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Carbon-based nanomaterials with multipurpose attributes for water treatment: Greening the 21st-century nanostructure materials deployment

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REVIEW ARTICLE

ABSTRACT

Nanotechnology is a top priority research area in a plethora of technological and scientific fields due to its economic impact and versatile capability. Among various applications, water treatment is considered among the most prospective utilization of nanotechnology, where a large number of nanostructured materials can remediate water using several different mechanistic ways. For achieving this, nanomaterials can be combined and modified with active moieties to develop different nanocomposites with structural diversity and unique physicochemical attributes. In addition, they have also been designed and integrated into membranes for improving water treatment performance. In this review, we provide an up-to-date overview of various nanostructured materials as nanoadsorbents, such as carbon-based nanomaterials, nanocomposites, and nanomembranes for remediating pesticide-based pollutants from aqueous systems using CNTs. Notably, nanomaterials are capable of efficiently removing environmental pollutants given their substantial surface area, high absorptive ability, and excellent environmental selectivity and compatibility.

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Introduction: Nanomaterials in water treatment

Nanotechnology has become a useful emerging technology in the past few decades. Researchers have employed nanomaterials to remove pesticides, toxic metals, pharmaceutical contaminants, organic compounds, and some other types of pollutants from the aquatic ecosystem (Ahmaruzzaman, 2019). Nanoadsorbents are nanoscale particles that are made up of inorganic or organic compounds and possess high power to adsorb substances on themselves. Nanoadsorbents possess certain characteristics due to which they can aggregate the pollutants with different sizes of molecules, hydrophobicity and these characteristics include small size, more numerous pores, and the active surface of nano adsorbents (Aguilar-Pérez et al., 2020; Zeb et al., 2020; Aguilar-Pérez et al., 2021; Rasheed et al., 2021). They also make manufacturing plants to be capable of using raw materials without releasing their hazardous freight (Pacheco et al., 2006). They have considerable pollutant-binding capacities and work expeditiously. They can also be regenerated chemically after being impoverished (Yang and Xing, 2007). Due to their small size, nanomaterials show unique characteristics, such as they possess much surface area and a large surface-to-volume ratio (Hristovski et al., 2007). Such properties of nanomaterials, including carbon nanotubes (CNTs), metal organic frameworks (MOFs), nanohybrids, MXene; graphene, and metallic nanoparticles increase their applied potential in different sectors of the modern world (Bilal et al., 2020; Zhao et al., 2021; Zhang et al., 2021; Gan et al., 2022). Properties like catalytic potential and high reactivity of nanoparticles improve their adsorption capacity as a result, they become good adsorbing materials than general materials. Due to the huge surface area, they possess numerous numbers of active sites to interact with various types of chemical species. So, nanoparticles are becoming the best alternatives to eradicate the contamination from wastewater (Santhosh et al., 2016). In our ecosystem, water pollution has become one of the most hazardous issues due to many pollutants, including pesticides, endocrine disruptive estrogens, and others (Bilal et al., 2021; González-González et al., 2022; Reyes-Calderón et al., 2022). Numerous methods such as floatation, flocculation, coagulation, electrochemical methods, precipitation of chemicals, adsorption, ion exchange, membrane filtration, etc., have been developed to remove these pollutants.

Metal nanoparticles possess the property of localized surface plasmon resonance (LSPR). With the help of this characteristic, these metallic nanoparticles can detect a variety of analytes (Sabela et al., 2017); also because of this special feature the colloidal nanoparticles show a high coefficient of extinction due to which they show a range of different colors in the visible spectral region (Ullah et al., 2018). The properties of the nanoparticles depend upon their size and shape. In this technique the colloidal NP's show color change with target particles. The most actively used nanoparticles for colorimetric detection are AuNPs and AgNPs. demonstrates the colorimetric detection mechanism using silver (AgNPs) and gold nanoparticles (AuNPs). In this process when the nanoparticles interact with the shift from wellspaced colloidal to the accumulated one, which graphically detects the pesticides in the sample under study. the nanoparticles show specific color changes as the silver nanoparticles turn brown-red from yellow and, the gold nanoparticle solutions show color change from wine red to a dark blue. Furthermore, the quantitative analysis of the concentration of these pollutants is done by using a UV/VIS spectrophotometer, and DLS and TEM techniques are used for the authentication of the process of aggregation. The colorimetric technique is considered more sensitive because the nanoparticles interact with the target through donor-acceptor and ligand exchange reactions, also by covalent and hydrogen bonding (Singh et al., 2020).

Nanoadsorption attributes

This is the simplest, easily manageable, inexpensive, and efficient method where a solid surface is used to adsorb the pesticides (Ali, 2012). The adsorption process depends upon surface morphology, sorbent's dose, and size, sorbate's structure, and concentration, temperature, and pH (Ali and Gupta, 2006). Many NPs are used as adsorbents such as nano zinc oxide, nano titanium oxide, and nanochitosans (Tan et al., 2015), which enhance the adsorption capacity and efficiency in removing the hazardous waste from water. The nano adsorbents are subdivided into two major carbon-based categories, and non-carbon derivatives nano adsorbents. The carbon-based nanomaterials like the carbon nanotubes, fullerenes, graphene, graphene oxides, and activated carbon are considered more efficient and eco-friendlier than the other nanoparticles which are metal oxides and metal-based adsorbents having no carbon. Benefits of carbon derived nanoadsorbants are that the activated carbon is easily available through the waste agricultural streams, and also through biomass sources. These NP's are cheaper and can be used at the nanoscale in adsorption. These adsorbents have enhanced adsorption capacity and a high rate of adsorption. On the other hand, the non-carbon derived nano adsorbents (metals and metal oxides) require a long process for their production and they are more expensive and are not easily available. The adsorption system designed for pesticide mitigation deals with some important relationships between these pollutant's residual concentrations in solution at equilibrium and adsorbed pollutant per unit weight of sorbent. To explain this relationship different models are proposed. The most important models proposed in this field for explaining the results of adsorption are Temkin, Langmuir, Hasley, BET, Dubinin-Radushkevich, Harkins-Jura model, Redlich-Peterson, Lagergren, and intraparticle diffusion (Hussain et al., 2021). These models also explain different thermodynamic parameters like Gibb's free energy, heat of sublimation, and change in entropy. This method is considered as the simplest and the useful way which is also used to remove organic and inorganic pollutants in water as it requires low cost for working, efficient, and also versatile for a variety of water systems (Qu et al., 2013). The nano-adsorbents have several qualities that's why these particles enhance the efficiency of the adsorption system, some of these qualities areas (Wang et al., 2012), non-hazardous, infinite recyclability, desorbability, selectivity towards low concentrations, and high adsorption capacity. A large variety of nanocomposites like magnetic metal-organic composites, adsorbents made of carbon, and metal oxides are now being used for removing the great amount of co-existing organic and inorganic pollutants (Kyriakopoulos et al., 2006). Carbon-based materials, metal oxide-based materials, nanocomposites, etc. are some of the types of nanomaterials that are employed to remove pesticides from wastewater.

