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## Chapter

# Starch-Based Hybrid Nanomaterials for Environmental Remediation

Ashoka Gamage, Thiviya Punniamoorthy and Terrence Madhujith

## Abstract

Environmental pollution is becoming a major global issue with increasing anthropogenic activities that release massive toxic pollutants into the land, air, and water. Nanomaterials have gained the most popularity in the last decades over conventional methods because of their high surface area to volume ratio and higher reactivity. Nanomaterials including metal, metal oxide, zero-valent ions, carbonaceous nanomaterials, and polymers function as adsorbents, catalysts, photocatalysts, membrane (filtration), disinfectants, and sensors in the detection and removal of various pollutants such as heavy metals, organic pollutants, dyes, industrial effluents, and pathogenic microbial. Polymer-inorganic hybrid materials or nanocomposites are highly studied for the removal of various contaminants. Starch, a heteropolysaccharide, is a natural biopolymer generally incorporated with other metal, metal oxide, and other polymeric nanoparticles and has been reported in various environmental remediation applications as a low-cost alternative for petroleum-based polymers. Therefore, this chapter mainly highlights the various nanomaterials used in environmental remediation, starch-based hybrid nanomaterials, and their application and limitations.

**Keywords:** environmental remediation, hybrid nanomaterials, nanomaterials, starch, starch-based hybrid nanomaterials

## 1. Introduction

Environmental pollution is becoming a serious global problem that society faces today. Ongoing anthropogenic activities, extensive food and agriculture practices, industrialization, and urbanization release huge amounts of pollutants into the environment that can cause air, water, and land pollution, consequently threatening to human, animal health, and ecosystem [1, 2]. These toxic pollutants can enter the human body either through inhalation, ingestion, or absorption and adversely affect health. Further, bioaccumulation of some heavy metals through the food chain and persistent organic pollutants in biota and fishes poses a huge threat to humans and wildlife and requires sustainable, efficient, and low-cost technologies to detect, monitor, and remediate the hazardous pollutants [1].

Different forms of pollutants are released into the environment; soil, water, and air. Organic substances (pesticides, insecticides, fertilizers, oil spills, phenols, chloro-form, hydrocarbons), heavy metals and metalloids (Cr<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, As, Hg), dyes, industrial effluents, sewage, as well as microbial pathogens are few contaminants in soil and water. While, contaminants such as toxic gases (nitrogen oxides, sulfur oxides, carbon oxides, ozone), suspended airborne particles, and volatile organic compounds are found in the atmosphere [3, 4].

These contaminants in soil, water, and air are remediated by using different conventional techniques, such as physical, chemical, and biological methods [4–6]. These techniques may be used in combination with one another to remediate contaminated sites. Adsorption (clay minerals, industrial wastes, biomass, biochar, activated carbon, biopolymer), chemical treatments, bioremediation, coagulation and flocculation, ion exchange, membrane-filtration, solidification/stabilization, electrokinetics, and electrochemical treatments technologies have been used in heavy metal removal from soil and water [7]. Bioremediation using microorganisms and plants helps to detoxify or remove crude oil, heavy metal removal, and pesticide degradation from soil and water [4, 5].

However, the majority of these conventional techniques are expensive, laborious, environmentally destructive, time-consuming methods, also involved in the consumption of chemicals and the generation of undesirable toxic by-products that are hazardous to the environment. Further, complexities of the mixture of different compounds, high volatility, and low reactivity of contaminants also limit the applications in environmental remediation [3, 5, 8]. New environmental remediation technologies are constantly being explored, and recent studies have focused on developing new environmental remediation technologies using various nanomaterials [3].

