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Nanotechnology for the bioremediation of organic and inorganic compounds in aquatic ecosystem/marine ecosystem

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ABSTRACT

There has been a rapid increase in the usage of carcinogenic organic and inorganic compounds such as dyes, heavy metals, and phenols due to the rise in industrialization. Around 70% of the industrial effluents are dumped into the aquatic system without being treated where they pollute the usable water supply. These elements can also harm the human health by entering the food chain. According to the current population growth rate, 3.5 billion people are expected to face water scarcity by 2025. Therefore, the need to eliminate these pollutants is growing day by day. Nano-bioremediation, a combination of bioremediation and nanotechnology is a competent way to remove contaminants from aquatic systems as it is a non-toxic, cost-effective, and less time-consuming approach. Nanotechnology has compelling capability, and thus, the applications of nanoparticles will escalate in the near future, and it will be a significant part of sustainable development. This review summarizes how various nanomaterials have the potential to degrade contaminants and how it can be used in the form of adsorbents, sensors, membranes, nano-catalysts, and nano-filters to remediate contaminants from marine systems. In addition to this, various limitations of nano-bioremediation and the factors responsible for efficiency of nanomaterials are also discussed in this review paper.

1. INTRODUCTION

As the human population is increasing, the need for economic and technological advancement is also growing and that is further leading to urbanization and industrialization [1]. According to the most recent United Nations estimates, the current world population is 7.9 billion as of March 2022 [2]. From the 19th century, industries started expanding and innovations were made without taking any precautionary measures for the environment [3]. According to The United Nations world water development report 2021, only 8% of municipal and industrial wastewater is treated in developing nations [4]. According to WWAP 2017, 80% municipal and industrial effluent is released in the environment without treatment [5]. Approximately 380 billion cubic meters of water can be recovered from annual effluent, and this type of water recovery is anticipated to reach 470 billion cubic meters by 2030 and 574 billion cubic meters by 2050 [6]. Many industries release lethal chemicals and organic and inorganic compounds daily into water, soil, and air. Humans, animals, flora, and fauna are all affected due to the release of contaminants through human activities [1]. Organic and inorganic pollutants accumulate in aquatic systems by the runoff from industries and the urban stretches. Irrigation systems are also being affected by the accumulation of heavy metals in sewage water. The presence of these contaminants in water affects all organisms and can have serious impact on humans and other ecosystems [7]. There is a serious impact on the aquatic life as there is a decrease in the concentration of dissolved oxygen due to the increase in pollution [8]. When contaminants enter the aquatic system, they are transported over thousands of kilometers because they get diluted very quickly. After dilution, they get accumulated in the organisms present in the marine system and are deposited in the sediments. These pollutants present in the sediments then get released into the water and cause toxicity to organisms, owing to the variations in the pH values, hydrological and external redox conditions [9]. These pollutants may also enter the food chain through biomagnification because of their toxicity, easy enrichment, and refractory degradation [10]. Phenols [11], polyaromatic hydrocarbons [12], azo dyes [13], pesticides [14], polychlorinated biphenyls [15], endocrine-disrupting chemicals, etc., are some of the organic pollutants. On the other hand, inorganic pollutants consist of a range of toxic heavy metals such as mercury [16], cadmium [17], lead [18], and chromium [19]. These have detrimental effects on human well-being, for example, contact with lead can cause neurotoxic effects [20], arsenic exposure can cause lung cancer [21], there can be damage to bones due to cadmium exposure [22], and phenols can cause a corrosive effect on the skin [23]. A case study done by Mărginean *et al*. showed that lead toxicity is a lethal illness as it has very critical and acute complications [24]. Another case study performed by Ruskeeniemi *et al*. showed that exposure to arsenic may be damaging to health [25]. A review by Wei *et al*., mentions that dose-dependent tumors were

