Chapter 9
Surface Engineered Magnetic Biosorbents for Water Treatment

Sofia F. Soares, Tiago Fernandes, Tito Trindade, and Ana L. Daniel-da-Silva

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Abstract Water pollution is a matter of concern because of the adverse impact of contaminants on environment and human health. Common polymer-based sorbents are difficult to separate from treated water, a limitation that has restrained their use. Nanomaterials with magnetic features appear as advantageous alternatives to these conventional biosorbents offering the advantage of fast and easy magnetically-assisted separation. Moreover owing to reduced dimensions magnetic nanomaterials possess large specific surface area that favours adsorption. The surface modification with biopolymers enhances the adsorptive capabilities of magnetic nanoparticles without compromising the low-cost. However, in order to attain high-performance, a rational design of the surface of the magnetic biosorbents is essential.

In this chapter we present an overview of the most recent developments on magnetic biosorbents for water treatment. Primary attention is given to the chemical

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G. Crini, E. Lichtfouse (eds.), *Green Adsorbents for Pollutant Removal*,
Environmental Chemistry for a Sustainable World 18,
https://doi.org/10.1007/978-3-319-92111-2_9

strategies used for the surface modification of magnetic nanoparticles with biopolymers aiming to obtain highly effective, robust and reusable biosorbents with magnetic properties. Two different strategies are distinguished, the *in situ* functionalization and the post-synthesis surface functionalization. The later comprises two distinct stages, the synthesis of the magnetic nanoparticles and the surface functionalization, and allows a better control of each stage individually. Surface functionalization can involve the simple coating of magnetic nanoparticles with biopolymers or the covalent attachment of the biopolymer chains to the surface. Overall covalent immobilization of the biopolymer onto the particles surface, either by crosslinking or grafting approach, is recommended to ensure successful recycling and reuse of the biosorbents without significant loss of adsorption capacity.

Appropriate selection of the biopolymer and the route for surface modification of magnetic nanoparticles are crucial to obtain effective magnetic biosorbents optimized and specialized in the targeted pollutants. The performance of several magnetic biosorbents in the uptake of heavy metal species and organic pollutants from water is discussed in this chapter.

9.1 Introduction

Magnetic nanomaterials have attracted increased attention in the last decade for application as biosorbents in water remediation processes (Sousa et al. 2015; Mehta et al. 2015; Simeonidis et al. 2016; Adeleye et al. 2016; Reddy and Yun 2016). Owing to reduced size, nanomaterials possess large surface area to volume ratio available, which is a desirable feature for adsorptive applications. Nanomaterials possessing magnetic features are easily and quickly separated from treated water in the presence of an external magnetic field, which clearly represents an advantage in relation to non-magnetic biosorbents. Iron oxides nanoparticles are the most used in research for treatment of polluted water owing to low cost and moderate environmental impact (Tang and Lo 2013; Su 2017). Enhancement of adsorptive capacity of magnetic nanoparticles (MNPs) and selectivity towards target pollutants can be achieved via the chemical functionalization of the particles surfaces.

The search for eco-friendly and low-cost biosorbents has prompted the interest for new biopolymer-based nanomaterials and their use in water decontamination (Crini 2005; Daniel-da-Silva et al. 2013; Dehabadi and Wilson 2014; Carpenter et al. 2015). Surface modification with biopolymers occurring in nature, provides to the particles surfaces novel functional groups that may confer affinity towards a wide diversity of pollutants (Xu et al. 2012; Boamah et al. 2015; Vandenbossche et al. 2015). A vast number of biopolymers are produced in natural environment during the growth cycles of living organisms, like green plants, animals, bacteria, fungi and algae. Besides being available on a sustainable basis, biopolymers present

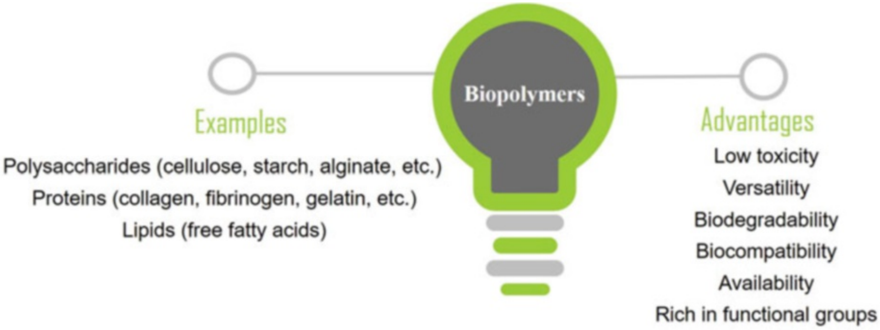

Fig. 9.1 Examples of biopolymers of different classes, such as polysaccharides, proteins and lipids. Polysaccharides include cellulose, starch and alginate among others. Collagen, fibrinogen and gelatin belong to the group of proteins and lipids include the free fatty acids. Biopolymers present several interesting environmentally friendly features such as low toxicity, versatility, biodegradability, biocompatibility, availability and they are rich in functional groups (Nair et al. 2017; Rebelo et al. 2017; Resch-Fauster et al. 2017)

the advantages of low cost, biodegradability and reduced toxicity (Nair et al. 2017; Rebelo et al. 2017; Resch-Fauster et al. 2017; Divya and Jisha 2017) (Fig. 9.1).

Ideally, a biosorbent for water remediation should fulfill the following requirements: specificity to target pollutants, high adsorptive performance, rapid adsorption, cost-effective, environmentally non-toxic, reusability and easy separation from treated water. Low-toxicity and easy magnetic separation can be in principle met by simple combination of biopolymers with magnetic iron oxides. However a rationale design of the surface of the MNPs is needed to attain specificity, high adsorption capacity and reusability. Advances in nanotechnology and in the field of colloidal science have extended the ability to tailor the surface of magnetic nanoparticles and to tune their physical-chemical properties to suit specific applications (Wu et al. 2015; Bohara et al. 2016). Appropriate selection of the biopolymer and the route for surface modification of magnetic nanoparticles are crucial to obtain effective biosorbents that meet the above mentioned requirements. For example, covalent immobilization of the biopolymer onto the particles surface, either by crosslinking or grafting approach, might be necessary to ensure successful recycling and reuse of the biosorbents without significant loss of adsorption capacity.

This chapter aims to provide a critical overview of the most recent developments in the field of magnetic biosorbents for application in water treatment. Primary attention is given to the chemical strategies used for the surface modification of magnetic nanoparticles with biopolymers aiming to obtain highly effective and robust biosorbents with magnetic properties. The main synthetic routes to prepare magnetic nanoparticles with controlled size and morphology are briefly enumerated. The performance of the magnetic biosorbents in the uptake of heavy metal species and organic pollutants from water is discussed. As a final note, the fate of the post-sorption magnetic biosorbents and its potential impact on the environment is put in perspective.

9.2 Magnetically Assisted Water Treatment

9.2.1 Magnetic Nanoparticles for Water Treatment

Magnetic separation relies on the fact that magnetic nanoparticles can be manipulated by an external magnetic field gradient. For the effective magnetic separation of micrometer or nanosized materials from a viscous flow, the magnetic force produced by the external magnetic field must overcome the drag force associated to the carrier fluid. The difference between the velocity of the magnetic nanoparticle and the velocity of the fluid ($\Delta \vec{v}$) can be expressed by Eq. (9.1) (Pankhurst et al. 2003; Sousa et al. 2015)

$$\Delta \vec{v} = \frac{R^2 \Delta\chi}{9\mu_0\eta} \nabla \left(\vec{B} \, . \, \vec{B}\right) \tag{9.1}$$

where R is the radius of the particle, $\Delta\chi$ is the difference between the magnetic susceptibility of the particle and of the diamagnetic fluid and η is the viscosity of the fluid. The constant μ_0 is the magnetic permeability of free space and B is the magnetic flux density. From the above equation it follows that larger magnetic nanoparticles with higher magnetic susceptibility yield larger velocities. In other words larger particles are more efficient for magnetic separation. On the other hand, for adsorptive applications, smaller magnetic particles are desirable, owing to high surface area to volume ratio.

Iron oxide nanoparticles, more specifically magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), are by far the most investigated magnetic nanoparticles for water treatment due to their adequate magnetic properties, low cost, chemical inertness and low toxicity (Xu et al. 2012; Kaur et al. 2014; Mehta et al. 2015; Su 2017). The easy synthesis, coating or surface functionalization, and the facility of tuning the size and particle shape, provide huge versatility to these materials. Both magnetic phases present inverse spinel crystal structure where the large oxygen ions are closely packed in a cubic order and the iron cations occupy the interstitial sites. Magnetite comprises both ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions in its structure. Half of the Fe^{3+} ions occupy tetrahedral sites, while the Fe^{2+} ions together with remaining ferric cations, occupy the octahedral sites. Maghemite results from the topotactic oxidation of magnetite. Other spinel ferrites have been also reported for magnetically assisted water treatment (Reddy and Yun 2016).

Magnetite nanoparticles exhibit unique size-dependent magnetic properties (Fig. 9.2). Bulk magnetite is a ferrimagnetic material composed by multiple magnetic domains. Due to such magnetic domains, bulk magnetite exhibits a hysteresis curve when magnetization (M) is plotted versus magnetic field (H) and a permanent magnetization in the absence of a magnetic field is observed. The external field needed to bring this remanent magnetization to zero is designated by coercivity and

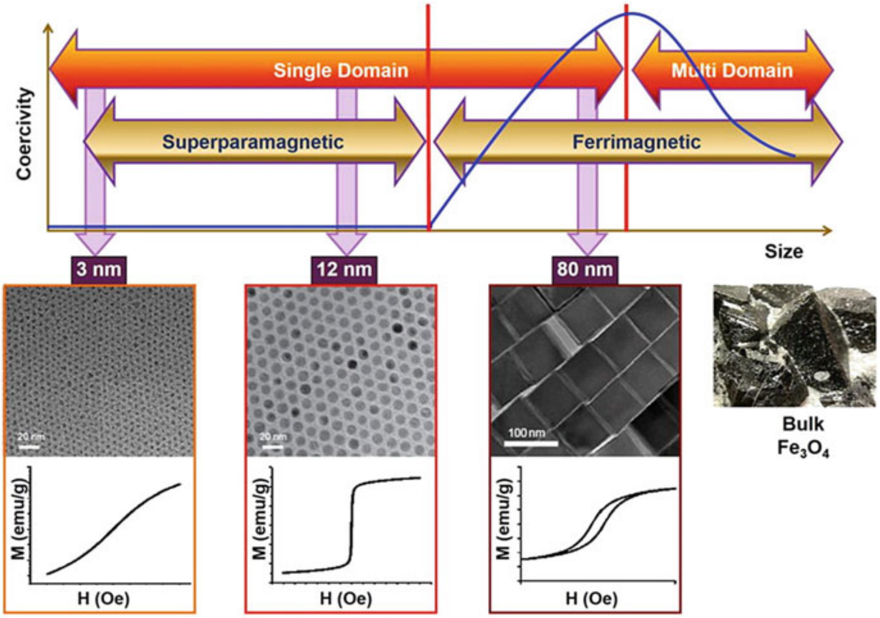

Fig. 9.2 Size-dependent magnetic properties of iron oxide nanoparticles. Inset TEM images and magnetization curves of magnetic nanoparticles. Bulk magnetite is a ferrimagnetic material composed by multiple magnetic domains. Magnetite particles become a single domain as the particle size decreases below 100 nm, where coercivity is maximized. When the particle size is smaller than 20 nm, the magnetization of magnetite nanoparticles is randomized so that they become superparamagnetic. (Adapted with permission from ref. Ling et al. (2015). *TEM* transmission electron microscopy)

in magnetite is maximized for sizes around 100 nm (Ling et al. 2015). The decrease of the particle size to the nanoscale brings consequences in terms of magnetic properties. Below a critical particle size (~25 nm for Fe_3O_4), it is energetically more favorable for magnetite particles to be composed by single magnetic domains and therefore exhibit superparamagnetic behavior. The magnetization curve of superparamagnetic nanoparticles does not exhibit hysteresis loop which means that in the absence of an external magnetic field these particles have zero magnetization, no coercivity and less tendency to agglomerate, an important feature for adsorptive applications.