### 2. Nanotechnology in environmental remediation

#### 2.1 Nanotechnology and its advantages and applications

Nanotechnology has gained much attention in environmental remediation over the last few decades [1]. Nanotechnology is an advanced technology that works on the material in nanometer scale (1–100 nm) and produces materials, devices, and systems with specific and novel properties and functions by controlling the size and the shape of matters [1, 4, 9]. The nanomaterials are broadly categorized as organic and inorganic nanomaterials. Some literatures is classified based on materials used in the synthesis process; inorganic (metal, metal oxide, zero-valent metals), carbon-based [graphene, carbon nanotubes (CNTs)], polymer-based (dendrimers or polyamidoamine), and composite based nanomaterials [3, 10].

Nanomaterials have several advantages in environmental remediation over conventional methods; cost-effective, simple to use, energy conservative, sustainable, and more effective methods. Due to the properties such as smaller size (1–100 nm) and higher surface area to volume ratio of nanomaterials, they provide more reaction surface area, which increases reactivity and thus its sensitivity and effectiveness. Nanoparticles have a high sorption capacity for inorganic and organic compounds because of their specific characteristics; large surface area, an increased number of surface activation sites, a good affinity to other species [11]. Further, nanotechnology helps in the development of remediation technologies that are specific and efficient for a particular pollutant [3, 9].

Nanotechnology has potential applications in many fields, including food and agriculture, packaging, pharmaceutical, drug delivery, energy, and pollution treatment [1, 12]. Of which, the application of nanotechnology in pollution control and environmental remediation has gained popularity over the last decade; wastewater treatment, cleaning groundwater, and remediation of soil contaminated with pollutants. In the field of environment, nanotechnology has been used in pollution detection (sensing and detection), prevention of pollution, and purification/remediation of contamination [9]. Thus, nanotechnology provides a sustainable solution to the global challenges of protecting water, soil and providing cleaner air [13].

### 2.2 Nanomaterials in environmental remediation

Various nanomaterials such as inorganic, carbonaceous nanomaterials, polymerbased nanomaterial are used in environmental remediation (air, soil, and water) as adsorbents, catalyst, photocatalyst, membrane (filtration), disinfectants, and sensors [1, 3, 14].

Metal (silver, gold), metal oxides (iron oxides, TiO<sub>2</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>), and zero-valent metals (Fe<sup>0</sup>, Zn<sup>0</sup>, Sn<sup>0</sup>, and Al<sup>0</sup>) based nanoparticles are mostly studied for environmental remediation including disinfection of water, treatment of drinking water, groundwater, wastewater, and air, because of their adsorption, antibacterial, antimicrobial, photocatalytic, reductive dehalogenation, desulfurization, and catalytic reduction activities [3, 15, 16]. Carbonaceous materials in different structural configurations; fullerene, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and graphene and used in the removal of organic and inorganic contaminants from air and water due to its adsorption and photocatalytic property [3].

Nanoscale zero-valent iron (nZVI) is the most widely studied nanoparticle in soil remediation [12] and is used for reductive immobilization of heavy metals in soil that decreases the bioavailability and mobility of heavy metals and prevents leaching into groundwater and transfers to the food chain [1]. Further, nanomaterials such as nanoparticles (NPs) (metal; Au, Ag, Fe, bimetal; Fe/Ni, Ag/Cu, metal oxides; TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>), nanotubes (carbon nanotubes, halloysite nanotubes), and nanocomposites (graphene oxide) have been reported to utilize in detection, degradation, and removal by adsorption of pesticides [17].

Emission of greenhouse gases (carbon dioxide, methane, nitrous oxide, and fluorinated gases), volatile organic compounds (ethylene, aniline, benzene), are controlled either by separation or capturing, such as filtration, absorption in liquids, adsorption on solids, or a combination of these processes. In addition, bioaerosols (aerosols of biological origin such as viruses, bacteria, and fungi), an indoor air pollutant, can rapidly spread with airflow and can cause numerous diseases, including infections and allergies. The air filtration process using antimicrobial materials such as Ag NPs, Cu NPs, CNTs, and natural products is the most applied and effective technique to remove bioaerosols [1].

