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Natural, biosynthesized, polymeric, and other remediation nanoreagents

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1. Introduction

The information age has brought major changes to our societies that exhausted our planet's energy and natural resources. Industrialization, consumerism, lifestyle improvements, and migration from rural to urban areas have also led to waste accumulation in air, soil, and water media [1–3]. In the previous chapters, we explored the role of nanotechnology in remediating the environment from different pollutants using different types of nanomaterials. These can be either engineered or naturally occurring; examples are metals and metal oxides [4–7], natural and synthesized zeolites [4,8,9], carbon nanotubes [10–13], and titania-based photocatalysts [4,14,15]. Over the last few decades, a new generation of biosynthesized nanomaterials have emerged as promising nanoremediation tools. Such materials can be naturally prepared by microorganisms such as bacteria and algae. Engineered materials usually exhibit better chemical and physical properties due to their uniform structure, purity, and high porosity. However, they are often more expensive and less abundant than natural materials. Despite their superior performance, the safety of engineered nanomaterials is currently under debate, and their use in the fields of soil and water treatment is faced by potential risks on the flora and fauna [16–19]. The excessive use of engineered nanomaterials could be either toxic or leading to soil eutrophication [4]. Therefore efforts are being made to develop nanomaterials that are biodegradable, ecofriendly, and

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safe. In this chapter, we extend our discussion into some ‘uncommon’ and novel nanomaterials that have recently drew high interest. This involves:

1. Alginates
2. Biosynthesized nanomaterials
3. Cellulose-based nanomaterials
4. Chitosan
5. Layered double hydroxides (LDH)
6. Nanoclays
7. Nanofibers
8. Nanoporous polymers and polyhydroxyalkanoates (PAH)

Fig. 9.1 shows the development of these nanomaterials through the number of scientific articles published in the last 20 years (2000–2020). Alginates, cellulose, and chitosan were at the top of scientists’ interest. These are naturally occurring materials that are considered ?>more ecofriendly when compared to engineered nanomaterials because of their low toxicity, low cost, and high biodegradability.

The nanomaterials in the list before are not fully segregated from each other. For instance, some chitosan and PAH can be biosynthesized by bacteria, some nanoclays can be made out from cellulose, and LDH are actually one type of nanoclays. On the other hand, scientists have developed nanocomposites that combine two or more of these categories. For instance, chitosan–alginate nanocomplexes and LDH/polymers show better performance than their individual components.

Due to its importance for living being’s life, water treatment lies at the top priorities in environmental remediation. Depending on the level of treatment, different technologies have been developed in the last decades. For the primary treatment of water,

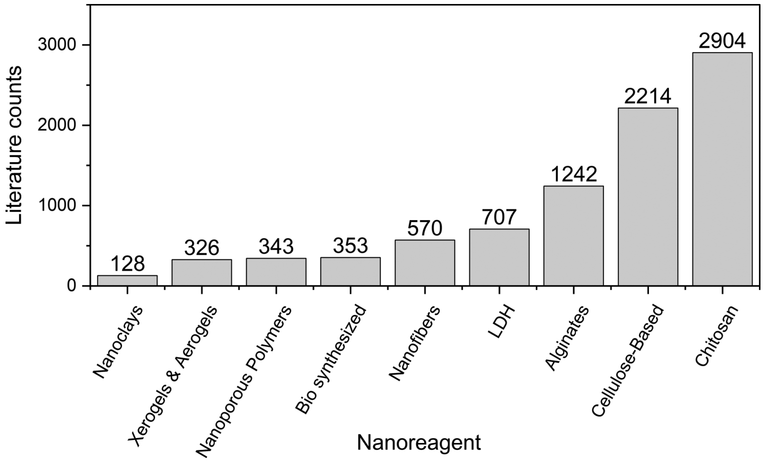


Fig. 9.1 Historical overview into some novel nanomaterials during the last 20 years (2000–20). Obtained from Clarative Analytics Web of Science.

which is typically heavily polluted, coagulation/flocculation, membrane filtration, adsorption, and settling are usually used [19]. For the secondary level of treatment, ion exchange, photocatalytic degradation, partial oxidation, and chlorination are used to further purify water [19]. In this chapter, we focus our attention on coagulation and adsorption because of their wide use in the removal of organic and inorganic pollutants. Coagulation can be visualized from daily observations such as the hardening of eggs upon boiling or the clotting of blood when exposed to air. Coagulation is defined as the destabilization of a given suspension or solution. Thus coagulation functions to overcome the forces holding the wastewater suspension in order to settle down the pollutants as a sludge. Flocculation, which typically accompanies coagulation, is a process where the destabilized particles are induced to assemble and agglomerate. Adsorption is defined as the process in which matter is extracted from one phase and concentrated at the surface of another [20].

In the following sections, we will discuss each of these materials, their synthesis, applications, and advantages.

