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Application of Nanotechnology in Pesticides Removal from Aqueous Solutions - A review

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Abstract

In recent years, water pollution and pesticide residues in the food chain have become a serious environmental and health hazard problem. Therefore, an efficient technology is essential for complete mineralization of pesticides to non-toxic forms. Nanotechnology offers many potential benefits to improve existing environmental technologies using new materials with effective performance, resulting in less consumption of energy and materials. The aim of this review is to compile and study current publications regarding pesticides removal by nanotechnology. This study discusses the applications, advantages and limitations various nanotechnology processes for removal of pesticides.

Keywords: *Pesticide, Removal, Nanotechnology, Environment, Water.*

1. INTRODUCTION

Pesticides are widely used in agricultural production throughout the world to protect plants against pests, fungi, and weeds. Therefore, residues of pesticides are extensively dispersed in drinking waters, groundwaters, and soils [1, 2]. There are various routes for pesticides contamination in the environment, including runoff from agricultural land, direct entry from the spray, industrial effluents, and dust. Residues of pesticides have significant environmental impacts on aquatic ecosystems and mammals [3, 4]. With regards to the quality of water intended for human consumption, the Drinking Water Directive (98/83/EC) determines a limit of 0.1 μg/L for any single pesticide, and 0.5 μg/L for the sum of all pesticides detected and measured through monitoring, regardless of hazard or risk [5].

In parallel with appropriate regulatory controls, there is an urgent need for determination and removal of pesticides from potable water sources. Chemistry based on bulk materials has primarily utilized the properties of adsorption, photocatalysis, membrane separation, or biodegradation [6-12]. Innovative water treatment methods have been developed to create more efficient systems. Nanotechnology has attracted a lot of attention recently, particularly in the research and industrial communities. Nanotechnology is the development and utilization of structures and devices with a size range from 1 nm (molecular scale) to about 100 nm where new physical, chemical and biological properties occur as compared to their bulk counterparts, such as extremely small size, high surface area to volume ratio, surface modifiability and excellent magnetic properties [13].

There are a broad range of physicochemical properties that make nanomaterial specific candidate and reactive media for pesticides removal. Nanomaterials can also be functionalized with various chemical groups to increase their efficiency for removal of desired target compounds [14, 15]. Here, we provide an overview of recent advances in nanotechnologies for removal of pesticides in three main capabilities: adsorption, filtration and degradation.

2. CURRENT APPLICATIONS FOR PESTICIDES REMOVAL

2.1. Adsorption

Adsorption is a well-known equilibrium separation process and an effective method for water cleaning applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility, and simplicity of design, ease of operation, and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. This process is a surface phenomenon that depends on the number of sites available, porosity and specific surface area of the adsorbent as well as various types of interactions.

2.1.1. Carbon Based Nano-Adsorbents

2.1.1.1. Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) represent a new class of nanomaterials and are composed of graphitic carbons with one or several concentric tubules. CNTs, as both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), are unique macromolecules that have a one-dimensional structure, thermal stability and special chemical properties [16, 17]. These nanomaterials have been shown to have good potential to remove various types of pesticides. The adsorption capacity of pollutants by CNTs is mainly affected by the pore structure and the existence of a broad spectrum of surface functional groups that can be achieved by chemical or thermal modifications to improve the optimal performance for a particular purpose [18]. Overall, the adsorption of organic chemicals on CNTs may involve one or more mechanisms, such as hydrophobic effect, covalent bonding, π-π interactions, hydrogen bonding, and electrostatic interactions [19-21]. Some organic molecules with C=C bonds or benzene rings, such as polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds adsorb on CNT through π-π interaction [22, 23]. Adsorption may also take place through hydrogen bonding between functional groups such as -COOH, -OH, -NH_2 and organic molecules [24]. Electrostatic attraction is one of the adsorption mechanisms that causes the adsorption of some organic chemicals such as antibiotics and dyes at suitable pH on the functionalized- CNTs [25, 26]. Functional groups can alter the wettability of CNTs surfaces and make them more hydrophilic and suitable for sorption of relatively low molecular weight and polar compounds. [27].