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observed in the lung tissues of pregnant mice that were treated orally with sodium arsenate [21]. The biological activities of native proteins in humans are damaged by the interference of heavy metals. The metals may interact and bind with the free thiols or other functional groups in proteins. According to some studies, pollutants are also responsible for inhibiting the process of refolding of denatured proteins [26]. Other than aquatic systems, there is hazardous impact of pollutants on soil as well. A study done in Italy confirmed the presence of organic and inorganic pollutants in soil [27]. Compounds like polyaromatic hydrocarbons that are not carcinogenic in character but become carcinogenic after fusion are a major problem as well [1]. Other than release of chemicals by industries, there are other reasons as well that lead to the contamination of environment such as wars and nuclear reactors in which radioactive substances are used. Strontium-90, Caesium-137, etc., are also formed by nuclear reactors [28]. A case study done in the aquatic system of Iraq showed the presence of radioactive compounds such as uranium [29]**.** According to a study conducted by Siddiqui *et al*., intensities of chromium, cadmium, lead, nickel, copper, and iron have gone beyond their respective standards in the middle and lower reaches of the river Ganga in India [30]. Another case study performed in western part of Punjab, India, showed that the groundwater in that region is alkaline and contaminated with arsenic, lead, uranium, nitrate, and fluorine and these contaminants are the potential cause for cancer [31]. Sometimes the pollutants enter the ecosystem accidentally as well, for example, oil spills which are unintentional but can pollute water and soil to a large extent [3]. All these reasons are responsible for environmental contamination. Bioremediation is the use of biological agents in the remediation of the environment [32]. This method is suitable for environmental cleanup because it is eco-friendly, cost-effective, and release no toxic by-products as it uses microorganisms to degrade or transform organic and inorganic pollutants in the aquatic/marine ecosystem [33]. Through bioremediation, organic wastes can be removed or transformed into less toxic compounds with the help of microorganisms [34]. Furthermore, through bioremediation the contaminants do not get transferred from one environmental medium to another gets fully degraded. Pollutants can be degraded on site as well without transferring it. It also is a non-invasive method and pollutants in very less concentration can also be degraded through this method which is not possible with physical or chemical method [35]. The main challenge of the 21st century is to save and clean our resources from pollution for our upcoming generations. The conventional techniques used for remediation have high cost and energy requirements. Hence, nanomaterials can be used for degradation of pollutants from water as it has the potential to reduce pollutants competently due to its small surface area and high adsorption and selectivity potential. Nanotechnology deals with assemblies of matter that have at least one dimension in the range of 1 to 100 nm [36]. Nanotechnology can be used for bioremediation because nanomaterial has many unique properties, for example, nanoparticles have large surface area and high surface energy [1] and hence they can absorb pollutants in maximum amounts. Furthermore, energy consumption during degradation is reduced as nanoparticles catalyses the reaction in faster rates as compared to bulk materials, they are not toxic, they improve microbial action in waste and toxic material, *in situ* remediation is possible because the contaminants become accessible due to its nanosized form, nanoparticles can be coated with different ligands [37] and, depending on the shape of the nanoparticles, the ratio between surface and volume can be controlled [38] and this enables the designing of sensors with high selectivity, sensitivity and specificity. For example, iron NP can be used to remove arsenic and prevent the release of harmful substances [39]. Another example can be the use of carbon nanotube in place of cathode ray tubes in computers to avoid to the use of lead, reduce consumption of energy and avoid poisonous and toxic bioproduct development [40]. Many nanomaterials can be used for bioremediation of contaminants from marine systems, for example, nanotubes [41], carbon dots [42], quantum dots [43], and nanoparticles [44]. In an experiment organic dye was removed from wastewater with the help of copper oxide nanoparticles synthesized from the leaves extract of *Citrus aurantifolia* [45]. In another experiment, Tabish *et al*. used graphene as an adsorbent for the removal of arsenic from water and found 80% efficiency [46]. Bioremediation combined with nanotechnology has proven to be an effective way for the removal of many organic/inorganic compounds from water, and wastewater and is being used today as it has the potential to protect and preserve natural resources [46]. Figure 1 demonstrates various uses of nanotechnology for bioremediation.

2. BIOREMEDIATION

Bioremediation is a technique used for the degradation and removal of pollutants such as heavy metals, hydrocarbons, azo dye, and pesticides into a less toxic/harmful form with the help of biological agents [47]. Bioremediation is a widely used method for the transformation of organic wastes into less toxic compounds [48]. Microorganisms are used for bioremediation as they have the potential to alter harmful contaminants into carbon dioxide [CO_2], water [H_2O], microbial biomass, and byproducts that are less fatal than the initial compound. Different kinds of microorganism can be used for bioremediation. Examples include, aerobic microbes such as Mycobacterium that are useful in degradation of pesticides and hydrocarbons [49]. The pollutants are being consumed as carbon and energy source by most of these microbes. Ligninolytic fungi, such as *Phanaerochaete chrysosporium,* have also been used for the bioremediation of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), chlorobenzene, and synthetic dyes. This white rot fungi generate extracellular oxidative enzymes that destroy lignin present in toxic substances [50]. An experiment performed by Shukla *et al*., demonstrated that chlorinated aliphatic trichloroethylene can be degraded by methanotrophs. According to the first-order kinetics, the

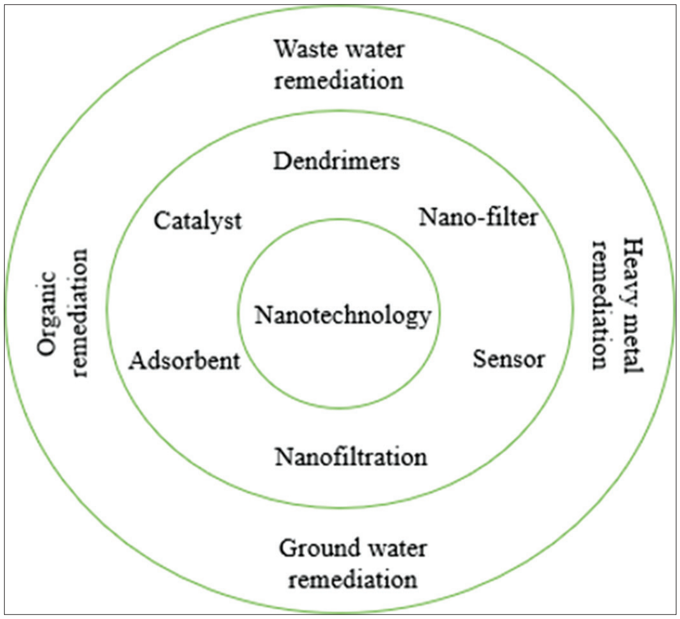

Figure 1: Schematic representation of nanotechnology for bioremediation.