1.1 Alginates

In 1980 alginates were introduced by Lim and Sun as a new microencapsulation procedure for drug delivery [21]. Since then this nontoxic polysaccharide material gained wide interest for many applications. Fig. 9.2 illustrates the main applications of alginates at both the biological and environmental levels. In addition to

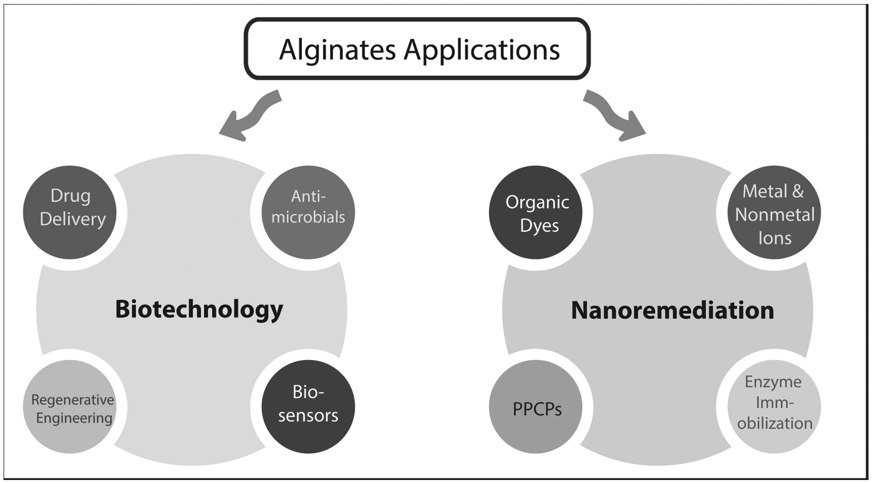


Fig. 9.2 Biological and environmental applications of alginates.

their applications in drug delivery, regenerative engineering, biosensing, and medicine, nanosized alginates have demonstrated good performance in the adsorptive removal of organic dyes, cationic and anionic pollutants, and pharmaceutical and personal care products (PPCP) from wastewater resources [18,21–23].

Alginates are naturally occurring anionic polymers that are typically obtained from aquatic creatures, such as seaweed and algae [23,24]. They are comprised of chains of polysaccharides with random arrangements of α-l-guluronate (G block) and β-d-mannuronate (M block) moieties. The arrangement of the G and M blocks can be consecutive (G–G–G, M–M–M) or alternating (G–M–G–M), as illustrated in Fig. 9.3. Because they are built from polysaccharides, alginates are biodegradable,

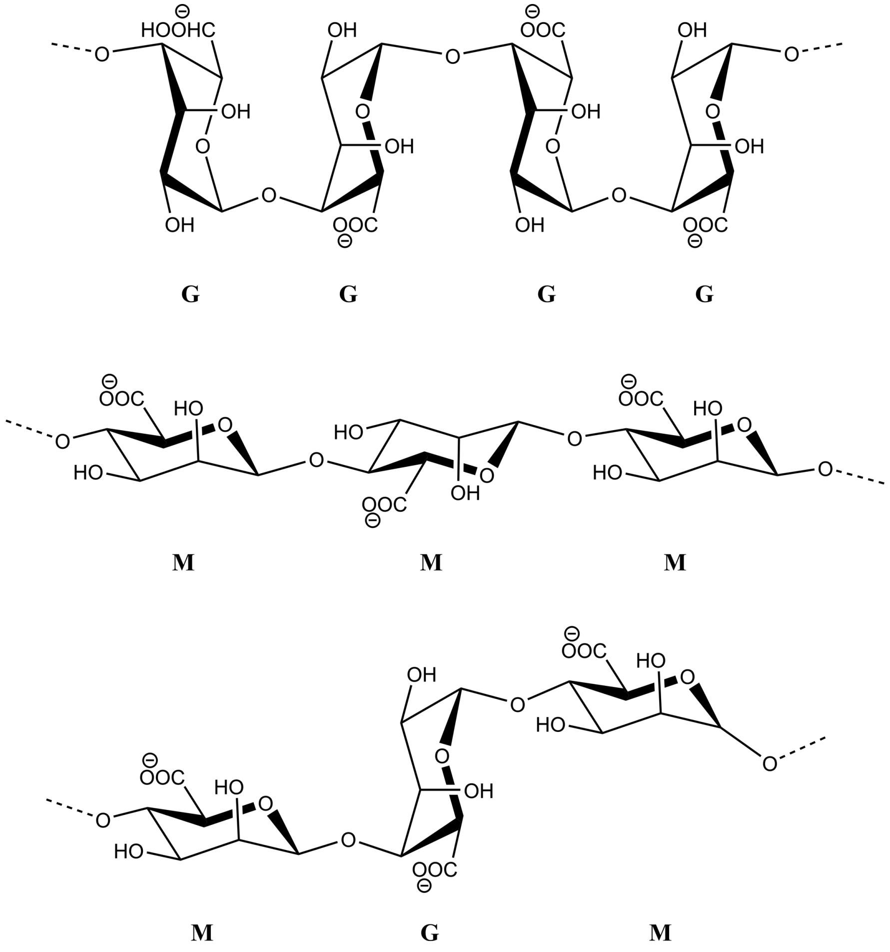


Fig. 9.3 Polymeric chain structures of alginates showing consecutive (G–G–G, M–M–M) or alternating (M–G–M) block.

hemocompatible, and have not shown to accumulate in living bodies [18,24–26].

