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REVIEW

Recent advances on magnetic biosorbents and their applications for water treatment

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Abstract

Water pollution threatens environment and human health. Common polymer-based sorbents are used to trap pollutants by these sorbents are difficult to separate from treated water and, in turn, their application is limited. Alternatively, nanomaterials with magnetic features offer the advantage of fast and easy magnetically-assisted separation. Moreover, the surface modification of magnetic nanoparticles with biopolymers enhances their adsorptive capabilities. We review recent developments on magnetic biosorbents for water treatment. We present chemical strategies for the surface modification of magnetic nanoparticles with biopolymers to obtain highly effective, robust and reusable biosorbents. This can be done by two strategies: in situ functionalization and post-synthesis functionalization. Post-synthesis functionalization is done in two distinct stages, the synthesis of the magnetic nanoparticles and the surface functionalization, thus allowing better control of each stage individually. Surface functionalization involves either simple coating or the covalent attachment of the biopolymer chains to the surface. Overall, covalent immobilization of the biopolymer onto the particle's surface is recommended to ensure successful recycling and reuse of the biosorbents without significant loss of adsorption capacity. Finally, we discuss the performance of several magnetic biosorbents in the uptake of heavy metal species and organic pollutants from water.

Keywords Biopolymers · Magnetic nanoparticles · Biosorbents · Bionanocomposites · Surface modification · Magnetic separation · Pollutant uptake · Heavy metal ions · Organic pollutants

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 (Madhura et al. 2019). 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 widely 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 and selectivity toward 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, i.e., polymers occurring in nature, provides to the particles surfaces novel functional groups that may confer affinity toward a wide diversity of pollutants (Xu

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et al. 2012; Boamah et al. 2015; Vandenbossche et al. 2015). Besides being available on a sustainable basis, biopolymers present 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. 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 ease of separation from treated water. Low toxicity and easy magnetic separation can be in principle met by the simple combination of biopolymers with magnetic iron oxides. However, a rational design of the surface of the magnetic nanoparticles 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).

This review 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 performance of the magnetic biosorbents in the uptake of heavy metal species and organic pollutants from water is discussed.

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Magnetically assisted water treatment

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 micrometric or nanosized materials from a viscous flow, the magnetic force produced by the external magnetic field must overcome the drag force associated with the carrier fluid. Larger magnetic nanoparticles present higher magnetic susceptibilities that originate higher particle 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 extensively 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. Magnetite nanoparticles exhibit unique size-dependent magnetic properties. Bulk magnetite is a ferrimagnetic material composed of multiple magnetic domains. Due to such magnetic domains, bulk magnetite exhibits a hysteresis curve when magnetization is plotted versus magnetic field and a permanent magnetization in the absence of a magnetic field is observed. The decrease in 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 particles to be composed by single magnetic domains and therefore exhibit

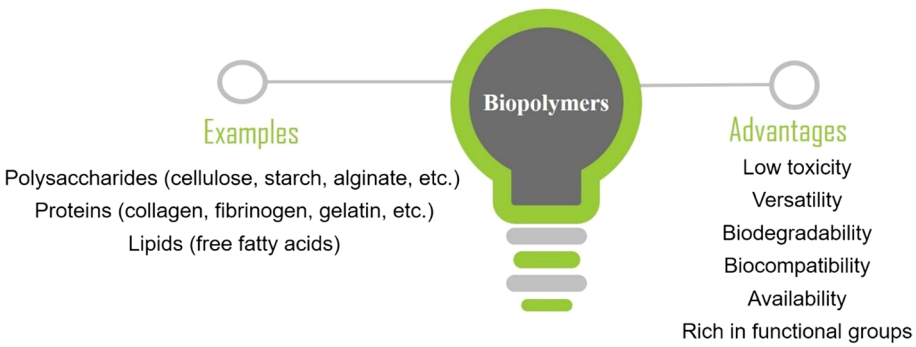

Fig. 1 Examples of biopolymers of different classes, such as polysaccharides, proteins and lipids. Polysaccharides include cellulose, starch and alginate among others. Collagen, fibrinogen and gelatin belong to the group of proteins, and lipids include the free fatty acids. Biopolymers present several interesting environmentally friendly features such as low toxicity, versatility, biodegradability, biocompatibility and availability, and they are rich in functional groups (Nair et al. 2017; Rebelo et al. 2017; Resch-Fauster et al. 2017)

superparamagnetic behavior. The magnetization curve of superparamagnetic nanoparticles does not exhibit hysteresis 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. However, for applications in magnetic separation ferromagnetic particles are usually preferable over superparamagnetic nanoparticles because they show higher magnetophoretic response, thus leading to faster separations.

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).

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 listed in Table 1. They can provide distinct ionic character such as neutral, anionic or cationic, variable chemical functionalities and physical properties to the magnetic biosorbents. Surface modification with polysaccharides allows to enhance and to tune the chemical affinity toward specific target pollutants.