The adsorption of diuron and dichlobenil on MWNTs was investigated [28]. The findings showed that the adsorption of diuron and dichlobenil increase with an increase in surface area and total pore volume of MWNTs. The presence of Pb^{2+} decreased the adsorption of diuron and dichlobenil. The values of adsorbed amount and surface coverage of diuron were larger than those of dichlobenil, while the surface area, molecular volume, and water solubility of dichlobenil are smaller. This may be due to larger van der Waals interaction of diuron than that of dichlobenil [29]. The adsorption of atrazine by surfactant-dispersed SWNTs and MWNTs demonstrated that surfactant treatment inhibited atrazine adsorption [30]. The hydrophilic fraction of the surfactant micelles faces in water cause the modified-CNTs to become more hydrophilic, which reduces the adsorption of atrazine significantly. The inhibitory effects of cationic (cetyltrimethylammonium bromide, CTAB) and anionic (sodium dodecylbenzene sulfonate, SDBS) surfactants on the adsorption of MWNTs were similar, although the inhibitory effect of SDBS on SWNTs was slightly greater than that of CTAB. For the SWNTs with lower purity and containing more oxygen content, the oxygen-containing functional groups may affect the affinity of cationic and anionic surfactants, and increase the difference in inhibition of atrazine adsorption. The high hydrophobicity of

MWNTs surfaces created an equal affinity for cationic or anionic surfactants, thus the inhibitory effects on atrazine adsorption were similar with both surfactants. Also, the surfactant treatment increased the diffusion of MWNTs, and consequently an increase in surface area would be expected [30]. The adsorption of diuron onto MWCNTs indicated that oxidation treatment of MWCNTs gave rise to a high surface area and pore volume and subsequently an increase in adsorption capacity. Also, the adsorption of diuron onto MWCNTs was spontaneous and exothermic [31]. SWCNTs have been demonstrated to have a higher adsorption capacity for 4-chloro-2-methylphenoxyacetic acid (MCPA), a phenoxy acid herbicide, than three kinds of MWCNTs with different average outer diameters and several nanoscale metal oxides (Al_2O_3, TiO_2, and ZnO); the adsorption kinetics usually followed pseudo-second-order kinetics, with the adsorption process being spontaneous and exothermic [32].

2.1.1.2. Graphene (G)

Graphene is a kind of carbon nanomaterial that has attracted tremendous attention in water purification and various fields due to its unique physical and chemical properties. Some literature shows the applications of graphene as an adsorbent for the removal of pesticides. Maliyekkal et al. studied the adsorption of pesticides by graphene [33]. They found that for effective interactions between graphene and a pesticide, water with its polar structure, plays an important role in mediating. Graphene has great adsorption capacities for pesticides (ranging from 600 to 2000 mg/g). Some researchers studied dehalogenation halogenation and removal of persistent halocarbon pesticides from water using graphene [34, 35]. Graphene and related carbon-based nanomaterials can adsorb contaminants with aromatic rings through π– π interactions [19, 22, 23, 36]. Graphene can combine with other materials to improve pesticide adsorption capacity [37-39]. Graphene-coated silica (GCS) as a highly efficient sorbent was used for removal of residual organophosphorus pesticides from water [37]. This study shows the mechanism of adsorption of OPPs on GCS is based on the electron-donating abilities of P, S, and N atoms and the strong π-bonding network of benzene rings.

2.1.2. Nanocrystalline Metal Oxides

Nanocrystalline metal oxides are highly effective adsorbents for a broad range of pesticides. Metal oxides such as ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides are effective and low cost adsorbents. Also, these materials were applied for a broad range of pesticides due to higher adsorption capacity, faster kinetics because of the higher specific surface area, shorter intraparticle diffusion distance and larger number of surface reaction sites as compared to their non-nano commercial counterparts [40-44]. Nanocrystalline metal oxides not only adsorb but also actually destroy many chemical hazards by converting them to much safer byproducts under a broad range of temperatures [45]. Their large surface areas and high activities are caused by the size quantization effect. The study on the effect of particle sizes on the adsorption and desorption of AS(III) and AS(VI) showed that as the particle size decreases from 300 to 12 nm, the adsorption capacity increases nearly 200 times [46]. However, as the size of metal oxides decreases from micrometer to nanometer levels, the increased surface energy inevitably leads to their poor stability [47]. Some researcher has studied the removal of organophosphorus pesticides by nano metal oxides. Although nano sized metal oxides are effective destructive absorbents for organophosphorus pesticides, production of high quality fine oxide powders is a relatively difficult task and can be costly [48, 49].