Carbon-based nanomaterials - multipurpose attributes

Carbon-based nano adsorbents show thermal stability and proved themselves as excellent adsorbents to remove pesticides, inorganic and organic contaminants among various nanomaterials-based adsorbents (Santhosh et al., 2016). Since the invention of carbon nanotubes (CNTs) and fullerene, nanomaterials have considerably employed as many effective adsorbents as possible but their application on large is not on a wide range on economic grounds. So, it is a great challenge to design the adsorbents at a lower cost. Multi-walled carbon nanotubes proved their efficiency with the help of magnetic materials for the effective removal of various contaminants (Yang et al., 2006).

Carbon nanotubes (CNTs): These are taken as many different structures as possible of carbon and one of the allotropes of carbon elements. These carbon nanotubes are made up of cylindrical shapes that roll up in tube form. CNTs are divided into two categories i.e., Single-walled CNTs (SWCNTs) and Multi-walled CNTs (MWCNTs). Single-walled CNTs consist of a single roll-up of graphene sheets while multi-walled carbon nanotubes consist of multiple roll-ups of graphene sheets (Mubarak et al., 2014; Santhosh et al., 2016), as shown in Figure 1. CNTs contain the excellent capability of sorption and have high sorption efficiency than general activated carbon, which is in the granules or powdered form, that possess intrinsic limitations like an active site on the surface and have an activation energy of sorption (Santhosh et al., 2016). It has been realized after studying vast, that capacity of adsorption of carbon nanotubes relies on two main things that are nature of sorbate that is being used and its surface functional group. For example, the quantity of carboxylic acid, phenolic acid, and lactonic acid on the surface favor adsorption of polar compounds (Wang et al., 2008), while un-functionalized carbon nanotubes like polycyclic aromatic compounds have excellent adsorption capacity to adsorb non-polar compounds (Stafiej and Pyrzynska, 2008). SWCNTs exhibit a strong attraction to adsorb many organic compounds as they have massive surface area. However, the high cost in the application of SWCNTs is a disadvantage in adsorption technologies. But as compared to SWCNTs, MWCNTs are low in cost but they have one disadvantage that they possess low adsorption decreases capacity which their potential applications. Scientists modified the multi-walled CNTs in such a way that they can modify the adsorption capacity of MWCNTs for a variety of organic compounds. MWCNTs can also improve by doing the selective functionalization process (Singh et al., 2018).



Figure 1. Structural and characteristic representation of (a) SWCNTs and (b) MWCNTs. Created with BioRender.com and extracted under premium membership.

The different types of contaminants such as pesticides can be removed from aqueous systems using CNTs as adsorbents (Chen et al., 2011; Taghizade Firozjaee et al., 2018). In the agricultural field, the most used organophosphorus pesticide is diazinon. It can easily reach the surface water and groundwater damaging the plant and animal biodiversity. The eradication of diazinon pesticides from water with the help of MWCNTs was studied. It was concluded from the study that diazinon pesticides can be efficiently removed from aqueous systems using MWCNTs as adsorbents (Dehghani et al., 2019). Using multiwalled carbon nanotubes, the removal of one of the other organophosphorus pesticides such as malathion from aqueous solutions has been studied. Various factors were kept in view while removing the maximum amount of malathion pesticides such as pH, temperature, time of contact, amount of nano adsorbent, and pesticide to get better results. It was shown that for the 100% removal of malathion, the concentrations of pesticide and malathion were 0.5 g/L and 6 mg/L, respectively. The results of this experiment confirmed the 100% removal of malathion pesticides from water using optimized conditions (Dehghani et al., 2017).

The eradication of dichlobenil and diuron from polluted water was reported using muti-walled carbon nanotubes. They followed the Polanyi Manes model and showed high adsorption on nanotubes at pH 6. The adsorption of both diuron and dichlobenil on the oxidized multi-walled carbon nano adsorbents from the water was studied. They showed the pseudo 2nd order kinetic model and also the Polanyi Manes model. The adsorption of these pesticides was high because of the large surface area and high pore volume of the oxidized MWCNTs (Deng et al., 2012). These modified nanotubes were used as solid-phase extraction nano adsorbents for the investigation of seventy-eight different residues of pesticides. These pesticides were then undergone detection through gas chromatography and mass spectrometry after extraction (Hou et al., 2014). The removal of 8

different types of organophosphorus pesticides from the water was investigated using MOF-ZIF-8/ magnetic MWCNTs. Based on adsorption isothermal models, the characterization and adsorption capacity of MWCNTs were noted (Liu et al., 2018). The extraction of carbamate pesticides with the help of carbon nanotubes modified with liquid ionic polymer by using the same type of extraction method (Hou et al., 2014). The carbon nanotubes were used as adsorbents for the removal of dicamba from water because it is acidic. The detection limit of dicamba was analyzed as 2 micrograms per liter in river water in favorable conditions. The efficient detection of metasulfuran and chlorosulfuran in aqueous solutions was studied with the help of capillary electrophoresis and MWCNTs under optimized conditions (Springer and Lista, 2010). The SWCNTs were investigated to have high adsorption capacity as compared to MWCNTs and other nanosized metal oxides such as alumina, zinc oxide, and titanium oxide for methyl phenoxy acetic acid herbicide from the water. The results showed that the adsorption method was exothermic and fast and followed the pseudo 2nd order kinetic model (De Martino et al., 2012). Indeed, carbon nanotubes possess contain a high potential as efficient adsorbents for removing pesticides and other contaminants from an aquatic system, but their practical use is restricted due to their relatively high cost. Chemically functionalized CNTs are not toxic but raw carbon nanotubes contain some toxicity because of the presence of a metal catalyst. Therefore, there is a need to do more research for a practical and economic solution for practicing carbon nanotubes in contaminated water treatment (Santhosh et al., 2016).