Naturally, alginates are produced by several bacteria such as *Pseudomonas aeruginosa* and *Azotobacter*. The synthesis is initiated by a bifunctional protein named *Phosphomannose isomerase/guanosine-diphosphomannose pyrophosphorylase* (PMI-GMP). This allows the formation of alginates as extracellular polysaccharide in aquatic plant cells [27]. Commercial alginates can be synthesized by several microorganisms such as *Ascophyllum nodosum, Durvillea antarctica, Ecklonia maxima, Laminaria digitate, Laminaria hyperborea, Laminaria japonica, Lessonia nigrescens, Macrocystis pyrifera,* and *Sargassum* spp. [24,28]. Gelification is one of the leading methods to produce high-quality alginate nanofibers. Since alginates are composed of anionic polymers with carboxylate functional groups (cf. Fig. 9.3), they can easily form gels with calcium ions (Ca^{2+}) and other divalent cations. This causes a crosslinking between the G blocks in alginates and the Ca^{2+} ions. Thus alginates with higher guluronate (G) content can form stronger gels. The advantage of this method is that it allows the functionalization of the nanofibers by different metals, metal oxides, and other types of adsorbents for environmental remediation, or even drugs and other biological materials for biological applications. For instance, magnetic alginate nanoparticles can be made by impregnating Fe_3O_4 (magnetite), Fe_2O_3 (maghemite), $MnFe_2O_4$ (jacobsite), or other magnetic compounds during the gelification process [24,29,30]. For remediation purposes, magnetic nanoparticles are favored because they can be easily separated at the end of the adsorption process. Alginates can also be produced by other methods, such as spray drying, self-assembly, electrospinning, electrospraying, thermally induced polyelectrolyte complexation, and phase separation. A full description of these methods was provided by Fernandoa et al. [24].

1.2 Biosynthesized nanomaterials

Living organisms have an endogenous ability to regulate and remove toxic compounds from their bodies. This feature is used for the disinfection of wastewater using microorganisms as detailed in Chapter 11. On the other hand, scientists have used this ability to biosynthesize organic and inorganic nanoparticles by algae, bacteria, fungi, and yeast [17,31,32]. These microorganisms, which can be visualized as small nanofactories, have revolutionized the nanoindustry. Biosynthesis has several advantages when compared with conventional chemical preparation methods. It is a clean, nontoxic, highly productive, and inexpensive. By replacing organic solvents and expensive chemical reagents with natural sources, biosynthesis is now considered ecofriendly. In addition, by controlling different parameters such as temperature, culture time, and pH, nanosized materials can be tailored for different applications.

Over the past years, advances in biosynthesis allowed the preparation of nanosized and symmetrical nanoparticles of different metals such as Fe, Cu, Zn, Pd, Pt, and Se. Composite semiconductors such as CdS and metal oxides like CuO, NiO, and Fe_2O_3 can also be produced [17]. Yet, most efforts were devoted to produce precious metals like silver, platinum, and gold, which can be done by using particular bacteria such as *R. capsulate, Ralstonia metallidurans, and B. subtilis*, or algae such as *Shewanella* and *Galaxaura elongata* [31,33,34]. Biosynthesis is not limited to metals and inorganic compounds. Organic structures such as polysaccharides, proteins, and nucleic acids, made mostly for biological use, can be prepared from particular microorganisms [17,31,34].

Among the nanoparticles of interest, zirconia (ZrO_2) is known for its superior physiochemical properties, including its hardness, high melting point, high chemical resistance, and low frictional resistance. Crystalline zirconia nanoparticles can be made by reducing its precursors such as hexafluorozirconate (ZrF_6^{2-}) complexes into ZrO_2 inside a fungus named *Fusarium oxysporum*. Similarly, high-quality spherical titania (TiO_2) from TiF_6^{2-} complexes can be prepared using the same fungus. Other oxides of aluminum, barium, copper, and zinc can also be prepared [31]. TiO_2 and ZnO are widely used as photocatalysts in the photocatalytic degradation of contaminated water. In this process, a semiconductor harvests light, typically in the UV region, to induce electronic excitations that lead to a chain of free radical reactions in a photocatalytic reactor. Organic pollutants are consequently removed by photooxidation. Photocatalytic degradation is highly successful in eliminating organic pollutants at very low concentrations, that is why it is used in the final stages of water treatment plants to produce water at drinking quality.

Biosynthesis can also be used to improve properties of some materials. For instance, three-dimensional solid scaffolds of carbon nanotubes (CNT) were fabricated using bacteria named *Magnetospirillum magneticum* (AMB-1) as a biotemplate [35]. The bacteria/CNT scaffolds were shown to exhibit high mechanical stability, large surface area, and high porosity. Molecular dynamics (MD) simulations showed that an interaction between the CNT and the proteins from AMB1, namely, the surface protein, MSP1, and the flagellum protein, was responsible for the fabrication process.

A question arises on how this transformation takes place within these microorganisms? How, for instance, a bacterium can convert metal ions into free metals? Several mechanisms were proposed to answer this question over the years. Generally, biosynthesis can be either intracellular or extracellular. In the former, positive ions diffuse through the cell membrane, which is negatively charged, under the force of electrostatic attraction. Consequently, enzymes, which are biocatalysts, reduce toxic cations into free metal nanoparticles [32]. In the extracellular mechanism, cell enzymes such as *nitrate reductase* or *hydroquinone* can do similar actions. For example, the coenzyme *nicotinamide adenine dinucleotide* (NAD), an essential cofactor for metabolism, can play a role in converting silver ions into silver metal. By donating an electron from the reduced form (NADH) into the oxidized form (NAD^+), Ag^+ ions can reduce into Ag nanoparticles in the fungus *Fusarium acuminatum* and some human pathogenic bacteria [31]. Similar enzyme reductions can transform selenite/nate and tellurite/rate to elemental Se and Te [17].

