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REVIEW

Applications of Nanomaterials for Adsorptive and Catalytic Removal of Chemical Pesticides: An Overview

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Chemical pesticides are one of the most frequently encountered pollutants in multiple water sources and made their way into biomagnification. Short-term exposure to pesticides causes headache, vomiting, nausea, blurred vision, pupil constriction, muscle tremors, excessive sweating, *etc*. whereas prolonged exposure can lead to severe neurological problems, coma and even death. However, conventional methods have been proved to be inefficient in complete removal of pesticides. Over the past few years, nanotechnology is considered to play a significant role in influencing the current environmental engineering and science owing to their excellent physico-chemical properties and tuneable functionalities. Nanomaterials are massively enrolled as adsorbents and photocatalysts for the removal of various chemical pesticides from different sources. In present article, the applicability of different nanomaterials for the removal of various pesticides *via* adsorption and photocatalytic degradation from aqueous environment was discussed. Furthermore, the influence of surface treatment to their functionalities and efficiencies was reviewed and highlighted.

Keywords: Adsorption, Nanobiocomposites, Nanoclays, Nanocomposites, Nanoparticles, Pesticides, Photocatalytic degradation.

INTRODUCTION

The expansion of agriculture practices has become a world phenomenon necessary to meet the increasing food demand by replacing traditional agricultural practices. In the course of such a transition, several complementary agrochemicals (fertilizers, plant growth stimulators, *etc*.) have been developed and extensively applied in crop farms, fields, forestry and orchards [1,2]. Among various agrochemicals, pesticides have been widely used against any pests including plant pathogens, insects, molluscs, mammals, weeds, microbes and nematodes (roundworms) that compete during the production, processing, storage, transport and marketing of agricultural commodities [3]. Among various categories of pesticides, chemical pesticides find huge demand in the agrochemical market and are classified into various types as shown in Fig. 1. While pesticides are directly applied on plants, only 2% of pesticide sprayed is delivered to the intended target whereas, remaining 98% of pesticide is accumulated in soil, ground water and air [4,5]. In addition, accidental release of pesticides due to spills, underground storage tanks, leaking pipes and waste dumps may lead to their persistence in the environment for a long time due to their long half-lives [6,7]. Over-exploitation of pesticides has raised serious concerns about environment, ecosystem and biomagnification due to their potential toxicological effects and bio-recalcitrant nature (Fig. 2). Annually, more than two million workers from the agriculture sector exhibited symptoms of pesticide poisoning [8,9]. Other adverse effects of chemical pesticides on the environment include declining biodiversity, threat to endangered species [10], reduced population of insect pollinators [11] and destruction of the habitat for birds [12].

In fact, more than 500 chemical compounds have been registered internationally as pesticides or their metabolites. In Asia, India ranks second position in manufacturing of various chemical pesticides. Globally, European countries are the leading consumer of pesticides. Several studies of water quality have reported the major classes of chemical contaminants of aquatic systems are metals, hydrocarbons and pesticides. In addition, pesticides and their products have also been designated as the

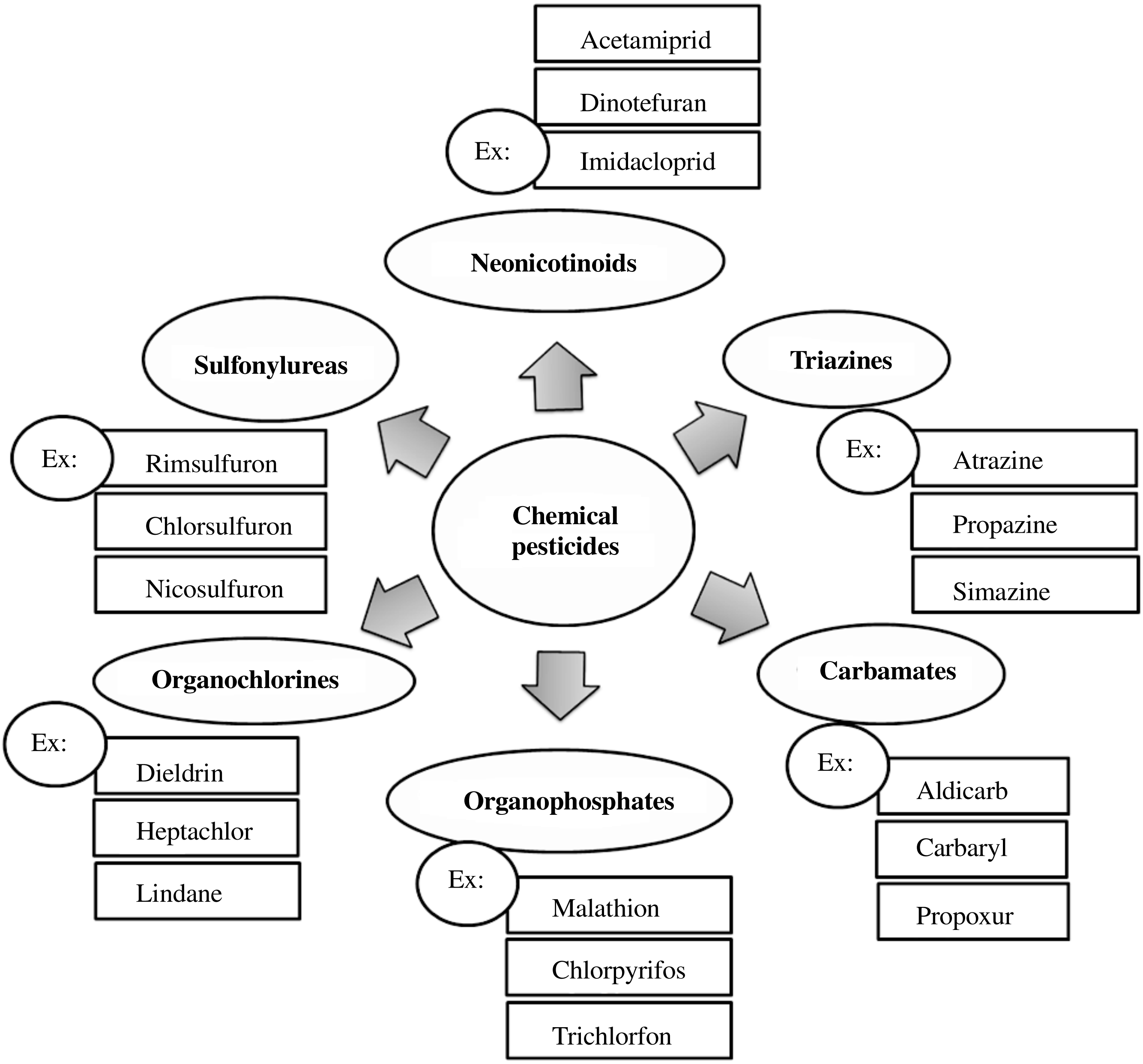

Fig. 1. Classification of chemical pesticides based on their chemical origin

most hazardous and persistent chemicals on the earth and referred as "dirty dozen chemicals" [13].

