Review

Recent Strategies for Environmental Remediation of Organochlorine Pesticides

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Abstract: The amount of organochlorine pesticides in soil and water continues to increase; their presence has surpassed maximum acceptable concentrations. Thus, the development of different removal strategies has stimulated a new research drive in environmental remediation. Different techniques such as adsorption, bioremediation, phytoremediation and ozonation have been explored. These techniques aim at either degrading or removal of the organochlorine pesticides from the environment but have different drawbacks. Heterogeneous photocatalysis is a relatively new technique that has become popular due to its ability to completely degrade different toxic pollutants—instead of transferring them from one medium to another. The process is driven by a renewable energy source, and semiconductor nanomaterials are used to construct the light energy harvesting assemblies due to their rich surface states, large surface areas and different morphologies compared to their corresponding bulk materials. These make it a green alternative that is cost-effective for organochlorine pesticides degradation. This has also opened up new ways to utilize semiconductors and solar energy for environmental remediation. Herein, the focus of this review is on environmental remediation of organochlorine pesticides, the different techniques of their removal from the environment, the advantages and disadvantages of the different techniques and the use of specific semiconductors as photocatalysts.

Keywords: organochlorine; emerging contaminants; photocatalysis; pesticides; degradation

1. Introduction

The conventional approach to the removal of pesticides from the environment are not effective for the complete removal of these pollutants. This is evident in the fact that despite their usage over the years, the negative impacts of pesticides on the environment and humans still remains a challenge. More than 17 million deaths has been reported to occur as a result of pesticide poisoning from 1960 till 2019 [1]. Despite the alarming statistics, this number is even assumed to be underestimated since majority of pesticide poisoning in the poor rural communities were not accounted for due to poor death registry [1]. Pesticides are used worldwide to prevent weeds, fungi and pests from attacking plants. Their wide usage has increased their enormous dispersal in soils, groundwater and drinking water [2]. The best way to identify them is through classification. The first method of classification is based on the use of the pest or organism they kill. For example, termites (termiticides), vegetation (silvicides), fishes (piscicides), birds (avicides) and nematode (nematicides). Others are
snail and slugs (molluscides), viruses (virucides), mites (acaricides), insects and mites (ovicides), weed (herbicides), bacteria (bactericides), fungi (fungicides) [3]. The second classification is based on the active components and chemical composition of the pesticides. Pesticides may be synthetic pyrethroid, carbamates, organophosphorus or organochlorine as shown in Figure 1 [4].

**Figure 1.** Types of pesticides based on chemical composition.

One of the most commonly used pesticides are organochlorine pesticides. Organochlorine pesticides are designed to specifically impede some particular living organisms. Just like other pesticides, they are different from other chemical pollutants because they are intentionally released into the environment. They are predictably toxic and disrupt the neural function of the pests, leading to their death [5]. Organochlorine compounds are part of persistence organic pollutants (POPs) and they are characterized by chlorine attachments, possession of functional groups that are polar, and the presence of cyclic structure which may be aromatic. They generally remain in an undegraded form in the environment for a long time. In addition, they can travel over long distance because of their semivolatile property and they are lipophilic (they mount-up in tissues that have fats like nerves) in nature [6]. When humans or animals consume fish that are contaminated with organochlorine pesticides, the active components of the pesticides could be released into the system which have detrimental effect. Due to their nature and properties, organochlorine pesticides are found in every part of the ecology including desert, snow, water bodies, soil and air despite the fact that their usage have been banned by several countries. Examples of organochlorine pesticides are furan (dibenzo-p-furans), dioxin (dibenzo-p-dioxins), polychlorinated biphenyls, chlordane, toxaphene, dichlorodiphenyltrichloroethane (DDT) and dieldrin. Others include aldrin, mirex, hexachlorobenzene, heptachlor [7,8]. New organochlorine pesticides such as imidacloprid have recently being reported [9]. The structures of some of the organochlorine pesticides are shown in Figure 2.
Their persistence in the environment could be attributed to the difficulty in hydrolyzing the carbon–chlorine bond of the aromatic compounds. This bond is strong due to the overlap of the p-orbital of chlorine and the pie bond of benzene. It has been reported that the more the number of chlorine attachments to the aromatic ring, the higher the stability of the organochlorine compounds to hydrolysis [11]. Other factors that affect their hydrolysis rate are catalysis by metal ions, ionic strength, presence of sediments, pH and temperature. A very important point to note about these organochlorine pesticides is that they are all toxic in nature and this makes their removal from the environment (water, soil and air) extremely important.
2. Toxicity of Organochlorine Pesticides

A link has been established, based on studies, between the infection rate and the quantity of organochlorine pesticides in the dietary intake of children. Children with higher organochlorine intake have lower immunity to infections [12]. Some of these organochlorine compounds have also been reported to be carcinogenic. In a similar study, DDT was found to be very high among people suffering from cancer [8]. In fact, the International agency for research on cancer (IARC)—a body that deals with cancer related studies—has classified organochlorine pesticides such as dieldrin and aldrin as human carcinogens based on the evidence from several investigations that linked them with cancer [13]. Exposure to high quantity of these two organochlorine pesticides was reported to cause kidney damage, detrimental effects on nervous system and could lead to convulsion. Even low dosage exposure, for an elongated period of time, could lead to involuntary movement of the muscles, vomiting, dizziness, headache, irritability and can also lead to convulsion [14]. Suppression of immune response and suppression of antibodies have been reported due to the exposure of the body to dioxins and other organochlorine pesticides [15]. Hornbuckle et al. have further emphasized that organochlorine compounds suppresses both the immune and antibody response, as evidenced in the studies conducted with animals [16]. Due to high toxicity of organochlorine pesticides to living organisms and the environment, one of them (2,3,7,8–tetrachlorodibenzo-p-dioxin) has been described as the most toxic pesticides by World Health Organization (WHO) [17]. Organochlorine pesticides have been linked to endocrine disruption and cardiovascular diseases such as pectoris and hypertension [18,19]. It was reported that about one billion people are suffering from hypertension worldwide, of which organochlorine in food was named as one of the causes [18]. It has equally been found that organochlorine pesticides can trigger reproductive problem and diabetes [19,20]. Other health problems reportedly linked to organochlorine compounds are neuropsychological impairment, atherosclerosis, transient hepatotoxicity, porphyria, peripheral and chloracne [19]. The toxic effects have also been reported among other living things apart from humans. For instance, death of fish has been observed in the presence of high dose of pesticides. One of the studies carried out with endosulfan, showed that the chemical became lethal within four hours of administering about 26.3 \( \mu \text{g/L} \) of the solution to fishes [8]. In a similar report, pesticides contamination have been discovered to lower the population of Alaskan Fur seal (Callorhinus ursinus) [21].