Biosynthesized nanoparticles have different applications as adsorbents, catalysts, transformers, and as photodegradation shuttles in the Fenton reaction.

1.3 Cellulose-based nanomaterials

Cellulose is the most abundant natural polymer. It is an organic polysaccharide with the general molecular formula $(C_6H_{10}O_5)_n$, where n extends to several hundred to many thousands of glucose units. Cellulose-based nanomaterials can be made from different sources such as fruit peels, rice husks, peats, plant residues, sugarcane bagasse, seeds, and some industrial waste like saw waste.

There is a common belief that metals, metal oxides, carbon nanotubes, and other conventional nanomaterials have little or zero negative impact on the environment. Studies showed that the toxicity of such materials should not be underestimated. Meanwhile the use of cellulose-based nanomaterials for environmental remediation is still limited. Future implementation of nanotechnology in waste mismanagement requires a greener approach with minimum or zero impact on the environment [36]. Cellulose meets the requirements of an ecofriendly nanotechnology. It is biocompatible, sustainable, highly effective, inexpensive, and almost nontoxic [18,31,36]. Furthermore, cellulose possesses a unique hierarchical structure consisting of macrofibers of cellulose, hemicellulose, and lignin. Using special techniques, different scaffolds can be prepared such as cellulose

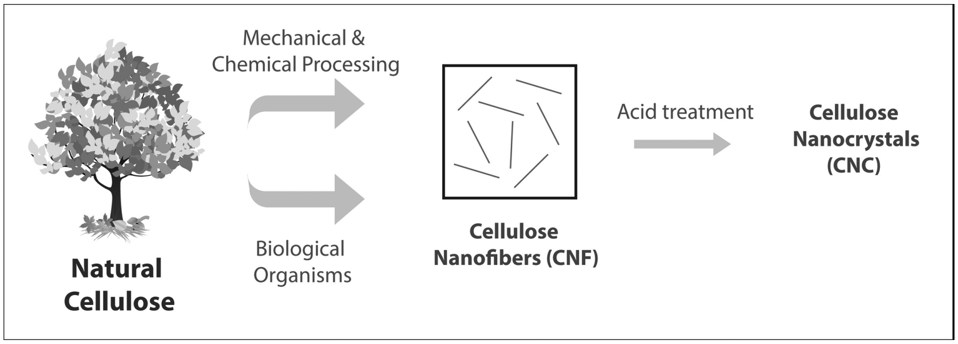


Fig. 9.4 Preparing cellulose nanofibers and cellulose nanocrystals from natural cellulose.

nanofibers and nanocrystals. Fig. 9.4 illustrates the main approaches to prepare such nanostructures. Using mechanical and chemical processing, the 3D macronetwork of natural cellulose is broken down into microfibers and next to cellulose nanofibers (CNF). Further acid treatment can remove the amorphous regions to form cellulose nanocrystals (CNC). As the name indicates, CNC possess highly crystalline structures that are highly favorable for delicate industries like electronics and aerospace. CNF are typically long fibers with 5–60 nm in diameter and lengths up to 1–100 mm. CNC are usually 5–70 nm in diameter and 100–250 nm in length. CNF and CNC are advantageous over single-walled (SWCNT) or multiwalled carbon nanotubes (MWCNT) due to several factors. They are biodegradable, less expensive, and renewable. Also, CNF and CNT have reported lower inflammations and health hazards than carbon nanotubes. On the flip side, SWCNT and MWCNT are still preferred for optical and electronic applications due to their higher tensile strengths, surface area, and electric conductivity. Based on this comparison, cellulose-based nanofibers and nanocrystals can be promising remediation shuttles for water treatment than carbon nanotubes.

Biosynthesis is another favored method to prepare CNF and CNC from natural cellulose. Bacteria such as *Gluconacetobacter xylinus* can be used to produce better quality fibers than those prepared by wood/plant chemical homogenization [36,37]. Cellulose and its derivatives have recognized applications in the fields of environmental remediation fields. Cellulose-rich products such as olive mill pomace, fruit peals, rice husks, and sugarcane bagasse can be used directly in wastewater treatment to remove highly toxic pollutants. This includes heavy metals like cadmium, nickel, selenium, copper, and mercury as well as anionic pollutants like phosphates and nitrates [38–41].

The direct application of cellulose for water treatment is not very efficient in removing micropollutants such as pharmaceuticals, food additives, pesticides, personal care products, and small-molecule industrial agents. To do that, cellulose derivatives can be used to synthesize better adsorbents or coagulants like activated carbon, grafted polymers, or graphene, which can remove micropollutants with efficiencies reaching 99% [42–44].

1.4 Chitosan

Chitosan is a linear aminopolysaccharide composed of (1,4)-linked *N*-acetylglucosamine units (Fig. 9.5). It is usually prepared by deacetylation of chitin, which is a long-chain polymer found in the shells of crustaceans such as shrimp, crab, and lobster, and considered to be the second most natural abundant biopolymer after cellulose. By the end of the twentieth century, chitosan attracted high scientific attention due to its unique physicochemical properties. It is a natural, biodegradable, and almost nontoxic material. The presence of the primary amino groups, the high cationic charge density, and long chains make it an effective coagulant for water treatment [19,45–47].