The removal of pesticides through several techniques classified under biological, chemical, physical and physicochemical processes of remediation from different types of matrices, such as water and soil. However, these approaches target diverse groups of environmental pollutants, which significantly affect the removal efficiency of these techniques. In addition, these methods fail to exhibit complete elimination of pesticide and further treatments are needed for their complete mineralization [14].

Nanoscience and nanotechnology: Over the past few years, the research community has witnessed an increasing interest in the field of nanomaterials, nanoscience and nanotechnology. Nanomaterials can be categorised into different classes based on their structure, physiochemical properties and field of application *viz*., nanostructured materials, porous nanomaterials, metal nanoparticles, bimetallic nanoparticles, polymer nanoparticles, nanoclay, layered nanomaterials, quantum dots, nanocomposites, polymer nanocomposites and so on (Fig. 3) [15,16].

Recent advancements in nanotechnology and nanoscience have received global attention in recent years for the detection and removal of organic and inorganic hazardous contaminants [17]. These approaches are known to be specific during partial or complete remediation of pesticides from the environment. Various types of metal and metal oxide nanomaterials have led to the massive research in the area through several methodologies [18]. Numerous nanomaterials have been used in abatement of organic and inorganic pollutants from various environmental media like soils, ground water and industrial effluents. The major mechanisms responsible for their remedial application are adsorption and photocatalytic degradation [19]. The

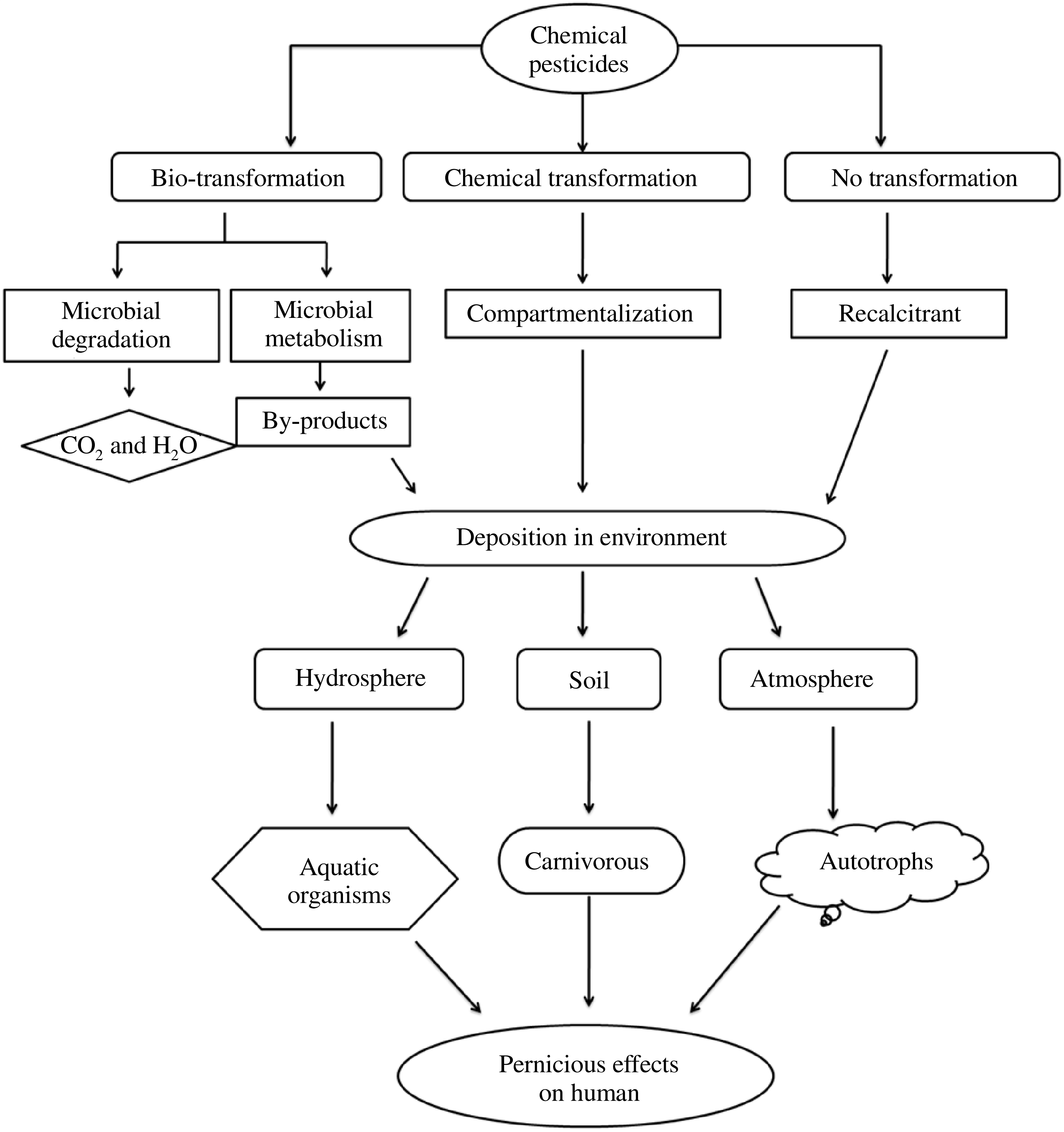

Fig. 2. Fate of chemical pesticides under environmental conditions

present article provides a brief compendium of the current research that focuses on the remediation of pesticides using several nanomaterials.

