticide known as Chlorpyrifos. Benfuracarb damaged human cell and called as cytotoxic. Hypothyroidism is caused by pesticides which are ant cholinesterase [20]. Carbamate acid derivatives are highly poisonous to vertebrates and destroy a limited range of insects.

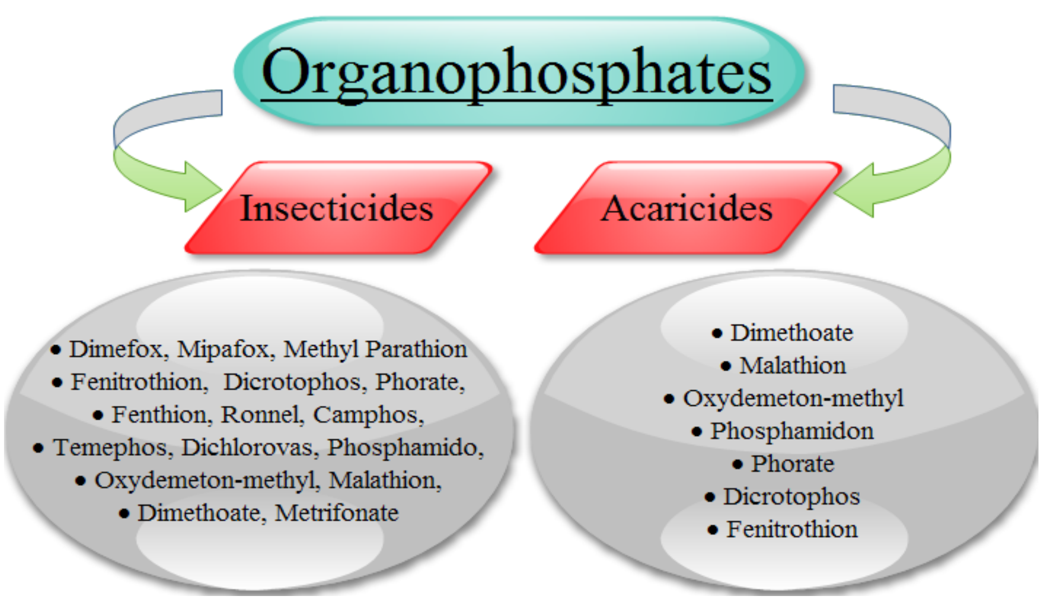

Figure 3. Organophosphate pesticides

Persistence is relatively low. Pyrethroids are obtained from the natural origin. They are derived from pyrethrins which are natural ester containing chrysanthemum. They have low toxicity and long environmental stability. They have long half-life than natural form. They have an effect on NS, they have short-life than other pest control chemicals, and often utilized as the household insecticides.

3. Functioning of Pesticides

Upon knowing working method of pesticide, one can find its effects on target or non-target organism [36]. Here, the working mechanism of three types of pesticides is discussed: insecticides, fungicide, and herbicides.

Pesticides according to their action can act as insecticides, which act on acetylcholine receptor, voltage-gated sodium ion channel, and acetylcholinestrase enzyme present in nervous system (NS) [37]. Insecticides show inhibition to acetylcholinesterase, and thus causes overstimulation in NS (*e.g.*, carbamates and OPPs) [38]. Some insecticides attach to the receptor of neurotransmitter (i.e. acetylcholine), and kill insect due to the long lasting stimulation (such as neonicotinoid pesticides) [39]. The OCs insecticides inhibit GABA (gamma-amino butyric acid) receptor, and thus regulate chloride channel. Pyrethroid insecticides get attach with sodium gates and causes tremor and ultimately death in insects. Certain insecticides act as hormones and block chitin production inside insects and kill insect at very initial developmental stage (embryonic development). Endocrine system that is responsible for growth in organisms gets affected by insecticides. Aliphatic OCs insecticides hinder electron transport channels in insects, and thus energy supply is broken. ATP that is the energy currency in an organism is blocked by blocking mitochondrial electron transport chains, and thus death of insect happens. This kind of action is performed by organoinseticides [40].

Cell membrane of fungi consists of ergosterol. Fungicides block ergosterol synthesis such as canazole fungicides [41]. Benzimidazoles fungicides inhibit proteins synthesis in fungi and mammals by affection reassembly of spindle microtubule [41, 42]. Fungicides also affect targeted fungi from multiple sides and different processes occurring in cells [43]. These processes involve the disturbance of redox reaction in cells and restrain respiration [44-46]. They also inhibit signal flow [47].