rate of trichloroethylene degradation was found to be 0.19 ppm/h in the experiment [51]. These microorganisms can be introduced to the contaminated site from an external site or they can be native to the contaminated location [52]. Pollutants in the environment are altered by microorganisms through reactions that take place as part of their metabolic process. The environmental conditions such as pollutant type, solubility, and bioavailability of pollutant to the microbe play a very vital part because for the microorganism to act, the polluted environment must allow its growth and action so that it can enzymatically attack the contaminant [48,52]. Numerous agents play a significant role in the success of bioremediation, for example, the presence of a population of microbes that can degrade contaminants, the accessibility of pollutants to the population of microbes and the environmental aspects [53]. An extensive range of contaminants can be degraded by microbes. Microorganisms transform harmful compounds into less toxic compounds naturally in a less expensive and eco-friendly manner without keeping any possibility of forthcoming liabilities that can be there due to treatment and clearance of polluted matter; hence, it is widely accepted by people [54,55]. However, there are several limitations to bioremediation as well. Bioremediation is a time taking and scientifically intensive method. Moreover, some substances are not responsive to biodegradation, such as, radionuclides, heavy metals, and some chlorinated compounds. Sometimes, microbial breakdown of pollutants may generate harmful metabolites [54]. Apart from this, many non-technical factors also cause hindrance, for example, regulatory barriers, scale-up process, the inability of regulators to consider the full range of remediation options or configurations and responsibility for failure to achieve goals [56].

3. ORGANIC AND INORGANIC POLLUTANTS

Industries release organic and inorganic compounds everyday into the aquatic system. There are many harmful effects of these compounds on aquatic life. Moreover, there are case studies that show the effect of these pollutants on human life as well. Table 1 shows different sources and harmful effects of organic and inorganic pollutants.

4. BIOREMEDIATION THROUGH NANOTECHNOLOGY

4.1. Nanobioremediation

Nanotechnology deals with assemblies of matter have at least one dimension in the range of 1−100 nm [57]. Nanotechnology is described as the usage of minuscule particles called nanoparticles. Compared to bulk material, properties of nanoparticles (NP) are much better because of their small dimension (1-100 nm). Nano-bioremediation has attracted attention because nanoparticles have diverse range of characteristics such as larger surface area and attractive chemical characteristics [58]. The nano size of the nanoparticles allows their penetration into the contaminated site and this provides better results compared to bioremediation methods [59]. Due to these reasons, the combination of nanoparticles and bioremediation is used as nanoparticles enhance the efficiency of bioremediation procedure [44]. Iron nanoparticles have gained significant interest over the years for bioremediation [60]. In an experiment, Thome *et al*. (2015) described various features that are significant to comprehend the performance of nanomaterial. These features include surface area, morphology, surface charge, and particle size distribution [61]. Some studies also show that nanotechnology can be combined with enzyme technology for better and efficient treatment of water [62].

4.2. Synthesis of Nanoparticles

Nanomaterials can be synthesized chemically, physically or through sol-gel method but the most eco-friendly method is synthesis through plants, bacteria, yeast, fungi and algae. This is called green approach for nanoparticles synthesis and it is a simple, low cost and non-hazardous method [63]. Nanomaterial synthesized by physical and chemical methods result in environmental and toxicity issues. Large amounts of space are required to perform synthesis through physical pathway and a lot of heat is also generated. The problem with chemical method is that a lot of toxic chemicals and solvents are being used during the synthesis. Due to these reasons, the green approach grabbed attention of researchers and various nanoparticles has been synthesized successfully synthesized with the same technology [64]. Table 2 shows different synthesis methods of nanoparticles.

5. APPLICATIONS OF NANOPARTICLE FOR BIOREMEDIATION OF ORGANIC/INORGANIC CONTAMINANTS IN AQUATIC SYSTEM

5.1. Adsorbents

There are many nanomaterials that can be used as adsorbents because of their high adsorbing capability, for example, dendrimers [65], nano-sorbents [66], and zeolites [67]. Many experiments have successfully proved that titanium oxides [68], magnesium oxides [69], and aluminum oxides [70] have the capability to adsorb pollutants such as dyes, arsenic, lead, mercury, copper, cadmium, chromium, and nickel from aquatic systems. In an experiment performed by Chen *et al*., successful adsorption of nickel from aqueous solution using oxidized multiwall carbon nanotubes was demonstrated [71]. Due to their low toxicity, strong magnetic property, regular shapes, chemical stability, uniform sizes, high specific surface area, easy surface modification, high dispersibility, and brilliant biocompatibility, Fe_3O_4 NP are considered to be the most suited for adsorption of heavy metals from marine system. According to a research, removal percentages of 98.8%, 96.4%, and 95.7% were observed for Hg(II), Pd(II), and Pb(II) ions, respectively, when Fe_3O_4 NP were used [72]. Graphene oxide nano-sorbents were used to effectively remove nickel, lead and chromium from waste effluents generated by pharmaceutical companies [73]. Table 3 shows different nanoparticles that were used for removal of organic and inorganic contaminant from water.