3. Methods for Removal of Organochlorine Pesticides from the Environment

The removal of pesticides from the environment has been a subject of intensive research, and this has remained for a period of time. Several techniques have been used to either degrade or remove the organochlorine pesticides from water, soil, food and air. Street [22] reported in 1969 that peeling, cooking, washing and blanching of food will reduce the organochlorine pesticides in food [23]. The study also reported that feeding animal with charcoal could lower organochlorine pesticides’ toxicity in animals. However, these methods cannot completely remove the organochlorine compounds due to their stability and persistence. Burial in deep well, landfill, use of cement kiln, land cultivation, evaporation ponds and open burning [7,24,25] have also been used for disposing organochlorine pesticides, but these pose serious environmental and health challenges [3]. Furthermore, land requirement, leaching, slow decomposition and varying climatic conditions are part of the factors that limit the use of these methods [3]. Due to these limitations, new strategies are now being adopted for the removal of organochlorine pesticides. These various methods that have been developed are the focus of this review. The advantages and disadvantages of each of the different techniques are presented in Table 1. It is important to note that most of these remediation strategies are still at pilot scale. Thus, further investigations are required in order to advance these strategies to full (commercial) scale [26]. However, strategies such as Fenton oxidation, adsorption, incineration, bioremediation and phytoremediation has been used on site.
## Table 1. Pesticides removal strategies with their advantages and disadvantages.

| Strategies                                      | Advantages                                                                 | Disadvantages                                                                 | Ref       |
|-------------------------------------------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------|
| 1 Phytoremediation: Removal of organochlorine from soil and water by using plants | Cost-effective; In situ treatment is possible; Excavator not needed, but excavator plant is used | Challenges of finding excavator plants that can effectively take-up pesticides | [27]      |
| 2 Bioremediation: Using microorganism to degrade organochlorine pesticides | Complete mineralization of contaminants to CO₂ and H₂O without buildup intermediate; Preliminary pollution site assessment is not needed | It is not effective when the growth of microbes is not supported by environmental conditions; can cause damage to the environmental balance | [28]      |
| 3 Incineration: Oxidation of organochlorine pesticides by applying heat and oxygen | Complete degradation of pesticides to ash | Problems of ash disposal; production and release of cyanide into the environment when pesticide contain nitrogen | [29]      |
| 4 Low temperature thermal desorption              | Removal of pesticides from sediments, soils and sludges is possible        | Costly since specialized facilities are needed; cannot completely destroy the pesticides | [30,31]   |
| 5 Adsorption: use of adsorbents                   | Fast and can be used on-site                                              | Pesticides are not being destroyed, but are being transferred from one medium to another | [32]      |
| 6 Supercritical oxidation                         | Toxic gases and particulates are not released                             | Problem associated with construction of super critical oxidation unit          | [33]      |
| 7 Ozonation: use of ozone                         | It is easy to operate and it works faster                                  | Consumes many energy; it is expensive                                         | [34]      |
| 8 Dechlorination: Removal of chlorine             | High boiling point organics like PCB can be degraded                      | Degradation efficiency is comparatively low compared to most techniques       | [35]      |
| 9 Electrochemical oxidation                       | It can degrade both soluble and insoluble organic feed of pesticide in any phase | Formation of multiple intermediate products                                    | [36]      |
| 10 Gas-phase chemical reduction                   | No possibilities for dioxin and furan formation since it happens in atmosphere without oxygen | It requires the removal of chlorine donor from the combustion air and effluent gas | [37]      |
| 11 Ultrasonic technology: use of sound            | No secondary pollutants; no need for extra chemicals; easy to use and improved remediation rate | Maintaining the temperature is challenging; attenuation problem               | [38]      |
| 12 Plasma arc techniques                          | It can be used to degrade recalcitrant organochlorine pesticides; is also appropriate when metal has mixed with pesticides | Challenge of getting appropriate scrubber to remove products of incomplete combustion and vaporized metals | [39]      |
| 13 Catalytic hydrogenation                        | Wide range of organochlorine pesticides can be degraded                   | Noble metal poisoning                                                         | [40]      |
| 14 Molten salt oxidation                         | Total transformation of organics to CO₂ and H₂O; It can be set up in a small scale | Organochlorine mixed with high inert materials cannot be treated             | [24]      |
| 15 Fenton oxidation                               | Effective in treating pesticides contaminated wastewater on the industrial scale | It is pH sensitive                                                            | [41,42]   |
| 16 Zero-valence iron                              | Iron is not expensive; its action decreases with time due to the formation of oxide layer that block the active site |                                                                       | [42,43]   |

One of the methods that has been used for the removal of organochlorine is phytoremediation. Phytoremediation is commonly carried out either by using plants or through the introduction of bacteria into the system. It is important to note that rhizoremediation, phytotransformation and
phytoremediation are involved in phytoremediation process. Removal of organochlorine pesticides may be via degradation occurring in the interior zone of the root or by the pesticide transformation taken place within the tissue of plants [44]. Rissato et al. carried out an assessment to estimate the phytoremediation potential of a tropical plant species *Ricinus communis* for the degradation of fifteen different persistence organic pollutants including organochlorine pesticides. The evaluation carried out after sixty-six days indicated that the roots of these plants successfully reduced the concentration of these contaminants. The highest removal was observed for hexachlorocyclohexane (HCH) [27].