Table 1 Main characteristics of 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; Ding et al. 2017)
	Dextran	Fermentation of sucrose	–OH	Aromatic hydrocarbons, As	(Cho et al. 2015; Kumar and Jiang 2017)
	Starch	Green plants	–OH	Cu, dyes	(Mahdavinia et al. 2016; Yang et al. 2016b)
Anionic	Alginate	Cell walls of brown algae	–OH, $–COO^-$	NaF, Sr, dyes	(Hong et al. 2016; Li et al. 2016b; Zhang et al. 2016)
	Carrageenan	Red seaweeds	–OH, $–OSO_3^-$	Dyes, heavy metal ions, pharmaceuticals, herbicides	(Gholami et al. 2016; Soares et al. 2016; 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; Fan et al. 2017)

Strategies for surface functionalization

The surface of magnetic nanoparticles, 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 magnetic nanoparticles with biopolymers, which can be carried out either in situ during nanoparticle 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 magnetic nanoparticles 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. 2).

In situ surface functionalization

This is a one-pot synthesis strategy where both the synthesis of magnetic nanoparticles and their surface functionalization are carried out. The biopolymer and the precursor of magnetic nanoparticles are added simultaneously 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 magnetic nanoparticles and from the nanoparticles' 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 in either the nucleation or particle growth steps. For example, starch was employed to effectively 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 nanoparticles was tuned from 15 to 100 nm by changing the time of starch addition to the reaction mixture. Starch acted as a kinetically control agent that affected the size, size distribution and aggregation state of the magnetic nanoparticles. Starch-coated Fe_3O_4 nanoparticles 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 in the presence of carrageenan, strongly depended on the type and concentration of carrageenan used (Daniel-da-Silva et al. 2007).

The in situ synthesis of magnetic nanoparticles 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 representative examples are described below that illustrate the usefulness of in situ strategy for the functionalization of magnetic

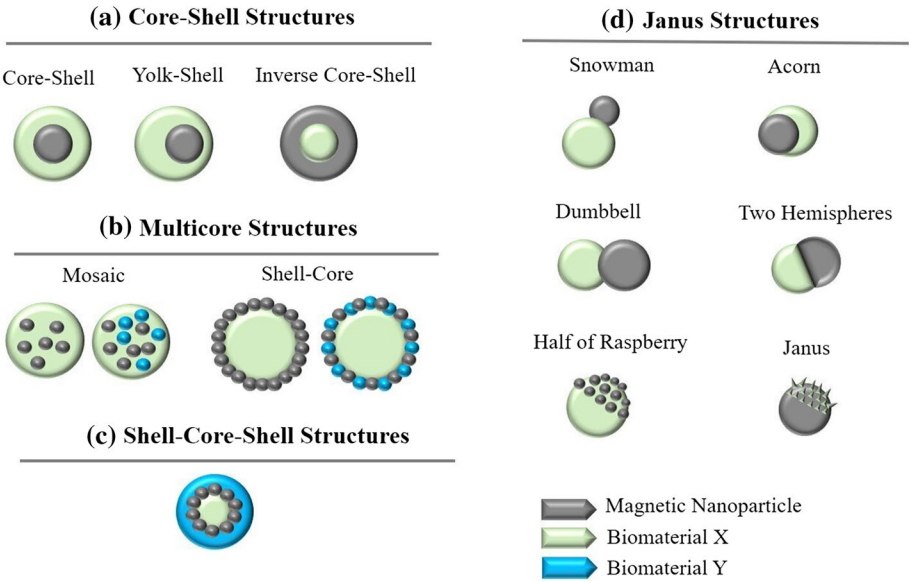

Fig. 2 Distinct structures of magnetic bionanocomposites: **a** core–shell structures include simple core–shell, yolk–shell and inverse core–shell structures; **b** multicore structures include mosaic and shell–core structures; **c** shell–core–shell structures; and **d** Janus structures comprise several types of arrangements such as snowman, acorn, dumbbell, two hemispheres, half of raspberry and Janus structures

nanoparticles aiming applications in the removal of pollutants from water.

Magnetic iron oxide nanoparticles were prepared by co-precipitation in the presence of chitosan, followed by the addition of the cross-linker 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. 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 cross-linking strategies are being explored. For example, κ-carrageenan-coated magnetite nanoparticles of 4 nm size were prepared by co-precipitation and then cross-linked with chitosan (Mahdavinia and Mosallanezhad 2016). The electrostatic interactions between positively charged amino groups of chitosan and negatively charged sulfate groups of κ-carrageenan could produce stable complexes, with affinity for cationic dyes.

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 a 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 cross-linker (Galhoum et al. 2015a, 2017). The materials showed binding affinity for uranyl and Dy(III) ions.