Various nanomaterials have also been studied for the treatment of drinking water and industrial wastewater, including adsorbents (nZVI or Fe, MnO, ZnO, MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Magnetite or Fe<sub>3</sub>O<sub>4</sub>, CNT), photocatalysts (ZnO, TiO<sub>2</sub>, metal-based nanocomposites such as Ag/ZnO and Pt/ZnO, CdS, ZnS: Cu, CdS: Eu, CdS: Mn), electrocatalysts (Pt, Pd, Au/metal oxides TiO<sub>2</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>), nano-membranes (MWCNTs, electrospun PVDF, PVC, sodium titanate nanobelt membrane), disinfectants with antibacterial effects (Ag NPs, chitosan NPs, TiO<sub>2</sub>), nanosensors (Au NPs, Ag NPs) [14, 16, 18].

#### 2.3 Hybrid nanomaterials

The term hybrid refers to fusion, joining, or mixing of characteristics at the molecular level, which generates a hybrid material owning the effective functionality of single components and eliminates undesirable characteristics [19, 20]. In this context, hybrid nanomaterials are defined as materials that are made up of two or more organic or inorganic components such as organic-organic (starch-cellulose), inorganic-inorganic (TiO<sub>2</sub>-Ag), and organic-inorganic (starch-TiO<sub>2</sub>) compounds, connected at the nanometer scale, combine the intrinsic characteristics of its individual constituents to additional properties due to synergistic effects between the components [21, 22]. These hybrid materials are synthesized by different methods such as covalent immobilization, electrostatic binding, polymerization methods, among others [21]. The properties of the hybrid material vary with the material (organic or inorganic), structure, and different component interface, and the optimum combination can enhance mechanical strength and thermosensitivity, improve thermal and chemical stability, and regulate optical, anticorrosive, magnetic, electrical, and thermal properties as well as fire retardancy [23]. Because of their excellent mechanical, physical, and tribological characteristics, hybrid nanomaterials are widely used in the area of food packaging, plant protection, electrochemistry, and various additional applications in the environmental, biotechnological, and agri-food sectors [19].

Generally, hybrid materials are classified into two categories depending on the intra- and intermolecular interactions among the organic matrix and cross-linking agent [21, 23];

- 1. Class I (organic and inorganic exhibiting weaker interactions such as noncovalent interactions; van der Waals and hydrogen bonding).
- 2. Class II (organic and inorganic exhibiting strong interactions such as covalent, ionic, ionocovalent, and coordinative bonding).

"Polymer-based composites" or "nanocomposites" can be defined as hybrid organic-inorganic composites when incorporating either component in nanoscale and generally obtained by incorporation of a small quantity of an inorganic component into an organic or a polymer matrix in order to form a new component with enhanced properties [24]. The "bio-nano composites" are the materials that comprise particles with at least one dimension in the range of 1–100 nm and a constituent(s) of the biological origin or maybe biopolymers.

Biopolymers (natural polymers) have received much attention in recent last decades due to their abundance, low toxicity, low cost, biodegradability, biocompatibility, and multiple functionalities [25]. A variety of biopolymers such as polysaccharides (cellulose, chitin, chitosan, pectin, starch, dextran, xanthan, guar gum, fucoidan, heparin, hyaluronan, and pullulan), proteins (albumin, casein, collagen, fibrinogen, and gelatin), polylactic acid (PLA), and nucleic acids have been used as alternative eco-friendly materials to replace synthetic polymers or petroleum-based polymers (PP, PE, and epoxies) partially or even totally [25–27]. Polysaccharidebased hybrid nanocomposites have become increasingly essential materials over the past decades [25, 27]. Many studies have reported the application of polysaccharidebased nanocomposites (natural polymer) in various fields such as food, biomedical, ecofriendly and sustainable food packaging, and environmental pollution control and remediation [28–30].