Graphene-based nanomaterials: a unique allotropic form of carbon named graphene was examined by the researchers which can also be used for the removal of pesticides (Santhosh et al., 2016). These graphene-based materials have brilliant electrical, mechanical, and thermal characteristics with excellent 2-D structures. It is made up of multi-layers of atomic carbon (Shahryari-ghoshekandi and Sadegh, 2014). Graphene-based materials are extensively used for the past few decades for the removal of pollutants from the environment. They possess many advanced properties which help in increasing the efficiency of the methods used for the purification of the ecosystem (Santhosh et al., 2016). Many researchers work on the oxides of graphite, as they are used as the cheap initiators for the production of nanomaterials based on graphene. Because of their unique character, these nanomaterials are used in different fields of science. The structure of their oxides highly resembles the layered structure of graphite. Both of them only differ in the carbon atom plane as there is the extreme saturation of groups containing oxygen atoms in the case of graphite oxides. Under normal ultra-sonication, these oxides exfoliate underwater. These sheets having one or a few more carbon atom layers will form graphene oxides. Nowadays, graphene and its oxides are considered more useful adsorbents for the removal of toxic contaminants from water (Kyzas and Bikiaris, 2015).

The graphene-based adsorbents are considered the best treatment for wastewater and also the ideal replacement for CNT's. Their use as an adsorbent provides many benefits as compared to CNTs (Rao et al., 2007; Stafiej and Pyrzynska, 2007; Zhao et al., 2014). The first advantage is that the graphene material with a single-layer structure specially designed for the adsorption in plants mainly consists of 2 basal planes. While on the contrary, the inner walls of CNTs are not accessible by the adsorbate. Secondly, the graphene its oxides, and reduced oxides can be prepared easily through chemical exfoliation of graphite, even in the absence of any metal crystal and complicated apparatus. Resultantly, the graphene material that is formed has no catalytic wastes, and also this manufacturing step doesn't need purifications (Zhao et al., 2011). Graphene oxides are used for the mitigation of the pesticides present in water. The adsorption of pesticides through graphene and its oxides has been studied. The results greatly explained the interactions between pesticides and graphene nanomaterials. The adsorption capacity of graphene ranges from 600-2000 mg/g against various pesticides. The eradication of assiduous halocarbon pesticides from aqueous systems was also studied (Sen Gupta et al., 2015). The adsorption of various pesticides is done through π - π bonding of graphene nanomaterials with aromatic compounds (Björk et al., 2010; Smith and Rodrigues, 2015). To enhance the adsorption capacity of pesticides, graphene nanomaterials can be combined with other different materials (Liu et al., 2013; Mahpishanian et al., 2015). The graphene-coated with silica can be used as an effective adsorbent to remove the residues of organophosphorus pesticides (Liu et al., 2013). By functionalizing magnetic graphene oxide with aminoguanidine, graphene-based nano adsorbents had been prepared for the effective removal of chlorpyrifos pesticide from agricultural contaminated water (Mahdavi et al., 2021). Similarly, another graphene-based adsorbent was synthesized by functionalizing it with magnetic NPs of iron oxide for the eradication of glyphosate (N- phosphonomethyl glycine) herbicide from the water. The adsorption capacity for glyphosate was noted to be 46.8 mg/g and followed pseudo 2nd order and Langmuir model (Santos et al., 2019). The composite materials are formed by the mixing of the nanosheets of graphene and its oxides. The metal oxides and graphene oxide composites are unique and act as efficient adsorbents in the mitigation of pesticides. In summary, Figure 2 shows carbon-based nano adsorbents to treat environmental pollunats of emerging concern.



Figure 2. Carbon-based nano adsorbents to treat environmental pollunats of emerging concern. Created with BioRender.com and extracted under premium membership.

Nanoparticles and nanocomposites

The efficiency of nanoparticles in real wastewater treatment can be improved by permeating them into particularly polymers to achieve matrices nanocomposite adsorbents (Pan et al., 2009). Nanocomposite has their application in the wide sector including water purification. The removal of pesticides can be improved by modifying the magnetic properties of nanoparticles by using functionalized polymer (Bhaumik et al., 2011a). Polypyrrole-based nanocomposite has been widely used (Bai et al., 2015). To formulate a magnetic polypyrrole nanocomposite, it is coated onto Fe₃O₄. These magnetic materials can be easily separated by applying an external magnetic field and need no other additional process. Polypyrrole magnetic nanocomposite coated with Fe₃O₄ is described to act as an efficient adsorbent (Bhaumik et al., 2011b). The researcher proposes a method for manufacturing cross-linked nanocomposite films of polyvinyl alcohol that are intermixed with functionalized multi-walled carbon nanotubes at varying concentrations. As multi-walled carbon nanotubes have some drawbacks such as poor surface chemistry, nonflexibility, poor water solubility, and their failure to form film composite by themselves, to overcome these limitations they are modified by mixing them with polyvinyl alcohol so that their applications in the environment can be enhanced and improved. So, after mixing, both form hydrophobic films which can capture pesticide, bacteria, and fungi from wastewater with good recyclability.