For applications in magnetic separation, ferromagnetic particles are usually preferable over superparamagnetic nanoparticles because they show higher magnetophoretic response thus leading to faster separations. Owing to their notable properties, superparamagnetic magnetite and maghemite nanoparticles have been widely investigated for bio-applications, including drug delivery, magnetic resonance imaging and magnetic hyperthermia (Laurent et al. 2008; Wu et al. 2015; Ling et al. 2015).

9.2.2 Preparative Methods of Magnetic Iron Oxides

As described in the previous section, the properties of magnetic nanoparticles are strongly dependent on the particle size and shape. Thus, a number of synthetic strategies have been developed for the synthesis of magnetic nanoparticles with uniform morphology, narrow size distribution and tailored properties, as extensively reviewed elsewhere (Laurent et al. 2008; Wu et al. 2015; Ling et al. 2015). Examples of methods for the synthesis of colloidal magnetite nanoparticles include the co-precipitation method (Roth et al. 2015; Pušnik et al. 2016; Lin et al. 2017), the oxidative hydrolysis (Girginova et al. 2010; Reguyal et al. 2017), the hydrothermal treatment (Cheng et al. 2016; Gyergyek et al. 2017; Bhavani et al. 2017) and the thermal decomposition of iron containing molecular precursors (Jiang et al. 2014a; Glasgow et al. 2016; Bartůněk et al. 2016). These methods will be briefly reviewed in this section.

Co-precipitation

This is a simple and widely used method to synthesize Fe_3O_4 nanoparticles from mixtures of ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions (molar ratio 2:1) in aqueous alkaline environment (pH 8–14) and non-oxidizing atmosphere. The global chemical reaction is depicted in Eq. (9.2).

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \tag{9.2}$$

The size, shape and composition of the magnetic iron oxides prepared via co-precipitation depend on the type of salts used (e.g. chlorides, sulfates, nitrates), the Fe^{3+}/Fe^{2+} ratio, the reaction temperature, the pH value and ionic strength of the medium (Laurent et al. 2008; Su 2017). For example, samples prepared at hypostoichiometric ratios of hydroxide ions with respect to iron ions in combination with a high Fe^{3+}/Fe^{2+} ratio tend to lead to a mixture of the iron oxyhydroxides lepidocrocite (γ-FeO(OH)) and goethite (α-FeO(OH)) (Roth et al. 2015).

The main advantage of the co-precipitation process is that a large amount of nanoparticles can be synthesized. By varying the reaction conditions particles with size ranging from 2 to 17 nm can be obtained (Laurent et al. 2008). However this method does not provide a tight control of the particle size and usually polydisperse size distribution is obtained. The formation of the nanoparticles involves two stages, the formation of nuclei (nucleation) and the growth of the nuclei by diffusion of the species in solution to the surface of the crystal. In the co-precipitation method these stages are not separated, and nucleation can occur during the stage of growth, thus leading to size polydispersivity. Molecules or polymers containing chelating groups, e.g. carboxylate, can be added during the formation of the nanoparticles to facilitate the control of the particle size and colloidal stabilization (Bee et al. 1995). Because co-precipitation process occurs at mild temperatures in aqueous conditions, from room temperature (RT) to water boiling temperature, this method is compatible with the presence of biopolymers.

Oxidative Hydrolysis

Another aqueous-based synthesis route to prepare magnetite is the oxidative hydrolysis of iron (II) salts, a method that was firstly reported by Sugimoto and Matijevic (1980). It consists of partially oxidizing, ferrous hydroxide suspensions with mild oxidizing agents, typically nitrate ions. In contrast with the co-precipitation method, the oxidative hydrolysis can be used to prepare particles in a wide range of sizes, from nanometric up to dimensions as large as 1 micrometer (Zhang et al. 2009). The manipulation of the synthesis conditions, such as the ratio between the concentrations of the oxidant and the iron precursor and the initial pH, defines the nanoparticle size. Using this approach our group has prepared spherical and cubic magnetite particles with mean size of 50 nm and 100 nm, respectively that were subsequently functionalized to obtain magnetic sorbents (Girginova et al. 2010; Pinheiro et al. 2014; Carvalho et al. 2016; Tavares et al. 2016). As in the co-precipitation, this method does not provide a tight control over the size distribution of the nanoparticles.

Hydrothermal Reaction

In the hydrothermal process the synthesis is performed for several hours and in autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200 °C (Laurent et al. 2008). The reactants are premixed before being transferred to the autoclave, to ensure complete solvation. The formation of ferrites can occur via the hydrolysis and oxidation of ferrous salts (Guin et al. 2005; Chen et al. 2008), or via neutralization of mixed metal hydroxides (Sue et al. 2011; Velinov et al. 2016). The particle size is controlled mainly through the rate processes of nucleation and grain growth, that will depend upon the reaction temperature. Nucleation might be faster than grain growth at higher temperatures and results in a decrease in particle size. On the other hand, prolonging the reaction time would favour grain growth. The elevated pressures generated in hydrothermal synthesis introduce safety concerns that are not present in atmospheric-pressure methods, especially as the reaction scale increases (Qiao and Swihart 2017).

Thermal Decomposition

The thermal decomposition of iron organic precursors using organic solvents and surfactants has been used to synthesize iron oxide nanoparticles with narrow particle size distribution and uniform in shape. Examples of precursors used include iron complexes such as iron cupferronate, iron pentacarbonyl and iron(III) acetylacetonate. Surfactants such as oleic acid and hexadecylamine provide colloidal stability to the particles. Typically a mixture composed of precursors, surfactants and high boiling solvents are heated from room temperature to high temperature, leading to the generation and accumulation of monomers, followed by burst nucleation (Ling et al. 2015) (Fig. 9.3). In some processes the organometallic precursor is injected into a hot surfactant solution, inducing the simultaneous formation of many nuclei (Mendoza-Garcia and Sun 2016). In both strategies, after the nucleation event the preformed nuclei start to grow from the remaining monomers, without additional nucleation events, leading to the formation of monodispersed nanoparticles (Laurent et al. 2008; Ling et al. 2015; Mendoza-Garcia and Sun 2016). The size and

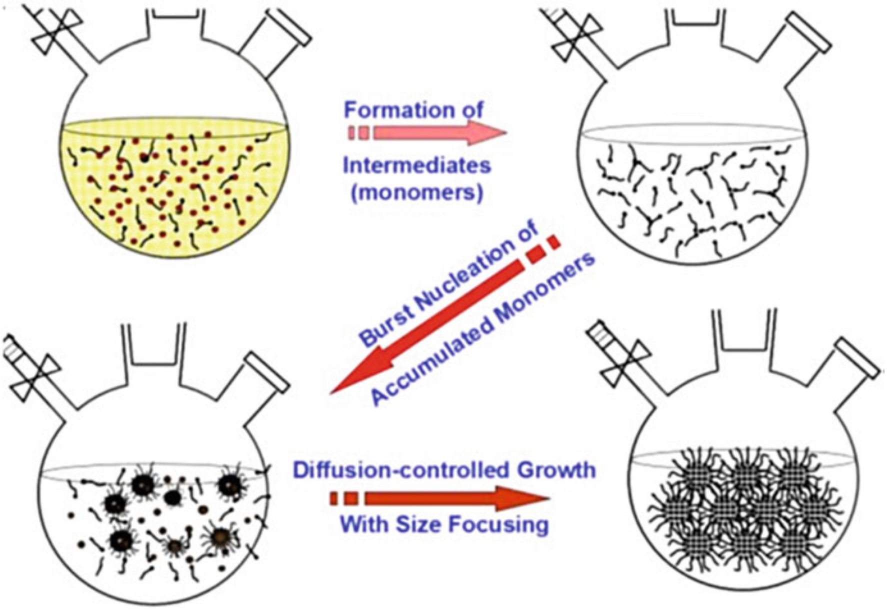

Fig. 9.3 Schematic illustration of the thermal decomposition method for the synthesis of uniformly sized iron oxide nanoparticles. Typically a mixture composed of precursors, surfactants and high boiling solvent are heated from room temperature to high temperature, leading to the generation and accumulation of monomers, followed by burst nucleation. The last step is the diffusion controlled growth of the nanoparticles. (Adapted with permission from Ling et al. 2015)

morphology of the nanoparticles can be controlled by adjusting the reaction times and the temperature but also the concentration and ratios of the reactants, namely the relative amounts of precursor and surfactants. The synthesis using thermal decomposition methods yields iron oxides nanoparticles compatible with organic solvents. For several applications, water-compatibility is required and thus surface modification is necessary using post synthetic methods such as ligand exchange reactions and encapsulation with amphiphilic polymers (Ling et al. 2015).

9.3 Surface Modification of Magnetic Nanoparticles with Biopolymers

Herein we will draw our attention on the synthetic procedures for the production of magnetic biosorbents, via the surface modification of magnetic nanoparticles with biopolymers. Preparative methods to obtain magnetic biosorbents in the particulate form, including composite nanoparticles, microparticles and hydrogel beads will be addressed.

Biopolymers extracted from natural sources present the advantages of biodegradability, reduced toxicity and low cost. Coating magnetic nanoparticles with biopolymers improves their stability against oxidation and provides functional groups to capture target pollutants from water (Avérous and Pollet 2012; Wu et al. 2015; Bohara et al. 2016). In addition, biopolymers improve the colloidal stability of the magnetic nanoparticles in aqueous media and prevent the formation of magnetic aggregates, which otherwise could contribute to diminish the available surface area and sorption capacity (Wu et al. 2008; Mehta et al. 2015). Colloidal stability is improved either due to steric shielding caused by biopolymer chains, or due to electrostatic repulsions between charged moieties present in the biopolymer.

