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Remediation of Pesticides using Nanomaterials : An overview

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Abstract: An intensive use of pesticides in agriculture has caused serious health and environmental problems. Various adsorbents and photocatalysts have been used for the remediation of pesticides from aqueous environment. In recent years, nanomaterials viz. nanocomposites and nano-biocomposites are playing a promising role towards the removal of pesticides. The present review focuses the updated information on pesticide removal using nanocomposites and nano-biocomposites through adsorption and photocatalytic degradation.
Keywords: Adsorption, nano-biocomposites, nanocomposites, photocatalytic degradation, pesticides.

1. Introduction

Leaching and persistence of chemical pesticides are the main reasons for the organic pollution in the environment[1]. Industrial wastewaters are also the significant sources of the pesticide pollution in aquatic system which is a great threat to general public health due to their high toxicity. Several approaches such as oxidation, fluid-extraction, biodegradation, ozonation, chlorination, and membrane separation were reported for the removal of pesticides from aquatic environment[2,3]. However, these techniques do not lead to the complete removal of pesticide and further treatments are needed to convert the pesticides into harmless products such as CO_2 and H_2O[4]. Hence, there is a need to develop efficient techniques which should be cost effective and eco-friendly offering high removal rates.

Adsorption has emerged as the most efficient, simple and promising fundamental technique in the waste water treatment process which certainly aims for the removal of organic pollutants[5].

In recent years, heterogeneous photocatalysis using a semiconductor and photon energy has been emerged as a new approach for the degradation of organic pollutants. It is based on the principle that when a semiconductor is exposed to a light source of particular wavelength, the electrons from valence band are promoted to the conduction band leaving the positive holes. The generated electron-hole pairs moves to the surface of semiconductor and degrades the organic pollutants into nontoxic products[6,7,8].

The impacts of nanotechnology are evident in all areas including the field of environmental studies and treatments. Nanoparticles being nano-sized exhibit advanced characteristics based on their properties such as size, morphology and other size dependent properties[9]. Due to the advanced properties, nanoparticles have been employed in water treatment systems[10].

With the recent developments in the field of nanotechnology, the correlation of material properties with filler size has become a point of great interest. Nanocomposites based on metallic nanoparticles have witnessed an exponential growth in the field of nanotechnology. They have also emerged as suitable alternatives to overcome the limitations of microcomposites and monolithics. The unique properties derived from the nano-composites can be exploited in various fields of science and technology[11].

In addition, biopolymers have also attracted a lot of research attention being nontoxic, low cost and eco-friendly. The physio-chemical characteristics of biopolymers favour the adsorption process in removal of various environmental pollutants. Based on the manufacturing process, biopolymers are classified into two categories viz. natural polymers and synthetic polymers. The natural polymers include polysaccharides (e.g. cellulose, chitosan, gums, alginate, agar, starch etc.) and some proteins from plant and animal origin. The synthetic polymers include polyhydroxy alkonates, poly vinyl alcohol, poly lactic acid, poly glycolic acid etc. However, the industrial performances of biopolymers are generally limited by the low thermal stability, poor mechanical and barrier properties[12]. To overcome the above disadvantages associated with biopolymers, a unique approach of incorporation the nanofillers into biopolymer matrix was introduced to improve their mechanical, barrier properties and thermal stability[13]. These 'nano-biocomposites' have received increasing attention as potential adsorbents towards reducing environmental pollution which incorporates the advantages of both biopolymers and nanoparticles. This article gives a brief overview on application of nanocomposites and nano-biocomposites towards the removal of pesticides from aqueous environment.

2. Adsorbents and photocatalysts for pesticides removal

A wide range of adsorbents for the removal of various pesticides have been reported in the literature which includes agricultural waste such as rice husk[14] and ground net shell[15]; carbonaceous materials *viz.,* activated carbon[16,17]; clay minerals such as zeolite[18,19], montmorillonite[20], bentonite [20], calcite[21], kaolinite[21]. In addition, biopolymers *viz.,* chitosan[22,23] and alginate[23] were also employed in the adsorption of pesticides.

Nanomaterials including silver[3], titanium dioxide[24], zinc oxide[25] were used as photocatalysts for the heterogeneous degradation of pesticides.

3. Nano-composites

Nanocomposites are prepared by reinforcing the nano sized inclusion (nanofiller) into the material which aims to improve the optical, catalytic, mechanical, magnetic, thermal, barrier and other properties. Depending on the type of nanofiller used, the nanocomposites could show the drastic modifications in their properties. Nanofillers are generally classified into three types based on their geometry and aspect ratio: Layered silicates (e.g. clays), spherical (e.g. silica) and acicular (e.g. CNT). At present, layered silicates are most widely studied due to the ease of availability, versatility and eco-friendly nature[26].

Based on the type of matrix used, the nano-composites are divided into three categories viz. Ceramic matrix nano-composites (e.g. Al_2O_3/SiO_3, SiO_2/Ni), Metal matrix nanocomposites (e.g. Co/Cr, Fe/MgO) and Polymer matrix nanocomposites (e.g. polyester/TiO_2). All the three categories of these nanocomposites have been exploited in field of environmental science where the applications are mainly focused on the removal of inorganic and organic pollutants from aqueous environment [27].