Some researchers studied the removal of pesticides by magnetic nanoparticles [43, 50-55]. Surface modified magnetic core–shell nanoparticles exhibit high adsorption efficiency and high rate of removal of contaminants [52]. C18 fabricated Fe_3O_4 core–shell nanoparticle is the most commonly used magnetic nanoparticle for removal of pesticides. They are suitable for extraction or cleanup of nonpolar and moderately polar pesticides due to their suitable separation ability, excellent stability, and convenient operation. Hao-Yu and partners used magnetics Fe_3O_4-C18 composite nanoparticle for removal of organophosphoerus pesticides [50]. After modifications of Fe_3O_4-C18 magnetic particles with C18-silane, the surface of the magnetite was covered with hydroxyl groups and C18 groups because of adsorption of both hydrophilic and hydrophobic compounds. OPs were captured by Fe_3O_4-C18 by a magnetic field. Also, alumina nanoparticle was applied for the removal of organophosphate pesticide [40, 56]. The results showed that nanocrystalline alumina can effectively adsorb organophosphate pesticides in a short period of time because of high surface area and the concentration of hydroxyl groups on the surface of nanocrystalline alumina. A list of nanocrystalline metal oxides with their adsorption parameters for pesticide removal is summarized in Table 1.

Table 1. *Nanocrystalline metal oxides for adsorption of pesticides.*

Nanocrystalline metal oxides	Modifier	Target pesticides	Adsorption amount	Ref.
Fe_3O_4	Polystyrene	Organochlorine Pesticides	The adsorption capacity of lindane, aldrin, dieldrin and endrin were calculated 10.2, 24.7, 21.3 and 33.5 mg/g, respectively.	[43]
Fe_3O_4	C18	Organophosphorous pesticides	The average recovery for organophosphorous pesticides were as high as 80%.	[50]
Fe_3O_4	Hexagonal Mesoporous silica (HMS)	DDT	The adsorption capacity of DDT was 2.77 µg/mg with the initial DDT concentration of 2.2 µg/ ml	[51]
Al_2O_3 and MgO	Activated carbon	Diazinon	The maximum initial adsorption rate of diazinon by ACNFs containing metal oxide was 19.36 µl/min.	[57]
Al_2O_3	Cerium Oxide	Dimethyl methylphosphonate (DMMP)	the adsorption amount of DMMP was only 775 µg/g at 25 °C,	[58]
Al_2O_3	—	Diazinon and Fenitrothion	The removal efficiency for diazinon and fenitrothion was 90% and 57% with initial concentration 0.32 mg/ml and 0.28 mg/ml within a period of 24 h,	[40]
LFCOs NPs	—	Vitavax	The calculated adsorption capacity of LFCO1 and LFCO2 NPs for the maximum investigated vitavax concentration (800mg/L) was 155 and 139 mg/g, respectively.	[42]
Zinc oxide	Chitosan	Permethrin	0.5 g of the bionanocomposite, at room temperature and pH 7, could remove 99% of the pesticide from permethrin solution (25 ml, 0.1 mg/l)	[41]

2.2. Filtration

Nanofiltration (NF) is the most recent technique of membrane filtration. The nanofiltration (NF) membrane is a type of pressure-driven membrane with properties between reverse osmosis (RO) and ultrafiltration (UF) membranes. It is a promising technology to remove hazardous organic micro-pollutants, such as pesticides, dyes, and many other synthesized products. Depending on the requirement, some manufacturers offer nanofiltration membranes to target different molecules based on their molecular weight. This provides consumers with many options for applications. The adsorption characteristics of organic matter on membrane surfaces are governed by a variety of factors including the physical and chemical properties of the membrane, pesticides properties, feed water composition and filtration system operating parameters.

2.2.1. Factors Affecting the Removal of Pesticides by NF Membranes

2.2.1.1. The Role of Membrane Characteristics

The physical and chemical properties of the membrane selected are an important factor for the removal of pesticide. When choosing a suitable membrane, the significant parameters to consider are the molecular weight cut-off (MWCO), desalting degree, porosity, and the membrane material. The molecular weight cut-off (MWCO), the molecular weight of a solute that corresponds to a retention of 90%, is commonly used by most membrane manufacturers as a measure of the retention properties of NF membranes [5, 59]. The rejection of uncharged pesticide molecules was positively correlated with membrane porosity parameters [60, 61]. This is also consistent with findings that the membrane pore size is a crucial parameter for pesticide removal by a specific membrane [62]. Some studies show the rejection of aromatic and non-phenyl pesticides was positively correlated with the desalination degree of commercial NF membranes; indeed, rejection was greatest in the case of the highest desalting membranes [63, 64]. The reported studies confirm that composite polyamide membranes exhibit far better rejection performance for several mixtures of micropollutants, including pesticides, compared to cellulose acetate, (CA) membranes [65-69]. This behavior has been attributed to the higher polarity of CA membranes which is responsible for the poor rejection of the highly polar pesticides [66].