5.2. Sensors

To control pollution in the environment, detection of the contaminant is a vital step. Gold nanoparticles are efficient to detect lead, mercury, and cadmium and silica nanoparticles are used for detection of pesticides [1]. Nanomaterial based sensors have many advantages like they are highly sensitive and selective, they are portable and they have the ability for on-site detection. In addition to this, to enhance the selectivity and ability to detect, molecular recognition probe can be deployed on the nanostructures [74]. Nanomaterial based biosensors are originated from stable, low-cost, biocompatible, and nontoxic inorganic reagents [75]. Silicon-based materials [76], metallic nanoparticles [77], and carbon-based materials [78] have been widely used in the design of sensors. Nano-sensors are categorized based upon the nanomaterial they comprise of, analyte they sense, and the signal transduction technique used to observe analyte recognition [79]. Colorimetric sensors are designed for the fast detection of lead by combining DNAzymes

Table 1: Different organic and inorganic pollutants.

Type of contaminant	Name of contaminant	Toxicity profile
Organic	Petroleum hydrocarbon	The most common petroleum hydrocarbon is polycyclic aromatic hydrocarbons, aliphatic, branched, and cycloaliphatic alkanes. Their source is refinery industries. Inhalation can cause memory loss, weakness, arrhythmia, and depression. Exposure to the skin can cause burns and dermatitis. Oral exposure can cause vomiting and diarrhea [19]. More than 30,000 Americans are affected by hydrocarbon toxicity per year. 20 deaths per year are attributed to hydrocarbon toxicity roughly [118].
	Pesticides	These are used to prevent or kill pests for better plant growth. Immune suppression, hormone disruption, and cancer can be caused by the exposure of pesticides. In developing countries 20,000 deaths are caused by the intoxication effects of pesticides in developing countries per year [19,119].
	Phenols	Red blood cells and liver can get damaged if exposed with even low concentrations of phenols. They act as carcinogens and new substitute compounds are formed when these interact with microorganisms, inorganic and other organic compounds in water. These substitutes are more toxic than the original phenolic compounds. For complaints about phenol exposure, 1000 calls/year are received by The National Poison Data System [120,121].
Inorganic	Lead	Contact with lead affects the nervous system, cause anemia, damages kidney, and liver and can cause miscarriage in pregnant ladies [122]. The maximum contaminant level of lead is 0.006 mg/ml. According to the WHO, the maximum tolerable limit value for metallic lead in drinking water is 0.05 mg/L. The Environmental Protection Agency allows the permissible limit value for lead in waste water to be 50 ppb. Several industrial processes related to storage batteries, mining, and mineral smelting are sources of lead contamination [123].
	Mercury	Mercury contamination is caused by the manufacture of chlorine and lye from brine, (chlor-alkali process) [124] and mining [125]. The maximum contaminant level of mercury is 0.00003 mg/ml. Mercury can damage the blood–brain barrier in the central nervous system, can affect the endocrine system and can damage the reproductive system [126]. A 2013 report documented 1300 single mercury exposures in the United States in 2013 [127].
	Zinc	Main sources of zinc pollution are discharge of municipal wastewater, coal-burning power plants, and industrial methods involving metals [128]. The maximum contaminant level of zinc is 0.80 mg/ml. The 2017 American Association of Poison Control Centers National Poison Data System Annual Report totals 1236 instances of exposure to zinc compounds. Cases of coagulopathy, liver necrosis, thrombocytopenia, and even demise have been reported because of severe exposure [129].

Table 2: Synthesis method of nanoparticles.

Synthesis methods	Advantage
Nanoparticles synthesized from plants	Plants are easily accessible, non-toxic to handle and have extensive range of metabolites that may help in reduction and may act as stabilizing agents. There are many molecules in plants that help in synthesis of nanoparticle such as alkaloids, carbonyl groups, phenolic, proteins, pigments, and amines [130]. Root, stems seed, and flowers can be used for synthesis. Leaves of *Euphorbia prostrata* were used to synthesis silver and titanium dioxide nanoparticle of spherical shapes [131]. Nanoparticle synthesis by plants includes washing and boiling of plant part with distilled water and then filtering and adding the nanoparticle solution. Biomimetic spherical gold nanoparticle was synthesized using *Gelidium pusillum* [132]. According to an experiment, uranium was removed from water sample by nano-scale zerovalent copper that was synthesized from *Anacardium occidentale* [133]. Another experiment demonstrated the removal of azo dyes from wastewater by palladium nanoparticles that were synthesized from agro-waste cotton ball peels [134].
Nanoparticles synthesized from bacteria	For synthesis of nanoparticle, bacteria are a well suited microorganism as there is no requirement of harmful and costly chemical materials. Metals can be mobilized, immobilized and also precipitated by bacteria. Gold, silver, platinum, titanium, etc., can be synthesized as bacteria are believed to be a potential bio factory for synthesis of these nanoparticles. Significant amounts of nanoparticles can be synthesized due to extracellular secretion of enzymes [100]. They have the ability to survive and grow at high concentration of metals as well. *Bacillus cereus* was used to synthesize silver nanoparticles of spherical shape [135]. In an experiment performed by Johnston, he explained how pure gold nanoparticles can be obtained from *Delftia acidovorans* [136]. Silver nanoparticles were reportedly generated intracellularly from *Bacillus licheniform* [137].
Nanoparticles synthesized from fungi	Fungi can be grown *in vitro* and this helps in the production of nanoparticles at larger scale. Furthermore, there is secretion of enzymes and proteins as reducing agents in fungi and fungus biomass grows at a faster rate. Interaction is also better because of the presence of mycelia. *A. niger* is used for the synthesis of gold nanoparticles of elliptical shape [138]. Other advantages associated with fungi are ease in biomass handling; very high wall binding capacity, intracellular and extracellular synthesis of nanoparticles is possible, good accumulation of metal and economic liability [131]. Silver nanoparticles generated using fungi enable the control of pathogens, with good biocompatibility and low toxicity [139]. Silver nanoparticles were synthesized from *Penicillium cyclopium* [140].
Nanoparticles synthesized from yeast	Yeast has the ability to accumulate metals as they have large surface area. Extracellular sequestration, bioprecipitation, bio-sorption, and chelation are some detoxification mechanisms used by yeast. These mechanisms are being used during nanoparticle synthesis [141]. Yeast threads are also sometimes being used for nanoparticle synthesis [142]. *C. glabrata* is used for the synthesis of cadmium sulfide nanoparticles of hexamer shape [138]. Selenium nanoparticles were synthesized from *Magnusiomyces ingens* [143]. It was seen that there was a link between the development of cadmium sulfide quantum dots and growth phase of yeast *Schizosaccharomyces pombe* cells [141].