It is reported that bentonites and their modified nanocomposites can efficiently remove inorganic pesticides from drinking water. They proved to be a better adsorbent as compared to existing commercial adsorbents in most cases. As they are present in nature abundantly so it makes them low cost, green, non-toxic adsorbents so they can be widely employed for the mitigation of various pollutants and thus providing pure drinking water for developing and developed (Pandey, 2017). Nanosized tungsten (WOx) is a multifunctional material and has many structures such as nanonanowires, hollow nano-spheres, plates, hierarchical flowers and nano-discs (Zhang et al., 2017). To eradicate pesticides from contaminated water, hierarchical porous ZnO-Al₂O₃ composites were used as adsorbents. The efficiency of the ZnO- Al₂O₃ composite depends on its composition and microstructure. These composites show higher adsorption performance as compared to pure ZnO and Al₂O₃. Hierarchically porous nickel-iron layered double hydroxide (NiFe-LDH) was also reported as an effective adsorbent. The researcher prepared the nanocomposite based on acrylic acid monomer and sodium alginate with varying concentrations of xonolite or calcite by irradiating with gamma rays. These nanocomposites were characterized by employing different techniques such as Scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The calcite and xololite were added to enhance the swelling capacity of hydrogel nanocomposite. This prepared nanocomposite was employed for the effective eradication of methomyl pesticides. The study reveals that the removal of methomyl by using the above nanocomposite is pH-dependent. The summary of various types of nanomaterials for the removal of pesticides is given in Table 1.

Nanomaterials/ composites	Pesticides	Adsorption/removal amount	References
Iron oxide	Organochlorine pesticides	Adsorption capacity of; Lindane= 10.2 mg/g Aldrin= 24.7 mg/g Endrin= 33.5 mg/g Dieldrin= 21.3 mg/g Removed in less than 20 minutes	(Rahmanifar and Dehaghi, 2014)
Zero valent metals(ZVI)s	Imidacloprid and Thiamethoxam	Removal efficiency more than 90%	(Lopes et al., 2008)
Titanium oxide	Dicofol	Removed in 2 hours completely	(Yu et al., 2008)
CNTs	Atrazine	More than 90%	(Yan et al., 2008)
Alumina	Fenitrothion, diazinon	Removal capacity within 24 hours of	(Armaghan and Amini,

		fenitrothion= 57% diazinon= 90%	2012)
ZnO	Permethrin	Almost 99% of pesticide is removed at neutral pH	(Dehaghi et al., 2014)
Iron oxide	organophoposrous	Almost 80%	(Shen et al., 2007)
Iron-palladium bimetal nanoparticle	Organochlorine lindane	Removed efficiently about 100 % in reduction method	(Joo and Zhao, 2008)
Alumina	Dimethyl methyl- phosphonate	Adsorption capacity= 775 µg/g	(Mitchell et al., 2004)
Iron metal	Dichloro-diphenyl trichloroethane	Completely degraded	(El-Temsah and Joner, 2012)
Cu metal	Endosulfan	Destroyed 100% in water	(Rani and Shanker, 2018)
Titanium oxide	Dichlorvos	100 % eradicated	(Gomez et al., 2015)
Copper oxide- chitosan	Malathion	Almost 99.9 % removed	(Rani and Shanker, 2018)
Ti- Fe oxides	parathion methyl	approx. 70%	(Henych et al., 2015)
Iron- zeolite	Carbamate	Completely removed	(Tomašević et al., 2010)
Manganese oxide	parathion methyl	Degraded 90% in 2 hours	(Šťastný et al., 2016)
Gold- titanium oxide	chloridazon	In 30 minutes, 50% eliminated	(Rani and Shanker, 2018)

Table 1. Various nanomaterials used for the removal of toxic pesticides.

Nanomembranes and filtration

The methods of filtration nanomembranes (NMs) are also extremely efficient in removing pollution from water bodies including the mitigation of bioproducts, organic wastes, inorganic ions, and pesticides (Zhang et al., 2018). Nanofiltration is in demand as it includes the production of advanced nanofiltration membranes (NFMs) via layer-bylayer modification, plasma treatment, photo grafting, and interfacial polymerization in coordination with the nanoparticles. These membranes can be divided into further categories depending upon the material used for their production. They may be organic like organic polymer-based nanomembranes. These are usually made up of synthetic polymers like polyamidoamine, polyacrilonitrle, polyethersulfone, and polyurethanes (Liu et al., 2014). Some of them are manufactured by using natural polymers like chitosan, and cellulose acetate. However, they can also be inorganic like graphene-based, zeolites, SiO₂ nanomembranes (Pedrosa et al., 2019). Prefiltration and other post-treatments are required along with the treatment of drinking water with nanofiltration and nanomembranes., however, they are not used in routine for water treatment as are a bit expensive. Their efficacy depends upon their pore size, weight, polarity, hydrophobic and hydrophilic nature and types of components used in their preparation (Rivera-Utrilla et al., 2013), so, organic polymers are now integrated with the inorganic membranes to improve their functionality (Bonné et al., 2000; Tepuš et al., 2009).

In a study on NFMs, four types of polyamides NMs were evaluated for the filtration of atrazine and dimethoate where both pesticides have been declared as the health concern by WHO. The best results were found for NF90 exhibiting a retention rate of 95% for atrazine and 85% for dimethoate (Ahmad et al., 2008). In another report, Nano-