Due to the poor barrier, mechanical, and processing properties, natural polymers (biopolymers) are incorporated with other synthetic polymers or nanomaterials to improve their properties and applications [31]. Polysaccharides such as cellulose, chitin, chitosan, and starch are the most studied biopolymers and used in biodegrad-able nanocomposites with metal nanoparticles (Au, Ag, Cu, and Pd), metal oxide nanoparticles (TiO<sub>2</sub>, ZnO, CuO, Cu<sub>2</sub>O, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>) and carbon nanomaterials (graphene and carbon nanotubes, CNTs) [25].

## 3. Starch hybrid nanomaterials for environmental remediation

#### 3.1 Starch

Starch, a natural, abundant, renewable, biocompatible, and biodegradable biopolymer, is naturally found in many plants as the primary source of energy and reserved in many parts of plants such as stalks, stems, roots, tubers, and seeds; main sources being cassava, wheat, rice, barley, maize or corn, banana, and potatoes, among others. Starch is a heteropolysaccharide that comprises D-glucose monomers joined with glycosidic bonds and can be denoted as  $(C_6H_{10}O_5)_n$  with the basic chemical formula. Starch is a heteropolysaccharide composed of two types of macromolecules: linear amylase (around 10–30% of starch granule) and branched amylopectin (remaining 70–90% of starch granule). Amylose is a linear polysaccharide chain of D-glucose units linked by  $\alpha$ -(1,4)-glycosidic bond with a degree of polymerization in a range of 300–10,000. Amylopectin is a very high-molecular-weight polymer with a backbone structure of amylase cross-linked through  $\alpha$ -(1,6) glycosidic bonds. The basic structure of amylose and amylopectin are shown in **Figure 1** [25, 32, 33].

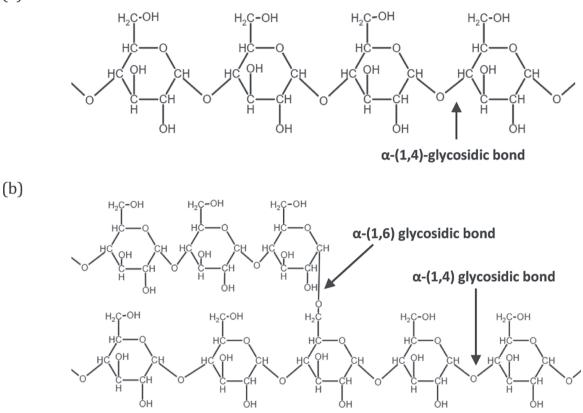
#### 3.2 Starch hybrid nanomaterials

Starch-based nanocomposites have wide applications in the fields of food and agriculture, packaging, biomedical, and environmental remediation as emulsion stabilizers, fat replacers, flexible films, carriers of bioactive compounds, drug delivery, and adsorbents in sewage treatment or wastewater treatment [34–36]. Starch nanoparticles are usually smaller than 300 nm in dimension with a high specific surface area. The various forms of starch-based nanoparticles are starch nanoparticles, starch nanoparticles, starch nanoparticles, starch nanoparticles, starch nanoparticles, starch nanoparticles, starch nanogels, and starch nanofibers [36].

Starch is a natural polymer, gained much attention because of its renewability, biodegradability, abundance, eco-friendly, relatively low cost, non-toxic, high adsorptive capacities, amenable to various chemical modifications, and cohesive film-forming properties. Starch molecules can bind with the heavy metal ions or contaminants through the functional (hydroxyl) groups on the starch structure [37, 38]. Further, high amylopectin content in starch has powerful swelling properties that are important in sorption-based applications [39]. In most published works, carbohydrates have been used as reducing, stabilizing, and/or complexing agents [40].

However, starch in a pure or native form has drawbacks such as poor processability, high brittleness, susceptibility to retrogradation, high viscosity, low adsorption capacity, and greater hydrophilicity or high-water absorption capacity, which limits its many applications in the environmental field. To overcome this problem and to obtain water-insoluble materials, starch is modified by physically [hydrothermal





#### Figure 1.

Structures of starch: (a) amylose and (b) amylose pectin.

processing (i.e. gelatinization)] or chemically (etherification, esterification, crosslinking, grafting, oxidation, and enzymatic hydrolysis) or a combination of these two methods [41–44]. Polysaccharides exhibit a great number of reactive hydroxyl groups, which can be exploited for direct esterification, etherification, and various chemical modifications [41].