and metallic nanoparticles as explained by Juewen Liu and Yi Lu in an experiment [80]. Pollutants such as heavy metals, toxic bacteria, harmful chemicals and pesticides can be detected by another type of sensor called cantilever sensors. The nanolayer of sensor interacts with the pollutant and this leads to the bending of sensor arm due to change in surface stress of the sensor [44]. For the detection of Cd^{2+} in water samples, an "ion imprinted" dual-emission QDs nanohybrid (CdTe@SiO2@CdSe) based ratio metric fluorescent probe was developed [81]. In an experiment, reduced graphene oxide (rGO) gold (AuNP)/colloid nanoparticles were synthesized by growing AuNPs in rGO via $HAuCl_4$ reduction on graphene oxide nanosheets. The nanoarchitecture of the colloid could be controlled by an in situ Pb^{2+} enhanced gold leaching reaction, making the colloid a flexible surface-enhanced Raman scattering (SERS) platform for Pb^{2+} detection [82].

5.3. Membranes

Membranes are used to manufacture nanomaterials as it allows permeability control and fouling resistance in numerous structures and relevant functionalities. Nanoparticles are either put together into porous membranes or are arranged through blending process for the manufacture of polymeric and inorganic membranes. Metal oxide nanoparticles like TiO_2 and carbon nano tubes are used to manufacture membranes as membranes manufactured from them have improved permeability and are bacteria resistant [83]. An adsorptive nanocomposite ultrafiltration membrane has been used for the removal of arsenate from water [84]. Recently, a research was done where heavy metal ion were removed from water using a nanofiltration membrane modified by curcumin boehmite nanoparticle [85]. For the synthesis of polymer composites membranes, carbon nanotubes are becoming a popular choice because of qualities such as large aspect ratio, tensile modulus, low mass density, high flexibility, and high strength. Due to these qualities, these membranes provide maximum performance [16]. Figure 2 shows the interaction of nanocomposite membrane and water for heavy metal removal [86].

5.4. Nano Catalysts

Nano-catalysts have excellent activity, greater selectivity, and high stability as compared to conventional catalysts as nanoparticles have large surface-to-volume ratio and smaller size [87]. In an experiment, silver NP deposition was carried out on the surface of Al-MOF/Fe_3O_4 functionalized with PDA and it was used as a nano-catalyst for the breakdown of organic pollutants. Al-MOF/Fe_3O_4/PDA@Ag displayed exceptional catalytic capability for removal of ciprofloxacin, norfloxacin, and methyl orange in water systems [88]. There are many researches going on for manufacturing of nano-catalyst using environmental-friendly and easy methods. For example, RT synthesis of broken porous nanosheets was carried out with CuO and used as catalysts to decompose organic contaminant (AR dye) using $NaBH_4$ as reducing agent in fluid system [89]. In addition to this, Fe_3O_4@SiO_2-Ag nanocomposite was prepared using an eco-friendly, inexpensive, and natural production technique using safflower flower aqueous extract excluding any stabilizers or surfactants. To carry out the catalytic reduction with $NaBH_4$, of MO, 4-NP, and MB, Fe_3O_4@SiO_2-Ag magnetic nanoparticles exhibited significant and stable activity. Moreover, the catalyst can be reused without any major activity loss 8 times and simply and rapidly separated using a magnet [90]. Table 4 discusses different nano-catalyst that is being used to remove contaminants.