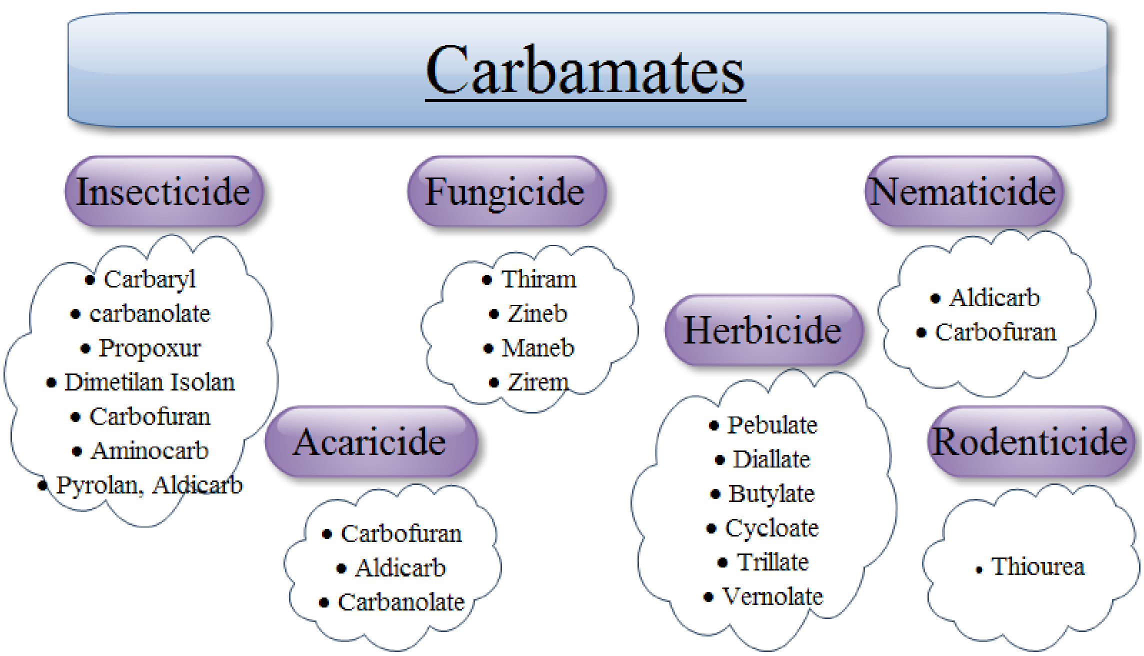

Figure 4. Carbamate pesticides

Herbicides are used as a replacement to the mechanical methods for the removal of weeds [48]. Growth regulating herbicides are useful for the broad leaf weeds. For seedling growth inhibition thiocarbamates and acid amides are used [46]. As they inhibit growth of plants at root and shoot. Plant metabolic pathway is disturbed by herbicides containing highly active components that interact with biomembranes [49]. Herbicides are also capable of blocking lipid production. Glyphosate suppresses the formation of amino acids (mainly tryptophan, tyrosine, and phenylalanine) [50]. Glyphosate is an active constituent of roundup herbicides. Cartenoids that are photosynthetic pigments protects chlorophyll from damaging. Cartenoids get blocked by clomazone herbicides.

4. Ways of Degrading Pesticides

Despite the large benefits of pesticides, their accumulation in food makes them highly harmful for humans and environment. Pesticide residues found in food are as active ingredients, their breakdown products or their metabolites have severe damaging effect on human health. The intake of various pesticides has various risks behind. Not only ingestion, but only the exposure to pesticides effects human heath e.g., pesticides sprays effect spray workers. When pesticides residues are consumed they start to store in human tissues and causes the muscle weakness, disorder endocrine secretions, paralysis, and respiratory problems [32]. To avoid the potential exposure of pesticides to human, pesticides residue should be removed from foodstuff and ground water; efficient strategies should be developed to degrade pesticides. The alternative tools to pesticides are IPM (integrated pest management), ICP (integrated crop management), the organic farming, and the sustainable agricultural control. Remediation of soil includes ex-situ, in-situ, and on-site methods. Ex-situ includes dig of soil and treated after transporting to another location. On-site method includes treatment of soil on-site after excavation. In-situ method involves treatment of soil without excavation. The selection of method is based upon pesticide distribution in soil either localized or distributed. Several methods are designed to degrade and get rid of pesticides due to their harmful nature. These methods include bioremediation [51], phytoremediation [52], electrokinetic remediation, advanced oxidation processes (AOPs), photolysis [53], photocatalysis [54], hydrogen-peroxide based methods [55], photochemical oxidation [56], adsorption, membrane filtration, and through microorganisms [51, 56-57]. Due to the ease

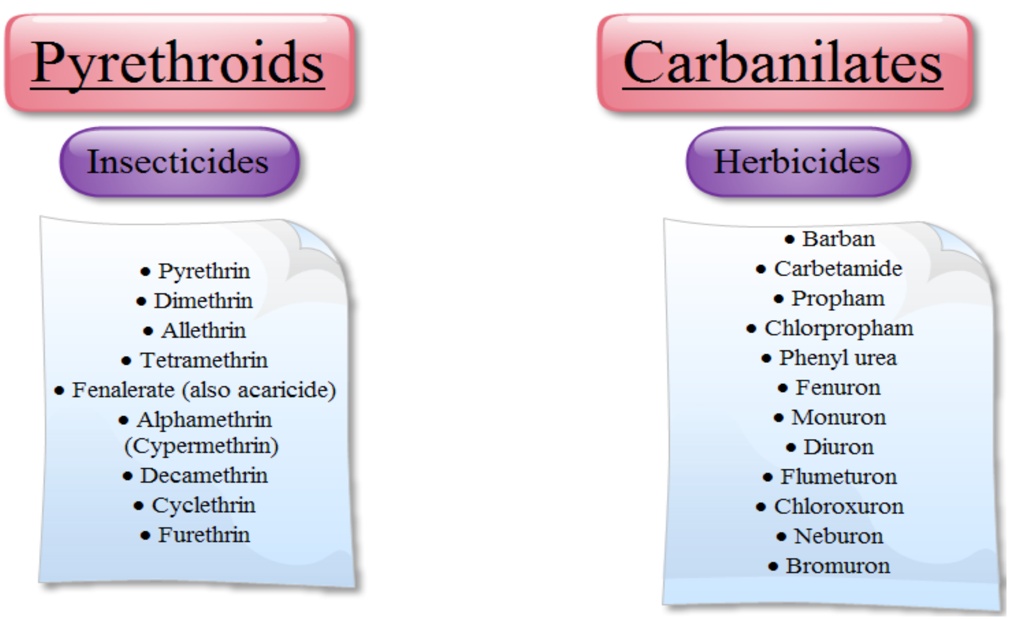

Figure 5. Pyrethroid and Carbanilate pesticides

and economically cheap approach, adsorption is the most accepted method [30]. Bioremediation decreases the pesticide defilement of soils by improving characteristic biodegradation measures by means of metabolic exercises of microorganisms, and it is getting well-known for being a productive, practical, and climate amicable in-situ treatment.