Polysaccharides are among the most commonly used biopolymers for preparing magnetic biosorbents. Examples of polysaccharides are chitosan, starch, carrageenan, alginate, cellulose and derivatives, dextran and natural gum (Table 9.1). They can provide distinct ionic character such as neutral, anionic or cationic, and variable chemical functionalities and physical properties to the magnetic biosorbents. Surface modification with polysaccharides allows to enhance and to tune the chemical affinity of magnetic biosorbents surfaces towards specific target pollutants.

Although an exhaustive description of the properties of these polysaccharides is out of the scope of this chapter and can be found in specific literature (Zafar et al. 2016; Pattanashetti et al. 2017; Saba et al. 2017; Park et al. 2017; Dickinson 2017; Divya and Jisha 2017), it is worth mentioning some properties of relevance for sorption applications for selected polysaccharides.

Chitosan is obtained by deacetylation of chitin, the most abundant natural polymer after cellulose. Its structure contains amine and hydroxyl groups than can interact with metal cations in neutral or alkaline conditions. In acidic environment the protonated amine groups promote the sorption of anions (Choi et al. 2016; Bano et al. 2017; Muxika et al. 2017). Furthermore chitosan can be chemically modified with distinct functionalities to improve the adsorption capacities as well as the mechanical and physical characteristics of the resulting biosorbents (Yong et al. 2013; Vakili et al. 2014; Boamah et al. 2015).

Alginate is extracted mainly from brown seaweeds and can form hydrogels. Its structure contains abundant carboxylate groups that can interact with multivalent metal cations, namely with calcium ions to form the so-called “egg-box structure” through a sol-gel transition (Schnepp 2013). Carrageenan comprises a family of anionic sulfated linear polysaccharides extracted from red seaweeds. Carrageenan undergoes gelation in the presence of monovalent and divalent cations due to the formation of a double helical configuration and helix aggregation (Piculell 2006). Besides hydroxyl groups, carrageenan possess anionic ester sulfate groups that can interact with cationic pollutants (Gholami et al. 2016; Mahdavinia et al. 2016; Fernandes et al. 2017; Soares et al. 2017b). The polysaccharides chitosan, alginate and κ-carrageenan form hydrogels under facile ionotropic gelation and can be easily combined with magnetic nanoparticles and moulded in the form of magnetic beads

Table 9.1 Main characteristics of the polysaccharides and derivatives commonly used for coating magnetic nanoparticles, according to their ionic character, source and functional groups, in the context of environmental applications

Ionic character	Polysaccharide	Source	Functional groups	Target pollutants	References
Neutral	Cellulose	Vascular plants	$-OH$	Heavy metal ions, resorcinol	Anirudhan and Shainy (2015), Luo et al. (2016) and Ding et al. (2017)
	Dextran	Fermentation of sucrose	$-OH$	Aromatic hydrocarbons	Cho et al. (2015) and Kumar and Jiang (2017)
	Starch	Green plants	$-OH$	Cu, dyes	Mahdavinia et al. (2015) and Yang et al. (2016b)
Anionic	Alginate	Cell walls of brown algae	$-OH$, $-COO^-$	NaF, Sr, dyes	Hong et al. (2016), Li et al. (2016c) and Zhang et al. (2016b)
	Carrageenan	Red seaweeds	$-OH$, $-OSO_3^-$	Dyes, heavy metal ions, pharmaceuticals, herbicides	Gholami et al. (2016), Soares et al. (2016) and Fernandes et al. (2017)
	Natural gum	Microorganisms	$-OH$, $-COO^-$	Dyes, heavy metal ions	Sahraei et al. (2017)
Cationic	Chitosan	Shells of shrimp/crustaceans	$-OH$, $-NH_3^+$	Dyes, heavy metal ions, pharmaceuticals, oils	Chen et al. (2017a), Xiao et al. (2017) and Fan et al. (2017)

for sorption applications (Zhang et al. 2015a; Li et al. 2016c; Bée et al. 2017). Cellulose is the most abundant biopolymer and is an important structural component of the primary cell wall of green plants. Its structure contains several hydroxyl groups that enables cellulose to be relatively stable (Ding et al. 2017). However, the adsorption ability of cellulose which is not modified is insufficient, and the adsorption stability is poor. Cellulose can be chemically modified through several chemical processes to improve the adsorption capability (Lu et al. 2016a; Ding et al. 2017; Daneshfozoun et al. 2017).

9.3.1 Strategies for Surface Functionalization

The surface of magnetic nanoparticles (MNPs), typically magnetic iron oxide nanocrystals containing surface hydroxyl groups, can react with different functional groups. Owing to this broad reactivity there is a range of strategies for the surface modification of MNP with biopolymers, which can be carried out either *in situ* during the MNP synthesis, or using post-synthesis routes, i.e. *ex situ* (Bohara et al. 2016; Su 2017). The main interactions that can be present in the adsorption mechanism of biopolymers onto MNP are electrostatic interactions, hydrophobic interactions and hydrogen bonding (Avérous and Pollet 2012; Bohara et al. 2016). As a result of the many strategies available for surface modification, several distinct structures of magnetic bionanocomposites can be obtained, including core–shell structure, multicores or matrix dispersed structure, shell–core–shell, and Janus-type hetero-structures (Wu et al. 2015; Bohara et al. 2016) (Fig. 9.4).

Core-shell structures are obtained when the magnetic core is encapsulated within the biopolymeric material that involves the whole particle. In particular, the core-shell can be called yolk-shell structure when the magnetic core is not located at the center of the functional coating. In the inverse core–shell structure, the magnetic material coats the surface of the nonmagnetic functional material. Multicore structures include two distinct structures: mosaic or matrix-dispersed structure and shell–

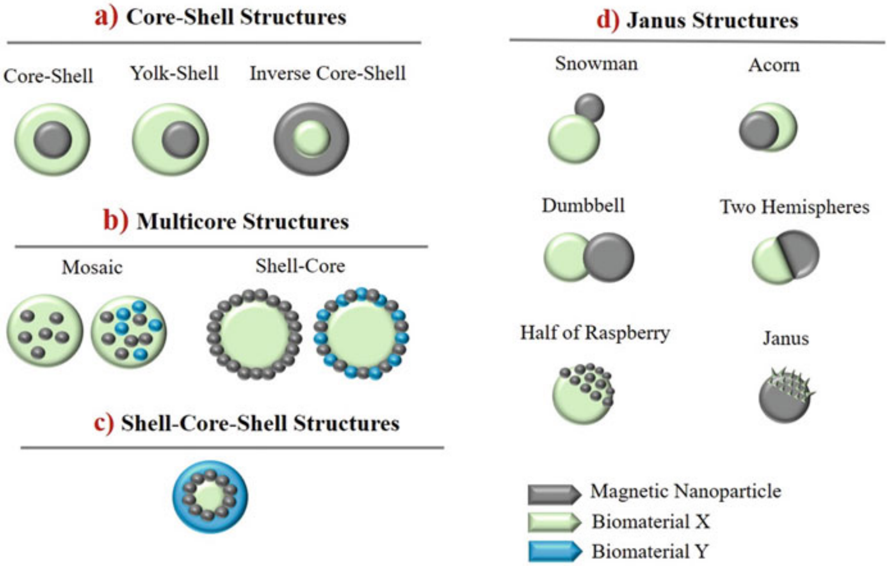

Fig. 9.4 Distinct structures of magnetic bionanocomposites: (**a**) core-shell structures include simple core-shell, yolk-shell and inverse core-shell structures; (**b**) multicore structures include mosaic and shell-core structures; (**c**) shell-core-shell structures; and (**d**) Janus structures comprise several types of arrangements such as snowman, acorn, dumbbell, two hemispheres, half of raspberry and Janus structures

core. The mosaic structure comprises a shell layer made of biopolymer molecules coated to any uniform MNP, i.e. MNPs are dispersed in a continuous biopolymer matrix. In a shell–core structure, MNPs decorate the surface of a core particle of biopolymer. In shell–core–shell structures, the location of MNPs is between the two biopolymeric materials. Magnetic Janus-type structures are hetero-structures where one of the spatial region provides magnetic features while the other compartment provides distinct functionality. Magnetic biopolymer-based Janus structures were barely explored for water treatment purposes. Nevertheless they offer huge potential for sensing applications, namely owing to the possibility of combining distinct analytical functions in a single particle that otherwise would interfere with each other (Fateixa et al. 2015; Pinheiro et al. 2018; Yi et al. 2016). In the context of sensing, Janus-compartmental alginate magnetic microbeads have been reported for the selective and convenient colorimetric detection of Pb(II) in water (Kang et al. 2014). The Pb(II) detection was possible owing to polydiacetylene liposomes embedded in the alginate matrix in the sensory compartment. The magnetic compartment provided convenient collection of the particles by applying magnetic field, after stirring for enhanced sensitivity and fast detection, while the alginate matrix provided additional feature of lead(II) removal.

9.3.1.1 *In situ* Surface Functionalization

This is a one-pot synthesis strategy where both the synthesis of magnetic nanoparticles (MNPs) and their surface functionalization are carried out in a single step. The biopolymer and the precursor of MNPs are added simultaneously to the reaction mixture and the coating process starts as soon as nucleation occurs, preventing further growth of the particles (Bohara et al. 2016). This method benefits from the ability of the biopolymer to interact with metal ions from the precursors of MNPs and from MNPs surface. The metal ion-biopolymer interaction may occur through different modes including complexation and hydrogen bonding (Boury and Plumejeau 2015). Hence, owing to these interactions the biopolymer can play a key role either on the nucleation or particle growth steps. For example, starch was employed to control and tune the size of Fe_3O_4 nanoparticles prepared by oxidation–precipitation of ferrous hydroxide (Tancredi et al. 2015). The size of the MNPs was tuned from 15 to 100 nm by changing the time period for starch addition to the reaction mixture. Starch acted as a kinetically control agent that affected both the size, size distribution and aggregation state of the MNPs. Starch-coated Fe_3O_4 NPs were water-dispersible, presenting good colloidal stability. In our group it has been observed that the particle size and the stability toward oxidation of Fe_3O_4 nanoparticles generated by co-precipitation of iron salts in the presence of carrageenan, strongly depended on the type and concentration of carrageenan used (Daniel-da-Silva et al. 2007). Overall the particle size decreased with increasing carrageenan concentration but the stability to oxidation followed distinct trend. The rheological state (hydrosol or hydrogel) of the final magnetic nanocomposite was found to be a relevant parameter. Considering that increasing biopolymer concentration resulted in smaller Fe_3O_4 nanoparticles and stronger gels and that magnetite oxidation follows a size-dependent diffusion mechanism, it was suggested that small particle sizes accelerate oxidation while strong gels have the opposite effect, as oxygen diffusion within the gel becomes more difficult.