Usually, the membrane surfaces are negatively charged, providing selective removal of charged contaminants [70]. Because many particles in water are also negatively charged, the negative surface charge enhances the removal of ionic compounds [71]. In general, the zeta potential of the membrane surface can change from a positive to a negative value as the solution pH increases. Subsequently, electrostatic interaction between ionic compounds and the membrane surface can also vary according to the solution pH. The electrostatic repulsion of negatively charged pesticides ($pH > pK_a$) at the membrane surface is expected to enhance the overall rejection performance [59, 72].

2.2.1.2. Effect of Pesticides Properties on Retention

The rejection of pesticides by NF membranes is affected by the molecular weight and size, polarity (dipole moment), acid dissociation constant (pK_a) and hydrophobicity/hydrophilicity. Molecular size is the main parameter that determines the retention of organic molecules with NF. Some studies showed that MW can be used for the rejection prediction of non-charged and non-polar compounds. A positive correlation exists between the rejections of eleven pesticides with their molecular weights [73, 74]. Some researchers confirmed that the size is not the single parameter influencing pesticide rejection: the shape of the molecule also influences the sorption properties of the membranes [64, 75]. Some interactions including hydrophobic and hydrogen bonding also influence pesticides retention on membranes. Hydrogen bonding and hydrophobic interactions can apparently act either independently or together. Kiso et al. examined and reported on the rejection properties of 11 kinds of aromatic pesticides by NF membranes [64]. They showed that strongly hydrophobic compounds, including aromatic pesticides, non-phenolic pesticides, and alkyl phthalates, were rejected at very high degrees even by the lowest desalting membrane. They also reported that while there was no significant correlation between retention of these pesticides and log K_{ow}, there is a good correlation between adsorption of these pesticides and log K_{ow} [64]. In some cases, adsorption may occur via hydrogen bonding between organic molecules and the hydrophilic groups of the membrane polymer [59].

The polarity effect of the pesticides is one of the most important parameters in predicting the retention of them on a membrane. Van der Bruggen et al. have successfully combined size exclusion and polarity effects to describe the retention of four pesticides [76]. The solute polarity effect is important for membranes with an average pore size larger than the size of compounds to be retained [60, 76, 77]. A greater dipole moment leads to a lower retention [62, 78]. Musbah et al. reported that the presence of more than one pesticide or metabolite (complex solutions) improves pesticide retention probably due to formation of macromolecular complexes [75].

2.2.1.3. Effect of the Feed Water Composition

The feed water quality including pH, ionic strength, and the presence of organic matter influences pesticide rejection. The pH value of the feed solution can also affect characteristics of the membrane especially charge of a membrane due to the dissociation of functional groups that can cause pore expansion or shrinkage of membrane pores [79-81]. In a study on removal of uncharged organic compounds (atrazine and terbuthylazine) at pH 3 and 7 the rejection was relatively constant. Also higher pH values caused a decrease in rejection rates in association with an increased in permeate flux. This behavior was a result of the pore expansion at higher pH values.

Some studies showed that the amount of adsorption increased with decreasing pH and increasing ionic strength [82, 83]. High ionic concentrations decrease the electrostatic forces inside the membrane and the actual size of the pores, leading to reduced membrane permeability; consequently, a better rejection could be observed due to reduced water flux [83]. Natural organic materials (NOMs) which are composed of a different group of compounds can affect the removal efficiency of pesticides depending on the type of NOM in the feed water. Some researchers have shown that the retention of pesticides in membrane-based systems tends to increase in the presence of NOM [84-87]. Boussahel et al. [88] indicated that the presence of a fraction of the high-molecular-weight organic matter such as humic acids in the feed water increases the elimination of the pesticides by NF. This result conforms with those of Plakas and Karabelas that indicated the combined nanofiltration of triazines (atrazine, prometryn) and naturally occurring humic substances facilitated the formation of complexes with triazines which in turn enhance their removal by nanofiltration [86].