4.1 Bioremediation

Biological method of remedy, also called bioremediation, is a capable skill that converts hydrocarbon containing compounds completely into the low poisonous end products like carbon dioxide or water. In contrast to the other techniques of pollutant removal, bioremediation is economic and beneficial to the environment. There are few types of bioremediation with microorganisms: remediation by native microorganisms, biological augmentation i.e. by using nonnative microorganisms, and also hereditarily tailored microorganisms [58]. Biological stimulation involves the nutrients increment or addition in e^- acceptors. Hydrocarbon pollutants can be degraded by various native microbes found in water and soil [59]. Bacteria [60], fungi, and archaea are the most common bio-agents that can disinfect a location [61]. The bacterial genus pseudomonas is considered effective at degrading a wide range of pollutants [62]. It has a 90-99 percent degrading capacity. Microbes having resistance gene to the pollutant usually stay alive in the polluted environment [63]. Microbes use pollutant for food, decompose it, or grow bio-mass. Because these microbes do not keep or accumulate the pesticide, this aids in the decontamination of the area. The biological technology includes biological remediation of soil for maintaining the environmental equilibrium and stability.

4.2 Phytoremediation

Plant absorbs CO_2 gas and releases oxygen gas. Rhizosphere microorganisms degrade interacting volatile organic compounds [64]. Leaf adsorption helps in the atmospheric particulates absorption. Plants also help in absorption of the insoluble salt precipitations formed in soil due to the combination of heavy metals with soils and sediments. Wetland is the transition zone between the aquatic and terrestrial ecosystem. It recycles nutrients, treat wastewater, and get rid of poisonous compounds, chemicals, and toxic metals [65]. Phytoremediation is sustainable due to these characteristics of soils. It also reinforces the

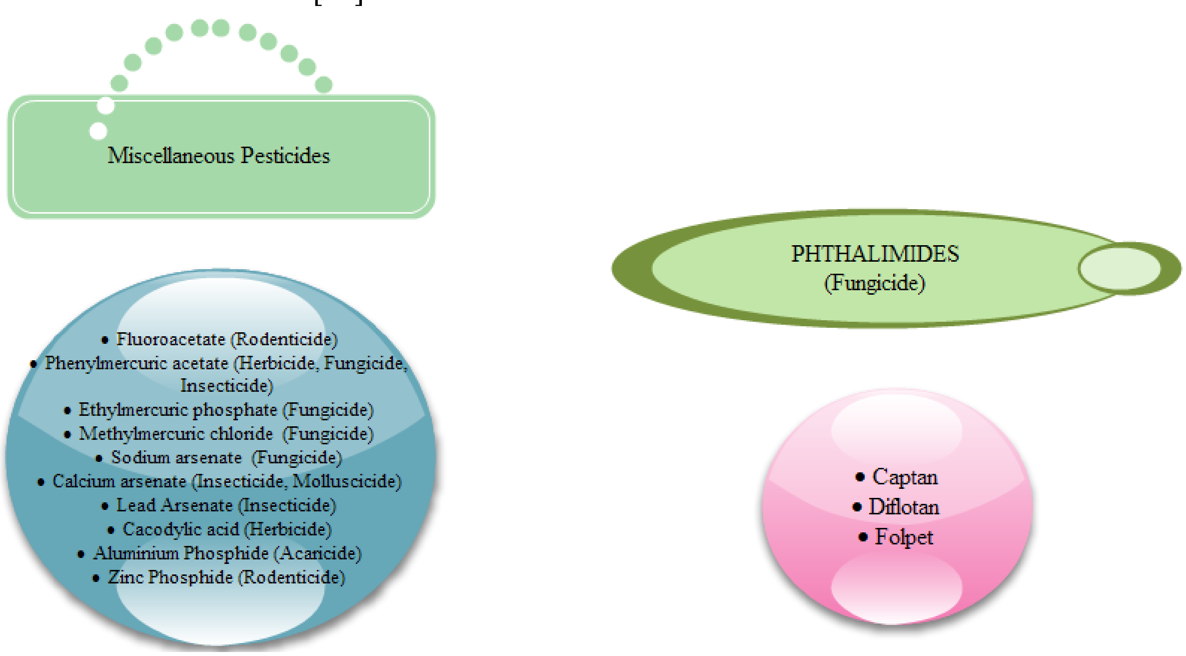

Figure 6. Phthalimides and miscellaneous pesticides

reduction oxidation processes linking microorganisms present in rhizosphere and flora. Plants also remove nitrogen and phosphorous content from water and helps in the eutrophication reduction of the aquatic ecosystem. For example, Litmus and Aspen removes nitrogen and phosphorous at the removal rate of 40-90% and 75-99%, respectively [12]. The microorganisms of rhizosphere remedy for PCBs, pyrene, decabromodiphenyls, phenanthrene, toxic metals, and dioxins have been described in several investigations. The employment of a mixture of microbial strains with species of plants has brought remediation to forefront. For POPs polluted soils treatment [65-67], microorganisms and phytoremediation are coupled [68, 69].

4.3 Electrokinetic method of soil flushing

Electrokinetic (EK) method of soil flushing is used for cleaning up soils that have been contaminated with various toxins [70]. The polluted soil can get rid of contaminants when passed through fluid flushing, and then treated/mobilized by electrokinetic methods like electro-osmosis, electromigration, and electrophoresis between anodes and cathodes in the presence of electric field [71, 72]. The EK procedure for treatment of contaminated soils has been integrated with the other techniques for decontamination like biological remediation or permeable reactive barriers (PRBs) [73]. Soil treatment that is impure by organic insoluble compounds, researchers are increasingly focusing on combining approaches for treatment, *e.g.*, the EK remediation coupled with the biological PRBs. Soils polluted by polycyclic aromatic hydrocarbons (PAHs) and heavy metals are treated by coupling ultrasound-assisted soil washing and bio-augmentation. To eliminate polybrominated diphenyl ethers from soils a microcosm was