Nanoparticles: Nanoparticles including metal and metal oxides are nanosized particles with one or more of its width, length and thickness is in the range of 1 to 100 nm which are usually synthesised using two approaches: (i) bottom-up and (ii) top-down. Bottom-up approach involves the assembling of atoms at their molecular level whereas; top-down approach involves the fragmentation of bulk materials using mechanical forces in presence or in absence of external catalyst. It is well known that the properties of nanoparticles are greatly influenced by their synthesis methods. Hence, different methods have been used by researchers to synthesize nanoparticles of desired dimensions and tunable properties (Fig. 4). Nanoparticles with their unique physico-chemical, optoelectronic and catalytic properties find applications in various sectors including medicine, agriculture, environment, pharmaceutical, *etc*. Nanoparticles are categorized in to different types based on their structure into dendrimers, liposomes, metal based, metal oxide based

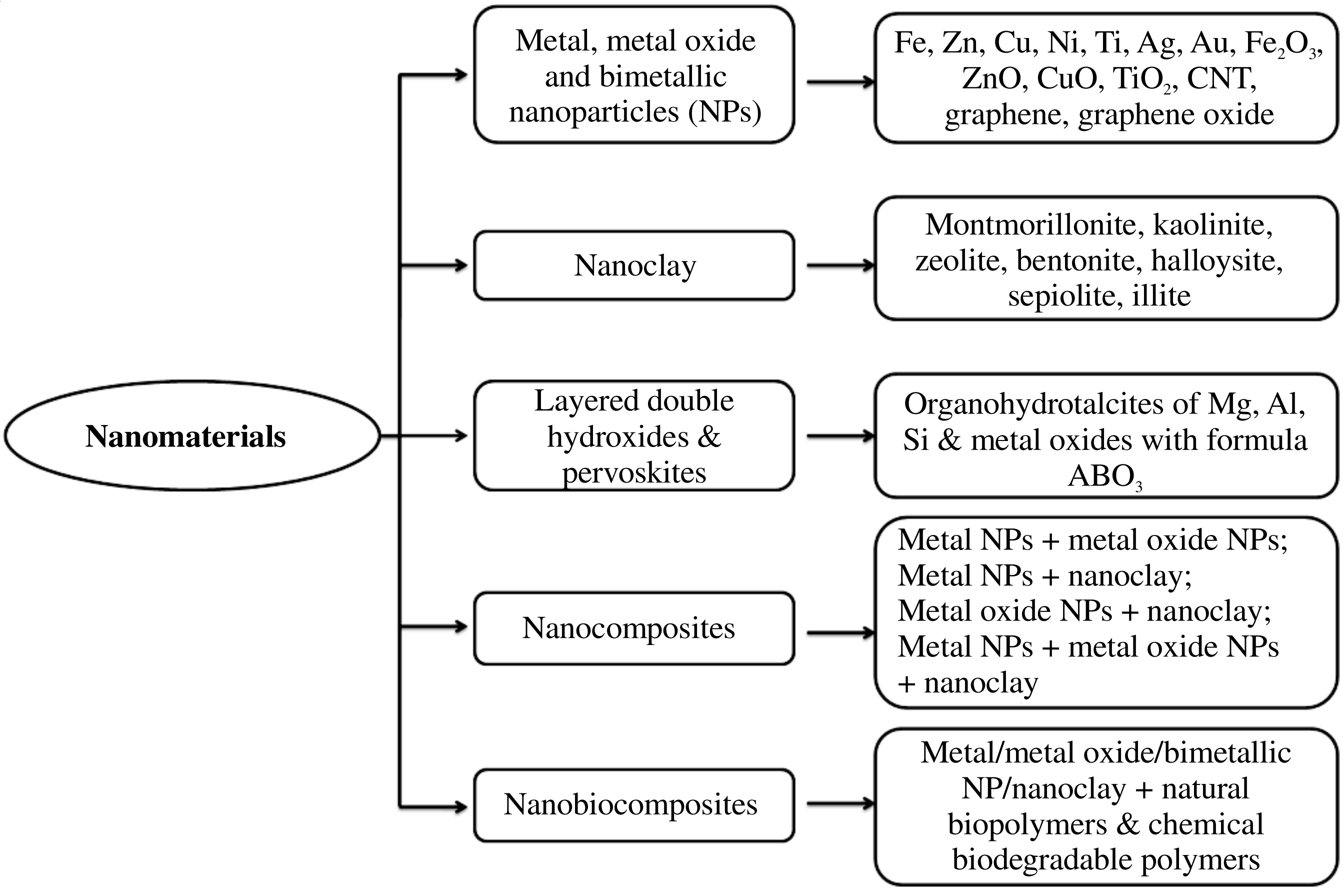

Fig. 3. Classification of nanomaterials for remediation of pesticides

carbon based, *etc*. Metal based nanoparticles are further classified into monometallic and bimetallic, according to the number of metal ions involved in nanoparticles constitution [20]. Transition and noble metal and metal oxide nanoparticles like iron [21,22], zinc [23-25], copper [26], nickel [27], titanium [28], cerium, silver [29-31], gold [32,33], palladium and platinum have been increasingly investigated for efficiency in detection, adsorption and photocatalytic degradation of various environmental pollutants. In addition to these metal nanoparticles, layered double hydroxides [34-39], perovskites [40,41] and carbonaceous nanostructures including carbon nanotubes, nano fibres, graphene and graphene oxide, *etc.* have gained great interest in remediation of environmental contaminants [42].

Monometallic iron oxide nanoparticles in the forms of hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_2O_3) with large surface area and low cost offers additional advantage of super-paramagnetism that makes them reusable materials. Guo *et al.* [43] applied biosynthesized iron oxide nanoparticles for the removal of 2,4-dichlorophenol from aqueous phase. Nanomaterials showed 20.6% of pesticide adsorption where removal efficiency increased to 64.4% when adsorption and Fenton like oxidation was integrated. Highly crystalline and hexagonal nanorods of iron hexacyanoferrate (FeHCF) synthesized from Sapindus-Mukorossi were investigated for the removal of malathion, chlorpyrifos and hexachoro cyclohexane *via* photocatalytic degradation. Highly active hydroxyl radicals favoured the maximum degradation of malathion (95%), chlorpyrifos (92%) and hexachoro cyclohexane (90%) with the release of nontoxic byproducts within 12 h of sunlight exposure [13]. Pre-treatment methodology using surface active agents have been utilized for to enhance the adsorption capacities. A polysterene coated magnetic nanospheres (Fe_3O_4-PS) were employed to remove four organochlorine pesticides. Fe_3O_4-PS with the diameter of 55 ± 11 nm showed the maximum adsorption of 7.93, 8.39, 8.28 and 8.33 mg/g for lindene, aldrin, dieldrin and endrin, respectively. In addition, a significant removal of 93.3% of mixed pesticides from wastewater was noted which suggested the applicability of Fe_3O_4-PS for the remediation of organic contaminants in water resources [44]. Zero-valent iron nanoparticles as well as polyaspartate (PAP) and polyacrylic acid (PAA) modified iron nanoparticles have been used to study the degradation kinetics of lindane. The polymers coating prevented the agglomeration of iron nanoparticles favouring availability of free active sites and reactivity. The degradation was well explained by pseudo-first reaction kinetic model where dehydro-halogenation and dichloro-elimination were the mechanisms involved in removal of lindane [45].