Chitosan's primary function in environmental remediation is as a coagulant to remove high concentrations of heavy metals or organic contaminants such as dyes. In order to use chitosan as an effective adsorbent to treat wastewater, scientists have developed several methods to synthesize nanostructures of chitosan such as beads, electrospun fibers, flakes, fiber membranes, and nanoparticles. In addition, nanocomposites made by coupling chitosan into magnetic metals oxides were developed. These materials have much larger surface area than the parent chitosan, which leads to much faster and effective adsorption. Some of the methods to prepare nanomaterials from chitosan are as follows [46,48]:

- Ionotropic gelation
- Polyelectrolyte complexation

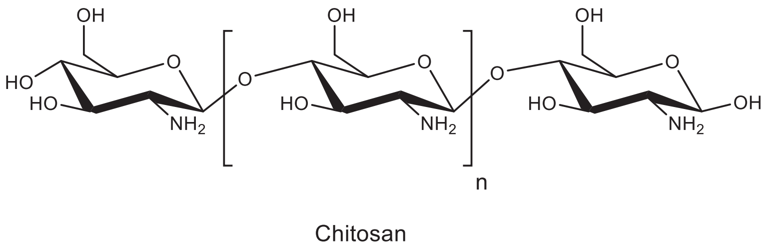


Fig. 9.5 Polymeric chain of chitosan.

- Reverse micellar
- Microemulsion
- Emulsification solvent diffusion

Microemulsion is one of the most effective methods to prepare chitosan nanoparticles. The method involves crosslinking the chitosan with a linker such as glutaraldehyde. An aqueous emulsion of chitosan is first prepared in weak acid, and then mixed with an organic solvent below room temperature (~7°C). The linker is then added to the emulsion and sonicated in the presence of a surfactant. When the final product is purified by centrifuging, high-quality chitosan nanoparticles can be obtained. The advantage of such adsorbents is their capabilities to removing pollutants with high adsorption capacities reaching 300–400 mg/g [46,48].

Because of the low water solubility of chitosan, it is not a very effective flocculate for heavily polluted water by itself. Thus a novel technique for preparing better chitosan nanomaterials is the coprecipitation with magnetic iron oxides such as maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4). By analyzing these nanoparticles, they were found to be highly crystalline and possess good magnetic properties. X-ray diffraction (XRD) analysis showed that the chitosan–iron composites have the same diffraction peaks of iron oxide, with slightly weaker intensities. This indicates the presence of gel or amorphous materials on the chitosan surface. Vibrating sample magnetometer (VSM) analysis showed good magnetic or paramagnetic properties for such nanoparticles, which are convenient enough to separate them at the end of the remediation process. As indicated by the scanning electron microscope (SEM) images, the size of these nanoparticles lies in the range of 20–80 nm. These properties allowed chitosan–iron composites to be excellent choice for nanoremediation of heavy metal ions and organic dyes [48–50]. Meanwhile, scientists succeeded in utilizing them in the dewatering of oil sands tailings ponds [47]. These are heavily oil-polluted water reservoirs formed as a by-product of the steam-assisted gravity drainage (SAGD), a process that is widely used in Canada and other parts of the world to produce petroleum from oil sands. Tailing ponds of oil sands typically contain sand, clay, bitumen, hydrocarbons, in addition to water [51–55].

Chitosan can also be used as a precursor to prepare biosynthesized nanomaterials. Some microorganisms such as *Metacarcinus magister* and *Penicillium oxalicum* are able to produce copolymers made of chitosan that can be used for drug delivery or water purification. Such materials can also be made from plants like *Catharanthus roseus*. The biosynthesis of these materials can be done in a solvent-free condition, which qualifies them to be biocompatible and fairly nontoxic remediation tools [17,56–58].

1.5 Layered double hydroxides

In 1824 a new mineral named hydrotalcite was discovered by Swedish mineralogists. Years later in 1915, hydrotalcite was characterized by Manasse to contain layered double hydroxides (LDH), which turn to be a very interesting material with superior properties [59,60]. LDH are two-dimensional (2D) materials that are described by the general formula $[M^{2+}{}_{(1-X)}M^{3+}{}_{(X)}(OH)_2]^{X+}$ $(A^{n-})_{X/n}$. mH_2O, where layers are made of M^{2+} and M^{3+} cations, while the A^{n-} anions, including OH^-, are located within the interlayer regions as illustrated in Fig. 9.6. Bivalent cations are usually Ca^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, or Ni^{2+}, while trivalent cations might be Al^{3+}, Fe^{3+}, Ga^{3+}, Co^{3+}, Cr^{3+}, Mn^{3+}, or Ni^{3+}. These cations are neutralized by counterions such as $CO_3{}^{2-}$ $NO_3{}^-$, or Cl^-, so the whole structure has no charge. The value of x is usually between 0.17 and 0.33 [59,61,62].