filtration was employed to separate glyphosate from saline wastewater (Song et al., 2013). A thin film composite poly piperazine amide nanomembrane was synthesized and evaluated to check the effect of trimethylamine and results demonstrated that their addition enhanced the rejection of diazinon, and water permeability improved from 95.2% to 98.8% (Karimi et al., 2016). In another study, controlled spherical ZrO₂ NPs were employed to synthesize yttria-stabilized ZrO₂ NFM efficiently fabricated with nanoparticles using reverse micelles-mediated sol-gel method to mitigate carbofuran from water with a proficient permeability of 3.9-4.2 L/m²/h for purified water, removal efficiency of 89% and reusability after alkali wash and low-temperature calcination (Qin et al., 2020). Two negatively charged organic NFMs (NF and OPMN-K) membranes were synthesized for the elimination of simazine, atrazine and diuron in humic acid presence where the outcome demonstrated that NF membrane provided more retention of pesticides in comparison with the OPMN-K membrane due to its smaller molecular cut-off (Saleh et al., 2020). Similarly, atrazine and simazine were evaluated for removal from different water samples such as river water, tap water and distilled water by nanofiltration by using four types of membranes where results showed that the rejection of atrazine in all cases was higher than simazine and was also higher in river water and tap water as compared to distilled water (Zhang et al., 2004). In a prominent study, a thin film nanocomposite membrane holding oleic acid treated silica NPs was synthesized through polymerization on polysulfone asymmetric membrane for the mitigation of prometryn, propazine and atrazine from water sample. Rejection and water flux studies were performed what revealed that addition of modified SiO₂ increases water flux and provides the best rejection among all membranes. Prometryn having largest size had maximum rejection at 99% and propazine had the lowest rejection (84.4–90.2%) due to higher dipole moment (Rakhshan and Pakizeh, 2015).

Conclusions

In summary, carbon nanotubes possess high hardness, mechanical and thermal stability, large surface area, corrosion resistance and high reactivity. Nanocatalysts, nano adsorbents, and nanomembranes are all three ways that are efficiently used for the removal of pesticides during wastewater treatment. The adsorption technique is considered the most useful and efficient technique to mitigate the pesticides and purify the wastewater by using the NPs. Most of the nano adsorbents now can eliminate 80% of the pesticides in a short interval of time. The most important parameters in the determination are the economic status, efficiency, and versatile nature of the adsorbent and activated carbon, Iron, and titanium dioxide are considered as the best nano adsorbents. As some pesticide contaminants and carbamates still need extensive study and a proper solution so it is suggested that for future the development of biopolymers based nanobiocomposites should be promoted to encourage eco-friendly, efficient and cheap nanocatalysts using green chemistry. As there is an urgent need to have a thorough comprehension of the multiple ways that lead towards the acute toxic effects of nanoparticles on vertebrate organisms, particularly humans. In that case, to get rid of the acaricidal and insecticidal impact of botanical and microbial products that are employed as capping and reducing agents, we can replace them by green fabrication process, which relies on some particular compounds like stearic acid, zein, and β -caryophyllene, which because of variation in tested green reducing agent, allows us to get rid of such results which are difficult to reproduce.

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Conflict of interests

The listed author(s) declare no conflicting interests.

Data statement

Not applicable

References

- Aguilar-Pérez, K. M., Avilés-Castrillo, J. I., Ruiz-Pulido, G., Medina, D. I., Parra-Saldivar, R., & Iqbal, H. M. (2021). Nanoadsorbents in focus for the remediation of environmentally-related contaminants with rising toxicity concerns. *Science of The Total Environment*, 779, 146465.
- Aguilar-Pérez, K. M., Heya, M. S., Parra-Saldívar, R., & Iqbal, H. M. (2020). Nano-biomaterials in-focus as sensing/detection cues for environmental pollutants. *Case Studies in Chemical and Environmental Engineering*, 2, 100055.
- Ahmad, A., Tan, L., & Shukor, S.A. (2008). Dimethoate and atrazine retention from aqueous solution by nanofiltration membranes. *Journal* of hazardous materials, 151, 71-77.
- Ahmaruzzaman, M. (2019). Nano-materials: novel and promising adsorbents for water treatment. *Asian Journal of Water, Environment and Pollution*, 16, 43-53.
- Ali, I. (2012). New generation adsorbents for water treatment. *Chemical Reviews*, 112, 5073-5091.
- Ali, I., & Gupta, V. (2006). Advances in water treatment by adsorption technology. *Nature protocols*, 1, 2661-2667.
- Armaghan, M., & Amini, M. (2012). Adsorption of diazinon and fenitrothion on nanocrystalline alumina from non-polar solvent. *Colloid Journal*, 74, 427-433.
- Bai, L., Li, Z., Zhang, Y., Wang, T., Lu, R., Zhou, W., Gao, H., & Zhang, S. (2015). Synthesis of water-dispersible graphene-modified magnetic polypyrrole nanocomposite and its ability to efficiently adsorb methylene blue from aqueous solution. *Chemical Engineering Journal*, 279, 757-766.
- Bhaumik, M., Leswifi, T.Y., Maity, A., Srinivasu, V.V., & Onyango, M.S. (2011a). Removal of fluoride from aqueous solution by polypyrrole/Fe3O4 magnetic nanocomposite. *Journal of hazardous materials*, 186, 150-159.
- Bhaumik, M., Maity, A., Srinivasu, V.V., & Onyango, M.S. (2011b). Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/Fe3O4 magnetic nanocomposite. *Journal of hazardous materials*, 190, 381-390.
- Bilal, M., Barceló, D., & Iqbal, H. M. (2021). Occurrence, environmental fate, ecological issues, and redefining of endocrine disruptive estrogens in water resources. *Science of The Total Environment*, 800, 149635.
- Bilal, M., Nguyen, T. A., & Iqbal, H. M. (2020). Multifunctional carbon nanotubes and their derived nano-constructs for enzyme immobilization–a paradigm shift in biocatalyst design. *Coordination Chemistry Reviews*, 422, 213475.