Zinc based nanoparticles have received great attention due to their eco-friendly nature and biocompatibility that pose zero risk to living organisms making them suitable materials in the field of environmental remediation [46]. Several researchers demonstrated the adsorbent and photocatalytic properties of ZnO nanoparticles owing to their surface and structural prop-

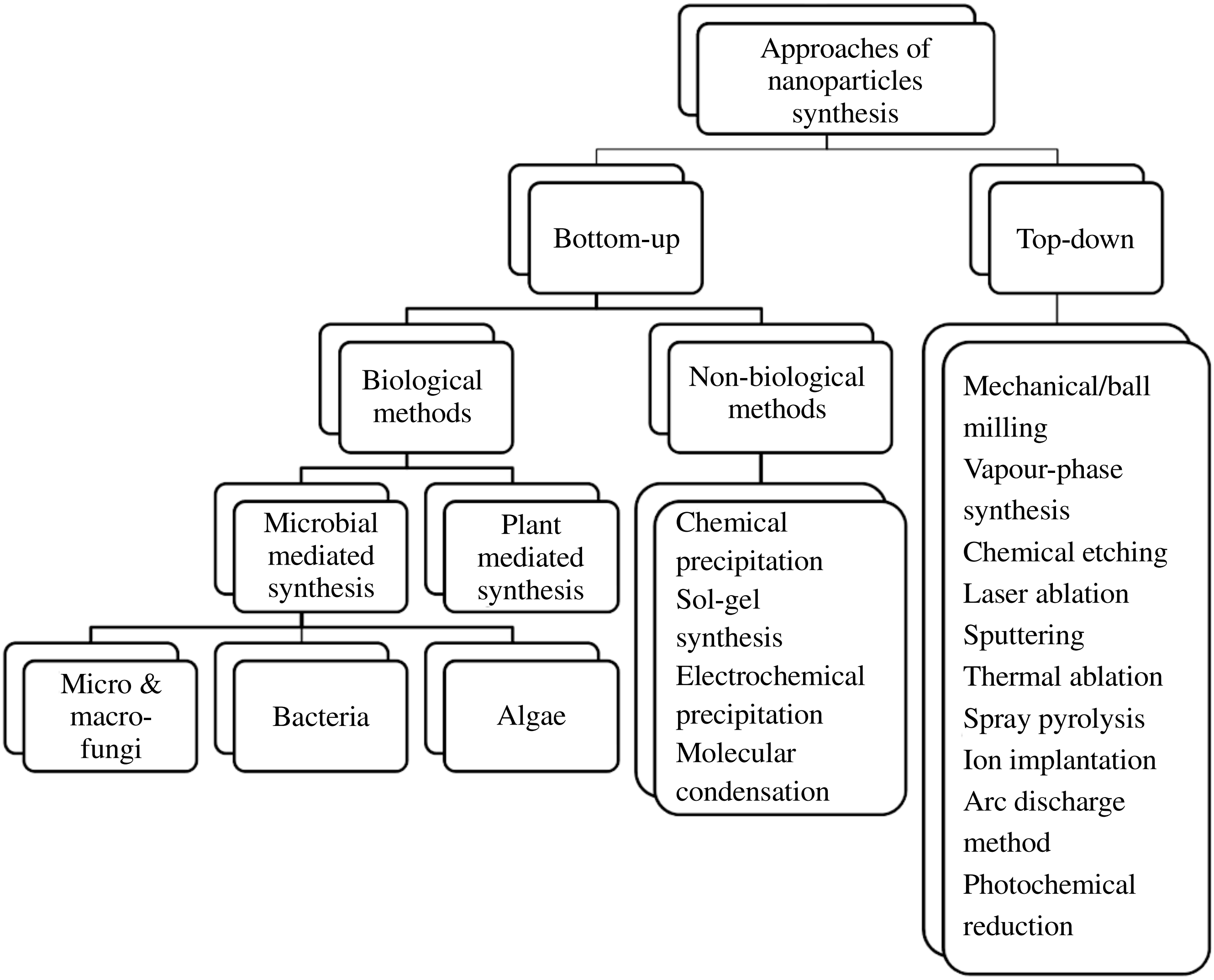

Fig. 4. Approaches involved in the synthesis of metal and metal oxide nanoparticles

erties. Chlorpyrifos, a widely used organophosphate was degraded from aqueous environment using ZnO nanoparticles embedded in a membrane filter. The process showed an increased rate of pesticide degradation by ZnO nanoparticles with membrane filtration under UV light irradiation as compared to ZnO mediated photocatalysis [47]. Another study showcased the suppression of chlorpyrifos induced immunotoxic effects and histopathological effects by addition of ZnO nanoparticles in drinking water [48]. ZnO nanoparticles synthesized from microoven technique were treated with cetyltrimethylammonium bromide (CTAB) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF) for improving their adsorption properties. The functionalization was effective where BMTF treated ZnO nanoparticles showed maximum adsorption of 148.3 mg naphthalene per adsorbent as compared with CTAB treated (89.9 mg/g) and untreated ZnO nanoparticles (66.8 mg/g) [49].

Currently, copper is being used for multiple applications in the field of electronics, optics, medicine, catalysis, *etc*. due to high natural abundance and low cost. In a recent study, green synthesized copper nanoparticles have been utilized as nanoadsorbent of pharmaceutical pollutants from real wastewater samples in batch studies. The removal percentage of ibuprofen, naproxen and diclofenac were found to be 74.4, 86.9 and 91.4%, respectively [50]. Endosulfan in acetonitrile solvent has been degraded using copper nanoparticles under γ-irradiation through heterogenous photocatalysis process. The photocatalytic degradation products identified as endosulfandiol, endosulfan sulphate and endosulfan ether. Further irradiation showed the complete degradation and mineralization of pesticide [51].