2.2.1.4. Effect of Membrane Fouling

Membrane fouling is considered as a major obstacle to efficient membrane operation due to a declining permeate flux, increased operational cost, and shortened membrane life. During operation, components present in source water such as particles, colloids, salts, natural organic matter (NOM), and soluble microbial products derived from biological wastewater treatment can adsorb and accumulate onto membrane surfaces resulting in membrane fouling. The effect of fouling on organic micropollutant retention has been the subject of rather extensive research in the past decade [78, 89-91]. Fouling may alter membrane surface characteristics in terms of the contact angle, zeta potential, functionality and surface morphology, which potentially affect the transport of contaminants compared to non-fouled membranes. NF will also experience a higher concentration polarization when fouling occurs, mainly when applications involve the presence of low molecular weight humic acids and, moreover, the presence of natural organic matter. Plakas et al. showed that the differences in pesticides retention between fouled and original membranes are related to the diffusion capacity of herbicides across the membranes [78, 90].

2.3. Degradation

2.3.1. Zero-Valent Iron

In recent years, zero-valent iron (ZVI) has been widely applied for treatment of contamination because of its easy accessibility, effective degradation of pollutants, generation of very little waste and secondary pollutants [3, 92]. ZVI is categorized into two types nanoscale ZVI (nZVI) and reactive nanoscale iron product (RNIP). nZVI particles have a diameter of 100–200 nm composed of iron (Fe) with a valence of zero, while RNIP particles include 50/50 wt% Fe and Fe_3O_4 [18]. The Elemental iron (Fe^0) and dissolved Fe^{2+} form a redox couple that has a standard reduction potential of 0.440V [93]. Studies have shown that many pesticides are vulnerable to degradation using ZVI. It also has been successfully used in dechlorination of highly recalcitrant pesticides and herbicides [94, 95]. When halogenated organic pollutants are treated with ZVI, oxidation of ZVI and Fe(II) provides electrons for dechlorination [96]:

$$\boldsymbol{Fe^{0} + R - Cl + H^{+} \rightarrow Fe^{2+} + R - H + Cl^{-}}$$

$$\boldsymbol{2Fe^{2+} + R - Cl + H_2O \rightarrow 2Fe^{3+} + R - H + OH^{-} + Cl^{-}}$$

The hydrophobic nature of organic pollutants, particularly halogenated organic compounds, appears to limit efficient electron transfer due to their immiscibility with water [3]. While ZVI was not effective in degrading cyclodiene pesticides, it did prove effective for other pesticide and herbicides. These include compounds containing nitrogen heteroatoms such as atrazine, molinate, picloram, chlorpyrifos, and, to a limited extent, diazinon and diuron [3, 97-99]. Young-Soo et al. studied the reduction of eleven nitroaromatic pesticides with zero-valent iron powder [100]. nitroaromatic pesticides were rapidly reduced with zero-valent iron to the corresponding amines as major reduction products. Intermediate products were found only in very small concentrations in some reactions. The results also showed that the reductive aromatic dechlorination was much slower than the reduction of nitro groups [100].

2.3.2. Photocatalysis

Photocatalytic oxidation is an environmentally friendly process used for removal of the wide range of organic pollutant. It is a suitable pretreatment for hazardous and non-biodegradable contaminants to enhance their biodegradability. Photocatalysis can also be used as a polishing step to treat recalcitrant organic compounds [101]. In a photocatalysis process, photoexcitation of semiconductor solid surfaces happens by irradiation, either by near UV or solar light. As a result, mobile electrons and positive surface charges are generated. These excited sites and electrons accelerate oxidation and reduction reactions, which are essential steps for pollutant degradation [102, 103]. Through the development of nanotechnology, semiconductor photocatalysts have been modified in terms of reactivity and selectivity. Based on this principle, a wide range of pesticides have been treated by photocatalytic degradation. There are various types of semiconductor materials including ZnO, TiO_2, Fe_2O_3, CdS and WO_3. Amongst these, titanium dioxide has been used most widely because of its low toxicity, chemical stability, low cost, and abundance a raw material.