Anandan et al[28] reported the preparation of ZnO/clay nanocomposites of different concentrations of ZnO and three different H-form of zeolites such as Y, β and ZSM-5 that differs in Si:Al ratios and their applications towards pesticide degradation. The results showed complete degradation of monocrotophos by ZnO/Hβ at 5 % loading of ZnO. Similarly, Fe/zeolite and TiO_2/zeolite nanocomposites were reported to show the complete removal of methomyl, monocrotophos and dichlorvos through photocatalytic degradation mechanism[29,30,31]. A polymer matrix nanocomposite was prepared by Jing et al.[32] using polystyrene and Fe_3O_4 nanofillers by in-situ polymerization method to investigate the efficiency of polystyrene in removal of organochlorine pesticides through adsorption mechanism. The nanocomposites exhibited the lower uptake of aldrin, endrin and lindane pesticides in batch studies and the performance of polymer matrix nanocomposites was low when compared with other alternatives. However, they could show the better performance in removing the ng ml^{-1} level of pesticides from contaminated water.

The applications of nanocomposites for pesticides removal are summarized in Table 1.

Table 1. Nano-composites used for the removal of pesticides

Pesticide Group	Target pesticide	NPs	Support	Mechanism of removal	Removal	Reference
Carbamate	methomyl	Fe	Zeolite	Photo catalytic oxidation	100 %	29
Organo Chlorine	Aldrin	Fe_3O_4	Poly styrene	Adsorption	24.7 mg g^{-1}	32
	Endrin	Fe_3O_4	Poly styrene	Adsorption	33.5 mg g^{-1}	32
	Lindane	Fe_3O_4	Poly styrene	Adsorption	10.2 mg g^{-1}	32
	Di and tri Chlorophenoxy acetic acid	ZnO/γ-Fe_2O_3	-	Photo catalytic degradation	55.2 and 57.0 %	33
	4-Chloro phenol	C/ZnO/ CdS	-	Photo catalytic degradation	98.0 %	8
	Lindane	Ag	Reduced graphene oxide	Degradation	99.9 %	34
Organo Phosphate	Monocrotophos	TiO_2	Zeolite	Photo catalytic degradation	100 %	31
		ZnO	Zeolite	Photo catalytic degradation	100 %	28
	Malathion	Au/TiO_2	-	Photo catalytic degradation	30.0 %	35
	Chlorpyrifos	$CoFe_2O_4$ @TiO_2	Reduced graphene oxide	Photo catalytic degradation	89.9 %	36
	Dichlorvos	CuO	MMT	Adsorption	83.2 %	37
		TiO_2	Zeolite	Photo catalytic degradation	100 %	31
Pyridazino ne	Chloridazon	Au/TiO_2	-	Photo catalytic degradation	50.0 %	35

4. Nano-biocomposites

Nano-biocomposites are the new class of composite materials where nanofillers are incorporated into biopolymer matrix using various techniques. The incorporation of appropriate nanoparticles into biopolymers will provide special properties which can be used for wide range of both conventional and emerging applications. The hydrophilic nature of biopolymers makes them potential adsorbents for remediation of pollutants from aqueous environment. Use of biopolymers is an innovating answer to replace the conventional and durable synthetic polymers[13].

The three major techniques involved in the incorporation of nanofiller into the polymer matrix are (i) in-situ polymerization, (ii) solvent intercalation and (iii) melt intercalation process. In in-situ polymerization, the polymerization of monomer solution is initiated in presence of layered silicates which increases the molecular weight of layered silicates showing fully exfoliated morphology. The solvent intercalation method involves the solvent in which the biopolymers are soluble. The biopolymer is added to an appropriate solvent followed by the nanofiller. Then, both the systems are pooled together leading to a polymer chains intercalation. This method is used to produce nano-biocomposites of polysaccharide/nanofiller and proteins/nanofiller. In melt intercalation process, both nanofiller and biopolymer are introduced simultaneously to the mixing system. This method is widely adopted due to its simplicity[13].

Saifuddin et al.[38] demonstrated the synthesis of Ag/chitosan nano-biocomposite by melt intercalation process in which both silver nitrate solution and chitosan solution was mixed together and subjected to microwave irradiation. The reduction of silver nitrate was noticed when exposed to irradiation thereby leading to the formation of Ag nanoparticles. Thus, the synthesised Ag/chitosan nano-biocomposite showed the higher removal of atrazine pesticide in column mode. Similarly, the chitosan based nano-biocomposites were proved to show the higher removal of organophosphate pesticides[2,39]. Preparation of nano-biocomposites using two nanofillers along with biopolymers and their applications on removal of dichlorvos has been reported recently by Sahithya et al[37]. Higher removal of dichlorvos by CuO-montmorillonite-chitosan and CuO-montmorillonite-gum ghatti nano-biocomposites suggested that biopolymers can play major role in the adsorption of pesticide. Reports are scanty on the use of nano-biocomposites on pesticide removal.

Table 2 summarizes the applications of nano-biocomposites on pesticides removal.

Table 2. Applications of nano-biocomposites for removal of pesticides

Pesticide group	Target pesticide	NPs	Biopolymer matrix	Mechanism of removal	Removal (%)	Reference
Organo phosphate	Malathion	CuO	Chitosan	Adsorption	99.9	2
	Dichlorvos	CuO-MMT	Chitosan	Adsorption	93.4	37
		CuO-MMT	Gum ghatti	Adsorption	87.8	37
		CuO-MMT	Poly lactic acid	Adsorption	63.3	37
Pyrethroid	Permethrin	ZnO	Chitosan	Adsorption	99.0	39
Triazines	Atrazine	Ag	Chitosan	Adsorption	94.0	38

5. Conclusion

This review presents the applications of nano-composites and nano-biocomposites towards the removal of pesticides from aqueous environment. The reported performances of nano- composites on pesticide removal are quite encouraging. Since industries are concerned with sustainable developments, and the production cost of biopolymers is decreasing, strong developments of biopolymers-based nano-biocomposites is needed in near future. Extensive research should be carried out to promote the large scale use of nano-biocomposites for the effective removal of pesticides from wastewater.

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