Starch-based hybrid materials have numerous functionalities and/or novel properties due to the interactions between the individual constituents, mostly associated with synergetic effects, and have been reported in environmental remediation applications [25]. Several starch-based composites have been reported to have a remarkable adsorption tendency for the removal of heavy metals and dyes [45].

#### 3.3 Starch-based hybrid nanomaterials in environmental remediation

#### 3.3.1 Starch/metal or metal oxides or non-valent metals

**Table 1** shows the recent examples of the combination of starch and different metal, metal oxide, zero-valent metal, CNTs, and other polymers nanoparticles, such as Au, Ag, Cu, Pd, ZnO, TiO<sub>2</sub>, nZVI, among others. Nanomaterials are widely used to treat different contamination because of their high specific surface area to volume ratio, rapid kinetics, and high reactivity. However, pure or unmodified nanoparticles tend to agglomerate easily into larger particles that decrease the available specific surface area and reactivity. To improve the colloidal stability of nanoparticles, surface modification has been done by coating with various polymers. Of which starch is one of the relatively cheap and green polysaccharides [53, 59].

Starch hybrid nanomaterials	Application	Reference
Starch-stabilized Fe/Cu	As <sup>2+</sup> and As <sup>5+</sup> removal from the contaminated water	[46]
Starch/Fe <sub>3</sub> O <sub>4</sub>	Removal of perfluorooctanoic acid (PFOA) in soil and groundwater	[47]
Starch/nZVI	Soil remediation—heavy metal removal, particularly Pb and Zn	[48]
Starch/nZVI	Removal of As <sup>3+</sup> and As <sup>5+</sup> from aqueous solutions	[49]
Starch-modified nZVI	Removal of Cr <sup>6+</sup>	[50]
Starch/SnO <sub>2</sub>	Water treatment—Hg <sup>2+</sup>	[51]
Starch/TiO <sub>2</sub>	Removal and determination of heavy metals such as Cd, Co, Cu, Pb, and Ni	[11]
Starch/glycidyl methacrylate	Adsorption of Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> and Cr <sup>3+</sup> in wastewater	[52]
Modified tapioca starch coated nZVI	Aqueous nitrate remediation	[53]
Starch-Fe-Pd	Water decontamination—trichloroethene	[37]
Starch xanthate	Water decontamination—Ni <sup>2+</sup> , Cu <sup>2+</sup> , Cr <sup>3+</sup>	
Carboxymethyl starch	Water decontamination—Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup>	
Polymerized starch with epichlorohydrin	Water decontamination—dyes	
Starch/polyvinyl alcohol (PVA)	Textile wastewater treatment—dye including methylene blue (cationic dye), methylene orange (anionic dye), starch, PVA	[54, 55]
PVA/corn starch hydrogel	Iron (Fe <sup>3+</sup> ) and arsenic (As <sup>3+</sup> ) removal in aqueous solution	[56]
Starch/TiO <sub>2</sub>	Removal of dye from water/wastewater	[32]
Starch-NiFe-layered double hydroxide	Adsorption of anionic dye methyl orange (MO) from aqueous solution	[45]
Starch/poly(alginic acid-cl-acrylamide) nanohydrogel	Adsorption of coomassie brilliant blue R-250 dye from the aqueous solution	[57]
Polyaniline/starch/hematite (PANI/ starch/Fe <sub>2</sub> O <sub>3</sub> )	Wastewater remediation—adsorption of different heavy metals, including $As^{3+}$ , $Zn^{2+}$ , and $Co^{2+}$ and antibacterial effect	[38]
MWCNT-starch-iron oxide	Adsorbent for removing methyl orange (MO) and methylene blue (MB) from aqueous solutions	[58]

#### Table 1.

Various starch-based hybrid nanomaterials and their applications in environmental remediation.