Another method that has been adopted is bioremediation, where specific attribute of microbes was used to degrade pesticides. The enzymes present in these microbes could attack the pesticides and convert them to fewer toxic substances. The degradation could be achieved either via an in situ or ex situ approach. The ex situ method may require the use of compost on farmland, biofilter or bioreactor, whereas the in situ method may require a system for delivering liquid, biosparging, bioventing and biostimulation [45]. Irrespective of the type of bioremediation method adopted, control of environmental conditions is very crucial. One of the studies that utilized bioremediation was reported by Watanabe et al. [28]. In the study, heptachlor, aldrin, endrin, dieldrin and HCB were successfully degraded by using anaerobic microbial strain. Although, the details of the metabolic pathways for the degradation of the pesticides was not given in the study [28, 46]. In a similar study, Matsumoto et al. utilized the aerobic bacteria *Cupriavidus sp.* and *Burkholderia sp.* to degrade dieldrin and endrin. The presence of 1, 2-epoxycyclohexane was found to enhance the efficiency of the degradation process [46, 47].

Incineration is another important strategy that has been utilized. This method utilizes a very high temperature, usually above 500 °C, and oxygen to completely degrade organochlorine pesticides to ashes. The high temperature is desirable because it leads to zero smoke generation. In addition, it prevents the production of noxious intermediate products [3]. For high organochlorine degradation efficiency, incinerators are being equipped with electrostatic filters, scrubbers, after burner and chamber as shown in Figure 3. This improves the process compared to the combustion of the pesticides in an open space, which releases enormous volume of substances such as smoke and toxic gases into the atmosphere [3, 48]. Fergusson et al. [29] reviewed the elimination of several pesticide wastes from the environment using incineration method. Low temperature thermal desorption method is similar to incineration since they both require heat. However, low temperature thermal desorption method requires less heat energy compared to what is needed for incineration method. This method has been utilized by Cong et al. [30] to remove pesticides from the clay of a manufacturing plant that was abandoned. Zhao et al. [31] used this method to degrade dichlorodiphenyltrichloroethane (DDT) from contaminated soil, while simultaneously monitoring polychlorinated dibenzodioxins (PCDD) formation.

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**Figure 3.** Incinerator designed for degrading municipal solid wastes (MSW) containing pesticides. Reproduced from [49]. (creative commons).
Adsorption process has been used to remove pesticides from water and the environment. One of the popular adsorbents that has been used is activated carbon. This adsorbent has been used for pesticides clean up and in the environment of pesticide-producing factories. Shankar et al. [34] removed pentachlorophenol pesticides from water by using chitosan as adsorbent. The removal of several pesticides from drinking water sources using activated carbon as adsorbent has also been reported by Biela et al. Different organochlorine pesticides have been removed from waste water using zeolite adsorbent [50] and the use of graphene oxide to adsorb pesticides from environmental samples have been reported [51].

An interesting technique is the use of supercritical oxidation. This involves the use of the solubility property of supercritical water. Supercritical water is prepared at high pressure and temperature. This approach also requires the introduction of an appropriate oxidizing agent such as nitrate, H$_2$O$_2$, O$_2$ or their combination. In this process, phosphate, sulfates, nitrates, chlorides, water, carbon dioxide are derived, respectively from oxidation of phosphorus, sulfur, nitro-compound, chlorinated compounds, hydrogen and carbon. Interestingly, organic substances and gases including oxygen dissolve totally in supercritical water. Another important thing about this method is that NO$_x$ ($x = 1$ or $2$), HCl and SO$_2$ are not part of the effluents. In fact, lower amount of CO is discharged without particulates being generated [25]. This strategy has been devised to degrade pesticides from wastewater at varying reaction conditions [33]. Reaction variables such as residence time, oxidant coefficient and reaction temperature affect the efficiency of waste water remediation. Another method that rely on oxidation process is ozonation. This involves the use of ozone, and it is usually combined with UV (ultraviolet) radiation, leading to the generation of hydrogen radicals capable of degrading the pesticides by oxidation [52]. Ozonation has been used to successfully degrade many pesticides present in the seed loading and wastewater [34]. The rate of the degradation process was observed to increase with increase in the ozone concentration. In addition, high ozonation time and the humidification of seed prior to ozonation positively increase the reaction kinetics.

Chemical dechlorination method involves the removal of chlorine from organochlorine pesticides by using reductant radical which have hydrogen that could be donated or the possible use of hydrogen for the dechlorination process. With variation in the reducing agent used, direct dechlorination may occur by using base catalyzed decomposition. Similar process involving the use of alkaline polyethylene glycolate or reduction in the gas phase has also been reported [25]. Recently, the use of ammonia with metals were considered for the dechlorination of pesticides through solvated electron technology. A base metal, such as Na, Ca and Li was dissolved in ammonia that was free of water. This leads to the unbounding of electrons which were consumed by organochlorine compounds to release chloride due to their high affinity for electrons. The chloride in the solution then reacted with sodium ion to form NaCl without leaving noxious agents [53]. For instance, Pittman et al. [35] remediated a soil from polychlorobiphenyls contamination using sodium and ammonia mixture. The volume of water in the soil and the concentration of the substrate were found to influence the rate of chlorine removal and amount of sodium consumed. This was also repeated in a different study using a mixture of calcium and ammonia. The efficiency with the use of calcium was observed to be greatly lower than when sodium was used. In both studies, chlorine was removed from organochlorine compounds which rendered the compound less toxic.