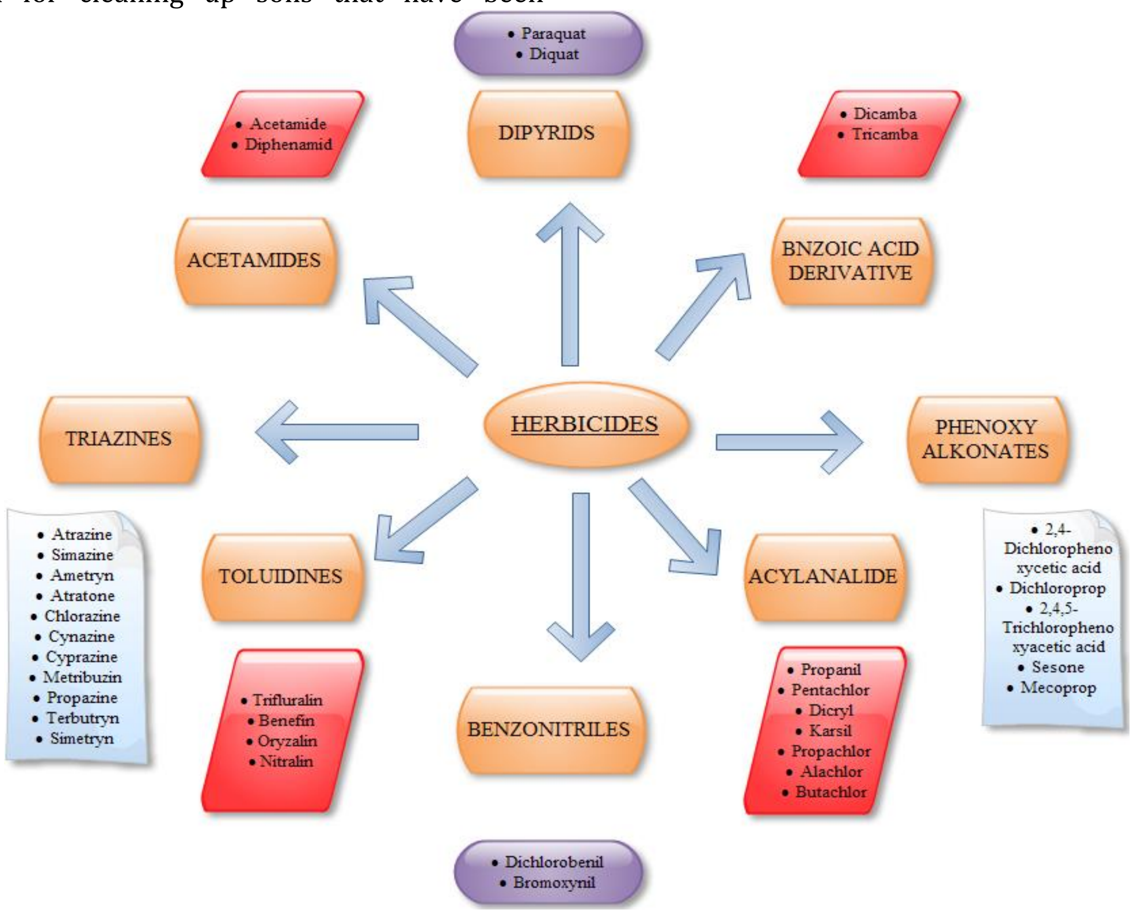

Figure 7. Common types of herbicides

achieved by using a TCFR (tourmaline catalyzed Fenton-like reaction) joint to TCFR+P (Phanerochaete chrysosporium). Nanoparticle based remediation (*i.e.* iron nanoparticles (0)) joint to EK was used.

4.4 Advanced oxidation methods

For wastewater and water treatment, the advanced oxidation processes (AOPs) have been employed involving the radical production during the reaction to degrade contaminants (**Figure 8**). Hydroxyl (OH) radicals are great oxidizing agents and they are not selective in attacking. This makes the basis of the advanced oxidation methods. Hydroxyl (OH) radicals have 2.8 V reduction potential which is significantly greater than other oxidizing agents. Hydroxyl radicals are commonly and widely accepted, indicating the ability to oxidize a lot of compounds during water treatment. Ozone with hydrogen peroxide, peroxone, UV with hydrogen peroxide, Ozone with UV, titanium dioxide photocatalysis, Fenton, Photo Fenton, Ultrasound, hydrodynamic cavitation, and persulfate processes are among the most commonly studied advanced oxidation processes. The process parameters, water quality, and radical scavengers all influence radical formation, attack, and degradation efficiency during reaction. Radicals like hydroxyl radical have a short half-life and react quickly to produce the other reaction products. Singlet oxygen radical, $O_2^{\bullet}$, or peroxone radical are produced as by-products. During AOPs including radicals, complete destruction, and mineralization of target, the organic contaminants is achievable. The ability to completely mineralize organics into carbon dioxide and water is one of the AOPs advantages. Complete mineralization may result in no waste sludge production based on reaction conditions and the oxidation process employed. A single oxidation process can be used to de-contaminate a lot of target