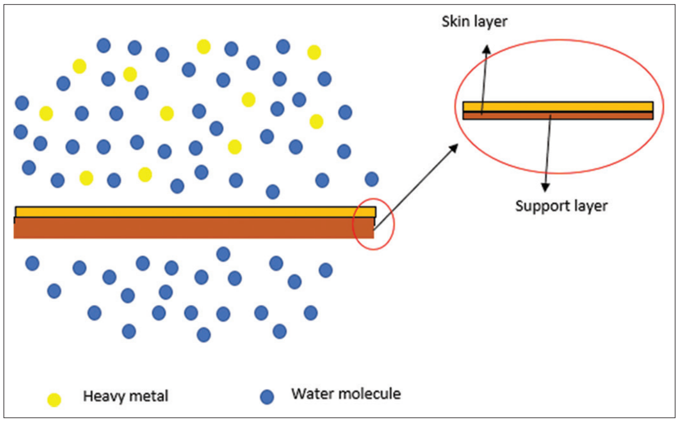

Figure 2: Nanocomposite membrane for heavy metals removal [86].

Table 3: Nanoparticles for removal of organic and inorganic contaminant from water.

Nanomaterial	Adsorbent	Metal removed	References
Iron oxide nanomaterial	CuO	Cd (II)	[144]
Metal oxide nanomaterial	γ-Al2O3	Ni (II)	[145]
Carbon based nanomaterial	MnO2-coated CNTs	Hg (II)	[146]
Polymer-based nanomaterials	Cellulose/ZrO2 nanohybrid	Ni (II)	[147]

Table 4: Nano-catalyst for contaminants removal.

Nano-catalyst	Pollutant removed	References
Pd nanoparticle	Reduction of organic contaminant	[148]
Pd-RGO nanocomposite	Degradation of dye contaminants	[149]
Nio nanoparticle	Removal of Pb (II)	[150]
CuO-CeO2-CoOx composite nanocatalyst	Ni (II)-citrate complexes	[151]
Vanadium and silver co-doped titanium oxide nanocatalyst	Methylene orange	[152]

5.5. Nanofilters

A controlled pressure filtration method that uses a semi-permeable organic membrane that has very tiny pore size usually ranging from 0.1~10 nm and 1~2 nm is termed as nanofiltration [91]. Nanofiltration membranes have a slightly charged surface at neutral pH. For the transportation mechanism and separation properties, this negative surface charge plays a crucial role. Nanofiltration is a pressure-driven cross-flow process characterized by a membrane pore size that has a molecular weight limit of roughly around 200–1000 Daltons and an operating pressure of 150–200 psi [92]. For wastewater treatment, nanofiltration is the most efficient and commonly used technique. It is used for the removal of organic and inorganic pollutants. There are many advantages associated with nanofiltration including high flexibility, low cost, and easy production. Polymeric membranes and ceramic membranes are the two types of nanofiltration membranes that are being used [93]. For the removal of pollutants from contaminated water sit, plastic bottles inserted with nano-filter are used. A commercially available technology to filter microbes of up to 15 nm size is LifeSaver Bottle which consists of super hydrophilic filter [94]. In an experiment, removal efficiencies of 97% for Cd, 99.9% for Cu, 84% Pb, 93% As (V), 89% As (III), and 98% for Mn were seen when nanofiltration membrane was used [95]. In recent research, carboxylated graphene oxide-incorporated polyphenylsulfone nanofiltration membrane was used to remove heavy metals [96]. A nanofiltration membrane was prepared by cross linking technology and layer by layer assembly of Polyethyleneimine (PEI) and sodium lignosulfonate on polysulfone (PSf) membrane surface. This nano filter membrane was able to remove more than 95% heavy metal ions such as cadmium, zinc, chromium, and copper. Figure 3 shows the procedure of PEI/LS membrane formation [97].