A method, known as electrochemical oxidation, involves the utilization of electron and current movement to remove pesticides from the environment. This method has been reported as one of the efficient methods for the degradation of organochlorine pesticides. An acid solution (usually HNO$_3$) is introduced to the anode of an electrochemical cell that liberates oxidizing species. The acid and this oxidizing agent, then degrade organochlorine pesticides to inorganic ions, CO$_2$ and H$_2$O under room pressure and temperature that is lower than 80 °C [25]. Samet et al. [36] removed pesticides by using this method, and the removal rate was found to increase with increase in the initial concentration of the pesticide and temperature of the system. Electrochemical oxidation was used to degrade 2,6-dichlorobenzamide pesticides using platinum as anode [54]. The intermediate products formed
during the degradation process were thoroughly investigated. A related technique that also utilizes current is the plasma arc technique, which involves the generation of thermal plasma field by passing electric current through a gas stream under low pressure. This leads to the generation of plasma heat that is above 5000 °C. This very hot plasma heat could be used to dissociate organochlorine pesticides to their atomic elements via pyrolysis. The three common plasma systems are plasma arc centrifugal treatment, plasma-electric waste converter and in-flight plasma arc system [25,53]. Misra et al. [39] were the first group to use plasma technology to degrade residues of pesticides from fresh agricultural produce. Mixtures of pesticides including pyriproxyfen, fludioxonil, cyprodinil and azoxystrobin were degraded from strawberries. In a similar study, Phan et al. degraded pesticide residue from mango by using plasma technology [55].

Reduction processes is another technique that has been reported for the removal of organochlorine from the environment. One of them, which is carried out in the gaseous state and is known as gas-phase chemical reduction reaction. This process involves the use of hydrogen at a temperature of about 1000 °C or more to degrade organochlorine pesticides to lower molecular weight hydrocarbon such as methane and HCl. Sodium hydroxide would then be used to neutralize the acid formed after cooling the gas. For efficient heat transfer, steam is used. Therefore, it is important to remove water from the input waste [56]. This method was implemented and patented by Eco Logic of Rockwood, Ontario. It is now internationally tested, accepted and in wide use. This method has been adopted for the degradation of hexachlorobenzene and other organochlorine compounds [37]. Approximately 100% degradation of these compounds were reported. Apart from light energy that has been investigated for pesticides degradation, sound energy via ultrasonic technology is now being explored.

Ultrasonic technology [57] is the use of acoustic wave with frequency beyond the hearing limit of humans (i.e., 20 KHz). When this sound wave passes through solution containing organochlorine pesticides, acoustic cavitation phenomenon is developed. This undergoes a series of processes that will eventually lead to the release of radicals capable of degrading the pesticides [4]. One interesting feature of this technique is that it could be combined with other techniques and their synergy would produce enhanced degradation of pesticide. In this light, ozonation and ultrasonic technology were combined by Wang et al. [38] for the degradation of pesticide. The acoustic frequency used for the degradation was 160 kHz. The degradation efficiency of the combined system was found to be better than when each of the methods were used for separate degradation of similar pesticide. In a similar fashion, Chitra et al. [58] used ultrasonic techniques to treat liquid waste containing ethylenediaminetetraacetic acid (EDTA). This reaction followed first-order kinetics and the rate of reaction increased at higher frequency. Hydroxyl radical was reported to be the most potent oxidizing radical among the radicals involved in the process. Interestingly, this group [58] proposed a probable mechanism that is involved in ultrasonic degradation of pollutants as shown in Equations (1)–(5):

\[
\text{Ultrasound} + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+
\]

\[
\text{Ultrasound} + \text{O}_2 \rightarrow 2\text{O}^-
\]

\[
\text{H}_2\text{O} + \text{O}^- \rightarrow 2\text{HO}^-
\]

\[
\text{O}_2 + \text{H}^+ \rightarrow \text{HO}^+ + \text{O}
\]

\[
\text{O}_2 + \text{H}^+ \rightarrow \text{HO}_2^-
\]

Catalytic hydrogenation has also been adopted for removing organochlorine pesticides from waste water. This involves the use of hydrogen over noble metal catalyst. The byproduct of the reaction are hydrogen chloride and low molecular weight hydrocarbon [53]. Endrin and some other organochlorine pesticides have been successfully degraded by hydrogenation, followed by deodorization [40]. Furthermore, the research conducted by Addisson and Ackman [7] removed polychlorinated biphenyl, DDT and dieldrin from margarine by dehydrogenation followed by deodorization.
Molten salt oxidation is also reported for the remediation of the environment from organochlorine pesticides. It involves the use of a bed of molten salt in alkaline medium (Na$_2$CO$_3$ in most cases) at a temperature of approximately 1000 °C. Any ash products, phosphorus, sulfur or chlorine in the pesticides are retained as inorganic salt in the bed [59]. Ernesto reported the use of this technique for the successful degradation of hexachlorocyclohexane [24]. The study showed that this technique was particularly useful for the removal of chlorine-containing compounds. Similarly, molten metal pyrolysis uses molten metal as both catalyst and solvent for the conversion of toxic organochlorine compounds into more useful substances. This technology was patented by Massachusetts Materials Technologies (MMT) in Walham. The metal that is commonly used is iron heated to a very high temperature. The high temperature breaks down the pesticides into their elements which may now be removed with the assistance of some selected materials and chemicals such as alumina and oxygen [25]. Patel et al. [60] reported molten metal pyrolysis as one of the methods that is effective for removing and degrading polychlorodibenzo-furan and polychlordibenzo-p-dioxin.

Fenton oxidation technique involves the degradation of organic pollutants, including organochlorine pesticides to different compounds. This is achieved through oxidation by hydroxyl radicals derived from the reaction between iron (II) and hydrogen peroxide [61,62] as presented in Equations (6) and (7) and shown in Figure 4.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \quad (6)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \quad (7)
\]

**Figure 4.** Photo–Fenton degradation of organochlorine pesticides. Adapted with permission from [63]. Copyright (2012) American Chemical Society.