Heterogenous photocatalysis employing semiconductors proved to be an efficient technique in complete mineralization of pesticides. At nanodimension, TiO_2 exhibits excellent photocatalytic activities under ultra violet irradiation with the band gap of 3.2 eV and also offers high surface area, thermal and chemical stabilities against different chemicals [52-54]. Chemical methods have been widely used for the synthesis of TiO_2 nanoparticles of varying size and tunable properties [55]. In a recent study, TiO_2 immobilized on solar still have been utilized for the degradation of organochlorine pesticides like endosulfan, DDT and hexachlorocyclohexane (HCH). In addition to this, degradation of pyrethroids like cyhalothrin, cyfluthrin, cypermethrin, fenpropathrin and fenvalerate were also investigated.

The process showed 82.9% degradation of HCH followed by cypermethrin (81.9%), endosulfan (80.3%) cyfluthrin (76.8%), fenvalerate (73.4%), cyhalothrin (75.5%), fenpropathrin (60.4%) and DDT (44.5%) [56]. The efficiency of bare TiO_2 nanoparticles and Au/TiO_2 metal-hybrid nanostructures in photocatalytic degradation of malathion was studied. Metal TiO_2 nanoparticles showed 68% of pesticide degradation in 1 h of UV irradiation at pH and initial pesticide concentration of 10^{-4} M, respectively. The doping process influenced the photocatalytic reaction rate where maximum (81%) degradation of pesticide was achieved at the reduced radiation time attributed to the ability of gold nanostructures to prevent of electron hole recombination that enhanced the photocatalytic degradation [57].

Graphene is one of the most popular nanomaterials with high density of functional groups including carboxyl, carbonyl, hydroxyl and epoxy in the lattice offers enhanced adsorption performance among carbon based nanostructures [58]. As early as 2012, graphite carbon nanostructures (GCN) synthesized from two different biomass were evaluated for adsorption efficiency against 2,4-dichlorophenoxy acetic acid (2,4-DCP). GCN synthesized from filter paper exhibited high adsorption potential as compared with GCN synthesized from cotton, which was attributed to higher surface area (182.4 m^2/g) and pore size (6.884 nm) [59]. Agarwal *et al*. [60] studied the adsorption behaviour of oxamyl on novel graphene quantum dots (GQD) synthesized by microwave assisted hydrothermal route. Experimental results suggested the superior adsorption capacity of GQD as compared to other activated carbon reported in the literature where maximum adsorption of 125 mg/g with in 25 min of contact time at pH 8.0 and adsorbent dosage 0.6 g was noted. Multiwalled carbon nanotubes have been utilized as nanosorbents to remove fenuron pesticide. Several hydrophobic interactions including one π-o, three π-alkyl, one π-π T shaped, seven π-π stacked facilitated the highest removal (90%) of fenuron at 100 µg/L concentration of pesticide at pH 7.0 and 2 g/L of catalyst concentration within 60 min of contact time [61]. The removal of pesticides mediated by several kind of nanoparticles are tabulated in Table-1.

Nanoclay: Nanoclays are the nanomaterials of layered phyllosilicates with a layer of ~0.7 nm thickness, formed as a result of rock-water interaction in the environment. They are primarily composed of multiple layers of tetrahedral and octahedral sheets of silica and alumina, respectively. In addition, phyllosilicates comprising exchangeable cations such as Mg^{2+}, Ca^{2+}, Fe^{2+}, Na^{2+}, O^{2+} and K^+ that balances the total negative charge generated due to the isomorphous substitution of Al^{3+} with Si^{4+} and Mg^{2+} with Al^{3+} in the tetrahedral and octahedral sheets [62-68]. These clay minerals are known to exhibit exceptional physical and chemical properties *viz.* crystalline network, high porosity, high surface area, high swelling capacity, electrical conductivity, mechanical and thermal stabilities, which can be easily modified to enhance their efficiency in various fields [65].

Several nanoclay minerals such as montmorillonite (MMT), kaolinite, zeolite, bentonite, halloysite, *etc*. were exploited for their efficiency as nanosorbent and photocatalysts in remediation of various chemical pesticides from aqueous environment and soil owing to their high abundance, layered structure, surface properties, environment-friendly nature and low cost [66-69]. Hexadecyltrimethylammonium bromide (HDTMA) treated montmorillonite was studied for the adsorption of ionic 2,4-D and non-ionic metoachlor pesticides. According to the results, maximum adsorption of both the compounds was observed on HDTMA treated montmorillonite due to the intercalation of surfactant that created the new functionalities in MMT [70]. Bojemueller *et al*. [71] reported the enhanced adsorption of metolachlor by bentonite clay calcined at 550 ºC for 12 h, which was attributed to the decomposition of clay edges creating mesopores followed by the increased interaction of exposed aluminium ions with herbicide ions. The adsorption of linuron, penconazole, alachlor, metalaxyl and atrazine by illite, sepiolote, montmorillonite, palygorskite and muscovite treated with cationic surfactant octadecyltrimethyl ammonium bromide was investigated. Results suggested the higher adsorption capacities of surfactant modified nanoclays where they could be used as natural barriers to decrease the mobility of hydrophobic pesticides in the soil [72]. Calcium rich Arizona montmorillonite treated with hexadimethrine exhibited maximum removal of clopyralid, diuron, fluometuron, mecoprop, 4-chloro-2-methylphenoxyacetic acid (MCPA), simazine and terbuthylazine as compared with hexadecyltrimethylammonium treated with montmorillonite [73]. Adsorption efficiency of commercial organoclay Cloisite 10A and bentonite modified with chitosan, Fe^+ and hexadecyltrimethylammonium was investigated against MCPA, terbuthylazine and tebuconazole [74]. The modified clay mineral displayed adsorption ranging from 30% to 100% whereas, adsorption of pesticides on Cloisite 10A ranged from 30% to 90%. Photo-Fenton degradation of methomyl insecticide using aluminium and iron pillared montmorillonite and iron zeolites were studied. The rate of photodecomposition of pesticide was higher in case of iron zeolites as compared to aluminium and iron pillared montmorillonite where complete degradation was noted under optimized conditions [75]. The removal of pesticides mediated by different kind of nanoclays are presented in Table-2.

Nanocomposites: Nanocomposites are engineered multiphase nanomaterials in which one phase has nanoscale dimension in the range of 10 to 100 nm like nanosheets, nanoparticles, nanotubes, nanospheres or lamellar structure. Nanocomposites with tailored functionalities have emerged as potential alternatives to overcome drawbacks of macro and microcomposites [76]. Despite of their short history, applications of nanocomposites in the fields of biomedical, biotechnological, engineering and electronics have been considerably increased owing to their superior physico-chemical properties such as enhanced surface area, improved optical properties, chemical resistance, electrical conductance, thermal and mechanical stabilities due to their unique structural combination of continuous bulk matrix phase and discontinuous nanodimensional phase. These nanomaterials based composites have attracted the attention of biotechnologists for the remediation of various organic and inorganic pollutants from the environment [77,78].