The *in-situ* MNPs synthesis is typically performed using wet chemical routes that require aqueous environment and mild conditions of temperature, compatible with the presence of the biopolymer. Among *in situ* strategies, the co-precipitation of ferric and ferrous ions under alkaline conditions is the most commonly used route to prepare biopolymer coated magnetite (Fe_3O_4) nanoparticles (Lee et al. 1996; Kim et al. 2014). Generally, nanocomposite structures obtained are core-shell structures or mosaic (matrix dispersed) structures (Wu et al. 2015; Bagheri and Julkapli 2016). Nevertheless the morphology and the thickness of the polymer shell are difficult to control using this methodology. Owing to these limitations and even though the one-step synthesis is less time-consuming, magnetic biosorbents prepared by *in situ* procedures have been less reported. Some recent examples are described below that illustrate the usefulness of *in situ* strategy for the functionalization of MNPs aiming applications in the removal of pollutants from water.

Magnetic iron oxide nanoparticles were prepared by co-precipitation of iron ions in the presence of chitosan, followed by the addition of the crosslinker glutaraldehyde (Yang et al. 2016a; Azari et al. 2017) to impart mechanical robustness to the biosorbent. Small nanoparticles, with an average size of 5 nm (Yang et al. 2016a) and 50 nm (Azari et al. 2017) and narrow particle size distribution were obtained. The nanoparticles were homogeneously dispersed and embedded in the biopolymer matrix, leading to the formation of magnetic nanocomposites of undefined morphology. These biosorbents showed good adsorption of mercury species (Azari et al. 2017) even in the presence of competitive cations. In alternative to glutaraldehyde addition, more environmental friendly crosslinking strategies are also being explored. For example, using *in-situ* co-precipitation κ-carrageenan coated magnetite nanoparticles with average size of 4 nm were prepared and then crosslinked with chitosan (Mahdavinia and Mosallanezhad 2016). The electrostatic interactions between positively charged amine groups on chitosan and negatively charged sulfate groups on κ-carrageenan could produce stable complexes, with affinity for cationic dyes such as methylene blue.

Magnetite nanoparticles coated with carboxylated cellulose were prepared using the co-precipitation method, wherein carboxylated cellulose acted as a template and stabiliser for the *in-situ* prepared Fe_3O_4 nanoparticles, preventing its aggregation (Lu et al. 2016a). The magnetic material showed high adsorption capacity of Pb (II) from water owing to carboxylic acid groups of carboxylated cellulose. The biosorbent could be regenerated and reused for at least 5 cycles. Nevertheless the removal capacity decreased with increasing cycle numbers, indicating poor stability of the coating. In another study (Ding et al. 2017) the co-precipitation method was used to prepare cellulose coated Fe_3O_4 nanoparticles that were subsequently reacted with polydopamine, providing a magnetic biosorbent whose surface was enriched in hydroxyl and amino functionalities. The biosorbent was tested in the removal of resorcinol from water showing better adsorption capacity at low pH. The biosorbent was reusable for 5 cycles, with small loss of adsorption capacity, after regeneration in alkaline conditions.

Several examples could be found concerning biopolymer coated magnetic nanophases obtained by in situ co-precipitation that were subsequently modified in post-synthetic steps. In those systems the biopolymer serves as springboard for the addition of reactive groups aiming to improve the adsorption capacity. For instance amino-acids and diethylenetriamine were grafted at the surface of chitosan coated magnetite nanoparticles (size 10–50 nm) prepared via co-precipitation, using epichlorohydrin as crosslinker (Galhoum et al. 2015a, 2017). The materials showed binding affinity for uranyl and Dy(III) species present in aqueous solutions. The highest uranyl sorption capacity was obtained with diethylenetriamine functionalized biosorbents, probably due to the increased density of reactive polyamine groups.

Li et al. (2017) prepared magnetic gelatin by *in situ* co-precipitation of magnetic iron oxide phases with an average size of 15 nm (Fig. 9.5a) and the gelatin was further cross-linked by transglutaminase to maintain its mechanical stability. Compared with other cross-linkers, transglutaminase had the advantage of its specificity towards reaction between lysine and glutamine residues of gelatin, without affecting many of amino groups that remain available for further modification and removal of heavy metals in water. After modification with a dicarboxylic acid, chitosan/polyethyleneimine (PEI) cationic copolymers were grafted on the surface of the nanoparticles, using carbodiimide chemistry, yielding a sheet structure with a mean diameter of 500 nm (Fig. 9.5b). Grafting of PEI greatly increased the number of

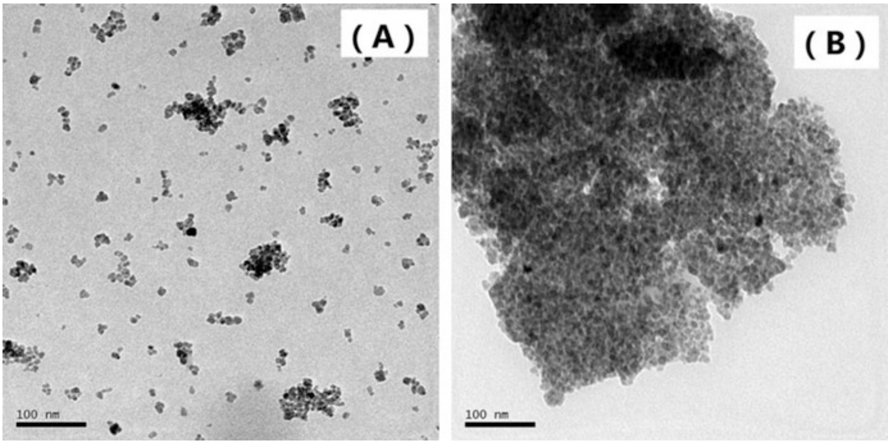

Fig. 9.5 TEM images of (**a**) magnetic gelatin particles with an average size of 15 nm and (**b**) chitosan/PEI-grafted magnetic gelatin sheet structure with a mean diameter of 500 nm. (Adapted with permission from ref. Li et al. (2017). *TEM* transmission electron microscopy, *PEI* polyethyleneimine)

surface amino groups and the adsorption capacity of lead and cadmium cations from water, as well as the stability of the biosorbent in strong alkaline or acidic conditions.

Using a simple one-pot polyol method, magnetic carboxymethylchitosan spherical composite particles with very uniform particle size have been prepared (Charpentier et al. 2016). The average diameter was nearly 500 nm, and each sub-micrometer sized particle was a cluster formed by the aggregation of many small Fe_3O_4 nanocrystals with sizes of 10–15 nm (Fig. 9.6). In this method the polyol (ethylene glycol) acts as high boiling point polar solvent and simultaneously reduces Fe(III) ions from the precursor, to form Fe_3O_4 nanocrystals (Cheng et al. 2009). The primary Fe_3O_4 nanocrystals aggregate into larger secondary particles. The resulting composite nanoparticles possessed high magnetic content and surfaces functionalized with carboxylic moieties and were used for the rapid removal of metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) from aqueous solutions.

9.3.1.2 *Ex situ* Surface Functionalization

Ex situ or post surface functionalization strategies are carried out using magnetic nanoparticles (MNPs) previously synthesized. The procedure is divided into two distinct stages, synthesis and surface modification, that allows a better control of each stage individually. It can involve the simple coating of MNPs with biopolymers, physically or chemically crosslinked or the covalent attachment of the biopolymer chains to the surface of MNPs. The latter usually requires the use of a linker ligand such as functional alkoxysilanes (Laurent et al. 2008; Sun et al. 2008; Begin-Colin and Felder-Flesch 2012).

Ionic Crosslinking of Biopolymer Coating

Several natural polyelectrolytes have the ability to undergo ionotropic gelation, i.e. to crosslink in the presence of counter ions to form hydrogels (Jiang et al. 2014b; Nie et al. 2016; Valle et al. 2017). This ability combined with extrusion or emulsification techniques has been widely explored for the encapsulation of magnetic nanoparticles, to form magnetic composite particles with different size and shapes.

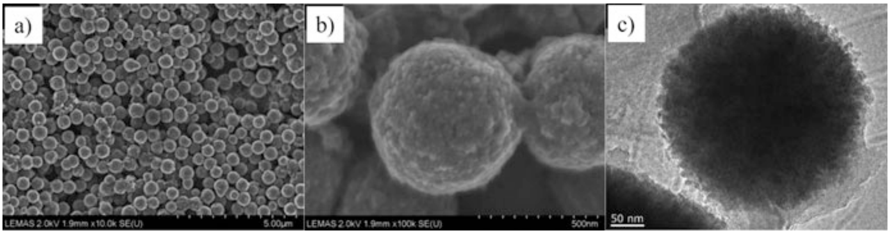

Fig. 9.6 SEM images of carboxymethylchitosan magnetic nanoparticles at (**a**) low and (**b**) high resolution, and (**c**) TEM image. The average size of the particles was 500 nm. (Adapted with permission from ref. Charpentier et al. (2016). *SEM* scanning electron microscopy, *TEM* transmission electron microscopy)

Magnetic alginate core-shell type particles were fabricated using a method of electro-coextrusion, and employed as an biosorbent for separation of fluoride from aqueous solution (Zhang et al. 2016b). In this method the solutions of alginate and Fe_3O_4 nanoparticles were injected simultaneously through a concentric nozzle using an electrostatic spinning machine and droped into a solution of $CaCl_2$ for alginate crosslinking. The resulting particles comprised a core of aggregated Fe_3O_4 nanoparticles coated by a shell of alginate. Because trivalent lanthanum (Lewis hard acid) shows high chemical affinity to fluoride anions (Lewis hard base), the Ca $^{2+}$ ions of the alginate were then replaced by La^{3+} ions, through cation exchange. The resulting particles were able to uptake F^- ions from solution owing to Lewis acid-based interactions. In another study magnetic alginate beads containing cobalt ferrite nanoparticles were prepared using Ca^{2+} crosslinking as well (Li et al. 2016c). The $CoFe_2O_4$ nanoparticles were firstly coated with polydopamine, which is a polymer that provides very good adhesion either to organic and inorganic substrates. Polydopamine coated ferrites were added to an alginate solution and the magnetic beads were obtained by injection into a $CaCl_2$ solution, to induce sol-gel transition. The beads were successfully used in the uptake of organic dyes from water. The adsorption was ascribed to negatively charged groups of the beads (carboxylate from alginate, catechol and amine groups from polydopamine) that could interact with cationic dyes through electrostatic interactions, hydrogen bonding, van der Waals interactions and π-π interactions between aromatic rings of catechol and organic dyes.

Martínez-Cabanas and co-workers (Martínez-Cabanas et al. 2016) have prepared magnetic chitosan beads containing magnetic iron oxide nanoparticles. The MNPs were dispersed in an acidic solution of chitosan and dripped into an alkaline solution under stirring to promote the formation of the beads. The materials were effective in the removal of arsenic from water with short equilibrium times and good adsorption capacity.