Ex situ surface functionalization

This procedure is divided into two distinct stages, synthesis and surface modification, which allows better control of each stage individually. It can involve the simple coating of magnetic nanoparticles with biopolymers, physically or chemically cross-linked or the covalent attachment of the biopolymer chains to the surface of the nanoparticles. The latter usually requires the use of a linker such as functional alkoxysilanes (Laurent et al. 2008; Sun et al. 2008; Begin-Colin and Felder-Flesch 2012).

Ionic cross-linking of biopolymer coating Several natural polyelectrolytes have the ability to undergo ionotropic gelation, i.e., to cross-link 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 composites particles with different sizes and shapes. For example, magnetic alginate core–shell type particles were fabricated using a method of electro-coextrusion and employed as a biosorbent for separation of fluoride from aqueous solution (Zhang et al. 2016). 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 dropped into a solution of $CaCl_2$ for alginate cross-linking. The resulting particles comprised a core of aggregated Fe_3O_4 nanoparticles coated by a shell of alginate. Because 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.

Magnetite nanoparticles were coated with κ-carrageenan and used to remove methylene blue from aqueous solutions (Salgueiro et al. 2013). The coating was performed by simple dispersion of the Fe_3O_4 nanoparticles in κ-carrageenan solution followed by the addition of K^+ ions to promote sol–gel transition by physical cross-linking. These biosorbents show high methylene blue adsorption capacity due to electrostatic interactions between the cationic dye and the ester sulfate moieties of carrageenan. Nevertheless, marked loss of adsorption capacity after regeneration and reuse was observed. This loss was ascribed to possible leaching of κ-carrageenan that was physically adsorbed at the surface of nanoparticles.

Covalent cross-linking 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 cross-linking 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 cross-linked magnetic biosorbents include cross-linked chitosan and quaternary chitosan particles prepared using a reverse-phase suspension cross-linking technique (Li et al. 2016a; Song et al. 2017; Funes et al. 2017). It is worth noting that glutaraldehyde is still one of the most frequently used cross-linkers, in spite of its known ecotoxicity (Leung 2001; Hu et al. 2017; Christen et al. 2017). Alternative and much less toxic cross-linkers 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).

Coating by complexation of polyelectrolytes Coating of magnetic nanoparticles can be also performed by the com-

plexation of 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 magnetic nanoparticles is mainly governed by strong but reversible electrostatic interactions, as well as hydrogen bonds. The layer-by-layer 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. Using a distinct approach, magnetic chitosan/carrageenan microspheres with high efficient adsorption capacity toward both cationic and anionic dyes and heavy metal ions in wastewater were prepared (Liang et al. 2017). The microspheres were fabricated via emulsification procedure from the homogeneous chitosan/carrageenan solution.

Grafting of biopolymers onto magnetic particles surface Another strategy explored for the preparation of magnetic biosorbents is the grafting of the biopolymer onto the surface of magnetic nanoparticles. The biopolymer can be directly grafted onto the surface of the particle (Badruddoza et al. 2011; Lu et al. 2016) or after surface functionalization with ligands that will subsequently link to the biopolymer (Bini et al. 2012; Rodriguez et al. 2017). This strategy might also involve the coating with a thin layer of amorphous silica (SiO_2). The 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 methylene blue adsorption due to electrostatic interactions between the carrageenan and the dye. Owing to the covalent immobilization of the carrageenan, the particles were reusable without significant loss of the adsorption capacity.

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, 2017a; Fernandes et al. 2017). 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. This method was successfully used with polysaccharides having distinct chemical nature and ionic character, namely κ-carrageenan (Soares et al. 2016, 2017b; Fernandes et al. 2017), chitosan (Soares et al. 2017a) and starch (Fernandes et al. 2017). In comparison with 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 hybrids prepared from chitosan were tested for the uptake of nonpolar organic solvents from water (Soares et al. 2017a).

Adsorptive applications of magnetic bionanocomposites in water treatment

In this section, the most recent magnetic bionanocomposites for the cleanup of emerging pollutants from water is reviewed taking into consideration adsorptive technologies. Table 2 provides an overview of several materials that have been successfully used for the removal of inorganic and organic pollutants.

Removal of heavy metal species

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 (Bashir et al. 2019; Malik et al. 2019).