Chlorophenoxyacetic acids such as phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic

TABLE-1
REMOVAL OF PESTICIDES MEDIATED BY NANOPARTICLES

Type of nanomaterials	Chemical presentation	Pesticide	Mechanism	Pesticide removal	Ref.
Metallic nanoparticles	Cu	Naphthalene	Adsorption	100%	[32]
	Ag	Naphthalene	Adsorption	100%	[32]
	MWCNTs	Fenuron	Adsorption	90%	[61]
	Polyaniline	Nicosulfuron	Adsorption	29.8 mg/g	[83]
	Tungsten trioxide	Chlorfenvinphos	Photoelectro-catalyzed degradation	60.5%	[23]
	Tungsten trioxide	Bromacil	Photoelectro-catalyzed degradation	42.8%	[23]
	MWCNTs	Diazinon	Adsorption	100%	[4]
	Iron hexacyanoferrate	α-Hexachloro cyclohexane	Photocatalytic degradation	90%	[13]
	Iron hexacyanoferrate	Malathion	Photocatalytic degradation	95%	[13]
	Iron hexacyanoferrate	Chlorpyrifos	Photocatalytic degradation	92%	[13]
	Ag	Chlorpyrifos	Adsorption	361 mg/g	[29]
	Ag	Malathion	Adsorption	204 mg/g	[29]
	Graphene quantum dots	Oxamyl	Adsorption	84%	[60]
	MWCNTs	Malathion	Adsorption	100%	[5]
	Au nanospheres	Dimethoate	Adsorption	456 mg/g	[30]
	Ag	Chlorpyrifos	Photocatalytic degradation	100%	[31]
	Ag	Malathion	Photocatalytic degradation	100%	[31]
	Cu	Endosulfan	Photocatalytic degradation	100%	[51]
	Au	Metsulfuron-methyl	Adsorption	83.9%	[33]
	Iron nanoparticles	Lindane	Photocatalytic degradation	98%	[45]
	Graphitic carbon nanostructures	2,4-dichlorophenoxyacetic acid	Adsorption	77 mg/g	[59]
Metal oxide nanoparticles	TiO_2	Fenvalerate	Photocatalytic degradation	96.4%	[56]
	TiO_2	Hexachloro cyclohexane	Photocatalytic degradation	82.9%	[56]
	TiO_2	Fenpropathrin	Photocatalytic degradation	60.4%	[56]
	CeO_2	2,4 dichlorophenoxyacetic acid	Adsorption	84.2 mg/g	[3]
	Fe_3O_4	Deltamethrin, Bifenthrin and Cyhalothrin	Magnetic separation	80.2%	[21]
	Iron oxide	2,4-Dichlorophenol	Adsorption and Fenton-like oxidation	64%	[43]
	ZnO	Naphthalene	Adsorption	66.8 mg/g	[49]
	TiO_2 doped with Fe and Si ions	Carbendazim	Photocatalytic degradation	98%	[22]
	ZnO	Methyl parathion and parathion	Photocatalytic degradation	93%	[24]
	TiO_2	Chlorpyrifos and monocrotophos	Photocatalytic degradation	>95%	[53]
	ZnO	Chlorpyrifos	Photocatalytic degradation	46%	[47]
	TiO_2	DDT	Adsorption	89.1%	[54]
	Fe_2O_3–Palygorskite	Fenarimol	Adsorption	70%	[63]
	Magnetic iron(II,III) oxide nanospheres	Organochlorine	Adsorption	93.3%	[44]
	ZnO	Malathion	Photocatalytic degradation	60%	[57]
	TiO_2	Malathion	Photocatalytic degradation	68%	[57]
	ZnO	Dimethylamine salt of 2,4-dichlorophenoxyacetic acid	Photocatalytic degradation	38.1%	[25]
Bimetallic nanoparticles	Ag/Cu	Chlorpyrifos	Photocatalytic degradation	100%	[26]
	Fe/Ni	Sulfentrazone	Dechlorination	100%	[16]
	Fe/Ni	Profenofos	Catalytic reduction	94.5%	[27]
Layered double hydroxides	Mg–Al hydrotalcite	Nicosulfuron	Adsorption	100%	[35]
	Mg–Al hydrotalcite	Mecoprop-P	Adsorption	100%	[35]
	Organohydrotalcites	S-Metolachlor	Adsorption	100%	[36]
	Mg–Al organohydrotalcites	Carbetamide	Adsorption	18%	[37]
	Mg–Al organohydrotalcites	Metamitron	Adsorption	14%	[37]
	$MgAl_2$-NO_3	Glyphosate	Adsorption	27 mg/g	[38]
	$Mg_3AlO_{4.5}$	2,4-D	Adsorption	62%	[39]
	$Mg_3AlO_{4.5}$	Clopyralid	Adsorption	75%	[39]
	$Mg_3AlO_{4.5}$	Picloram	Adsorption	90%	[39]
Perovskite nanoparticles	$LaNiO_3$	Dichlorvos	Photocatalytic degradation	71.0%	[40]
	$LaFe_{0.9}Co_{0.1}O_3$	Vitavax	Adsorption	100%	[41]