Magnetite nanoparticles were coated with κ-carrageenan and used as magnetic biosorbents for the removal of methylene blue from aqueous solutions (Salgueiro et al. 2013). Coating of MNPs (size around 12 nm) was obtained by simple dispersion of the nanoparticles in κ-carrageenan solution, addition of K^+ ions to promote sol-gel transition by physical crosslinking, followed by particle separation. These biosorbents show high methylene blue adsorption capacity due to electrostatic interaction of the cationic dye MB with the ester sulfate moieties of carrageenan. Nevertheless marked loss of adsorption capacity after regeneration and reuse was observed for these biosorbents. This loss was ascribed to possible leaching of the external layer of κ-carrageenan molecules during adsorption/desorption stages, owing to lack of stability of the carrageenan layer that was physically adsorbed at the surface of MNPs.

Covalent Crosslinking of Biopolymer Coating

The mechanical and chemical stability of the biosorbent is an important aspect to consider, namely to ensure successful recycling and reuse of the biosorbents without loss of adsorption capacity. Covalent crosslinking is a versatile method to improve the robustness of the biosorbents. It results in the enhancement of the mechanical properties and insolubility of the biopolymer coating, as the chains are tied together by strong covalent linkages (Maitra and Shukla 2014). Some recent examples of covalently crosslinked magnetic biosorbents are described below. It is worth noting that glutaraldehyde is still one of the most frequently used crosslinkers, in spite of its known ecotoxicological issues (Leung 2001; Hu et al. 2017; Christen et al. 2017). Alternative and much less toxic crosslinkers such as genipin (Muzzarelli 2009; Pujana et al. 2014) have been barely investigated for applications in water remediation (Laus and de Fávere 2011; Mondal et al. 2015).

Magnetic crosslinked-chitosan microparticles were prepared using a reverse-phase suspension cross-linking technique (Funes et al. 2017). The process encompassed the preparation of a water-in-oil emulsion, the aqueous phase comprised an acidic solution of chitosan containing Fe_3O_4 nanoparticles (280 nm in size) dispersed. Glutaraldehyde was added to crosslink the biopolymer and the particles were gathered using a magnet. The microparticles were spherical in shape and polydisperse in size, with a mean diameter of 4.8 μm (Fig. 9.7a). The cross-sectioned particles revealed a homogeneous distribution of Fe_3O_4 nanoparticles within the chitosan microspheres indicating that the embedding process resulted in little Fe_3O_4 aggregation (Fig. 9.7b). These biosorbents were tested in the removal of phosphorous in the form of phosphates from water.

Magnetic biosorbents of a quaternary chitosan, N-(2-hydroxyl)propyl-3-trimethyl ammonium chitosan chloride were prepared using a similar emulsion technique (Li et al. 2016a; Song et al. 2017). Overall, quaternary chitosans provide enhanced adsorption affinity towards anionic pollutants in comparison to unmodified chitosan. The biopolymer coating was covalently crosslinked using glutaraldehyde (Li et al. 2016a) or a combination of formaldehyde and glutaraldehyde (Song et al. 2017). The magnetic biosorbents were used for the removal of anionic pollutants from water such as As(III) (Song et al. 2017) and Cr(VI) (Li et al. 2016a) anionic species and anionic dyes (Li et al. 2016a).

Aiming to prepare chitosan based biosorbents with high specific surface area, Xiao et al. used a distinct approach and produced sub-micron-sized polyethylenimine modified polystyrene/Fe_3O_4/chitosan magnetic composite particles for the uptake of Cu(II) ions from water (Xiao et al. 2017). Polystyrene particles (~300 nm) whose surface was decorated with small Fe_3O_4 nanoparticles (~10 nm) were firstly synthesized. Magnetic polystyrene particles were then coated with chitosan thin-film which was crosslinked by glutaraldehyde, followed by grafting of polyethylenimine (Fig. 9.8). Owing to small particle size and a surface highly enriched in amine groups, these biosorbents exhibited very high Cu(II) adsorption capacity when compared with other magnetic biosorbents, reaching the equilibrium within very short time (15 min).

Besides chitosan and chitosan derivatives, glutaraldehyde was also used to prepare magnetic biosorbents derived from other biopolymers such gum tragacath (Sahraei et al. 2017).

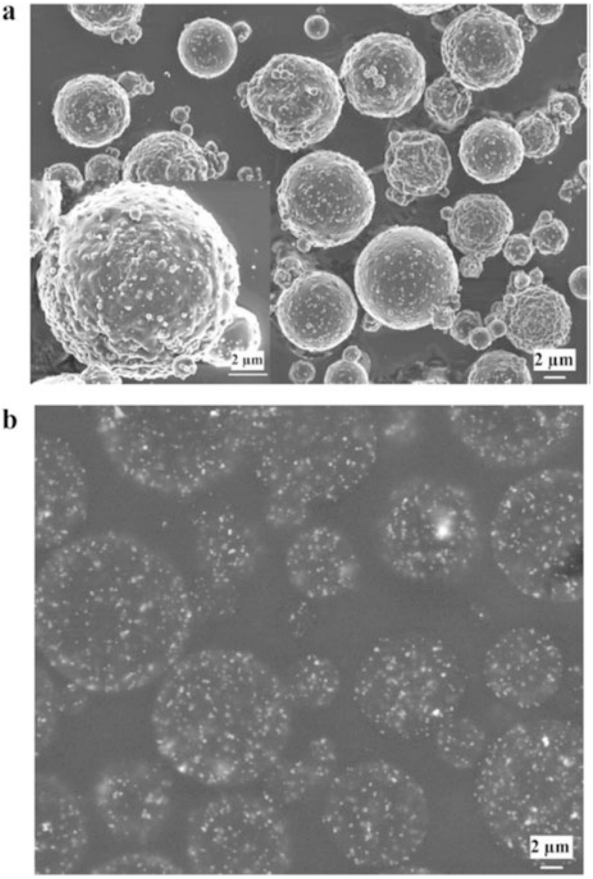

Fig. 9.7 SEM images of (**a**) magnetic chitosan microparticles with an average size of 280 nm and (**b**) cross-sectioned magnetic chitosan microparticles showing a homogeneous distribution of the magentic nanoparticles within the chitosan microspheres. (Adapted with permission from ref. Funes et al. (2017). *SEM* scanning electron microscopy)

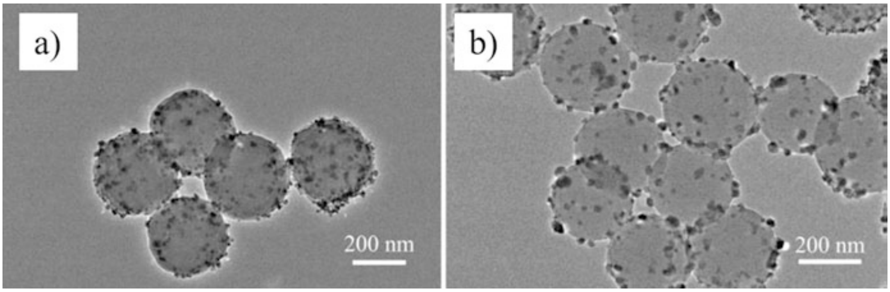

Fig. 9.8 TEM images of (**a**) PS/Fe$_3$O4/CS and (**b**) PS/Fe_3O_4/CS-PEI microspheres. The average size was 300 nm and 10 nm for PS and Fe_3O_4 particles, respectively. (Adapted with permission from ref. Xiao et al. (2017). *TEM* transmission electron microscopy, *PS* polystyrene, *CS* chitosan, *PEI* polyethylenimine)

Coating by Complexation of Polyelectrolytes

Coating of magnetic nanoparticles can be also performed by assembling polyelectrolytes oppositely charged. Most of biopolymers are polyelectrolytes i.e., macromolecules that are either charged or, under suitable conditions, can become charged. Hence biopolymers can undergo complexation in the presence of other oppositely charged biopolymers (Luo and Wang 2014) or synthetic polyelectrolytes (Gentile et al. 2015). The assembly of oppositely charged polyelectrolytes and MNPs is mainly governed by strong but reversible electrostatic interactions, as well as hydrogen bonds. The layer-by-layer (LbL) assembly technique is a simple and versatile method for the fabrication of polymer-based coatings and has been widely used to modify spherical and planar inorganic substrates (Srivastava and Kotov 2008). This method involves the sequential adsorption of oppositely charged biopolymers onto the surface of the nanoparticles. The thickness of the polymer coating can be tuned by varying the number of layers deposited and the properties of the polymer solutions. Most of magnetic bionanocomposites prepared by LbL technique were developed envisaging biomedical application (Xiong et al. 2013; Luo and Wang 2014; Gentile et al. 2015). Nevertheless examples of magnetic biosorbents for water treatments have been also reported (Mu et al. 2013; Shi et al. 2016). For example polyelectrolyte-coated magnetic composites were prepared by LbL self-assembly of chitosan and cysteine modified β-cyclodextrin on the surface of Fe_3O_4 nanoparticle-decorated attapulgite, and investigated for the adsorption of precious metal ions (Mu et al. 2013).

Using a distinct approach Liang et al. have prepared magnetic chitosan/carrageenan ampholytic microspheres that showed highly efficient adsorption capacity towards both cationic and anionic dyes and heavy metal ions in wastewater (Liang et al. 2017). The microspheres were fabricated via emulsification procedure from the homogeneous chitosan/carrageenan solution in LiOH/KOH/urea aqueous system, showing homogeneous network structure. In alternative to the use of acidic solutions, chitosan was dissolved in the alkali/urea solution via the freezing- thawing process. The dissolution was caused by destruction of the intermolecular hydrogen bonds rather than protonation of the amino groups, and as a result chitosan displayed the neutral feature and no flocculation occurred in chitosan/carrageenan blend solution. The ampholytic chitosan/carrageenan composite matrix played an important role in adsorption of pollutants, and the Fe_3O_4 nanoparticles uniformly embedded in the matrix afforded sensitive magnetic responsiveness.

Grafting of Biopolymers onto Magnetic Particles Surface

Another strategy explored for the preparation of magnetic biosorbents is the grafting of the biopolymer to the surface of magnetic nanoparticles. The biopolymer can be directly grafted onto the surface of the iron oxide particle (Badruddoza et al. 2011; Lu et al. 2016b) or after surface functionalization with ligands such as functional alkoxysilanes that will subsequently link to the biopolymer (Bini et al. 2012; Rodriguez et al. 2017). This strategy might also involve the coating of MNPs with a thin layer of amorphous silica (SiO_2). The method for the encapsulation with SiO_2 shells is well established and involves the hydrolysis of alkoxysilanes (e.g.

tetraethylorthosilicate-TEOS) and subsequent condensation of silica oligomers in the presence of an acid or base catalyst. The amorphous SiO_2 shells protect magnetic iron oxides from oxidation and ion leaching, and provide a suitable surface for further chemical modification aiming the grafting of the biopolymers onto its surface. For example carboxymethylated carrageenans were grafted onto the surface of amino-functionalized silica coated magnetite nanoparticles, via carbodiimide chemistry (Daniel-da-Silva et al. 2015). The biosorbents showed good adsorption of methylene blue due to electrostatic interactions between the sulfonate groups of carrageenan and the dye. Owing to the covalent immobilization of the carrageenan to the magnetic support, the particles prepared with κ-carrageenan were reusable for six adsorption cycles without significant loss of the adsorption capacity.