Rashid et al. reported that modified tapioca starch could be used as an effective surface modifier for nZVI particles for aqueous nitrate removal [53]. Starch-stabilized Fe/Cu nanoparticles in arsenic ( $As^{2+}$  and  $As^{5+}$ ) removal from the contaminated water where Cu as a metal catalyst was incorporated with Fe<sup>0</sup> (nZVI) to form an iron bime-tallic nanoparticle; then, the surface was modified to prevent the agglomeration [46].

Well stabilized (dispersed) iron oxides nanoparticles offer greater specific surface area and sorption capacity than the nanoparticles without any stabilizer towards a wide range of pollutants. Starch-functionalized magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles showed much higher  $As^{2+}$  and  $As^{5+}$  sorption capacity than pristine magnetite nanoparticles [59]. Starch-stabilized Fe<sub>3</sub>O<sub>4</sub> nanoparticles can be used as a "green" adsorbent for the effective removal of perfluorooctanoic acid (PFOA) in soil and groundwater [47]. Baysal et al. reported that starch-coated TiO<sub>2</sub> NPs can be successfully used as adsorbents for the removal and determination of heavy metals such as Cd, Co, Cu, Pb, and Ni [11]. The starch-based SnO<sub>2</sub> nanocomposite material can be used as an adsorbent for the removal of highly toxic Hg<sup>2+</sup> metal ions from an aqueous medium [51].

## 3.3.2 Starch/carbon nanotubes (CNTs)

CNTs have gained increased attention in multidisciplinary studies because of their unique physical and chemical properties. However, the hydrophobicity of CNTs may limit their application. The hydrophilicity and biocompatibility of CNTs can be improved by incorporating biopolymers such as starch in the composite system. Incorporating CNTs with starch also helps to overcome the limitation of starch, i.e. weak mechanical properties and poor long-term stability [60, 61]. MWCNT-starch-iron oxide has been reported as a better adsorbent for removing anionic dye methyl orange (MO) and cationic dye methylene blue (MB) from aqueous solutions than MWCNT-iron oxide. The hydrophilic property of soluble starch improved the hydrophilicity of MWCNTs and the dispersion of MWCNT-starch-iron oxide in the aqueous solution. In addition, the increased contact surface between magnetic MWCNT and dyes reduced the aggregates of MWCNTs and facilitated the diffusion of dye molecules to the surface of MWCNTs. Nanoparticles, ZnO, TiO<sub>2</sub>, or Ag or their complex decompose the adsorbed organic contaminants on MWCNTs as the photocatalysts [60].

## 3.3.3 Blending starch nanoparticles with different biopolymeric matrices

Starch-based hydrogels have a good adsorption capacity, which can be used for wastewater treatment by removing various cationic or anionic dyes after modification with functional groups [44]. The incorporation of starch into synthetic polymer hydrogel networks improves their swelling and adsorption capacity [44]. Hydrogel as an adsorbent is one of the best candidates for removing soluble dyes from an aqueous solution. The study of methylene blue (MB) adsorption efficiency of NaOH-treated starch/ acrylic acid hydrogel showed high dye-capturing coefficients, which increase with the starch ratio and indicates the possibility of the hydrogels' application for removing dyes from aqueous solution. In which, starch can be a natural-polymer superabsorbent because of a large number of hydrophilic groups (-OH) and other benefits such as renewable, very cheap, and biodegradable [62]. Biodegradable polymers, starch/cellulose nanowhiskers hydrogel composite, showed outstanding adsorption capacity to be employed in the remediation of methylene blue contaminated wastewaters [63]. Pectin-starch magnetite hybrid nanoparticles could be potential adsorbents for methylene blue dye with higher adsorption efficiency at a low polymer concentration and starch-pectin ratio and can be used to recycle water from the textile industry [58].