The most interesting feature of LDH is the ability to replace the interlayer anions easily. This can be done by exchanging the host anions ($CO_3{}^{2-}$, $NO_3{}^-$, Cl^-) with a desired functional group such as EDTA, glutamate, sulfides, or humates. This allows LDH to have different chemical multifunctionalities to be used in drug delivery, catalysis, fuel cells, adsorption, and many other applications [59–62]. In terms of using LDH for wastewater treatment, they demonstrated high performance to adsorb heavy metals, organic dyes, and micropollutants. For instance, by replacing the LDH host anions with glycerol (propanetriol), the LDH demonstrated high adsorption performance for methyl orange, a model molecule for toxic organic dyes. The adsorption was enhanced through

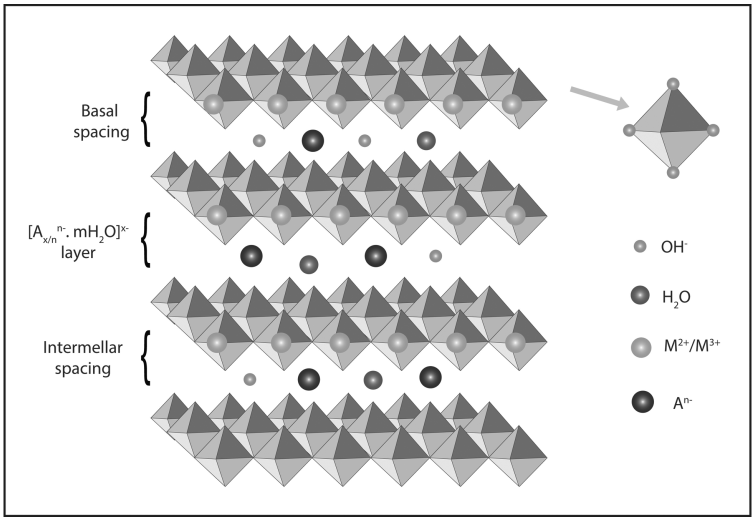


Fig. 9.6 General structure of layered double hydroxides (LDH).

hydrogen bonding between the –OH groups of glycerol and the sulfonate group in the dye [63].

LHD are also thermochemically stable, reusable, easy to synthesize or obtained naturally, and most importantly, having a magnetic memory effect [59,61,62,64]. This is a reversible change in the ferromagnetic magnetization upon applying a stress, which can be released when the stress is lifted [65]. Thus LDH can be easily separated from the adsorption bulk in water treatment tanks.

Artificial LDH can be synthesized in the lab in situ by different methods such as calcination, coprecipitation, hydrothermal, solvothermal, ion exchange roasting reduction, and the sol–gel method [59,61,62,64]. In addition, nanocomposites of LDH and other materials such as carbon nanotubes, graphene, glycerol, or other polymers can be prepared to target specific pollutants. For instance, composites of LDH and poly(m-phenylenediamine) have shown excellent performance in removing diclofenac sodium, a common antiinflammatory drug, from water resources with adsorption capacities exceeding 500 mg/g and nearly 100% removal efficiency [64].

One of the effective methods to prepare high-quality LDH is the exfoliation-restacking process. This involves the exfoliation (peeling off) the LDH surface and depositing the delaminated LDH layers to the surface of the target substrate in the presence of an organic solvent. The product can then be calcinated at high temperatures (400–600°C) to obtain a higher surface, higher number of active sites, and more thermally stable nanoparticles [62,66,67].

Today, the main challenge facing the LDH manufacturing process is scaling up these batch processes. More efforts are needed to construct a continuous process that integrates batch techniques and tabular reactors to produce high yield of LDH materials at good standards.

So, what is the origin of the high adsorption efficiency of LDH? There are different adsorption mechanisms that were proposed to explain this. Fig. 9.7 illustrates the different ways LDH interacts with water pollutants such as heavy metal, organic compounds, and bacteria. These mechanisms induced chemical bonding (like hydrogen bonding), physical interaction in the form of van der Waal forces, adsorption, ion exchange, or hydroxide precipitation. In ion exchange, toxic metal ions like Cr^{3+}, Cd^{2+}, or $Hg_2{}^{2+}$ are replaced by nontoxic Mg^{2+} and Ca^{2+} in the LDH network. The exchanged ions can then be precipitated and washed out as hydroxide salts. The different variety of mechanisms that LDH materials can use to remove pollutants makes them versatile, highly effectible, and convenient for waste removal.

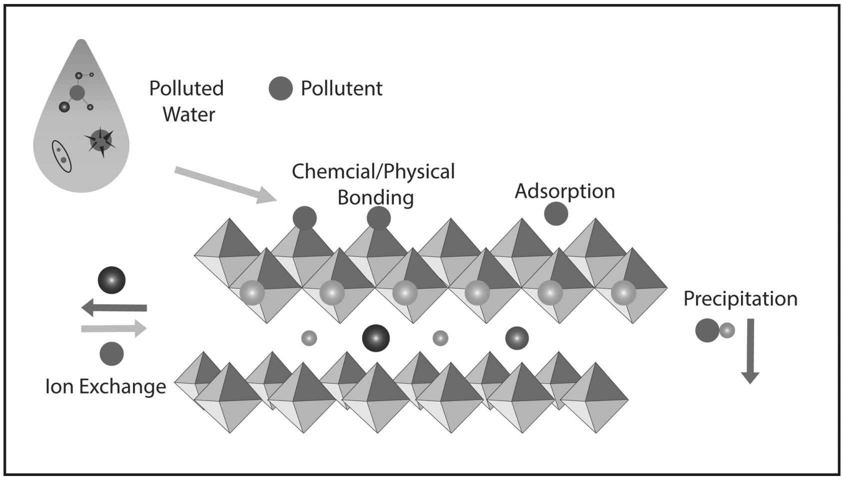


Fig. 9.7 Adsorption mechanisms in layered double hydroxides (LDH).