Many researchers have reported pesticides photodecomposition by TiO_2 [104-109]. Binbin et al. investigated the photocatalytic degradation of organochlorine pesticides carried out on nano- TiO_2 coated films under UV irradiation in air [104]. All pesticides could be completely degraded in a short time. Also, the degradation rate was greatly enhanced by using the higher power UV lamp. Another study on the photocatalytic degradation of dicofol with TiO_2 nanoparticles under UV light irradiation showed that dicofol could be completely degraded and active hydroxyl radicals (·OH) could react with dicofol to produce chloride ions and less toxic compounds that contain less chlorine content [107]. The photoactivity of nano-TiO_2 can be improved by optimizing particle size and shape, reducing e^-/h^+ recombination by noble metal doping, maximizing reactive facets, and surface treatment to enhance adsorption capacity [110]. Many researchers investigated the possible extension of its absorption range in to the visible region with a various compounds including metal and nonmetal surfactants etc [111-115]. Police et al. studied photocatalytic degradation of isoproturon pesticide on C, N and S doped TiO_2 [112]. The results showed that the prepared catalysts are anatase type and nanosized particles. The catalysts exhibited stronger absorption in the visible light region with a red shift in the adsorption edge. It appears that metal doping is more effective in shifting the absorbance range to a visible region relative to nonmetal doped titania [116]. Degradation efficiency of Th-doped TiO_2 photocatalysts were investigated under UV and solar light illumination [117]. These results indicate that Th-doped TiO_2 with its modified electronic properties is a good photocatalyst for the degradation of oryzalin in surface water under solar light irradiation. However, these modifications show very slight differences in photocatalytic rates under UV irradiation. All the photodegradation reactions follow first order kinetics. In addition to titania, many other photocatalysts (ZnO, WO_3, etc.) have also been applied to degradation of pesticides [118-120]. For instance, Photodegradation of eight pesticides in leaching water (the water is polluted with pesticides and other dissolved chemicals when moving through the soil.) at pilot plant scale using tandem $ZnO/Na_2S_2O_8$ as photosensitizer/oxidant and compound parabolic collectors under natural sunlight has been reported [121]. The results showed that the use of solar photocatalysis in the presence of ZnO as photosensitizer constitutes a very effective method for the reduction and even elimination of the selected pesticides in leaching water. Table 2 summarizes recent research on improving photocatalyst activity and expanding photoactivity range.

3. CONCLUSIONS

Pesticides residues which have been detected in various natural waters in many countries are of special concern because of their persistence in the aquatic environment and potential adverse health effects. It is an emerging problem in developing countries, and there is an essential need for efficient technologies. Research indicated that there is a significant potential for pesticides removal by the use of the different processes of nanotechnology. In this study, three main processes categories for pesticides removal including adsorption, filtration and degradation were discussed. The researchers applied nanomaterials either individual or composite. In many cases, the multitude of parameters has been considered for nanomaterial chemical reactivity enhancement and its use in aqueous solution for removal of pesticide:

***Table 2.** Photocatalyst activation in degradation of pesticides*

Photocatalyst	**Modifier**	**Target pesticides**	**Optimization**	**Ref.**
TiO_2	C, N and S	Isoproturon	Lower electron-hole recombination, high surface area and the better adsorption in visible light range.	[112]
ZnO	$Na_2S_2O_8$	azoxystrobin, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil (fungicides), primicarb (insecticide), and propyzamide (herbicide)	Reduction in treatment time and enhance the rate of degradation	[121]
TiO_2	N	Lindane	Better photocatalytic activity in visible light	[111]
TiO_2	$CdSO_4$	Methomyl	Strong electrons capturing and lower electron-hole recombination	[122]
TiO_2	Ag	Organochlorine pesticides (α-hexachlorobenzene (BHC) and dicofol)	High surface area and lower electron-hole recombination	[123]
TiO_2	Au–Pd	Malathion	Effective separation of photo-generated charge carriers and the higher synthesis rate of H_2O_2	[124]
TiO_2	V, Mo, Th	Chlorpyrifos	High surface area, lower electron-hole recombination	[114]

shape-controlled synthesis procedures, increase in specific surface area, increase in reactivity and incorporation of nanoparticle on support structures. Overall, different processes of nanotechnology have similarities to natural processes including energy efficiency, use of smaller quantities of materials, conversion efficiency, etc. Although it needs to be studied further about to large scale application of nanotechnology process in water and wastewater treatment to eliminate of pesticide and other pollutants associated with the investigation on potential risks of nanomaterials for environmental and human health.

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