Kim et al. prepared carboxymethyl chitosan-modified magnetic-cored dendrimers with enhanced adsorption capacity and magnetic properties (Kim et al. 2016). Magnetite nanoparticles were first functionalized with amine groups using an amine functionalized alkoxysilane. Amine terminated dendrimers were then built at the surface of the MNPs. Finally carboxymethyl chitosan was grafted to the dendritic structure upon the reaction between –COOH and $–NH_2$ groups, using the carbodiimide reaction. The resulting material contained carboxylic acid groups and amino groups as terminal sites and showed satisfactory adsorption capacity of both cationic and anionic organic dyes.

Bio-hybrid Coatings

In alternative to the grafting of biopolymers at the surfaces of silica coated nanoparticles, the biopolymer can be introduced in the silica network, yielding an organic-inorganic hybrid material enriched in biopolymer, herein designated by bio-hybrid material. Our group has developed a method for the encapsulation of Fe_3O_4 nanoparticles with bio-hybrid siliceous shells comprising a polysaccharide covalently grafted to the siliceous network (Soares et al. 2016; Fernandes et al. 2017; Soares et al. 2017a). The encapsulation was performed through a one-step procedure, involving the hydrolysis and condensation of a mixture of tetraethyl orthosilicate and an alkoxysilane covalently bound to the biopolymer, in the presence of the magnetic particles and a base that acts as catalyst. Core-shell composite particles comprising a magnetic core of Fe_3O_4 uniformly coated by a thin shell of bio-hybrid siliceous material were obtained (Fig. 9.9). This method was successfully used for the encapsulation using polysaccharides having distinct chemical nature and ionic character, namely κ-carrageenan (Soares et al. 2016; Fernandes et al. 2017; Soares et al. 2017b), chitosan (Soares et al. 2017a) and starch (Fernandes et al. 2017). In comparison to the post encapsulation grafting, this method allowed to obtain surfaces highly enriched with biopolymer functional groups. The resulting magnetic biosorbents were highly effective in the removal of the organic pollutants Paraquat, Methylene Blue and Metoprolol from aqueous solutions (Soares et al. 2016, 2017b; Fernandes et al. 2017). Magnetic hybrid particles prepared from chitosan were tested for the uptake of non-polar organic solvents from water (Soares et al. 2017a).

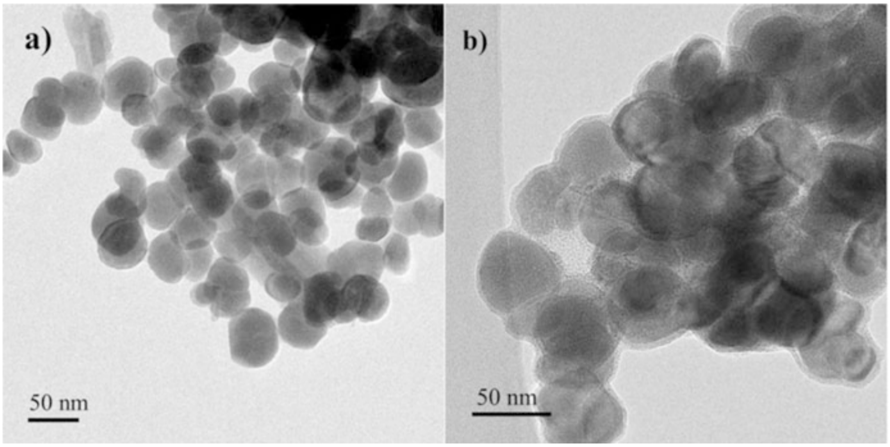

Fig. 9.9 TEM images of (**a**) Fe_3O_4 particles with an average size of 47 nm and (**b**) Fe_3O_4 coated with κ-carrageenan hybrid siliceous shell with a shell thickness of 6 nm. (Adapted with permission from ref. Soares et al. (2016). *TEM* transmission electron microscopy)

9.4 Adsorptive Applications of Magnetic Bionanocomposites in Water Treatment

In this section, the most recent magnetic bionanocomposites for the clean-up of emerging pollutants from water is reviewed taking into consideration adsorptive technologies. The Table 9.2 provides an overview of several materials that have been successfully used for the removal of inorganic and organic pollutants.

9.4.1 Removal of Heavy Metal Species

Although there is no clear classification, heavy metals can be defined as metallic elements that possess a high density (higher than 5 g/cm^3). Herein, metalloids, such as arsenic, will be included in this discussion given their chemical nature and ability to also induce similar toxic effects even at low concentrations (Tchounwou et al. 2012; Chen et al. 2015). Heavy metals have been used for many human applications for at least 5000 years, including for agricultural, mining, industrial or domestic operations. Their accumulation in the environment, i.e. plant tissues, fish, mammals, soil, air and water, poses a serious threat to human health. Even though heavy metals are naturally occurring elements, their unintended environmental accumulation is originated from the uncontrolled disposal of these elements arising from anthropogenic activity. Although some heavy metals have an important biological role (e.g. Cu(II) as cofactor), the excessive exposure to such elements or a simple change on their oxidation state can result in detrimental effects to the ecosystem and human

Table 9.2 Recently reported magnetic bionanocomposites for the uptake for several inorganic and organic pollutants

Biosorbent	Pollutant	Adsorption capacity	pH	References
Magnetic chitosan-graphene oxide	Acid red 17 (AR17) and bromophenol blue (BPB)	8.1 and 9.5 mg.g^{-1}	2, 6	Sohni et al. (2017)
Imprinted Fe_3O_4-quaternay ammonium chitosan	As(III)	12 mg.g^{-1}	6	Song et al. (2017)
Fe_3O_4-chitosan beads	As(V)	147 μg.g^{-1}	6–8	Martínez-Cabanas et al. (2016)
Fe_3O_4-chitosan-PAC-clay	Atenolol, ciprofloxacin and gemfibrozil	15.6, 39.1 and 24.8 mg.g^{-1}	10, 7, 4	Arya and Philip (2016)
8-hydroxyquinoline anchored imprinted γ-Fe_2O_3@chitosan	Co(II)	100 mg.g^{-1}	8	Hossein et al. (2016)
Pyridinium-diethylenetriamine magnetic chitosan	Cr(VI)	176 mg.g^{-1}	3	Sakti et al. (2015)
Fe_3O_4-quaternary ammonium chitosan	Cr(VI) and methyl orange	3.25 and 2.5 mmol.g^{-1}	2	Li et al. (2016a)
Fe_3O_4-κ-carrageenan-g-poly(methacrylic acid) hydrogel	Crystal violet	28.24 mg.g^{-1}	7	Gholami et al. (2016)
Polyethylenimine(PEI)-modified polystyrene/Fe_3O_4/chitosan	Cu(II)	204 mg.g^{-1}	6	Xiao et al. (2017)
Starch-g-polyacrylonitrile/montmorillonite/Fe_3O_4	Cu(II)	164 mg.g^{-1}	4.7	Mahdavinia et al. (2015)
Fe_3O_4-chitosan	Cu(II)	236 mg.g^{-1}	6	Neeraj et al. (2016)
Fe_3O_4@ aminopropyl-functionalized silica-chitosan	Demulsification	n/a	n/a	Lü et al. (2017)
Magnetic cellulose ionomer/layered double hydroxide	Diclofenac	268 mg.g^{-1}	9	Hossein et al. (2016)
Gelatin based magnetic beads	Direct red 80 and methylene blue	380 and 465 mg.g^{-1}	n/a	Saber-Samandari et al. (2017)
Fe_3O_4-alanine or –serine or –cysteine grafted-chitosan	Dy(III)	14.8, 8.9, and 17.6 mg.g^{-1}	5	Galhoum et al. (2015a)
Magnetic chitosan modified with glutaraldehyde	Hg(II)	96 mg.g^{-1}	5	Azari et al. (2017)

(continued)

Table 9.2 (continued)

Biosorbent	Pollutant	Adsorption capacity	pH	References
Itaconic acid-grafted-magnetite nanocellulose	Hg(II)	240 mg.g^{-1}	8	Anirudhan and Shainy (2015)
Fe_3O_4-cysteine-chitosan	La(III), Nd(III), and Yb(III)	17, 17, 18 mg.g^{-1}	5	Galhoum et al. (2015b)
Chitosan/Al_2O_3/Fe_3O_4 microspheres	Methyl orange	419 mg.g^{-1}	6	Tanhaei et al. (2016)
Glutaraldehyde cross-linked chitosan-coated Fe_3O_4 nanoparticles	Methyl orange	758 mg.g^{-1}	6–10	Yang et al. (2016a)
Fe_3O_4@SiO_2-κ-carrageenan	Methylene blue	530 mg.g^{-1}	9	Soares et al. (2017b)
Fe_3O_4-OMWCNT-κ-carrageenan	Methylene blue	1.24×10^{-4} mol.g^{-1}	6.5	Duman et al. (2016)
Fe_3O_4-κ-carragenaan crosslinked with chitosan	Methylene blue	123 mg.g^{-1}	2–12	Mahdavinia and Mosallanezhad (2016)
Magnetic chitosan/clay beads	Methylene blue	82 mg.g^{-1}	> 9	Bée et al. (2017)
Carboxymethyl chitosan-modified magnetic-cored dendrimers	Methylene blue and methyl orange	20.85 and 96.31 mg.g^{-1}	3; 11	Kim et al. (2016)
Magnetic ampholytic polyelectrolyte microspheres	Methylene blue, Congo red, Cu (II) and Cr(III)	124, 212, 20 and 12 mg.g^{-1}	>9, <5 (org. Only)	Liang et al. (2017)
$CoFe_2O_4$ alginate beads	Methylene blue, crystal violet and malachite green	466, 456, 248 mg.g^{-1}	5	Li et al. (2016c)
Fe_3O_4@SiO_2-κ-carrageenan	Metoprolol	447 mg.g^{-1}	7	Soares et al. (2016)
Ion-imprinted magnetic chitosan/poly(vinyl alcohol)	Ni(II)	500 mg.g^{-1}	5.5	Zhang et al. (2015a)
Fe_3O_4-corn stalk	NO^{3-}	102 mg.g^{-1}	6–9	Song et al. (2016a)
Fe_3O_4@SiO_2-κ-carrageenan	Paraquat	257 mg.g^{-1}	7.3	Fernandes et al. (2017)
Magnetic cellulose beads	Pb(II)	5 mg.g^{-1}	2–3	Luo et al. (2016)
Magnetic graphene oxide coated with chitosan	Pb(II)	79 mg.g^{-1}	5	Wang et al. (2016)
Chitosan/PEI-grafted magnetic gelatin	Pb(II) and Cd(II)	341 and 321 mg.g^{-1}	6–7	Li et al. (2017)
Fe_3O_4-chitosan and -caboxymethylchitosan	Pb(II), Cu(II) and Zn(II)	243, 232, 131 mg.g^{-1}	5.2	Charpentier et al. (2016)