Because they are originated from natural minerals in the earth crust, LDH are considered safe and nontoxic materials. Up to date, there is no documented evidence for potential hazards of LDH to human health. Therefore LDH have found many applications in the pharmaceutical industry as well as carriers for drug delivery into cancer cells [61,62,68].

1.6 Nanoclays

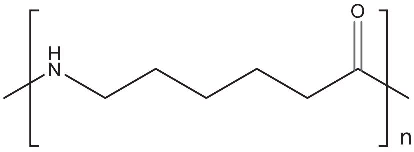
The term ‘clay’ covers a wide spectrum of naturally occurring deposits. Within this framework, we focus our attention on kaolinites which are natural particles that are made mostly of silicates and aluminums. Kaolinites are classified as nanomaterials because they have at least one dimension within the nanometer scale. Earth deposits that are rich in kaolinite are known as kaolin or china clay. We have already covered a special type of clays, which is the layered double hydroxides (LDH). Another special component of kaolin is montmorillonite. This is a hydrated soft phyllosilicate with the general chemical formula $(Na,Ca)_{0.33}$ $(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$. The name originated from Montmorillon, France. The terms clay, kaolin, kaolinite, and montmorillonite are used interchangeably in the scientific literature to describe natural clay. In the following discussion, we will use the word kaolin [4,16,69,70].

Kaolins offer the advantage of being naturally abundant and available at low cost. This allowed them to play a role in many industries such as the ceramics, paper, paints, rubber, and constructions [71–73]. Like chitosans, kaolins are considered good coagulants that are used to destabilize heavily polluted water. However, kaolins have lower adsorption capacities than conventional adsorbents because they are highly hydrophilic. So, nonpolar organic compounds, such as benzene, toluene, and oil, cannot compete with water for kaolin's adsorption sites. Furthermore, the use of kaolin-based materials in environmental remediation can generate secondary waste which leads to another environmental pollution. Thus kaolin needs to be treated, modified, or mixed with other materials to enhance their adsorption efficiency [16,69,70,74–76].

Kaolin minerals can interact with different types of organic and inorganic compounds. The penetration of such compounds into the interlayer of the clay is called intercalation. Similar to LDH, the interlayer cations in kaolin can be exchanged by different types of metals or organic species. For instance, scientists have introduced ammonium (NH_4^+), humic acid, poly(acrylamide), and iron oxides into the kaolin structure in order to build nanocomposites that target specific water pollutants [4,16,69,70,77]. To achieve that, several methods are used. For example, coprecipitation is done by heating a mixture of kaolin with salts of the desired metal in the presence of concentrated NaOH. For instance, the iron salts, $FeCl_3.6H_2O$ and $Fe_SO_4.7H_2O$, can be used to build a magnetic iron–kaolin nanoparticles [70]. Another novel method is the ultrasound-assisted emulsion polymerization, in which polymers such as poly(acrylamide) can be impregnated into kaolin to build a highly robust composite [69]. Experimental studies showed that such nanocomposites have a greater affinity in removing heavy metals and dyes from wastewater than the parent kaolin.

1.7 Nanofibers

Over the past few decades, nanoparticles have demonstrated excellent performance in the adsorptive removal of heavy metals, organic pollutants, and inorganic anions from water, air, and soil. However, implementing nanoparticles in industrial adsorption columns has a drawback. The solid-phase extraction process in these columns has high backpressure, which makes it difficult to apply high flow rates [16,78]. Therefore the nanoparticle adsorbents are usually supported in packed bed columns filled with silica or alumina. Nanofibers can overcome this problem by combining the nanoscale advantage in one dimension with having long chains in other directions. We have already explored one type of these materials which was cellulose nanofibers (CNF). Such



Nylon-6

Fig. 9.8 Polymeric chain of nylon-6.

materials can be used in adsorptive columns as adsorbents as well serving as support. In addition, CNF are natural, ecofriendly, and relatively nontoxic.

One of the widely used nanofibers is Nylon-6 (Fig. 9.8). It is a semicrystalline polyamide with the systemic name poly(azepan-2-one); poly(hexano-6-lactam). Nylon-6 is one of the most produced polymers worldwide and has many applications in the automotive, aircraft, clothing, medical, and electronic industries. The polymer has attracted attention recently for remediation prospects due to its high surface-to-volume ratio, length-to-diameter ratio, and high specific surface. It has also an interesting structure with carbonyl ($C{=}O$) and amide (NH) groups both in planar orientation. This allows maximum hydrogen bonding interactions within the polymer as well as outer polar groups. In addition, the hydrophilic polar amide groups are expected to enhance the solid-phase extraction in adsorption columns by increasing water flow and mass transfer [16,79,80].