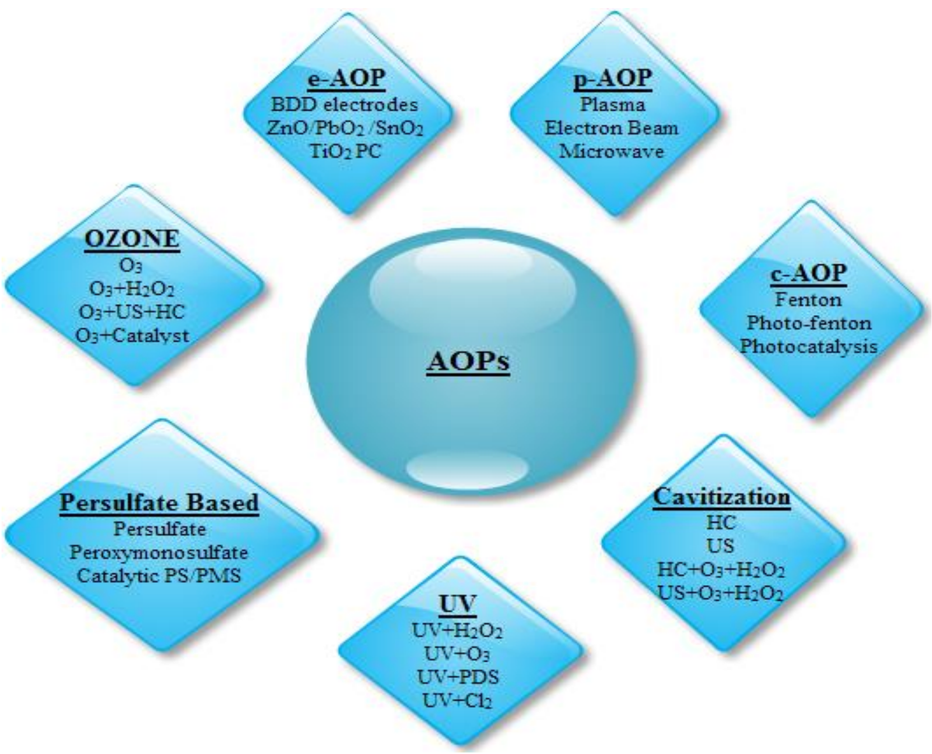

Figure 8. Reactor, tools, catalysts, radical production, and chemicals combined to give different types of AOPs. Numerous combinations of the aforementioned sorts of processes are feasible, with the potential for the synergy between them. The e$^-$/current assisted AOPs uses electrodes and redox reactions are referred to as *e*-AOPs. Catalysts are used in *c*-AOPs, and physical approaches are utilized in *p*-AOPs to increase the radicals' formation.

contaminants in the complicated combinations. AOPs are non-selective while degrading contaminants i.e. they are capable of refractory compounds degradation, excellent efficiency, and efficiency to degrade a variety of DOM (dissolved organic matter). The cost of reagents and processes are relatively greater when using AOPs on a wide scale. In ozonation, ozone is used to degrade organic pollutants. With an oxidation potential of 2.07 V, it has a high oxidation potential. When alkaline circumstances, UV radiation, or transition metal catalysts are used to activate ozone, the production of great reactive radicals (hydroxyl and hydroperoxyl) occur that destroy contaminants readily. Hydrogen peroxide has 1.77 V oxidation potential and its operation is not much useful. Hence, it is usually employed coupled as the AOPs strategy. The hydroxyl radical is generated via titanium dioxide photocatalysis or the UV assisted titanium dioxide photocatalysis, $FeSO_4$, or ozone activation, it improves the efficiency for degradation. Although, the utilized activation method is determined by the contaminants presence and the characteristics of the solution [74, 75], organic pollutants have also been observed to be degraded via cavitation based accelerated oxidation. Significant characteristics of cavitation process include ability to oxidize at room temperature, the utilization of diverse cavitating device configurations, and the suppleness of their joint with AOPs. Once more, the solitary operation of cavitation is never believed to be successful, and thus oxidant joining has been required, so increase in deterioration degree can be achieved [76]. The ultrasound-induced cavitation also produces hydroxyl radicals, which aid in the breakdown or oxidation of pollutants [77]. The ultrasound-induced cavitation has been used to degrade numerous organic molecules and pollutants such as trichlorophenol and rhodamine B, similar to microwave [76]. The inclusion of a catalyst or oxidants is further predicted to improve the efficacy of sonochemical treatment. Microwave-based oxidation technologies have a lot of promise for degrading pollutants in wastewater. Microwaves do not have enough ability for bond breakage, particularly of surfactant like chemicals, but combining them with other degrading materials like oxidizing agents that are able to increase absorption of microwave radiations, induce hotspot and can produce radicals, hence result in intensity in degradation. Microwaves are able to speed up the reactions with effects (including thermal or other) and they have sparked curiosity in microwave-assisted techniques such as ruining of contaminants and wastewater treatment [78].

4.5 Photocatalysis

Certain chemical reaction proceeds by absorbing photon or light in certain wavelength in the range of ultraviolet or visible region (10 nm-750 nm). Light absorption depends on the structure of compound and location of double bond. Electrons in the valence band absorb photons and excite to conduction band. Due to the electron excitation, a positive charged hole is generated on the valence band in place of electron. This excited electron may join hole after some times or it may produce a radical, after reduction, on surface of compound. Photoreactions are speed up by the presence of catalyst called as photocatalyst, and such acceleration is called photocatalysis [79]. It is an approach to photochemical detoxification. Mostly, semiconductors are used as photocatalyst. Photocatalyst can be defined as a substance than can produce the chemical transformation of reactants upon absorbing photons and can attain the original chemical composition after each interaction with reaction participants. It is efficient in stoichiometric amounts. Hence, photocatalysis can be defined as “an alternation in time of a reaction or start of a reaction on interaction with UV, visible, IR radiations in the photocatalyst presence, which is responsible for the light absorption and transformation of reactants.” Photocatalysis is employed in organic synthesis, water, and air decontamination and hydrogen production [24]. Photocatalyst used in decontamination of air and water are classified in two groups; semiconductors and organic compound and their complexes with metals. Semiconductor photocatalyst are used in heterogeneous photocatalysis. In photocatalysis, electron promotion causes charge separation between conduction and valence band which then helps in radical formation. For degradation of organic pollutants involving photocatalysis, the radicals' formation, for example, superoxide radicals ($O_2^•$) or hydroxyl radical ($OH^•$) is necessary. These radicals are essential for organic compounds degradation because they act as electron transport channel from photocatalyst to organic compound. Hydroxyl radical is produced by water oxidation through hole, also produced from hydrogen peroxide due to its interaction with light or other superoxide radicals. The excited electrons in the conduction band reduce oxygen molecule results in the superoxide formation. Reduced oxygen species are produced as indicated in the following equations steps:

1. $material(semiconductor) \overrightarrow{\boldsymbol{hv}} holes + e^-$
2. $O_2 + e^- \rightarrow O_2^{-•}$
3. $H_2O + holes \rightarrow HO^• + H^+$
4. $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$
5. $O_2^{-•} + H_2O_2 \rightarrow OH^- + O_2 + HO^•$

4.6 Semiconductor based photocatalyis

AOPs are divided into two categories: homogeneous AOPs and heterogeneous AOPs. When phase of sample is different to catalyst, the heterogeneous AOP can be used to remove pesticides. Photocatalysis based on semiconductors is a low-cost heterogeneous AOP [80]. Semiconductor based photocatalysis has following benefits; cost-effectiveness, non-toxicity, proficient light absorbance, and extended life without a significant photocatalytic pastime [81]. Under the solar/UV irradiation, photocatalytic semiconductors such as ZnO and TiO_2 are commonly employed for pesticide breakdown [82]. The TiO_2 semiconductor is less hazardous, less expensive, and has been indicated as effective catalyst to degrade poisonous compounds [81]. On the other hand, the E_g value of TiO_2 *i.e.* 3.2eV, results in electron-hole pairs recombination, ineffective adsorption, and limited recovering ability afterward degradation are limitations that restrict its commercial potential [83]. ZnO, a semiconductor with a band gap similar to TiO_2, is also utilized as a photocatalyst [84]. The results achieved by using ZnO provide excellent satisfaction in terms of high-scale water treatment, environmental pollution removal, and toxic organic species detoxification. In addition, ZnO has a broad band gap in UV and also recombination is fast. As a result, the created active charge carriers aggregate very quickly, slowing down the reaction rate. The photocatalytic breakdown of pesticides is also aided by the CuO semiconductor. Catalytic potential of semiconductors decreases over time because of recombination and adsorption capacity decreases. The alternative ways for overcoming these constraints take account of doping of metal or non-metal in semiconductor, mixing the semiconductor in other partly-conductor with a dissimilar value of band gap, and creating any composite material that has compounds (dual/ternary) [85-87].

4.7 Adsorption

For polluted soils treatment, principle of adsorption is employed using in-situ amendments and considered as an economic solution. Biochar is a popular modification that is both environmentally beneficial and includes the broad spectrum sources of raw materials [88]. Porous carbon containing solid made by without oxygen pyrolyzing of biomass is called biochar [89]. Biochar is most commonly used as a soil additive to minimize irrigation, enhance its quality, increase rate of crop output, less emissions of greenhouse gas and fertilizer needs. Two major factors, surface area and porosity, influence biochar's sorption capacity for organic contaminants such as pesticides [90]. Higher sorption capabilities will arise from more porous materials and more surface area. The sorption capacity of biochar is dependent on presence of amide, carboxylic (–COOH), lactonic, hydroxyl (–OH), and amine groups on surface. The amount of these groups on surface of biochar is influenced by two important factors: pyrolysis temperature and source material [90-93]. The alkali catalysis mechanism in biochar can speed up the OP insecticide hydrolysis and carbamate insecticides hydrolysis in the soil [94]. Biochar is alkaline, in general, and its pH rises as the pyrolysis temperature rises. However, depending on the source material, there are a few exceptions, for example, biochar made through sludge of wastewater or straw obtained from wheat relatively on low temperatures i.e. 400 °C was acidic in nature (pH 4.87-6.11). Functional groups are essential elements impacting biochar's pesticide sorption capabilities, and aromatic structure is also important for biochar's long-term behavior in the soil. In fact, the pyrolysis temperature determines the majority of biochar features, and the ratio of hydrocarbons reflects structure of the aromatic compound present that can also determines size of pores and surface area of adsorbent. Concerning the treated biochars for soils remedy, it is necessary considering if treatment processes are economic or not, albeit they have a good sorption ability [95]. In addition, biochar found as an effective pesticide amendment for its sorption ability which is able to reduce the biological degradation of pesticides within soils. In contrast, a lot of microbial stimulation can be caused by biochars making a high microbial degradation of pesticides. Consequently, the dominant action of biochar determines its effect of on biodegrading pesticides [96].

4.8 Membrane filtration

Separation systems based on membranes (pressure assisted) offer a great removal aptitude, economic, and operational flexibility, the membrane's material is available feasibly and energy consumption is low [97, 98]. Membrane methods, on the other hand, are plagued by the production of cake layers, which eventually block pores of membrane and make it dirty. The significant reductions in water flux, increase in energy consumption, and cost of treatment are fouling aftermaths [99]. Furthermore, the membrane dependent filtering methods focus contaminants keen on high-concentration remains, which should be treated further before final discharge.

Pesticide residues cause's harmful effects to human health that is mentioned in **Table 1**.

Table 1. Representative studies on different pesticides

Pesticide Group	Pesticide Name	Negative Effects	Degradation Studies	Ref.
OCs	Dichlorodiphenyltrichloroethane (DDT)	Nausea and Seizures.	Production of oxidative radicals (SO_4^-, OH) and reductive radicals ($S_2O_8^-$) during oxidation technologies involving thermally activated persulfate gave best degradation of DDTs.	[100]
OCs	Dichlorodiphenyldichloroethylene (DDE)	Affect adipose tissues and serums.	Microbial fuel cells are able to degrade DDE in 60 days. After 60 days, MFCs stop proper functioning due to a decrease in water content.	[101]
OCs	Dicofol	Nausea and damage the skin.	Ni/Zn dopped multi-walled carbon nanotubes were able to maximally degrade dicofol in 90 minutes, at pH 6 and 318 K.	[102]
OCs	Lindane	Damage CNS and immune system.	For degrading organic contaminants in water sulphate radical based AOPs was employed. The efficiency of the UV assisted persulfate procedure to degrade lindane in water was explored with 93.2 percent. 720 mJ/cm^2 was the UV facility during lindane elimination. It was found to be the first-order kinetics for pesticide breakdown during proton abstraction by sulphate and chloride remobel via carbon chloride bond by using ultraviolet-C light.	[103]