(continued)

Table 9.2 (continued)

Biosorbent	Pollutant	Adsorption capacity	pH	References
Magnetic hydrogel beads with gum tragacanth	Pb(II), Cu(II), crystal violet and Congo red	81, 69, 101, 94 $mg.g^{-1}$	2–6 (M^{+}) 2–8 (CV) 5–8 (CR)	Sahraei et al. (2017)
Fe_3O_4-β-cyclodextrin-bearing dextran	Phenanthrene and pyrene	K_d: 6095.5, 21,965 $l.kg^{-1}$	n/a	Cho et al. (2015)
Magnetic chitosan microspheres	Phosphorous	4.84 $mg.g^{-1}$	7	Funes et al. (2017)
Fe_3O_4 –NH_2 modified cellulose	Reactive Brilliant red K-2BP, methyl Orange and acid red 18	101, 222 and 99 $mg.g^{-1}$	2–3, 6, 6, >8,	Song et al. (2016b)
Cellulose functionalized with poly(dopamine)	Resorcinol	258 $mg.g^{-1}$	3	Ding et al. (2017)
Carbon nanotubes–C@Fe–chitosan	Tetracycline	104 $mg.g^{-1}$	6	Ma et al. (2015)
Carbon disulfide-modified magnetic ion-imprinted chitosan-Fe(II)	Tetracycline and Cd(II)	516 and 194 $mg.g^{-1}$	7–8	Chen et al. (2017a)
Fe_3O_4-alanine or –serine grafted chitosan	U(VI)	85, 116 $mg.g^{-1}$	3.6	Galhoum et al. (2015c)

health. In addition, many heavy metals are considered non-essential elements and have been linked to several diseases in humans (Järup 2003; Khan et al. 2008; Tchounwou et al. 2012; Chen et al. 2015; Tóth et al. 2016; Wasana et al. 2017).

Since water is one of the main routes for human exposure to excessive levels of heavy metals, in this section, a review is provided regarding the most recent magnetic bionanocomposites for their water remediation. Due to their well-known toxicity, heavy metals such as lead, cadmium, arsenic, mercury and chromium have been considered priority pollutants since they pose the greatest concern regarding human exposure.

A wide variety of magnetic bionanocomposites have been proposed for the effective removal of Pb(II) from water under several operating conditions (Charpentier et al. 2016; Luo et al. 2016; Wang et al. 2016; Li et al. 2017; Sahraei et al. 2017; Sengupta et al. 2017; Chen et al. 2017b). It is now well documented that Pb(II) can have a serious impact on human health mainly due to increased oxidative stress, with a highly detrimental effect on the hematopoietic, renal, reproductive and central nervous system (Flora et al. 2012). Moreover, even at very low environmental concentrations (<7.5 $\mu g.dL^{-1}$), lead can induce neuro–behavioural problems in children (Järup 2003; Lanphear et al. 2005). Despite the limited evidence on humans, lead has been classified as possible human carcinogen (Rousseau et al. 2007). Since that lead poisoning has been considered a major public health risk, several biosorbents have been recently presented for water remediation. Recently, a chitosan/PEI–grafted magnetic composite has been reported with an impressive capacity for the removal of Pb(II) and Cd(II) with a maximum adsorption capacity of 341 and 321 mg.g^{-1} respectively (Li et al. 2017). With an optimum performance in pH range 6–7, the isotherm studies indicated a good agreement with the Langmuir isotherm for both metals. In addition, under the temperature range of 297 to 303 K, the chitosan/polyethylenimine–grafted magnetic composite exhibited negative ΔG° and positive ΔH° values indicating that the adsorption process is thermodynamically favourable and endothermic. It was also found that this material possessed a pseudo-second order kinetics, suggesting that chemisorption is the rate-limiting step. It was proposed that the good removal efficiency could be attributed to presence of biopolymer at the surface of the particles, which resulted in a higher number of amines groups with superior uptake efficiency. Besides the good performance, the chitosan/polyethylenimine–grafted magnetic composite could be effectively regenerated for 5 cycles while keeping the good performance and stability.

Magnetic hydrogel beads containing gum tragacanth in its composition, have also been reported for the effective clean-up of Pb(II) and Cu(II) from water (Sahraei et al. 2017), with a maximum adsorption capacity of 81 and 69 mg.g^{-1} respectively, at pH 6. The good removal capacity of the particles was attributed to the presence of several chelating sulfonic acid, carboxylic acid, hydroxyl and amine groups. The isotherm experiments suggested a good agreement with the Langmuir model and the kinetic studies were more precisely defined by a pseudo-second order kinetics. Besides of the interesting performance, these beads could be regenerated for 3 cycles, maintaining their good performance and stability.

Magnetic carboxymethylchitosan (CMC) nanoparticles have also been proposed for the clean-up of Pb(II), Cu(II) and Zn(II). By preparing the materials through a simple one-step chemical precipitation method, their adsorption efficiency was determined with values of 243, 232 and 131 mg.g^{-1} at pH 5.2 (Charpentier et al. 2016). The good sorption capacity of magnetic carboxymethylchitosan nanoparticles was attributed to the availability of a large number of carboxyl groups which are able to coordinate to metal ions. The isotherm and kinetic experiments revealed that these bionanocomposites follow the Freundlich isotherm and a pseudo-second order kinetics. In addition, the interaction between the metal ions and the biopolymer could be reversed under mild conditions for at least 3 cycles without any loss in their activity or stability.

It is well-known that Cd(II) is a highly toxic metal, where its exposure even at very low concentrations has been linked to several diseases in humans (Satarug et al. 2009). Cadmium is also classified as a human carcinogen (class I) (McMurray and Tainer 2003; Järup 2003; Joseph 2009; Yu et al. 2016). Recently, a novel composite of carbon disulphide-modified magnetic ion-imprinted chitosan-Fe(III) has been reported for the simultaneous clean-up of Cd(II) and tetracycline from water. With an impressive maximum adsorption capacity of 194 and 516 mg.g^{-1} for Cd(II) and tetracycline, respectively, the optimal uptake efficiency was observed on the pH range of 7–8 (Chen et al. 2017a). The presence of pores in the composites along with the functional groups of the biopolymer resulted in good uptake efficiency due to large number of binding sites in the structure. The isotherm experiments indicated that the Langmuir model provides the best fit and that the kinetic profile is characterized by a pseudo-2nd order kinetics. After magnetic clean-up, the composite could be easily regenerated for at least 5 cycles while keeping its optimal adsorption capacity and magnetic behavior.

Arsenic has a wide distribution in nature, either in rocks, soil or water arising from natural and anthropogenic activity. For example, many natural occurring organic arsenic compounds (e.g. arsenobetaine) can be widely found in fish without significant toxic effects. In addition, several organic and inorganic forms of arsenic exist with distinct oxidation states, however the forms with As(III) (arsenite) and As (V) (arsenate) are the ones that raise the greatest concern. It is well-documented that these forms of arsenic are toxic for aquatic systems (Kumari et al. 2017) and are related with several diseases in humans and with well-known carcinogenic effects. Millions of people worldwide are exposed to one of these forms of arsenic due to the contamination of drinking water sources above the established permissible levels (WHO 2001; Hughes 2002; Järup 2003; Shi et al. 2004; Sharma and Sohn 2009).

An As(III) imprinted magnetic Fe_3O_4-N-(2-hydroxy)propyl-3-trimethyl ammonium chitosan (HTCC) composite has been presented for the removal of As(III) from water (Song et al. 2017). The use of HTCC resulted in improved solubility of the composite in water and delivered a high number of cationic biding sites that promoted the removal of As(III) species under optimal pH conditions (pH 6). The isotherm experiments agreed well with the Langmuir-Freundlich model, indicating a maximum adsorption capacity of 12 $mg.g^{-1}$. With a kinetic profile characteristic of pseudo-2nd order kinetics, this biosorbent was recycled for 10 cycles without any significant loss in performance.

Magnetic-chitosan beads have also been proposed for the removal of As(V) from water (Martínez-Cabanas et al. 2016). The isotherm experiment indicated a good agreement with the Langmuir-Freundlich model and a maximum adsorption capacity of 147 $\mu g.g^{-1}$. The material could also be recycled for 4 cycles while maintaining the performance.

Mercury is a heavy metal with a well-known toxicity. It is a natural element with a wide distribution in nature, however a great portion of mercury bioaccumulation is originated from anthropogenic activity. This metal exists in several inorganic (e.g. metallic mercury or mercuric salts (Hg^{2+})) and organometallic forms (e.g. methylmercury). The toxicity of mercury in humans is variable depending on the mercury form, where several forms are known to have a severe impact on human health. Mercury and its several forms have been identified as priority hazardous substance by the European Union (directive 2008/105/EC) and EPA (Clean Water Act). Water contamination of mercury is a serious threat to human health and aquatic ecosystem. For example, the toxic form methylmercury is a major source of human exposure to mercury through the ingestion of contaminated water or fish. This form of mercury is originated from the microbiological conversion of inorganic mercury in aquatic environments, which can then easily accumulate on fish. Moreover, this lipophilic form of mercury is of great concern, given its long retention in the human body (half-life of 70 days) (Zahir et al. 2005; Bernhoft 2012). Since water contamination with mercury is a serious problem, several nanomaterials have been purposed for its remediation. A itaconic acid-grafted-magnetite nanocellulose composite has been purposed for the removal of mercury from water (Anirudhan and Shainy 2015). The maximum adsorption capacity obtained was 240 mg.g^{-1}, where the experimental data fitted well with the Freundlich isotherm model. The material also exhibited a good reuse capacity, being recycled for 6 cycles. Recently, magnetic chitosan modified with glutaraldehyde was also purposed for the Hg(II) water remediation (Azari et al. 2017). Showing a maximum adsorption capacity of 96 mg.g^{-1} (pH 5) and a good agreement with the Langmuir isotherm, the material could be recycled for 12 cycles while maintaining the good performance. In this case, glutaraldehyde was important to promote the fixation of chitosan, resulting in superior stability and, consequently, in a large number of strong chelating sites.