- Björk, J., Hanke, F., Palma, C.-A., Samori, P., Cecchini, M., & Persson, M. (2010). Adsorption of aromatic and anti-aromatic systems on graphene through π - π stacking. *The Journal of Physical Chemistry Letters*, 1, 3407-3412.
- Bonné, P., Beerendonk, E., Van der Hoek, J., & Hofman, J. (2000). Retention of herbicides and pesticides in relation to aging of RO membranes. *Desalination*, 132, 189-193.
- Chen, H., Yang, S., Yu, K., Ju, Y., & Sun, C. (2011). Effective photocatalytic degradation of atrazine over titania-coated carbon nanotubes (CNTs) coupled with microwave energy. *The Journal of Physical Chemistry A*, 115, 3034-3041.
- De Martino, A., Iorio, M., Xing, B., & Capasso, R. (2012). Removal of 4-chloro-2methylphenoxyacetic acid from water by sorption on carbon nanotubes and metal oxide nanoparticles. *RSC advances*, 2, 5693-5700.
- Dehaghi, S.M., Rahmanifar, B., Moradi, A.M., & Azar, P.A. (2014). Removal of permethrin pesticide from water by chitosan–zinc oxide nanoparticles composite as an adsorbent. *Journal of Saudi Chemical Society*, 18, 348-355.
- Dehghani, M.H., Kamalian, S., Shayeghi, M., Yousefi, M., Heidarinejad, Z., Agarwal, S., & Gupta, V.K. (2019). High-performance removal of diazinon pesticide from water using multiwalled carbon nanotubes. *Microchemical Journal*, 145, 486-491.
- Dehghani, M.H., Niasar, Z.S., Mehrnia, M.R., Shayeghi, M., Al-Ghouti, M.A., Heibati, B., McKay, G., & Yetilmezsoy, K. (2017). Optimizing the removal of organophosphorus pesticide malathion from water using multiwalled carbon nanotubes. *Chemical Engineering Journal*, 310, 22-32.
- Deng, J., Shao, Y., Gao, N., Deng, Y., Tan, C., Zhou, S., & Hu, X. (2012). Multiwalled carbon nanotubes as adsorbents for removal of herbicide diuron from aqueous solution. *Chemical Engineering Journal*, 193, 339-347.
- El-Temsah, Y.S., & Joner, E.J. (2012). Ecotoxicological effects on earthworms of fresh and aged nano-sized zero-valent iron (nZVI) in soil. *Chemosphere*, 89, 76-82.
- Gan, J., Li, X., Rizwan, K., Adeel, M., Bilal, M., Rasheed, T., & Iqbal, H. M. (2022). Covalent organic frameworks-based smart materials for mitigation of pharmaceutical pollutants from aqueous solution. *Chemosphere*, 286, 131710.
- Gomez, S., Marchena, C.L., Renzini, M.S., Pizzio, L., & Pierella, L. (2015). In situ generated TiO₂ over zeolitic supports as reusable photocatalysts for the degradation of dichlorvos. *Applied Catalysis B: Environmental*, 162, 167-173.
- González-González, R. B., Sharma, A., Parra-Saldívar, R., Ramirez-Mendoza, R. A., Bilal,

M., & Iqbal, H. M. (2021). Decontamination of emerging pharmaceutical pollutants using carbon-dots as robust materials. *Journal of Hazardous Materials*, 423, 127145.

- Henych, J., Štengl, V., Slušná, M., Grygar, T.M., Janoš, P., Kuráň, P., & Štastný, M. (2015). Degradation of organophosphorus pesticide parathion methyl on nanostructured titania-iron mixed oxides. *Applied Surface Science*, 344, 9-16.
- Hou, X., Lei, S., Qiu, S., Guo, L., Yi, S., & Liu, W. (2014). A multi-residue method for the determination of pesticides in tea using multiwalled carbon nanotubes as a dispersive solid phase extraction absorbent. *Food Chemistry*, 153, 121-129.
- Hristovski, K., Baumgardner, A., & Westerhoff, P. (2007). Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media. *Journal of Hazardous Materials*, 147, 265-274.
- Hussain, C.M., Kecili, R., & Hussain, C.G. (2021). Sample Preparation with Nanomaterials: Next Generation Techniques and Applications. John Wiley & Sons.
- Joo, S.H., & Zhao, D. (2008). Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: effects of catalyst and stabilizer. *Chemosphere*, 70, 418-425.
- Karimi, H., Rahimpour, A., & Shirzad Kebria, M.R. (2016). Pesticides removal from water using modified piperazine-based nanofiltration (NF) membranes. *Desalination and Water Treatment*, 57, 24844-24854.
- Kyriakopoulos, G., Xiarchos, I., & Doulia, D. (2006). Treatment of contaminated water with pesticides via adsorption. *International journal of environmental technology and management*, 6, 515-524.
- Kyzas, G.Z., & Bikiaris, D.N. (2015). Recent Modifications of Chitosan for Adsorption Applications: A Critical and Systematic Review. *Marine Drugs*, 13, 312-337.
- Liu, G., Li, L., Huang, X., Zheng, S., Xu, X., Liu, Z., Zhang, Y., Wang, J., Lin, H., & Xu, D. (2018). Adsorption and removal of organophosphorus pesticides from environmental water and soil samples by using magnetic multi-walled carbon nanotubes@ organic framework ZIF-8. Journal of Materials Science, 53, 10772-10783.
- Liu, T., Li, B., Hao, Y., & Yao, Z. (2014). MoO₃nanowire membrane and Bi₂Mo₃O₁₂/MoO₃ nano-heterostructural photocatalyst for wastewater treatment. *Chemical Engineering Journal*, 244, 382-390.
- Liu, X., Zhang, H., Ma, Y., Wu, X., Meng, L., Guo, Y., Yu, G., & Liu, Y. (2013). Graphene-coated silica as a highly efficient sorbent for residual

organophosphorus pesticides in water. *Journal* of Materials Chemistry A, 1, 1875-1884.