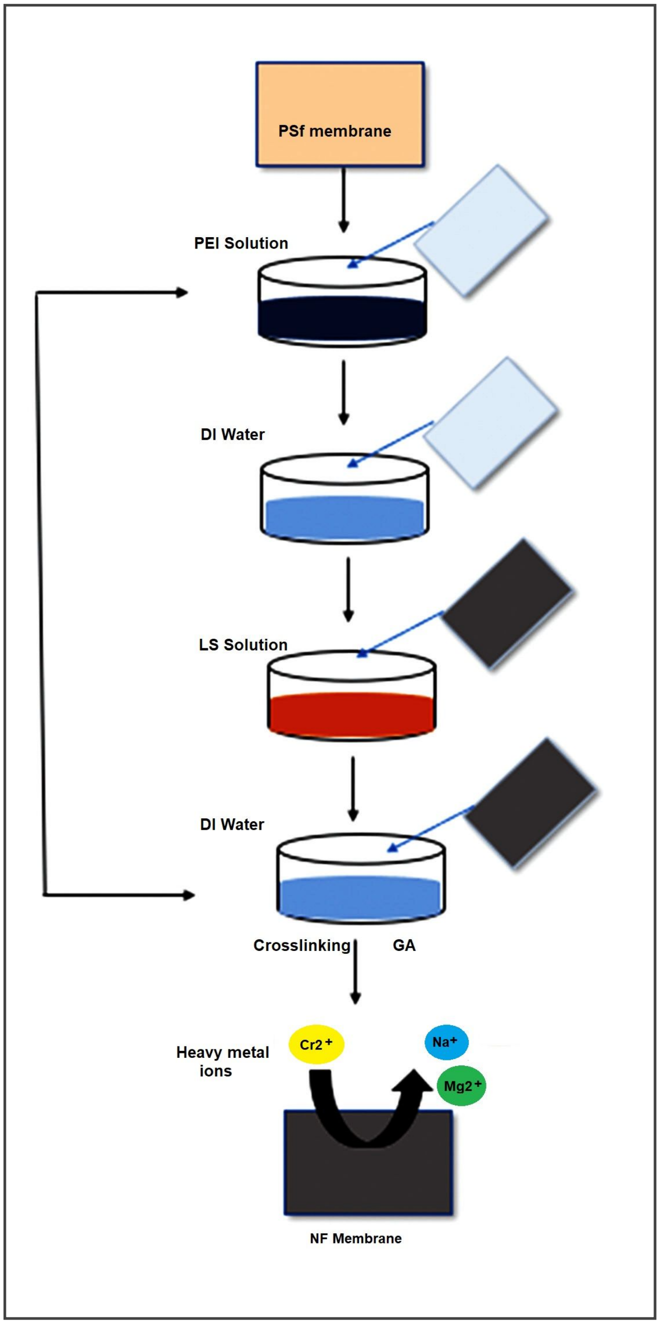

Figure 3: Process of PEI/LS membrane formation [97].

6. ENVIRONMENTAL FACTORS FOR NANOMATERIAL EFFICIENCY

Numerous factors play a significant role in nanomaterial efficiency. The competence of nanomaterials depends on environmental conditions. Nanomaterials need convenient conditions to show its potential. Table 5 shows various environmental factors that affects the effectiveness of nanomaterials for remediation of aquatic systems.

7. LIMITATIONS OF NANOPARTICLES FOR AQUATIC REMEDIATION

Although there are many advantages of using nanotechnology for waste water treatment, there are several limitations as well. Given below are some of the limitations.

7.1. Nanomaterial Toxicity

Chemical and physical properties determine NP toxicity. These include presence or absence of a shell and groups active on the surface, size, specific surface area, shape, catalytic activity and surface charge [98]. As nanomaterials are very small in size, they penetrate through endothelial and epithelial barriers into the blood and lymph and from there they reach organs. Other routes by which nanomaterials can be exposed include the skin, eyes, and gastrointestinal tract [99]. Through cell membrane they can diffuse into cells or are transported into cells by transcytosis mechanisms [98]. The capability of engineered nanoparticles to be ingested by organisms, transported into food chains and influence microbial ecosystem, plant, invertebrate or fish communities as well as ecosystem processes require further systematic investigation [100].

7.2. Nanomaterial Transformation Risk

The fate of nanomaterials is administered by mode of interaction between biotic nanomaterials and abiotic factors [101]. Furthermore, as nanoparticles such as carbon nanotubes and fullerenes are highly insoluble in water, they can easily be removed using water columns. Engineered nanomaterial gets transformed to other forms [93]. Nanomaterials can undergo photochemical transformation on coming in contact with light and oxidation reduction can sometimes be favored [102]. The interactions between nanomaterials and the environment can get altered due to these transformations, which ultimately direct the adsorption and desorption of pollutants in aquatic system [93].

7.3. Self-toxicity of Nanomaterials

Although nanomaterials have various applications in water remediation, they also possess self-toxicity properties. Even at low concentrations, few metal oxides show some toxic character. Moreover, the toxicity of carbon nanotubes depends on various factors such as initial concentration of material, length, distribution ratio, aggregation degree, and surface area. In addition to this, double walled carbon nanotubes are more toxic than single walled carbon nanotubes. Diseases such as fibrosis, pulmonary and basic inflammation, granuloma in lungs, apoptosis, and oxidative stress, are all associated with it. In case of TiO_2, initial concentration and time is responsible for the toxicities of different composition ratio of

Table 5: Environmental factors that affects nanomaterial efficiency.

Environmental factor	Description
pH	pH plays and important role in the efficiency of nanomaterial for the removal of pollutants. The pH value of the solution influences the surface charge of the nanomaterial and thus its adsorption capacity. Moreover, bioavailability and existing forms of heavy metal ions are also determined by the pH value [153]. Environment of aquatic system has a pH range of 5–9, and adsorption of heavy metal ions by NZVI-based materials can occur between pH range of 5–9 [154]. At a lower pH value, more protons react with nanomaterials and convert H+to H2 and that can lead to more reactive atomic hydrogen and a faster rate of reduction [153].
Contact time	To know the effect of contact time on metal ion sorption, Lagergren kinetic models, pseudo first-order, Zeldowitsch, Elovich, and pseudo-second-order, are employed [155]. According to a study by Lv *et al*., within 2 h, Cr (VI) was quickly removed by NZVI–Fe3O4 nanocomposites within 2 h and then slowed down until equilibrium. The kinetics model was described well by the pseudo-second-order model [156].
Absorbent dose	The adsorbent dose is very important owing to its capability to indicate the capacity of the adsorbent for a certain original amount of the adsorbate. According to an experiment conducted by Arshadi *et al*., removal percentage of Pb (II) increased with increasing the adsorbent dosage because number of adsorption sites also increased [157].
Temperature	Energy of reaction activity is determined by temperature and hence temperature plays an important role in adsorption process. Equilibrium adsorption capacity of nanomaterials can change due to increase and decrease in temperature. The distance between nanoparticles can get reduced and the redox reaction rate can increase due to rising of temperature [153]. According to an experiment conducted by Dubey *et al*., the removal efficiency of Hg (II) by chitosan–alginate nanoparticles, increased with the increasing temperature until 30 degree C and then started to decrease [158].
Particle shape and size	The properties of nanoparticle are dependent on the particle size. According to a study, the melting of NP decrease when the size of the NP reaches the nanometer scale [159]. The chemical properties of NP are influenced by the shape and nature of the synthesized NP [102].