Chromium is another natural occurring heavy metal, being Cr(III) the most stable form with a wide distribution in nature. Cr(VI) does not occur naturally, being its bioaccumulation associated from anthropogenic activity. Chromium(III) is an essential nutrient playing a crucial role in several metabolic processes in the human body. Humans and other animals are capable to convert inorganic inactive Cr(III) into biologically active forms. Even though Cr(III) has an important biological role, it is now accepted that the exposure to high levels have been linked to adverse health effects. It is difficult to differentiate the toxic effects of Cr(III) and Cr(VI) since that Cr(VI) is mainly reduced into Cr(III) by the cells. The presence of Cr(VI) in drinking water is of serious concern, since that this form of chromium can easily enter the cells when compared with Cr(III) (Barceloux and Barceloux 1999; Wilbur et al. 2012; Ni et al. 2014). A pyridinium-diethylenetriamine magnetic chitosan (PDFMC) was proposed for the efficient removal of Cr(VI) from water (Sakti et al. 2015). The experimental data agreed well with the Langmuir isotherm, indicating maximum adsorption capacities of 176 mg.L^{-1} (pH 3) and 124 mg.L^{-1} (pH 6). The use of pyridinium units along with chitosan delivered several functional groups (amines and quaternary amines) that promoted the electrostatic interaction with the metal. Moreover, this material could be recycled for 5 cycles without any significant loss in performance.

Several magnetic bionanocomposites have also been proposed for the clean-up of other types of heavy metals where its bioaccumulation may result on detrimental effects to the human health or the ecosystem. The most recent reported materials are summarily presented on Table 9.2.

9.4.2 Removal of Organic Compounds

The impressive diversity of organic compounds commercially available result in their widespread occurrence where some of them possess a long-term persistence, high-bioaccumulation and a significant impact on human health and ecosystems. With the advent of advanced analytical techniques, there was an increase in the scientific public awareness regarding the contamination of water sources of not only hydrophobic persistent pollutants but also of polar contaminants that can deeply affect the water quality criteria. Every day, different classes of organic pollutants are discharged with the potential to contaminate drinking water sources. Some examples include dyes, pharmaceuticals, pesticides, solvents or many other organic by-products originated from industrial manufacturing (Dsikowitzky and Schwarzbauer 2014; Cizmas et al. 2015). Moreover, with the increased limitation of available potable water, there is an added need to implement closed-water cycles involving the reuse of treated wastewater. Unfortunately, many organic pollutants and their by-products are not monitored at water treatment plants. There are now great evidences that a large diversity of hazardous organic pollutants are present in drinking water sources, with an alarming negative impact on human health or aquatic ecosystem. To address this problem, different types of bionanocomposites have been purposed for the water remediation of organic pollutants.

In the last decade, a greater attention has been given to the remediation of organic dyes due to their widespread use and uncontrolled discharge. Some dyes or their by-products have been found to be toxic, mutagenic or carcinogenic (Rai et al. 2005). Furthermore, many bionanocomposites have been explored for the uptake of several common less toxic dyes, given their prevalent use as molecular models for preliminary assessment of material performance. A well-known example of such case is methylene blue. As detailed in Table 9.2, several works have investigated the performance of bionanocomposites for the uptake of this dye from water. Recently, our group explored the ability of hybrid magnetic biosorbents containing a siliceous shell with covalently liked κ-carrageenan for the uptake of methylene blue from water (Soares et al. 2017b). The experimental results indicated a Z-type isotherm, with a maximum adsorption capacity of 530 $mg.g^{-1}$. In addition, the material could be recycled for 6 cycles without loss in performance or stability. It was also revealed that the biopolymer had an important role in the removal of methylene blue by providing functional groups (anionic ester sulfate groups) that could establish electrostatic interactions with the cationic dye under optimal pH conditions.

A gelatin-based magnetic nanocomposite comprising carboxylic acid functionalized carbon nanotube has also been reported for the uptake of methylene blue and direct red 80 (Saber-Samandari et al. 2017). The experimental results indicated a good agreement with the Freundlich isotherm and a maximum adsorption capacity of 380 and 465 $mg.g^{-1}$ for methylene blue and direct red 80 respectively. The authors proposed that the gelatin (type A) delivered cationic functional groups that can remove the organic pollutants from water through electrostatic interactions.

Alginate beads containing dispersed polydopamine coated $CoFe_2O_4$ particles were reported for the uptake methylene blue, crystal violet and malachite green (Li et al. 2016c). The experimental data indicated a good agreement with the Freundlich (methylene blue and crystal violet) and Langmuir (malachite green) isotherm models with maximum adsorption capacities of 466, 456 and 248 $mg.g^{-1}$. It was shown that the presence of carboxylate, catechol and amine groups in these beads, provided important binding sites for the removal of the organic dyes through electrostatic interactions.

Glutaraldehyde cross-linked chitosan-coated Fe_3O_4 nanocomposites were used to efficiently uptake methyl orange (Yang et al. 2016a). Exhibiting a maximum adsorption capacity of 758 mg.g$^{-1,}$ the experimental data fitted well with the Freundlich isotherm. The material could be reused for 6 cycles without loss in performance.

In addition to dyes, other organic pollutants have also been investigated for water remediation, given the rising concerns regarding their impact on human health and the ecosystems. For example, our group explored the ability of hybrid magnetic nanoparticles containing κ-carrageenan for the uptake of metoprolol (MP, beta-blocker) (Soares et al. 2016) and paraquat (PQ, herbicide) (Fernandes et al. 2017). The good performance of the material, 447 (MP) and 257 mg.g^{-1} (PQ), and recycling capacity (4+ cycles), make it as a good candidate for the water remediation of these pollutants. It was shown that the biopolymer had an important role in the removal of these pollutants by establishing electrostatic interactions at optimal pH conditions.

Magnetic cellulose ionomer/layered double hydroxide has been successfully used for the removal of diclofenac from water (Hossein et al. 2016). The material exhibited a maximum adsorption capacity of 268 mg.g^{-1}, with a good reuse capacity for 3 cycles. The pyridinium rings of cellulose ionomer provided several binding sites for the removal of diclofenac. Different adsorption mechanisms were proposed by the authors, including π-π interaction, hydrogen bonding as well as anion exchange and electrostatic interactions.

Cellulose functionalized with magnetic poly(dopamine) was reported for the uptake of resorcinol from water (Ding et al. 2017). The adsorption process fitted well the Freundlich isotherm, indicating a maximum performance of 258 mg.g^{-1}. The material showed a good reusability for 5 consecutive cycles. The cellulose-poly (dopamine) units provided abundant functional groups (hydroxyl and amino groups) that were important for the successful uptake of resorcinol through electrostatic interactions.

A composite material based on chitosan and magnetic carbon nanotubes has been employed for the removal of tetracycline from water (Ma et al. 2015). The adsorption profile fitted well with the Freundlich isotherm model with a maximum performance of 104 mg.g^{-1}. In addition, the biosorbent could be recycled for 10 cycles while keeping the performance above 99.3 mg.g^{-1}. The kinetic studies along with the FTIR characterization indicated that the chemisorption was the rate-limiting step.

9.5 Fate of Magnetic Biosorbents

The effective recovery of nanosorbents used in from treated water is essential to ensure the absence of nanosized particles in the purified water and in the waste streams of the treatment process (Simeonidis et al. 2016). The use of magnetic biosorbents presents clearly an advantage in comparison to non-magnetic biosorbents since magnetic nanoparticles can be simply and quickly separated from aqueous dispersions using high-gradient fields (Moeser et al. 2004; Yavuz et al. 2006). However in the accidental case of release of the sorbents, the use of magnetic nanoparticles in water treatment may introduce unknown health effects to humans and other living organisms. The effects of the magnetic iron oxide nanoparticles in terms of ecotoxicity and cytotoxicity have been investigated in the last years (Handy et al. 2008; Su 2017). However studies addressing the effect of the magnetite nanoparticles on plants are still scarce (Zhu et al. 2008; Wang et al. 2011). Also few studies have addressed the effects of iron oxide nanoparticles on aquatic living organism (Zhang et al. 2015b; Blinova et al. 2017). More attention has been devoted to potential human exposure and a large number of works investigates the cytotoxicity and genotoxicity of magnetic iron oxide nanoparticles (Singh et al. 2010; Liu et al. 2013; Shen et al. 2015; Zhang et al. 2016a). Parameters such as the size, shape, surface coating and surface charge of the magnetic nanoparticles affect the interaction with cells and living organisms. Generally, neutral surfaces are the most biocompatible, whereas cationic surfaces, which have higher affinity to phospholipid in cell membranes, are more likely to induce undesirable hemolysis (Liu et al. 2013).

Upon release of the magnetic biosorbent particles into the aquatic environment, their potential impact on the environment and human health will largely depend on the particle colloidal stability that is determined by particle surface charge. Environmental factors such as the pH, the salinity and the presence of organic matter will also affect (Handy et al. 2008). For example humic acid, that is a major organic constituent of soil and aquatic environments, if present in high levels, is capable to coat Fe_3O_4 nanoparticles giving rise to particle zeta potential values similar to its own and therefore much more stable nanoparticle suspensions (Hu et al. 2010).

Another concern is the fate of nanoparticles recovered after water treatment. Although magnetic biosorbents are reusable after adequate regeneration treatment, generally after multiple cycles lose adsorptive abilities, generating solid waste that needs to be handled (Gómez-Pastora et al. 2014). Most recently alternative strategies for the effective utilization of pollutant loaded post-sorbents have been reported (Harikishore et al. 2017) and include applications in catalysis, as fertilizer or feed additives. For example, biochar decorated with magnetic nanophases developed for phosphate recovery, at its end-life improved plant growth and the application as fertilizer was proposed (Li et al. 2016b). Nevertheless before implementation of any post-sorption valorization strategy it is critical to investigate the leaching behavior of captured pollutants following experimental protocols that characterize solid wastes as inert, non-hazardous or toxic (Simeonidis et al. 2016).

9.6 Conclusions

The application of magnetic bionanocomposite particles for the uptake of pollutants in water treatment has emerged as an interesting alternative to conventional sorbents. These biosorbents offer clear advantages of magnetic separation and tuned affinity for a variety of pollutants. The rational design of the surface of these materials is essential, in order to attain robust and reusable biosorbents with high adsorption capacities. Thus, this chapter dedicated a specific section to the most relevant chemical strategies for the surface modification of magnetic nanoparticles with biopolymers, aiming the production of magnetic biosorbents optimized and specialized in the targeted pollutants. A direct outcome of the use of optimized biosorbent particles is the reduction of quantities of solids needed in the water treatment, which apart from bringing down the costs of water remediation, also reduces the potential environmental effects of the exhausted sorbents disposed. The successful implementation of magnetic biosorbents based water remediation technology needs of the evaluation of the impact of these materials on the environment and human health. However the use of natural occurring biopolymers anticipates potential bio- and eco-compatibility of the magnetic biosorbents.

Acknowledgements This work was developed in the scope of the exploratory project IF/00405/2014 and the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC, and when appropriate cofinanced by the European Regional Development Fund (FEDER) under the PT2020 Partnership Agreement. S. F. Soares thanks the Fundação para a Ciência e Tecnologia (FCT) for the PhD grant SFRH/BD/121366/2016. T. Fernandes thanks FCT for the PhD grant SFRH/BD/130934/2017. A. L. D.-d.-S. acknowledges FCT for the research contract under the Program 'Investigador FCT' 2014.

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