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). 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). Recently, a chitosan/polyethylenimine-grafted magnetic composite has been reported with an impressive maximum adsorption capacity 341 mg g^{-1} of Pb(II) and 321 mg g^{-1} of Cd(II) (Li et al. 2017). With an optimum performance in pH range 6–7, the isotherm studies indicated a good

Table 2 Magnetic bionanocomposites for the uptake for several inorganic and organic pollutants (*PAC* powered activated carbon, *OMWCNT* oxidized multiwalled carbon nanotube)

Biosorbent	Pollutant	Adsorption capacity	pH	References
Magnetic chitosan–graphene oxide	Acid red 17 and bromophenol blue	8.1 and 9.5 mg g^{-1}	2, 6	(Sohni et al. 2017)
Imprinted Fe_3O_4–quaternary 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-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. 2016)
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)
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-carrageenan cross-linked 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)

Table 2 (continued)

Biosorbent	Pollutant	Adsorption capacity	pH	References
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. 2016b)
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. 2015)
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/polyethylenimine-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)
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, 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)

agreement with the Langmuir isotherm for both metals. The adsorption process was thermodynamically favorable and endothermic in nature. The good removal efficiency could be attributed to the biopolymer at the surface of the particles, which resulted in a higher number of amino groups with superior uptake efficiency. Furthermore, the chitosan/polyethylenimine-grafted magnetic composite could be effectively regenerated for five cycles while keeping good performance and stability. Magnetic hydrogel beads containing gum tragacanth in its composition have also been reported for the effective cleanup 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 was ascribed to the presence of several chelating sulfonic acid, carboxylic acid and hydroxyl and amino groups.

Magnetic carboxymethyl chitosan nanoparticles have also been proposed for the cleanup 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 was attributed to the availability of a large number of carboxyl groups which are able to coordinate to metal ions.

Cadmium is a highly toxic heavy metal, and its exposure even at very low concentrations has been linked to several diseases in humans (Satarug et al. 2009). Recently, a composite of carbon disulfide-modified magnetic ion-imprinted chitosan–Fe(III) has been reported for the simultaneous cleanup of Cd(II) and tetracycline from water (Chen et al. 2017a). The presence of pores in the composite along with the functional groups of the biopolymer resulted in good uptake efficiency (194 and 516 mg g^{-1} for Cd(II) and tetracycline, respectively).

Arsenic, which is a metalloid that can induce toxic effects even at low concentrations (Tchounwou et al. 2012; Chen et al. 2015; Bibi et al. 2017), has a wide distribution in nature. Several 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. These forms are toxic for aquatic systems (Kumari et al. 2017) and are related to several diseases in humans and with carcinogenic effects. An As(III)-imprinted magnetic Fe_3O_4–N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan composite has been presented for the removal of As(III) from water (Song et al. 2017). The use of this quaternary chitosan resulted in improved dispersion 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). Magnetic chitosan beads have also been proposed for the removal of As(V) from water (Martínez-Cabanas et al. 2016).

Mercury is a heavy metal with 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. Mercury and its several forms have been identified as priority hazardous substance by the European Union (directive 2008/105/EC) and the United States Environmental Protection Agency. An 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} and the material exhibited a good reuse capacity, being recycled for six cycles. Recently, magnetic chitosan modified with glutaraldehyde was also purposed for the Hg(II) water remediation (Azari et al. 2017). 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 and widely distributed in nature. Even though Cr(III) has an important biological role, it is now accepted that the exposure to high levels has been linked to adverse health effects. The presence of Cr(VI) in drinking water is of serious concern since it 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 was proposed for the efficient removal of Cr(VI) from water (Sakti et al. 2015). The use of pyridinium units along with chitosan delivered several functional groups (amines and quaternary amines) that promoted the electrostatic interaction with the metal.

Removal of organic compounds

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; Crini et al. 2019). There is now great evidence that a large diversity of hazardous organic pollutants is 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 adsorption of organic pollutants. 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. Recently, our group explored the ability of hybrid magnetic biosorbents containing a siliceous shell with covalently linked 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 six cycles without loss in performance or stability. The biopolymer had an important role by providing 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 authors proposed that the gelatin delivered cationic functional groups that can remove the organic pollutants from water through electrostatic interactions. Alginate beads containing dispersed polydopamine $CoFe_2O_4$ particles were reported for the uptake methylene blue, crystal violet and malachite green (Li et al. 2016b). It was shown that the presence of carboxylate, catechol and amino groups provided important binding sites for the removal of the organic dyes through electrostatic interactions.

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 (beta blocker) (Soares et al. 2016) and paraquat (herbicide) (Fernandes et al. 2017). The good performance of the material, 447 and 257 mg g^{-1} for metoprolol and paraquat, respectively, and recycling capacity make it as a good candidate for the water remediation of these pollutants. Magnetic cellulose ionomer/layered double hydroxide has been successfully used for the removal of diclofenac from water (Hossein et al. 2016). The pyridinium rings of cellulose ionomer provided several binding sites for the removal of diclofenac. A composite material based on chitosan and magnetic carbon nanotubes has been employed for the removal of tetracycline (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 ten cycles while keeping good performance.

Conclusion

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 article 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 in 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 use of nature occurring biopolymers anticipates potential bio- and eco-compatibility of the magnetic biosorbents.

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