## 3.4 Limitations and future studies for using starch hybrid nanomaterials in environmental remediation

Increased nano-waste release in the environment, bioaccumulation, occupational exposure, and nanotoxicity are the major problems associated with the increased use of nanomaterials in environmental remediation. Nanoparticles incorporated in starch-based hybrid nanomaterials such as Ag, Au, nZVI, TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, CNTs, metal chalcogenides (CdS, CdSe), polymeric nanoparticles, among others, shows toxicity (acute or chronic) in high dose; growth inhibition of microalgae, disruption of membrane integrity, reactive oxygen species generation, oxidative stress, genotoxicity, and mutagenicity up to reproduction impairment in aquatic species and many health complications in human [41, 64–67].

Because of the very small size, nanoparticles are capable of entering the human body by inhalation, ingestion via food, drink, and drugs, skin penetration, or injections and they have the potential to interact with intracellular structures and macromolecules for long periods [68]. Exposure to nanoparticles is associated with a range of acute and chronic effects ranging from inflammation, exacerbation of asthma, and metal fume fever to fibrosis, chronic inflammatory lung diseases, and carcinogenesis [64].

The effect of surface modification of nanoparticles such as nZVI is not clear. Sun et al. reported that surface modifiers enhance the stability of the nZVI that either increase the toxicity due to prolonged exposure to the living organisms or decrease the toxicity via reducing the adhesion of nZVI to living organisms or preventing the release of toxic ions. Starch stabilized nZVI produced higher phytotoxicity compared to bare nZVI, this may be due to the higher dispersity, hydrophilicity, and anti-aggregation of starch/nZVI that enhances their affinity to root surfaces and the oxidability of the Fe<sup>0</sup>, forming a coating of insoluble Fe<sup>3+</sup> compounds on the root surface, and thus interferes the absorption of water and nutrients [69].

In the future, attention will be given to the green synthesis of nanomaterials because not all nanomaterials are produced in an eco-friendly way, as involves acid hydrolysis in multiple steps. There are several systems and methods for the green synthesis of nanoparticles, particularly enzymes, vitamins, microwave, bio-based methods, and from plants and phytochemicals [67, 70]. Green synthesis of nanoparticles using various natural sources, non-toxic solvents, and techniques (ultrasound, microwave, hydrothermal, magnetic, and bioproduction by fungi and other microorganisms) promote eco-friendly, sustainable, less expensive, and free of chemical contaminant production and applications [68].

Nano-wastes should be diluted and neutralized before disposal as they are extraordinarily toxic, hazardous, and/or chemically reactive. Proactive nano-waste management strategies need to be adopted to prevent long-term unintended consequences, and, where possible, nano-waste should be recycled [64].

### 4. Conclusion

Remediation is the science of removal or reduction of pollutants from the environment using chemical or biological means. Starch-based hybrid materials are a costeffective and eco-friendly solution over petroleum-based polymers in environmental remediation. Though starch is a natural polymer with many benefits, including renewability, biodegradability, abundance, eco-friendly, relatively low cost, nontoxic, poor barrier, and mechanical properties, poor processability, high brittleness, and high hydrophilicity are major drawbacks of raw starch. Therefore, starch is modified by physical and/or chemical methods, including gelatinization, etherification, esterification, crosslinking, grafting, oxidation, and enzymatic hydrolysis.

Starch-based hybrid materials have numerous functionalities and/or novel properties, mainly associated with synergetic effects and reported in environmental remediation applications. Starches are incorporated with metal NPs, metal oxide NPs, zero-valet metals, CNTs, and other polymers as reducing, stabilizing, and/or complexing agents to remove various toxic contaminants such as heavy metal, organic contaminants, and dye wastewater and groundwater.

In future studies, various natural starch sources, green synthesis of nanomaterials, recyclability, and toxicity effect of nano-waste should be considered. Further development of biodegradable starch-based hybrids and nanomaterials focusing on new functional materials, processing technology, and cost reduction needs to be studied for commercial application.

## **Conflict of interest**

The authors declare no conflict of interest.

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