- Lopes, R.P., de Urzedo, A.P., Nascentes, C.C., & Augusti, R. (2008). Degradation of the insecticides thiamethoxam and imidacloprid by zero-valent metals exposed to ultrasonic irradiation in water medium: electrospray ionization mass spectrometry monitoring. *Rapid Communications in Mass Spectrometry*, 22, 3472-3480.
- Mahdavi, V., Taghadosi, F., Dashtestani, F., Bahadorikhalili, S., Farimani, M.M., Ma'mani, L., & Khaneghah, A.M. (2021).
 Aminoguanidine modified magnetic graphene oxide as a robust nanoadsorbent for efficient removal and extraction of chlorpyrifos residue from water. *Journal of Environmental Chemical Engineering*, 9, 106117.
- Mahpishanian, S., Sereshti, H., & Baghdadi, M. (2015). Superparamagnetic core-shells anchored onto graphene oxide grafted with phenylethyl amine as a nano-adsorbent for extraction and enrichment of organophosphorus pesticides from fruit, vegetable and water samples. *Journal of Chromatography A*, 1406, 48-58.
- Mitchell, M.B., Sheinker, V.N., Cox, W.W., Gatimu, E.N., & Tesfamichael, A.B. (2004). The room temperature decomposition mechanism of dimethyl methylphosphonate (DMMP) on alumina-supported cerium oxide– participation of nano-sized cerium oxide domains. *The Journal of Physical Chemistry B*, 108, 1634-1645.
- Mubarak, N., Sahu, J., Abdullah, E., & Jayakumar, N. (2014). Removal of heavy metals from wastewater using carbon nanotubes. *Separation* & *Purification Reviews*, 43, 311-338.
- Pacheco, S., Medina, M., Valencia, F., & Tapia, J. (2006). Removal of inorganic mercury from polluted water using structured nanoparticles. *Journal of Environmental Engineering*, 132, 342-349.
- Pan, B., Pan, B., Zhang, W., Lv, L., Zhang, Q., & Zheng, S. (2009). Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*, 151, 19-29.
- Pandey, S. (2017). A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment. *Journal of Molecular Liquids*, 241, 1091-1113.
- Pedrosa, M., Drazic, G., Tavares, P.B., Figueiredo, J.L., & Silva, A.M. (2019). Metal-free graphene-based catalytic membrane for degradation of organic contaminants by persulfate activation. *Chemical Engineering Journal*, 369, 223-232.

- Qin, H., Guo, W., Huang, X., Gao, P., & Xiao, H. (2020). Preparation of yttria-stabilized ZrO₂ nanofiltration membrane by reverse micellesmediated sol-gel process and its application in pesticide wastewater treatment. *J. Eur. Ceram. Soc.* 40, 145-154.
- Qu, X., Alvarez, P.J., & Li, Q. (2013). Applications of nanotechnology in water and wastewater treatment. *Water research*, 47, 3931-3946.
- Radic, S., Geitner, N.K., Podila, R., Käkinen, A., Chen, P., Ke, P.C., & Ding, F. (2013). Competitive binding of natural amphiphiles with graphene derivatives. *Scientific reports*, 3, 1-8.
- Rahmanifar, B., & Dehaghi, S.M. (2014). Removal of organochlorine pesticides by chitosan loaded with silver oxide nanoparticles from water. *Clean Technologies and Environmental Policy*, 16, 1781-1786.
- Rakhshan, N., & Pakizeh, M. (2015). Removal of triazines from water using a novel OA modified SiO₂/PA/PSf nanocomposite membrane. *Separation and purification technology*, 147, 245-256.
- Rani, M., & Shanker, U. (2018). Degradation of traditional and new emerging pesticides in water by nanomaterials: recent trends and future recommendations. *International Journal of Environmental Science and Technology*, 15, 1347-1380.
- Rao, G.P., Lu, C., & Su, F. (2007). Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. *Separation and purification technology*, 58, 224-231.
- Rasheed, T., Ahmad, N., Ali, J., Hassan, A. A., Sher, F., Rizwan, K., ... & Bilal, M. (2021). Nano and micro architectured cues as smart materials to mitigate recalcitrant pharmaceutical pollutants from wastewater. *Chemosphere*, 274, 129785.
- Reyes-Calderón, A., Pérez-Uribe, S., Ramos-Delgado, A. G., Ramalingam, S., Oza, G., Parra-Saldívar, R., ... & Sharma, A. (2022). Analytical and regulatory considerations to mitigate highly hazardous toxins from environmental matrices. *Journal of Hazardous Materials*, 423, 127031.
- Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M.Á., Prados-Joya, G., & Ocampo-Pérez, R. (2013). Pharmaceuticals as emerging contaminants and their removal from water. A review. *Chemosphere*, 93, 1268-1287.
- Sabela, M., Balme, S., Bechelany, M., Janot, J.M., & Bisetty, K. (2017). A review of gold and silver nanoparticle-based colorimetric sensing assays. Advanced Engineering Materials, 19, 1700270.
- Saleh, I.A., Zouari, N., & Al-Ghouti, M.A. (2020). Removal of pesticides from water and wastewater: Chemical, physical and biological

treatment approaches. *Environmental Technology & Innovation*, 101026.

- Santhosh, C., Velmurugan, V., Jacob, G., Jeong,
 S.K., Grace, A.N., & Bhatnagar, A. (2016).
 Role of nanomaterials in water treatment applications: a review. *Chemical Engineering Journal*, 306, 1116-1137.
- Santos, T.R., Andrade, M.B., Silva, M.F., Bergamasco, R., & Hamoudi, S. (2019). Development of α -and γ -Fe₂O₃ decorated graphene oxides for glyphosate removal from water. *Environmental technology*, 40, 1118-1137.
- Sen Gupta, S., Chakraborty, I., Maliyekkal, S.M., Adit Mark, T., Pandey, D.K., Das, S.K., & Pradeep, T. (2015). Simultaneous dehalogenation and removal of persistent halocarbon pesticides from water using graphene nanocomposites: a case study of lindane. ACS Sustainable Chemistry & Engineering, 3, 1155-1163.
- Shahryari-ghoshekandi, R., & Sadegh, H. (2014). Kinetic study of the adsorption of synthetic dyes on graphene surfaces. Jordan J. Chem 9, 267-278.
- Shen, H.-Y., Zhu, Y., Wen, X.-E., & Zhuang, Y.-M. (2007). Preparation of Fe₃O₄-C18 nanomagnetic composite materials and their cleanup properties for organophosphorous pesticides. *Analytical and bioanalytical chemistry*, 387, 2227-2237.
- Singh, N., Nagpal, G., & Agrawal, S. (2018). Water purification by using adsorbents: a review. *Environmental technology & innovation*, 11, 187-240.
- Singh, R., Kumar, N., Mehra, R., Kumar, H., & Singh, V.P. (2020). Progress and challenges in the detection of residual pesticides using nanotechnology based colorimetric techniques. *Trends in Environmental Analytical Chemistry*, 26, e00086.
- Smith, S.C., & Rodrigues, D.F. (2015). Carbonbased nanomaterials for removal of chemical and biological contaminants from water: A review of mechanisms and applications. *Carbon*, 91, 122-143.
- Song, J., Li, X.-M., Figoli, A., Huang, H., Pan, C., He, T., & Jiang, B. (2013). Composite hollow fiber nanofiltration membranes for recovery of glyphosate from saline wastewater. *Water Res.* 47, 2065-2074.
- Springer, V.H., & Lista, A.G. (2010). A simple and fast method for chlorsulfuron and metsulfuron methyl determination in water samples using multiwalled carbon nanotubes (MWCNTs) and capillary electrophoresis. *Talanta*, 83, 126-129.
- Stafiej, A., & Pyrzynska, K. (2007). Adsorption of heavy metal ions with carbon nanotubes. *Separation and purification technology*, 58, 49-52.