TABLE-2
REMOVAL OF PESTICIDES MEDIATED BY NANOCLAY

Chemical presentation	Pesticide	Mechanism	Pesticide removal	Ref.
Fe^{3+}-Bentonite	Terbuthylazine	Adsorption	38%	[74]
Fe^{3+}-Bentonite	Tebuconazole	Adsorption	88%	[74]
Fe^{3+}-Bentonite	MCPA	Adsorption	38%	[74]
Hexadecyltrimethyl ammonium modified bentonite	Terbuthylazine	Adsorption	44%	[74]
Hexadecyltrimethyl ammonium modified bentonite	Tebuconazole	Adsorption	82%	[74]
Hexadecyltrimethyl ammonium modified bentonite	MCPA	Adsorption	98%	[74]
Montmorillonite	2,4-Dichlorophenoxyacetic	Adsorption	185.1 mg/g	[70]
Montmorillonite	Metolachlor	Adsorption	84.7 mg/g	[70]
BEA zeolite (SiO_2/Al_2O_3)	Glyphosate	Adsorption	92.2 mg/g	[67]
Halloysite doped with Fe_3O_4 NPs	Pentachloro-phenol	Catalytic decomposition	100%	[68]
Halloysite nanotubes	4-*n*-Nonylphenol	Photo-decomposition	>90%	[69]
Hexadecyltrimethyl ammonium modified montmorillonite	Fluometuron	Adsorption	90%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	Diuron	Adsorption	95%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	Terbuthylazine	Adsorption	77%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	Simazine	Adsorption	28%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	Mecoprop	Adsorption	95%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	MCPA	Adsorption	94%	[73]
Hexadecyltrimethyl ammonium modified montmorillonite	Clopyralid	Adsorption	84%	[73]
Fe-ZSM-5 zeolite	Methomyl	Photo-Fenton degradation	100%	[75]
AlFe-pillared montmorillonite	Methomyl	Photo-Fenton degradation	63%	[75]
Montmorillonite	Penconazole	Photo-Fenton degradation	40.3 mg/g	[72]
Sepiolite	Linuron	Photo-Fenton degradation	327 mg/g	[72]
Sepiolite	Alachlor	Photo-Fenton degradation	122 mg/g	[72]
Sepiolite	Atrazine	Photo-Fenton degradation	247 mg/g	[72]
Illite	Metalaxyl	Photo-Fenton degradation	14.4 mg/g	[72]

acid and 4-chlorophenoxyacetic acid, widely used herbicides was removed by nanocomposites of ZnO and γ-Fe_2O_3 synthesized *via* co-precipitation method. Under optimum conditions, maximum photocatalytic degradation was achieved owing to the synergistic interaction between ZnO and γ-Fe_2O_3 [79]. $CoFe_2O_4$-TiO_2 decorated reduced graphene oxide nanocomposites have been exploited for the removal of chlorpyrifos, a commonly used organophosphate insecticide. Metallic nanoparticles increased the partition of electrons and protons which enhanced the production of hydroxyl and superoxide radicals that participated in the degradation of pesticide [80]. A strong hydrophobic, electrostatic and π-π interactions of nanocomposite with organic pesticide is the mechanism behind the adsorption by Fe_3O_4/graphene nanocomposites towards triazine pesticide [81].

Chemically treated zeolites are extensively used as supports for the preparation of nanocomposites with metal and metal oxides attributed to their exceptional features such as stable chemical and physical properties, enhanced surface area, high thermal stability, hydrophilic and hydrophobic properties and eco-friendly nature. A series of sodium forms zeolites with Si/Al ratio of 3, 15 and 53 prepared to support TiO_2 and ZnO nanoparticles were explored for their efficiency in the adsorption and photocatalytic degradation of monocrotophos from the aqueous solution. The hydrophobicity of zeolites favoured the maximum adsorption of pesticide on to the nanocomposites followed by their photocatalytic degradation carried by TiO_2 and ZnO [82]. In another study, nicosulfuron was degraded in water samples by BEA zeolite/polyaniline nanocomposite synthesized by chemical oxidative polymerization. Electrostatic interaction of amino groups of polyaniline chains and anionic groups of pesticides in addition to hydrogen bonding of O- and N-containing groups of pesticide with -OH groups of BEA zeolites were the mechanisms behind the maximum removal of pesticide [83]. The removal of pesticides mediated by different kind of nanocomposite are tabulated in Table-3.

Nanobiocomposites: Nanobiocomposites are also known as natural composites derived from inorganic nanomaterials and biodegradable polymers. Owing to the nano-dimensional particles dispersed in a polymer matrix, these nanobiocomposites exhibit exceptionally enhanced physiochemical properties such as optical, thermal, mechanical, water sensitivity, *etc*. At present, most of the studies concerned to nanobiocomposites have focused on two categories of biodegradable polymers *e.g.* natural biopolymers such as cellulose, starch, chitosan [86,87], cyclodextrin, gelatin, alginates [88], casein, natural gums [89], *etc.* and chemical synthesized biodegradable polymers like poly glycolic acid, poly lactic acid, poly vinyl alcohol, *etc*., Nanobiocomposites have replaced conventional nanocomposites and hydrocarbon based composites that significantly contributed to the sustainable development in connection with lower risk of environmental pollution [90,91].

Remediation of environmental pollutants using nanobiocomposites has started gaining attention in past few years. Biopolymer nanocomposites especially, chitosan based metallic nanobiocomposites have been used for the elimination of various pesticides. *S. cerevisiae* and magnetic iron (Fe_3O_4) nanoparticles coated chitosan nanobiocomposites encapsulated in alginate have been used for adsorption of atrazine. Live *S. cerevisiae* as well as thermal inactivated *S. cerevisiae* were

TABLE-3
REMOVAL OF PESTICIDES MEDIATED BY NANOCOMPOSITES

Chemical presentation	Pesticide	Mechanism	Pesticide removal	Ref.
TiO_2/GO/$CuFe_2O_4$	Dichlorodiphenyl-dichloroethylene	Photocatalytic degradation	96.5%	[28]
BEA Zeolite and polyaniline	Nicosulfuron	Adsorption	18.4 mg/g	[83]
Silica/Polyaniline	Chloridazon	Adsorption	30.0 mg/g	[1]
12-Tungstophosphoric acid/BEA zeolite	Nicosulfuron	Adsorption	25.8 mg/g	[76]
Polyethylenimine capped CuO/montmorillonite	Atrazine	Photocatalytic degradation	95.6%	[14]
Reduced graphene oxide–silver	Chlordane	Photocatalytic degradation	100%	[84]
Graphene oxide-zirconium	Glyphosate	Adsorption	482.6 mg/g	[8]
Fe_3O_4/graphene	Ametryn	Adsorption	93.6%	[81]
Fe_3O_4/graphene	Prometryn	Adsorption	91.3%	[81]
Fe_3O_4/graphene	Simazine	Adsorption	88.5%	[81]
Fe_3O_4/graphene	Simeton	Adsorption	81.2%	[81]
Fe_3O_4/graphene	Atrazine	Adsorption	75.2%	[81]
Graphene oxide-Ag	Chlorpyrifos, endosulfan & DDE	Adsorption	100%	[42]
CuO-Montmorillonite	Monocrotophos	Adsorption	40.8%	[94]
TiO_2/Zeolite	Dichlorvos	Photocatalytic degradation	100%	[85]
$CoFe_2O_4$@TiO_2 decorated reduced graphene oxide	Chlorpyrifos	Photocatalytic degradation	96.0%	[80]
Reduced graphene oxide–silver	Lindane	Photocatalytic degradation	100%	[58]
C/ZnO/CdS	4-Chlorophenol	photocatalytic degradation	100%	[55]
CuO-Montmorillonite	Dichlorvos	Adsorption	83.2%	[86]
ZnO/γ-Fe_2O_3	2,4-Dichlorophenoxyacetic acid	Photocatalytic degradation	55.2%	[79]
ZnO/γ-Fe_2O_3	2,4,5-Trichlorophenoxyacetic acid	Photocatalytic degradation	57%	[79]
ZnO/γ-Fe_2O_3	Peracetic acid	Photocatalytic degradation	47.1%	[79]
ZnO/γ-Fe_2O_3	4CA	Photocatalytic degradation	59.4%	[79]
Au/ZnO	Malathion	Photocatalytic degradation	79.0%	[57]
Au/TiO_2	Malathion	Photocatalytic degradation	81.0%	[57]
Poly-*o*-toluidine Zr(IV) phosphate	2,4,5-Trichlorophenoxy acetic acid	Adsorption	1.2 mg/g	[7]
β-Zeolite-ZnO	Monocrotophos	Photocatalytic degradation	14.9 mg/g	[82]
TiO_2/β-Zeolite	Monocrotophos	Photocatalytic degradation	100%	[78]