OCs	Pentachlorphenol	Negative effect on liver, kidney, and CNS.	Using crosslinked modified chitosan based activated charcoal, pentachlorophenol degradation proved exothermic, practical, and spontaneous. The pseudo-second order reactions were used in the mechanism.	[104]
OPP	Monocrotophos (MCP)	Strong cholinesterase inhibitor.	By using a one-pot solvothermal technique 2-dimensional/2-dimensional TiO_2 mounted on Fe (MIL-88) semiconductor hetero-junction was created and grafted. Through visible light irradiation, the TiO_2/Fe (MIL-88) composite degraded this herbicide. Fe (MIL-88) and TiO_2/Fe (MIL-88) have specific surface areas; 1175 and 935 m^2g^{-1} and pore volumes; 0.69 and 0.57 m^3g^{-1} respectively. Various parameters were used to confirm the TiO_2/Fe (MIL-88) oxidizing ability for the breakdown ability of MCP that include pH(1-12), temperature (27.3 °C), and starting MCP concentrations of 20 to 60 mg/L.	[105]
OPP	Malathion	Blurred vision, diarrhea, and breathing problems.	Malathion degradation efficiency was examined by utilizing Fenton (Fe^{2+}/H_2O_2), ultrasound/UV with Fenton (Fe^{2+}/H_2O_2/UV/US) and UV with Fenton (Fe^{2+}/H_2O_2/UV) methods. Fe^{2+}concentration, pH, H_2O_2 concentration, and Malathion concentration, these all investigated as operational parameters that affect the degradation rate. In subsequent ideal situations: hydrogen peroxide conc. 0 to 700 mgL^{-1}, pH (3), Malathion conc. 0-20 mgL^{-1}, conc. of Fe^{2+} 0 to 20 mgL^{-1}, 98.79 percent for (Fe^{2+}/H_2O_2/UV/US), 70.92 percent for the (Fe^{2+}/H_2O_2/UV), and 55.94 percent for (Fe^{2+}/H_2O_2) was founded degradation ability.	[106]
OPP	Glyphosate	Oral or nasal discomfort, skin irritation, and mild conjunctivitis.	At pH 4, glyphosate has a maximal adsorption capacity of 2.855$mmolg^{-1}$ on UiO-67/GO. It followed Langmuir model of adsorption. It also obeys the pseudo-second-order kinetic model also. UiO-67/GO performed adsorption of this pesticide by many Zr-hydroxyl groups present on graphene oxide surface, vast surface area of accessible graphene oxide helped impounding of the objective OPPs.	[107]
OPP	Methyl Parathion	Reparatory and eye sight problems.	The produced nanocomposite (GO-Fe_3O_4/Bi_2MoO_6) had 2.5 eV band gap that was appropriate for visible light photocatalytic action. This nanocomposite photocatalyst showed >95% degrading ability for methyl parathion, after 120 minutes. The photocatalyst was recovered from the solution after the reaction concerning its magnetic property. Even after five cycles, this nanocomposite could decompose methyl parathion with competence >90%.	[108]

OPP	Dimethoate	Blurred vision, diarrhea, and breathing problems.	Through a one-step hydrothermal technique, built Ag NPs ornamented CNG (GO-Graphite N_2 carbide). These are self-assembled micro-flowers from nano-sheets. The Ag-nps alteration not only enhanced the uptake of visible region, but also successfully boosted the movement of photo-generated electrons via the SPR action and the plasmonic heterojunction produced, according to different physical/chemical characterizations. The dimethoate breakdown rate of Vis/Ag@CNG/sulfite has found to be 15.8 times > Vis/Ag@CNG.	[109]
Carbamate	Carbaryl	Vision and stomach problems.	In varied growing circumstances, the breakdown of carbaryl by Xylaria sp. was investigated. While cytochrome P450 was effective in liquid culture, 99 percent of the additional carbaryl was removed, which was equivalent to the degradation rate of fungus (Pleurotusostreatus) with excellent bio-remediation capabilities. Carbaryl decomposition is aided by the presence of Mn^{2+}. In non-sterile soil, 59 percent carbaryl was removed, compared with 72.17 percent in sterile soil, signifying that Xylaria sp. BNL1 can withstand environment and related infection. Moreover, carbaryl was rapidly digested by intracellular fractions comprising laccase, CYP450, and carbaryl esterase.	[110]
Carbamate	Carbofuran	It is fatal and leads to hypertension.	For the photo-degradation of carbofuran driven by LED light, the mixed nanostructure Fe_3O_4-SnO_2-gC_3N_4 was used. Under the visible light, the catalyst demonstrated excellent photocatalytic performance, with an efficiency of 89 percent and rate constant was 0.015 min1 (the pseudo first-order). Addition of Fe_3O_4 increased the catalyst's magnetic separation after repeated periods of operation, enhancing the system's practical value in combating organic contaminants.	[111]
Carbamate	Aldicarb	Weakness, headache, sweating, tearing, blurred vision, tremors, and nausea.	By sol-gel precipitation approach, high visible light sensitive anatase nitrogen and sulphur combine doped and only nitrogen doped nano-titania was created. It was discovered that when exposed to visible light for half an hour NS doped catalyst system (1.5 gL^{-1}), more than 80% of the aldicarb degraded. This increased activity is related to the symbiotic influence of two contaminants in its framework (both N and S) that reduces the band gap.	[112]
Acylanalide	Alachlor	Malignancy, mutagenic, and thyroid effect.	Utilizing CuS- $BiFeO_3$ heterojunction materials, a photo (visible light) assisted catalytic method has been formed for degradation of alachlor insecticide. $BiFeO_3$ nanostructures and nanorods of Copper-Sulphide made heterojunction material. By photo illumination, hetero-junction material successfully catalyzed the degradation of alachlor herbicide, achieving >95% breakdown in 60 minutes. Use of sustainable power, relatively inexpensive, high performance, durability, and reusability of the catalyst material are all appealing properties of the devised photocatalytic process.	[113]