- Stafiej, A., & Pyrzynska, K. (2008). Solid phase extraction of metal ions using carbon nanotubes. *Microchemical Journal*, 89, 29-33.
- Šťastný, M., Štengl, V., Henych, J., Tolasz, J., Vomáčka, P., & Ederer, J. (2016). Mesoporous manganese oxide for the degradation of organophosphates pesticides. *Journal of Materials Science*, 51, 2634-2642.
- Taghizade Firozjaee, T., Mehrdadi, N., Baghdadi, M., & Nabi Bidhendi, G. (2018). Application of nanotechnology in pesticides removal from aqueous solutions-a review. *International Journal of Nanoscience and Nanotechnology*, 14, 43-56.
- Tan, K.B., Vakili, M., Horri, B.A., Poh, P.E., Abdullah, A.Z., & Salamatinia, B. (2015). Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. *Separation and Purification Technology*, 150, 229-242.
- Tepuš, B., Simonič, M., & Petrinić, I. (2009). Comparison between nitrate and pesticide removal from ground water using adsorbents and NF and RO membranes. *Journal of hazardous materials*, 170, 1210-1217.
- Tomašević, A., Kiss, E., Petrović, S., & Mijin, D. (2010). Study on the photocatalytic degradation of insecticide methomyl in water. *Desalination*, 262, 228-234.
- Ullah, N., Mansha, M., Khan, I., & Qurashi, A. (2018). Nanomaterial-based optical chemical sensors for the detection of heavy metals in water: Recent advances and challenges. *TrAC Trends in Analytical Chemistry*, 100, 155-166.
- Wang, X., Guo, Y., Yang, L., Han, M., Zhao, J., & Cheng, X. (2012). Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. J. Environ. Anal. Toxicol., 2, 154.
- Wang, X., Lu, J., & Xing, B. (2008). Sorption of organic contaminants by carbon nanotubes: influence of adsorbed organic matter. *Environmental science & technology*, 42, 3207-3212.
- Yan, X., Shi, B., Lu, J., Feng, C., Wang, D., & Tang, H. (2008). Adsorption and desorption of atrazine on carbon nanotubes. *Journal of Colloid and Interface Science*, 321, 30-38.
- Yang, K., & Xing, B. (2007). Desorption of polycyclic aromatic hydrocarbons from carbon nanomaterials in water. *Environmental Pollution*, 145, 529-537.
- Yang, K., Zhu, L., & Xing, B. (2006). Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environmental science & technology*, 40, 1855-1861.
- Yu, B., Zeng, J., Gong, L., Yang, X., Zhang, L., & Chen, X. (2008). Photocatalytic degradation investigation of dicofol. *Chinese Science Bulletin*, 53, 27-32.

- Zeb, S., Ali, N., Ali, Z., Bilal, M., Adalat, B., Hussain, S., ... & Iqbal, H. M. (2020). Silicabased nanomaterials as designer adsorbents to mitigate emerging organic contaminants from water matrices. *Journal of Water Process Engineering*, 38, 101675.
- Zhang, S., Bilal, M., Adeel, M., Barceló, D., & Iqbal, H. M. (2021). MXene-based designer nanomaterials and their exploitation to mitigate hazardous pollutants from environmental matrices. *Chemosphere*, 283, 131293.
- Zhang, S., Yang, H., Huang, H., Gao, H., Wang, X., Cao, R., Li, J., Xu, X., & Wang, X. (2017).
 Unexpected ultrafast and high adsorption capacity of oxygen vacancy-rich WOx/C nanowire networks for aqueous Pb²⁺ and methylene blue removal. *Journal of Materials Chemistry A*, 5, 15913-15922.
- Zhang, Y., Van der Bruggen, B., Chen, G., Braeken, L., & Vandecasteele, C. (2004). Removal of pesticides by nanofiltration: effect of the water matrix. *Sep. Purif. Technol.* 38, 163-172.

- Zhang, Y., Wei, S., Hu, Y., & Sun, S. (2018). Membrane technology in wastewater treatment enhanced by functional nanomaterials. *Journal* of Cleaner Production, 197, 339-348.
- Zhao, G., Li, J., Ren, X., Chen, C., & Wang, X. (2011). Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environmental science* & technology, 45, 10454-10462.
- Zhao, J., Wang, Z., White, J.C., & Xing, B. (2014). Graphene in the aquatic environment: adsorption, dispersion, toxicity and transformation. *Environmental science & technology*, 48, 9995-10009.
- Zhao, Y., Qamar, S. A., Qamar, M., Bilal, M., & Iqbal, H. M. (2021). Sustainable remediation of hazardous environmental pollutants using biochar-based nanohybrid materials. *Journal* of Environmental Management, 300, 113762.



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