The efficiency of Fenton oxidation largely depend on the pH, concentration of both iron(II) and the hydrogen peroxide [61,62]. The favorable pH for Fenton oxidation ranges from 3–5. One of the studies that investigated the degradation of pesticides by Fenton oxidation was carried out by Barbusinsky et al. [62]. The study reported more than 90% removal efficiency of organochlorine compounds. Four different pesticides, 4-chlorophenoxyacetic acid, 4-chloro-2-methylphenoxycetic acid, fenitrothion and atrazine have been successfully degraded using this Fenton oxidation technique by Kassino et al. [41]. Similarly, iron in the oxidation state of zero has been used for organochlorine remediation. The use of iron for the removal of contaminants is based on its cost-effectiveness, nontoxicity, abundance and ease of its preparation. Different mechanisms have been proposed for this reaction, such as zero-valence iron mechanism, which involves the transfer of electrons from zero-valence iron to the organochlorine pesticide. This leads to the mineralization of the pesticides to less-toxic or nontoxic species [64]. Different mechanism occurs in the presence of oxygen. One zero-valence iron transfers two electrons to oxygen, which then reduces the oxygen to hydrogen peroxide, while the zero-valence iron is oxidized to iron(II). Another zero-valence iron donates two electrons to the hydrogen peroxide generated from the first reaction to form water. The last step involves the reaction between iron (II) and hydrogen peroxide to generate the hydroxyl radicals.
The generated highly oxidizing hydroxyl radical degrades the pesticides to nontoxic or less-toxic substances [64]. Equations (8)–(10) present the reactions that occur in the process:

\[
\begin{align*}
H^+ + O_2 + Fe^0 & \rightarrow H_2O_2 + Fe^{2+} \quad (8) \\
2H^+ + H_2O_2 + Fe^0 & \rightarrow 2H_2O + Fe^{2+} \quad (9) \\
H_2O_2 + Fe^{2+} & \rightarrow OH^- + OH^- + Fe^{3+} \quad (10)
\end{align*}
\]

Shoifu et al. [42] used zero-valence iron and iron oxide to destroy organochlorine pesticides (aldrin, lindane and DDT) from water. The products obtained were investigated and the degradation pathway for p,p-DDT was proposed (Figure 5). However, the intermediate products of lindane and aldrin were not identified. It was noted that within 12 h, about 79.81% and 100% of aldrin, HCH and DDT were successfully degraded, respectively. Cong et al. [43] also dechlorinated soils that has been contaminated with organochlorine pesticides. This was carried out by using iron at oxidation state of zero at an abandoned production site.

![Figure 5. Degradation pathway of p,p-dichlorodiphenyltrichloroethane (DDT) using zero-valence iron. Reprinted from [42]. Copyright (2016), with permission from Elsevier.](image)

Other reported methods that have been used for the treatment of organochlorine compounds include thermal desorption, air stripping, settling, membrane filtration, hydrolysis, vitrification, solar destruction, reverse osmosis and solvent extraction [25]. Each of these methods have their advantages and shortcomings. For example, solvent extraction cannot destroy the organochlorine pesticides, but transfers it from one medium to another, which requires another complementary remediation method with solvent extraction. Sometimes, more than one method may be combined to get a better removal
efficiency of organochlorine pesticides. Example was the degradation of DDT using both plasma and thermal desorption strategies, reported by Ma et al. [65].

The continuous search for new strategies for the remediation of the environment from organochlorine pesticides led to the emergence of heterogeneous catalysis as one of the preferred environmental remediation techniques. It is preferred to other methods that had been discussed because it utilizes solar light which is abundantly available. In addition, it can degrade pesticides at ambient pressure and temperature instead of transferring them from one medium to another which could lead to secondary pollution problem. It is one of the advanced oxidation processes which requires the use of suitable photocatalyst. As shown in Figure 6, an ideal photocatalyst should be chemically and biologically inert, stable to photo corrosion, utilizable in the visible or near UV light region, cheap, nontoxic and photoactive [66]. Example of semiconductors that have been utilized as photocatalysts are metal oxides, metal sulfides, noble metals, graphene oxide, graphitic carbon nitride or their composites.

Figure 6. Properties of ideal photocatalysts.

4. Mechanism of Heterogeneous Photocatalysis

The mechanisms of heterogeneous photocatalysis has been reported in several studies [63,67–71]; only a summary of these mechanism will be highlighted in this review. All semiconductors (SC) have energy band with low empty conduction band (CB) and high occupied valence band (VB) in their electronic band structure. The separation between the CB and VB is called band gap energy. Upon the irradiation of a semiconductor photocatalyst with light energy which is equal to or more than its band gap energy ($E_g$), a pair of valence band hole ($h^+$) and conduction band electron ($e^-$) is formed as the electron is excited from VB to CB. The pair may either recombine or move to the surface of the semiconductor photocatalyst and react with acceptor or donor species. It should be noted that the prevention of the charge carrier recombination is important for photocatalyzed reaction to proceed favorably. The reason being that fast recombination of the charge carriers will merely dissipate heat.
Holes of the valence band are strong oxidizing agent, which can oxidize the pesticides or attack the donor species. These attacked donor species can be readily oxidized to generate hydroxyl radicals from hydroxide ion at the surface or from water. On the contrary, electrons of the conduction band are reducing agent. They can react with dissolved oxygen to form superoxide anion radical $\text{O}_2^\cdot-$. This may also lead to the formation of hydroxyl radicals. These radicals can oxidize pesticides on the surface of the SC, which eventually brings about the mineralization of the pesticides. The entire mechanism is presented in Figure 7 and summarized Equations (8)–(16).

$$SC + \text{photon} \rightarrow SC(e^-_{CB}) + SC(h^+_{VB})$$  
(11)

$$H_2O + SC(h^+_{VB}) \rightarrow H^+ + OH^\cdot + SC$$  
(12)

$$OH^- + SC(h^+_{VB}) \rightarrow SC + OH^\cdot$$  
(13)

$$SC(e^-_{CB}) + O_2 \rightarrow SC + O_2^\cdot$$  
(14)

$$O_2^\cdot- + H^+ \rightarrow HO_2^\cdot$$  
(15)

$$HO_2^\cdot + H^+ + SC(e^-_{CB}) \rightarrow H_2O_2 + SC$$  
(16)

$h^+_{VB}$ + Pesticide $\rightarrow$ products of oxidation  
(17)

$e^-_{CB}$ + Pesticide $\rightarrow$ products of reduction  
(18)

$OH^\cdot$ + Pesticide $\rightarrow$ products of degradation  
(19)

**Figure 7.** Mechanism of decomposition of pesticide involving heterogeneous photocatalysis.

5. **Photocatalysts for Pesticides Degradation**

The photocatalysts that will be the focus of this review include titanium oxide, ZnS, graphitic carbon nitride and graphene oxide-based photocatalysts. These are representative of semiconductor metal oxides, metal sulfides, metal free semiconductor and materials that serve as substrate in the use of composite materials as photocatalyst, respectively. They all meet the requirements stated in Figure 5.