1.8 Nanoporous polymers and polyhydroxyalkanoates

According to the International Union of Pure and Applied Chemistry (IUPAC), nanoporous polymers are defined as glassy or rubbery polymer that contains a large number of macropores (50 nm to 1 μm in diameter) that persist when the polymer is immersed in solvents. These polymers are extensively studied in the literature due to their superior mechanical and chemical properties. They can be found under different nomenclatures, for example [81,82]:

Covalent organic frameworks (COF)
Covalent organic polymers (COP)
Covalent triazine-based frameworks (CTF)
Metal–organic frameworks (MOF)
Microporous organic polymers (MOP)
Porous aromatic framework (PAF)

Porous carbons, porous graphene, and carbon nitrides
Polymeric organic frameworks POF
Polymer nanosieve membranes (PNM)
Porous polymer frameworks PPF
Zeolites and zeolitic Imidazolate frameworks (ZIF)

Nanoporous polymers are versatile compounds. Their chemistry can be tuned to specific purpose by modifying their structure and the functional groups present. They can be either hydrophilic or hydrophobic depending on their surface modification. In addition, most nanoporous polymers are biodegradable, biocompatible, and generally nontoxic. This versatility allowed these materials to find their way into many applications such as catalysis, ion exchange, adsorption, chromatography, electrolysis, fluorescence probes, hydrogen and methane storage, and CO_2 capturing [16,83–86].

The science of nanoporous polymers is so big to fit into the scope of this context. Nonetheless, we focus on one type of polymers that attracted extensive attention in the last decade, which is polyhydroxyalkanoates (PHA, Fig. 9.9). These are a family of biodegradable polyesters that accumulate naturally in different types of microorganisms. PHAexist in more than 300 bacteria inside the living cell and acts as an intracellular energy reservoir. They also can be biosynthesized in the lab via microbial aerobic fermentation using inexpensive nutrients like sugar, cellulose, and vegetable oil. In sewage sludge treatment plants, PHA are the key constituents of the excess sludge produced by aerobic oxidation. So present research is focused on either recycling these valuable nanomaterials or biosynthesize them from particular bacteria. Because of their biocompatibility and biological origin, they are commonly referred to as bioplastics [17,81,83,87].

Conventional fossil fuel plastics such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), and polyvinyl chloride (PVC) are nonbiodegradable, and they are posing a global threat to the environment. PHA, instead, are natural, biodegradable, and sustainable source of robust plastics that can

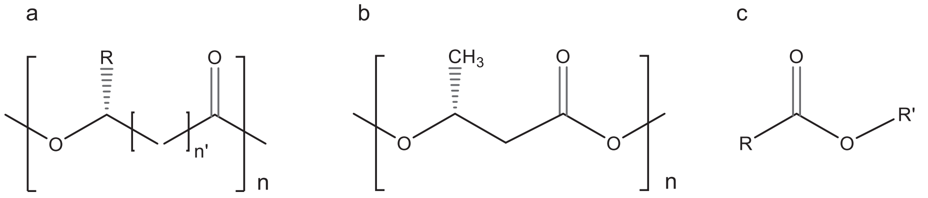


Fig. 9.9 Different forms of Polyhydroxyalkanoates (PHA). *n* is the number of subunits, *n′* is the number of carbons within subunit, R and R′ are the alkyl groups.

overcome this problem. Furthermore, the toxicity of PAS is low. Studies showed that PAH ingestion into mammals showed no harmful effects [83,88,89].

Environmental remediation is not limited to waste removal by adsorption or similar methods. The modern concept of waste management is based on a reduce–reuse–recycle approach. In this context, the conversion of waste to value-added products plays a central role within this approach. Investing in the in situ PHA recycling from waste is a promising solution to today's plastic problem. PHA provides a special advantage in this framework by being completely biodegradable. The final products of its degradation are mostly H_2O and CO_2. The unique advantage PHA provide is that the carbon released as CO_2 is already part of the natural carbon cycle, in contrast to the uncontrolled sudden release of CO_2 from fossil-fuel plastics [81,88,89].

2. Conclusions and future perspective

The nanomaterials presented in this chapter can provide safe, economic, and ecofriendly alternative to conventional treatment technologies. Their applications in nanoremediation extend from treating wastewater, soil, and air into waste conversion, catalysis, and recycling. Natural materials such as alginates, chitosan, and cellulose are built from polysaccharide blocks and thus offer the advantage of being natural, biodegradable, and almost nontoxic. In recent years, extensive research on these materials showed that they are very effective in treating different types of pollutants, including metals, ions, organic dyes, pharmaceuticals, and personal care products. Layered double hydroxides exhibit superior physiochemical properties that make them very attractive for nanoremediation. Their structure, which is constructed from different cations, anions, and hydroxide layers, allows them to be modified easily to target particular contaminates. Also, nanocomposites made of LDH and other nanomaterials, such as CNT or graphene, have demonstrated higher performance than their parents.

Some of the conventional laboratory methods that are used in nanoparticle preparations involve the use of expensive and toxic organic solvents. Biosynthesis offers a promising route to replace such methods. This can be done by utilizing the power of some microorganisms, such as bacteria, fungi, and algae, to prepare high-quality nanoparticles. Nanomaterials made from kaolins, nanofibers, and polyhydroxyalkanoates are also promising remediation tools, not only to treat wastewater, but also to convert waste into fuel or value-added commodities.

The future implementation of the materials discussed in this chapter at the industrial scale requires further efforts. During the last few years, laboratory results demonstrated excellent performance of these materials. However, experimental bench work neglects major elements of industrial production, such as heat and mass transfers, thermal and mechanical stability, hazards, and cost. In addition, laboratory work is done over a short period of time, and therefore the long-term stability, safety, and functionality of these materials need to be assessed.

Because of the rapid development in this field, the nomenclature of these materials and the terms used in the literature are overlapping and confusing. A systematic classification system needs to be formulated for easy scalable manufacturing and transport industry. Finally, regional and international legislations that govern the handling and safety of these materials need also to be formulated.

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