Phenoxy-Alkanoates	2,4-D (2,4-dichlorophenoxyacetic acid)	Headache, nervousness, and unconsciousness.	The degradation of 2,4-D was first attempted electrochemically by using Blue-TiO_2 nanotubes anode with the minimum power utilization (0.14kWhm^3) yielding rate constants 2.57 times larger than that produced by BDD (boron-doped diamond) anode also 6.32 times larger than that produced by using DSA (dimensionally stable anode). On Blue-TNT, the input of the accountable radicals for 2,4-D degradation was 95 percent by hydroxyl radical and just 2 percent by sulphate radical, in contrast to the BDD anode (radical assisted or non-radical based).	[114]
Phenoxy-Alkanoates	2,4,5-Trichlorophenoxyacetic acid	Liver damage.	Electrochemical also photo-electrochemical oxidation techniques were used to investigate for degrading this pesticide. TiO_2 has structure of nanotube whether PbO_2 NPs are present or not. For PEC oxidation TiO_2-PbO_2 was utilized. The total organic carbon was often used to determine the height of decomposition. PE behavior changes with potential in 0.5M sulphuric acid which was measured by using LSV method at 5 mVs^{-1} (slow sweep of linear scanning voltametry) for PEC studies. After 120 minutes of electrolysis at 30 mAcm^2, oxidation of pesticide by Sb-SnO_2 was 100% and 95 percent on PbO_2, indicating that the EC is an effective treatment approach for removing this pesticide from effluents.	[115]
Triazines	Atrazine	Kidney failure and heart collapse.	Atrazine decomposition was affected differently by ashes and biochar. Compost was made from SBA; sugarcane bagasse ash (5 and 10%), RHA; rice husk ash (5 and 10%), and WBC; wheat straw biochar (1 and 5%). RHA lowered the half-life of atrazine at lower concentrations (50 gg^{-1}) compared with control bio-mixtures, while SBA and WBC (1 percent) had no effect. WBC (5%) increased the half-life of atrazine by 200 percent (50 gg^{-1}) and 300 percent (100 gg^{-1}). The addition of pesticide-degrading cultures to bio-mixtures improved atrazine breakdown.	[116]

Triazine	Simazine	Reproductive disarray and kidney collapse.	The effect of H_2O_2, Fe and photo situations for breakdown of this pesticide employing AOPs was studied by using the D-optimal model. In AOPs that use sunlight, the effect degree of the operational variables is set in the following order: H_2O_2<Fe<time, whilst in AOPs with ultraviolet assistance the increasing order is Fe<H_2O_2<time for degradation ability. In addition, due to the creation of reactive intermediates, degradation was larger than mineralization. After analyzing the kinetic constants obtained, it was determined that UV/H_2O_2 with 2.5 ppm H_2O_2 would be the best technique to use in the conduct of water.	[117]
Dipyrid	Paraquat (PQT)	Kidney failure.	rGO (reduced graphene oxide) GO (graphene oxide) with chitosan (CS) were produced by using a simple co-precipitation technique. CS/rGO was able to degrade 85.49 percent of PQT solution in 60 minutes when exposed to the visible light, and this capacity maintained at 82 percent after 5 repetitions under the same circumstances. The pseudo-first order kinetics was used to determine the kinetics and rate of reaction for degradation process of PQT.	[118]
Dipyrid	Diquat	Skin irritation.	By simultaneous adsorption and photo-degradation procedures, OH-GCN (hydroxyl assisted graphite carbon nitride) samples were used as bi-functional substances for the effective elimination of diquat dibromide pesticide. The active sites for this pesticide sorption process were hydroxyl groups on surface, as revealed by the structural characterization. The study of adsorption showed 110 times greater adsorption capacity (159.3 mgg^{-1} at pH 7 and 25 °C) than perfect CN. After 240 minutes of visible-light irradiation, the overall degradation ratios were 97.1 percent.	[119]
OPP	Chlorpyrifos	Nausea, dizziness, and confusion. Also, respiratory paralysis and death in the case of major accidents like spills.	Halloysite Nanotubes (HNT) functionalized with chitosan (CTS) was used as responsive nano-supports for the grafting of copper (Cu) and laccase (Lac) for chlorpyrifos breakdown. At neutral pH and room temperature, chlorpyrifos decomposition with the nanocomposite was as high as 97 percent for 50 g/mL chlorpyrifos. Even at different temperatures and pH levels, the nano-composite maintained 97 percent breakdown ability. The recyclability investigation was repeated five times, with the breakdown percentage remaining the same (95%) after each round.	[120]

5. Conclusion

Pesticides are used to boost crop yield, prevent vector illnesses, and kill, or inhibit dangerous pests. On the other hand, they have the unmistakable negative consequences. Destruction of water and soil quality harmfully affects the environment inhabitant because they are considerably affecting the environment and mammals. Biodiversity get affected by pesticides and their contact either directly or indirectly but on long-term basis pose the solemn health risks for human beings. Cancer, abnormality in reproduction, diabetes mellitus, illnesses of respiration, and problems of neurology are just some of the acute health concerns they might cause. To remediate the polluted ecosystem, various remediation approaches have been documented, including adsorption, biological remediation, AOPs, and so on. Adsorption and biological remediation, on the other hand, are mentioned to be the ideal treatments since they are ecologically benign, economically effective, and produce less harmful byproducts. To lessen the risk of pesticide poisoning, governments should work together. By enacting the rigorous legislation and toxicity standards, the necessary steps should be done to ensure the efficient management of pesticides. The integrated pest management (IPM) can aid with pesticide use plus control of chemicals. Manufacturing of pesticides should include more care and a higher safety profile to have a lower detrimental influence on the environment and humans.

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