5.1. **Titanium Oxide-Based Photocatalyst for Pesticide Degradation**

The most widely used heterogeneous photocatalyst is titanium oxide. This is because its holes are selective to oxidation and reduction reaction. In addition, it is highly oxidizing, non-toxic, stable under light and it is not expensive [72,73]. The major challenge with its usage is that due to its wide band gap energy, it cannot absorb visible light which makes up almost 40% of the solar spectrum. To surmount this challenge, capping, coupling, doping and dye sensitization approaches have been
intensely studied [72]. Linlong et al. [74] used light emitting diodes (LEDs) as light source to irradiate titanium oxide photocatalyst, which was used to destroy four different organochlorine pesticides [2,4-dichlorophenol, 4-chlorophenol, 2-methyl-4-chlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid] in water. Further evaluation was done on 2,4-dichlorophenoxyacetic acid in order to determine the effect of light intensity and photocatalyst loading on the rate of degradation. Furthermore, the use of LED irradiation was compared with irradiation from mercury discharge lamp and complete pesticides mineralization was observed with the LED. A reduction in the rate of degradation was observed when mixture of pesticides was degraded. In a related study, Fiorenza et al. [75] selectively degraded the insecticide imidacloprid and the herbicide 2,4-D. The photocatalyst used for the degradation was molecularly imprinted titanium oxide made via sol–gel method with the pesticide molecule as template. The uniqueness of their approach was achieving the selective trapping of the pesticides by molecular imprinting process, while pesticide degradation was simultaneously achieved through heterogeneous photocatalysis. Other works that utilized titanium oxide-containing nanocomposite as heterogeneous photocatalyst for degrading pesticides and other pollutants with more than 50% removal efficiencies are summarized in Table 2. Particularly, up to 85% mineralization efficiency was reported for neat titanium oxide photocatalyst [76].

Table 2. TiO$_2$-based photocatalysts and the pesticides removed.

| Photocatalysts | Organochlorine and Other Pollutants Destroyed | Solar rad. Used | Ref. |
|---------------|---------------------------------------------|----------------|-----|
| F and N co-doped TiO$_2$ | Representative pesticide | UV [77] | |
| Nanocrystalline $\gamma$-Fe$_2$O$_3$/TiO$_2$ nanoparticles | Propachlor | UV [78] | |
| GO-TiO$_2$ | Atrazine, isoproturon, alachlor and diuron | UV [79] | |
| Titanium oxide and lanthanum oxide composite | Parachlorophenoxyacetic acid | UV [80] | |
| Carbon-doped TiO$_2$ on zeolite | Atrazine and others (and 18 drugs) | UV [81] | |
| TiO$_2$ + HZSM-5 zeolite combine | Parachlorophenol | UV [82] | |
| TiO$_2$ on zeolite support | 2,4-dichlorophenoxyacetic acid | UV [83] | |
| TiO$_2$ on different support (activated carbon, silica and zeolite) | 3,5-dichloro-N-(3-methyl-1-butyn-3-yl) benzamide(propyzamide) | UV [84] | |
| Silver-doped TiO$_2$ | Acetamiprid | Visible [85] | |
| nano-TiO$_2$ coated film | Cypermethrin, dicofol and $\alpha$-, $\beta$-, $\gamma$-, $\delta$-hexachlorobenzene (BHC) | UV [86] | |
| GO/TiO$_2$/Ag nanotube | 2-chlorophenol and (dyes) | UV [87] | |
| mesoporous GO-Fe$_3$O$_4$/TiO$_2$ | Fenitrothion | Visible [88] | |
| TiO$_2$/ZnO | Trichloroethanoic acid | UV [89] | |
| Aqueous TiO$_2$ suspension | Irgarol, prometryn, cyanazine, propazine, atrazine and other pesticides | UV [90] | |
| TiO$_2$ | Dichlorvos in gas phase | UV [76] | |
| Nitrogen-doped anatase TiO$_2$ | Endosulfan from soil | UV [91] | |
| TiO$_2$ and oxygen system | Lindane and DDT | UV [92] | |

UV: ultraviolet; HZSM-5: Heterogeneous Zeolite Socony Mobil-5; DDT: dichlorodiphenyltrichloroethane.
5.2. Zinc Sulfide-Based Photocatalyst for Pesticides Degradation

The utilization of ZnS as photocatalyst has been applauded as a result of its outstanding structure. It is a polymorphous material that exists in two crystalline forms, wurtzite and zinc blende. While the wurtzite has band gap energy of 3.91 eV, zinc blende has a band gap energy of 3.54 eV. Interestingly, ZnS is not only stable to oxidation and hydrolysis, but it is also not toxic and it has high natural abundance [93]. Due to its high band gap energy, it absorbs in the UV region, but could be made to absorb in the visible light region by doping with transition elements. These properties make its maximum use as a photocatalyst in the degradation of organochlorine pesticides to be highly feasible [94]. In the studies conducted by Fenoll et al. [95], eight miscellaneous pesticides including tolclofos-methyl, propanil, pendimethalin, pencycuron, metribuzin, metalaxyl, isoxaben and ethoprophos were destroyed by zinc oxide and zinc sulfide photocatalysts. The concentration of all the pesticides remaining was lower than 0.8 \( \mu g \ L^{-1} \) at the end of the investigation. Tran et al. [96] used ZnS-containing nanotube array, which was sensitized by titanium oxide, to destroy anthracene-9-carboxylic acid and 2,4-dichlorophenoxyacetic acid. This laboratory-scale investigation showed that all the contaminants were completely removed from water after 150 min of visible light irradiation. Toxic organic pollutants have also been degraded by using nanoparticles made from zinc sulfide and chitosan as the photocatalyst [97]. Zinc sulfide-cellulose nanocomposite have been used to degrade pollutants with high degradation efficiency [98]. Thin film of zinc sulfide was also reported to degrade organic contaminants by Pedanekar et al. [99]. By using a nanocomposite composed of zinc sulfide and molybdenum sulfide as photocatalyst, under visible light irradiation, Ahamad et al. degraded the pesticide dicofol [100]. Their result showed maximum removal efficiency. In addition, the reusability efficiency of the photocatalyst was very good. Chlorpyrifos pesticides was recently degraded along with other organic pollutant by using photocatalyst made of zinc sulfide, iron oxide and cadmium oxide [101]. Further studies on the effect of various parameters on the degradation efficiency were also carried out.