TiO_2. Generally, even at high concentrations for 24 h, it is considered as non-toxic [103].

7.4. Ecotoxicity

Nanoparticles have to undergo aging processes like aggregation, chemical transformation, and disaggregation. A strong aggregation was observed in silver nanoparticles when they interacted with a minimally defined medium [104]. The interplay between the nanoparticles transport and these processes governs the fate and eventually the ecotoxicological ability of nanoparticle. The fate and ecotoxicological potential of nanoparticle is determined by their interaction with the abiotic surrounding in the environment [100]. Schwab *et al*. reports an increase in toxicity induced by herbicide (diuron) applied at concentrations that are environmentally relevant in the presence of NP based on carbon [105]. Likewise, in the presence of fullerene nanoparticle, the acute toxicity of the insecticide bifenthrin was escalated, but there was no effect on the chronic effects. Moore [106] as well as Hund-Rinke and Simon [107] proposed that detrimental effects can be caused by nanoparticles by the formation of reactive oxygen species in the biota that further affect biological make-ups.

7.5. Water pollution

Characteristics that make nanoparticles useful are also responsible for inducing toxic effects on aquatic organisms. Concerns about the effects on genotoxicity of NM have increased in the last years [108]. Carbon nanotube-induced genotoxicity can be ascribed to various factors such as direct interaction with cellular components, direct interaction of the particles with the DNA, the release of toxic ions and indirect destruction caused by ROS [109]. Cimbaluk *et al*. concluded that the commercial sample of multi-walled carbon nanotubes can be toxic in *Danio rerio* and *Astyanax altiparanae* fish models after acute and sub chronic exposure to water [110]. Likewise, Khan *et al*. concluded that significant damage to the genetic material in the test fish was stimulated by Ag nanoparticles which caused nuclear alterations in blood erythrocytes. In addition to this, Ag nanoparticles also generate oxidative stress [111].

8. FUTURE PROSPECTS OF BIOREMEDIATION BY NANOTECHNOLOGY

The concept of nanotechnology for a contaminant free and clean environment has drawn attention of researchers owing to its multidisciplinary approach. In the last decade, many electrochemical biosensors coupled with nanomaterials such as nanowires, nanorods, and nanospheres are being developed [112]. These biosensors offer many advantages such as high sensitivity and real-time detection of heavy metals. Such biosensors will be widely used in the future for monitoring environmental metal pollution. Among nanomaterials, usage of zerovalent iron is rapidly increasing [113]. Recently in a study acid orange 7 was successfully removed using porous adsorbent-supported zerovalent iron [114]. Another recent study demonstrated the effective removal of chromium from marine system with the help of $CaCO_3$ coated nanoscale zerovalent iron [115]. Synthesis of modified nanomaterials that are eco-friendly, effective, easy to handle and having high efficiency is also gaining attention [103]. There are however many limitations to using nanomaterials for bioremediation and hence, their toxicology, transport, fate, and bioaccumulation needs to be further explored and understood [116]. The main apprehension that arises today is the disposal of NP after they have served their purpose in water treatment. The potential risk of NP is not known and its field-scale implementation has unpredictable risk therefore more research needs to be done on this concept [117].

9. CONCLUSION

Various pollutants enter the aquatic ecosystem through industries and cause damage to the aquatic life and to humans as well. Water contamination is a big problem in today's world and it needs to be solved. The application of nanomaterials in treatment of water and pollutant removal has a very bleak and promising future in comparison to their traditional equivalents. The effectiveness of nanotechnology has been extended to the degradation of contaminants from various sectors, for example, medicine, dyes, and pharmaceuticals. Properties such as small surface area and high adsorption and selectivity potential make nanomaterials advantageous for removal of organic and inorganic contaminants such as dyes and heavy metals from water. Several nanomaterials have been successfully developed for wastewater treatment. These include titanium oxide nanoparticles, carbon nanotubes, and zerovalent ions. Nanomaterial approaches such as nano-sorbents, nanostructured membranes, sensors, filters, and catalyst are very efficient, eco-friendly and less time and energy consuming methods. There are, however, many risks associated with nanotechnology such as ecotoxicity, transformation risk, and nanoparticle toxicity. For water treatment, nanotechnology has a promising and great future, but a sincere and committed monitoring from the government and scientific community are needed. More efforts and research are needed to re-evaluate the ecotoxicity potential for each new NP modification. Moreover, for developing green methods of synthesizing nanomaterials, further research is required.

10. AUTHORS' CONTRIBUTIONS

All authors made substantial contributions to conception and design, acquisition of data, or analysis and interpretation of data; took part in drafting the article or revising it critically for important intellectual content; agreed to submit to the current journal; gave final approval of the version to be published; and agreed to be accountable for all aspects of the work. All the authors are eligible to be an author as per the International Committee of Medical Journal Editors (ICMJE) requirements/guidelines.

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This study does not involve experiments on animals or human subjects.

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