employed for this purpose. Nanobiocomposites containing live yeast exhibited 88% removal of pesticide at pH 7.0 at 25 ºC and initial atrazine concentration of 2 ppm as compared with nanobiocomposites containing inactivated yeasts [92]. Similar study was conducted using *Pseudomonas* sp. strain ADP adsorption onto LDH [93]. In another study, montmorillonite and copper oxide nanoparticles coated chitosan, gum ghatti and poly lactic acid were evaluated for monocrotophos removal from aqueous environment. Polymer matrix enhanced the surface area and also provided active sites exposed with multiple functional groups that favoured the maximum adsorption of pesticide [94]. Similarly, zinc and silver nanoparticles embedded in chitosan have been used as adsorbents to remove permethrin [95] and atrazine [96], respectively. A novel single layer graphene oxide (GO)-magnetic iron (Fe_4O_3) nanoparticles have been developed for the removal of neonicotinoid pesticides where β-cyclodextrin (β-CD) has been used as a biopolymer matrix. The synthesised GO- Fe_4O_3-β-CD showed of 2.8 mg/g adsorption of imidacloprid followed by acetamiprid (2.9 mg/g), thiamethoxam (2.8 mg/g), clothianidin (2.8 mg/g), nitenpyram (2.5 mg/g) and dinotefuran (1.7 mg/g). A further investigation of neonicotinoid pesticides removal from spiked (0.1, 0.2 and 0.5 mg/L) tap water with showed complete adsorption of pesticide ions. High surface area of GO-biopolymer and superparamagnetism of Fe_4O_3 nanoparticles enabled the rapid removal of pesticides from aqueous medium suggesting the employability of nanobiocomposite in remediation of pesticides from environmental waters [97]. The removal of pesticides mediated by various kind of nanobiocomposites are tabulated in Table-4.

Conclusion

The applications of nanomaterials are quite interesting and encouraging. The widespread exploitation of nanomaterials in the form of nanoclays, nanoparticles, nanocomposites and nanobiocomposites for adsorption and degradation of numerous pesticides suggested their higher efficiency than the conventional methods. Till now, numerous nanomaterials are available for environmental applications and currently fabrication of these nanomaterials into suitable biopolymers is still a topic of high interest. In addition, further insights into the compatibility and interplay of nanomaterials in nanocomposites and nanobiocomposites are still required. Certainly, the interaction between the target contaminant and nanomaterials should be further revealed with the help of sophisticated analytical tools like atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray absorption spectroscopy (XAS), which may give further insights into the underlying mechanism, at micro scale level.

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TABLE-4
REMOVAL OF PESTICIDES MEDIATED BY NANOBIOCOMPOSITES

Chemical presentation	Type of bio-support	Pesticide	Mechanism	Pesticide removal	Ref.
Polyaniline nanoparticles	Barley husk	2,4-dichlorophenol	Adsorption	24.5 mg/g	[88]
Iron oxide nanoparticles	*S. cerevisiae*-Chitosan-Alginate	Atrazine	Adsorption	88.0%	[92]
Magnetic iron nanoparticles	Laccase	Chlorpyrifos	Enzyme-based catalysis	99.0%	[90]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Thiamethoxam	Adsorption	2.8 mg/g	[97]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Imidacloprid	Adsorption	3.1 mg/g	[97]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Acetamiprid	Adsorption	2.9 mg/g	[97]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Nitenpyram	Adsorption	2.5 mg/g	[97]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Dinotefuran	Adsorption	1.7 mg/g	[97]
Magnetic-graphene oxide nanoparticles	β-Cyclodextrin	Clothianidin	Adsorption	2.8 mg/g	[97]
$LaNiO_3$ nanoparticles	Carboxy methyl cellulose	Dichlorvos	Adsorption and photocatalytic degradation	100%	[40]
Montmorillonite-CuO nanoparticles	Chitosan	Monocrotophos	Adsorption	71.6%	[94]
Montmorillonite-CuO nanoparticles	Gum ghatti	Monocrotophos	Adsorption	62.1%	[94]
Montmorillonite-CuO nanoparticles	Poly lactic acid	Monocrotophos	Adsorption	83.9%	[94]
Montmorillonite-CuO nanoparticles	Chitosan	Dichlorvos	Adsorption	93.4%	[89]
Montmorillonite-CuO nanoparticles	Gum ghatti	Dichlorvos	Adsorption	87.8%	[89]
Montmorillonite-CuO nanoparticles	Poly lactic acid	Dichlorvos	Adsorption	63.4%	[89]
ZnO nanoparticles	Chitosan	Permethrin	Adsorption	99.0%	[95]
Iron nanoparticles	Carboxy methyl cellulose	Lindane	Photocatalytic degradation	95%	[45]
Montmorillonite (SWy-2)	Chitosan	Clopyralid	Adsorption	55.0%	[86]
Montmorillonite (SWy-2)	Chitosan	Clopyralid	Adsorption	38.0%	[86]
Cu	Chitosan	Parathion	Adsorption	100%	[87]
Cu	Chitosan	Methyl parathion	Adsorption	100%	[87]
Mg_RAl Layered Double Hydroxides	*Pseudomonas* sp.	Atrazine	Adsorption	100%	[93]
Ag	Chitosan	Atrazine	Adsorption	98.0%	[96]

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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