5.3. g-C₃N₄-Based Photocatalysts for Pesticide Degradation

Since most existing semiconductors used in heterogeneous photocatalysis only absorb in the UV region. The search for a good semiconductor photocatalysts that will utilize visible light, which is approximately forty percent of the solar spectrum, led to the emergence of graphitic carbon nitride (g-C₃N₄) [102]. It is a polymeric materials and with a band gap energy of approximately 2.7 eV [103]. As a result of high condensation grade and its structure, it exhibits photochemical, chemical and thermal stability [104]. In addition, its synthesis is simple since it can be prepared from nitrogen-rich precursors such as melamine, thiourea and urea. Interestingly, chemical doping can be used to modify its band structure [102,104]. This important photocatalyst (g-C₃N₄) has been utilized to destroy an emerging organochlorine pesticide (imidacloprid). The urea derived graphitic carbon nitride was able to degrade almost 90% of the pesticide within 5 h, in the presence of visible light. Further studies revealed that change in precursor type affects the photocatalytic efficiency of graphitic carbon nitride. The degradation route for imidacloprid degradation using graphitic carbon nitride was proposed (Figure 8) [71].

Another interesting study was carried out by Raisada [9], where Z-scheme silver-doped g-C₃N₄/Bi₂O₃ nanocomposite was prepared through a hydrothermal process for degrading imidacloprid. The nanocomposite was used to completely mineralize the organochlorine pesticides within 10 h under visible light irradiation. This degradation followed pseudo-first order kinetics and the photocatalyst was stable even after 10 recycle times. A nanocomposite of bismuth oxide and graphitic carbon nitride was synthesized, but without doping by Yeping et al. [105]. The nanocomposite was successfully used to degrade 4-chlorophenol under the visible light irradiation. This organochlorine compounds has also been degraded by mesoporous graphitic carbon nitride in a study by Cui et al. [106]. Vigneshwaran et al. [107,108] degraded pesticides by using graphitic carbon nitride and also by using its nanocomposite with chitosan. This photocatalyst was able to degrade 85% of the toxic pesticide. Four different graphitic carbon nitride-based nanocomposites have been fabricated [109]. The nanocomposites were phosphorus-doped
graphitic carbon nitride with graphene oxide, phosphorus-doped graphitic carbon nitride with fullerene, phosphorus-doped graphitic carbon nitride with carbon nanotube and phosphorus-doped graphitic carbon nitride with graphene. Each of these was used to degrade four different pesticides including organochlorine pesticides. They were all found to be good photocatalysts for removing pesticides. These nanocomposites were also used for inactivating Pseudomonas aureus, Staphylococcus aureus, Pseudomonas fluorescens, Bacillus subtilis and Escherichia coli bacteria. Guan et al. [110] used graphitic carbon nitride nanovessel to remove pesticides from juice. More than 80% of the pesticides were removed from soil and food samples by using graphitic carbon nitride nanosheet [111]. Graphitic carbon nitride that was doped with carbon was fabricated by Zheng et al. [112] This photocatalyst was found to be very potent in degrading persistence organic pollutant from both wastewater and natural water better than when pure graphitic carbon nitride was used for the same purpose. Fluazaindolizine was degraded in aqueous solution with the use of nanosheet of graphitic carbon nitride under visible light irradiation [113]. An improvement in the half-life to 2.7 h was recorded when 5 mg of the catalyst was used.

![Figure 8. Imidacloprid degradation route with graphitic carbon nitride as the photocatalyst. Reproduced with permission from [71]. Copyright (2015) American Chemical Society.](image)

A nanocomposite composed of peroxymonosulfate, graphitic carbon nitride and activated carbon was prepared and used to degrade pesticide (atrazine). A higher efficiency was obtained compared to when the nanocomposite without peroxymonosulfate was used as photocatalyst [114]. Tang et al. [115] fabricated AgI/g-C3N4/Ag3PO4 which was a z-sceme, and the catalyst achieved a better pesticides degradation than when only ordinary graphitic carbon nitride, silver iodide or silver phosphate was used as the catalyst. Recalcitrant polychlorinated biphenyl (PCB) was removed from water sample by using velvet-like nanocomposite of graphitic carbon nitride [116]. The nanocomposite showed good reusability potential, which made it even more interesting. Seven different insecticides have been degraded by nanocomposites prepared by co-doping of oxygen and sulfur with graphitic carbon nitride [117]. Over 90% degradation rate of some of these insecticides were achieved under 30 min. Zou et al. [118] degraded ortho-dichlorobenzene by using photocatalyst composed of vanadium pentoxide and graphitic carbon nitride. About 62.4% of the organochlorine was degraded within 8 h when just 2% of the nanocomposite was used. In addition, the removal efficiency was found to be 2.18- and 2.77-fold better than when pure vanadium pentoxide and pure graphitic carbon nitride were used for the degradation. Jo et al. [73] also prepared TiO2/g-C3N4 nanotubes and nanopores which were used to separately degrade pesticides. The nanotube-containing nanocomposite was reported to successfully degrade 90.8% of the pesticide under 4 h reaction time.

Other reported studies involved the use of activated carbon supported graphitic carbon nitride to activate peroxymonosulfate, which was used for pollutant degradation [119]. Trihalomethane and haloacetonitrile have been degraded under visible light by using g-C3N4 as photocatalyst [120]. g-C3N4
modified with β-cyclodextrin has recently been used for pollutants degradation [121]. Zheng et al. [112] degraded persistence organic pollutants under visible light irradiation by using graphitic carbon nitride. Graphitic carbon nitride was also used to degrade fluazaindolizine under simulated irradiation. The pathway for fluazaindolizine was comprehensively discussed [113]. Bi_2WO_6 and g-C_3N_4 nanocomposite has been used to photocatalytically degrade 2,4-dichlorophenol pesticide under visible light irradiation [122]. Nanohybrid of NiO/WO_3 decorated on graphitic carbon nitride has been reported for the degradation of some organic pollutants [123]. Platinum nanoparticles deposited on carbon nanotube of g-C_3N_4 were used for destroying p-chlorophenol under visible light irradiation [124]. Both Z-scheme nanotube and nanoparticles of g-C_3N_4/TiO_2 have been used to decompose isoniazid by Jo et al. [73]. The degradation pathway for isoniazid degradation was also proposed.

5.4. Graphene Oxide-Based Photocatalyst for Pesticide Degradation

The use of graphene oxide in heterogeneous photocatalysis for degrading organochlorine pesticide was favored due to its large surface area. It is metal free, since it contains only carbon, hydrogen and oxygen and can disperse easily in water [125]. Delocalization of conjugated π (pie) electrons throughout its layers have positive impact on charge transport. In addition, the presence of functional group such as OH and COOH, hydrophilicity, low conductivity and chemical stability are desirable properties of graphene oxide. In actual fact, graphene oxide is mostly used as co-catalyst because limited information is available about its ability to be activated by light [126]. However, it has been reported that their presence significantly improved the photocatalytic removal efficiency. This can be attributed to the role played in adsorbing the pollutant, acting as an electron acceptor, surfactant and support for the semiconductor [127–129]. Graphene oxide can be reduced to form reduced graphene oxide [130,131]. Both graphene oxide and reduced graphene oxide have similar properties; however, reduced graphene oxide have high defects and low oxygen-to-carbon ratio unlike graphene oxide that has high oxygen-to-carbon ratio. Apart from this, graphene oxide has the appearance of brown powder, whereas reduced graphene oxide is a black powder. Either of the two could be combined with other semiconductors to degrade organochlorine pesticides with improved degradation efficiency [130,132]. The improved efficiency could be attributed to better light absorption, narrowed band gap, limited recombination of charge carrier and improved separation of charge carrier [133]. Graphitic oxide and graphene oxide have been used to degrade 4-chlorophenol in water. About 92 and 97% were successfully degraded at optimum conditions, respectively [125]. El-Shafai et al. [134], prepared nanocomposite from both titanium oxide and graphene oxide which was used to degrade two poisonous insecticides (imidacloprid and carbaryl). The prepared nanocomposites possessed smaller band gap and superior photodegradation of the insecticides than ordinary graphene oxide or pure titanium oxide. In a similar study, Sharma et al. [107] prepared nanocomposite of Ni, Co and La supported on graphene oxide through microwave method. This catalyst was utilized to degrade 2-chlorophenol under sunlight irradiation. Within 300 min, 71% of the organochlorine was destroyed. However, when the experiment was carried out without graphene oxide, about 57% degradation was obtained within the same time. The presence of graphene oxide in the nanocomposite resulted in the lowering of the ability of holes and electrons to recombine and charge transfer efficiency was tremendously enhanced. Cruz et al. [79] also degraded four different pesticides (atrazine, isoproturon, alachlor and diuron) from water, by using a nanocatalyst made from the combination of titanium oxide and graphene oxide. It was observed from their investigations that the photocatalytic efficiency of this nanocomposite was not affected by water matrix variation. There was an enhanced degradation when ultra-pure water and natural water were separately used. Conversely, the photocatalytic efficiency of pure titanium oxide catalyst was altered with change in water matrix. Visible light irradiation was used throughout the experiment. Similarly, Mostafa et al. [88] destroyed fenitrothion, which is an organochlorine pesticide, by using mesoporous GO-Fe_3O_4/TiO_2 as a visible light active photocatalyst.
6. Conclusions and Recommendations

Increasing efforts have been directed towards improving the methods of removal and destruction of the organochlorine pesticides. This has resulted into the emergence of facile strategies for remediating the environment from the toxic effect of these organochlorine pesticides. Different techniques have been developed, and their advantages and drawbacks have been highlighted. One of the promising methods that is currently used is heterogeneous photocatalysis. There are numerous reports on the removal of pollutants using heterogeneous photocatalysts. However, a lot still remains to be achieved in order to develop photocatalysts that are capable of utilizing visible light of the solar system. In addition, photocatalysts that can degrade organochlorine pesticides in a mixture of pollutants needs to be explored. This is because these pollutants sometimes exist together as mixtures, especially in wastewater. The development of other eco-friendly strategies is needed in order to remove the pollutants in environmentally sustainable ways. Furthermore, many studies on the different intermediate products of the degradation process of most organochlorine pesticides is necessary. There are limited reports on the degradation pathways of the organochlorine pesticides. Studies on the molecularly imprinted titanium oxide, graphene oxide and graphitic carbon nitride needs to be carried out and their use as photocatalyst for destroying pollutants thoroughly explored. In addition, the design used for the reactors of some of the removal methods need to be improved upon. For example, the use of more than one transducer may be considered for sonochemical reactor because this will lead to improved activity of cavitation. Control system and the radiating surface area could also be improved \[58\]. The improvement on the methods described in this review is needed in order to overcome the various disadvantages that have been highlighted. A synergy between two or more methods for efficient removal of organochlorine pesticides should be further researched. Additionally, the nanocomposite between graphitic carbon nitride and ternary metal chalcogenides for organochlorine pesticide degradation has received minimal attention. It is very important that concerned audience (especially farmers) be enlightened on the dangers of organochlorine pesticides to minimize its discharge into the environment. Government should further promulgate laws controlling the use of organochlorine pesticides and it should be backed-up with serious enforcement in efforts towards minimizing the harmful effects of organochlorine pesticides.

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