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Guibal Eric, Vincent Thierry, Ricardo Navarro. Biopolymer-Based Sorbents for Metal Sorption. Advanced Separations by Specialized Sorbents, pp.358 Pages, 2015, 9781032240572. ⟨hal-04673642⟩

HAL Id: hal-04673642

<https://imt-mines-ales.hal.science/hal-04673642v1>

Submitted on 26 Aug 2024

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Biopolymer-Based Sorbents for Metal Sorption

Eric Guibal, Thierry Vincent, and Ricardo Navarro

9.1 INTRODUCTION

The regulations concerning the levels of concentration of metals in drinking water are becoming more and more stringent. As a consequence, the discharge levels for industrial wastewater are strictly controlled. Conventional processes such as precipitation, solvent extraction, membrane processes, and ion-exchange and chelating resins can be inappropriate for technical limitations (difficulty to reach discharge levels), environmental reasons (production of toxic sludge), or economic criteria. Biosorption has retained a great attention for the last decades as an alternative to conventional processes. This technique consists in using materials of biological origin for the sorption of metal ions, dyes, etc. The concept is based on the use of functional groups present at the surface of these materials for binding metal ions through adsorption, ion exchange, chelation, reductive precipitation, etc. A wide diversity of materials have been tested including agriculture subproducts, waste materials from food industry, and valorization of wastes from water compartments (e.g., invading algal biomass). Algal and fungal materials represent emblematic examples of biomass that were tested for metal sorption (Gonzalez Bermudez et al. 2012, Guibal et al. 1992, 1995, Kleinuebing et al. 2010, 2011, Svecova et al. 2006, Yipmantin et al. 2011). For example, algae are mainly constituted of cellulosic compounds, alginate, fucoidan biopolymers (Davis et al. 2003), and diatomaceous materials. Fungal material is characterized by the presence of proteins, carbohydrates, and more specifically chitin-based materials as main constituents of cell wall. However, the main commercial source of chitin-based products comes from the valorization of crustacean shells. The complexity of the structure of these raw materials, the possible interactions between their different components, and the possible variation in their composition (e.g., depending on the extraction process, on the growing conditions) may explain, in some cases, their limited efficiency, the variability in their sorption properties, and also the difficulty to elaborate some advanced materials based on these resources. This may also explain that a great attention has been paid to the extraction of their main active components (i.e., alginate for algae and chitin/chitosan for fungi and crustacean shells). Among the great diversity of biopolymers available in nature, the present work focuses on these two emblematic polysaccharides because of their wide availability and because they are complementary in terms of functional groups (i.e., carboxylic acid groups for alginate, basic amine groups for chitosan), stability range (acidic solutions for alginate, neutral/alkaline solutions for chitosan), and application (affinity for different metal ions due to the difference in their functional groups, with regard to hard and soft acid–base theory). Though these biopolymers can be readily modified by chemical grafting of specific reactive groups to improve their reactivity and their selectivity (Guibal et al. 2000b), the present study is limited to the use of raw materials (with the exception of chitosan grafting that is required for using the biopolymer in acidic solutions) (Alves and Mano 2008, Guibal et al. 2000b, 2002, Yang et al. 2011). These materials can be also used for the encapsulation and immobilization of liquid or solid compounds for preparing new sorbents (Guibal et al. 2009, Krys et al. 2013).

After describing the properties of these biopolymers, their ability to be conditioned under different forms will be discussed. The second part deals with sorption mechanism considering the different mechanisms involved in metal binding, the parameters that control sorption performance, the possibility to recycle the sorbent, and the different modes of application. The third section focuses on the encapsulation properties of these materials for immobilizing liquid compounds (ionic liquids, extractants) or solid compounds (mineral sorbents and ion exchangers). Finally, some examples are given regarding the possible use of composite materials (i.e., biopolymers combined with metal ions) for the synthesis of advanced materials. The aim of this chapter is not to draw an exhaustive compilation but to illustrate the wide diversity of possibilities opened by these materials of biological origin.

9.2 ALGINATE AND CHITOSAN: STRUCTURE AND PROPERTIES

9.2.1 ALGINATE

Alginate (or alginic acid) is an anionic polysaccharide, which is present in large quantities in the cell wall of brown algae. It is extracted from algal biomass by a three-step procedure consisting of (1) successive contact with formaldehyde solution and hydrochloric acid solution (to remove phenolic compounds), (2) treatment with sodium carbonate (to solubilize sodium alginate), and (3) reprecipitation of alginate in ethanol (Hernandez-Carmona et al. 1998, 1999, McHugh et al. 2001). Actually, alginic acid is a linear copolymer constituted of two blocks of 1,4-linked hexuronic acid residues: mannuronic acid residues (β (1 \rightarrow 4)-linked-D-mannuronopyranosyl, M) and guluronic acid residues (α -L-guluronopyranosyl, G) (Yang et al. 2011). These residues are assembled as blocks of repeating G units (GG blocks), repeating M units (MM blocks), and blocks of mixed M and G residues (MG blocks) of different distributions (Figure 9.1). The properties of the biopolymer can thus be controlled by the

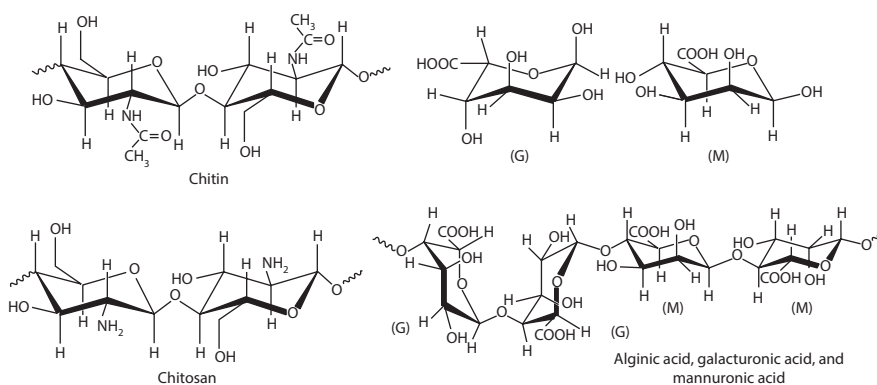


FIGURE 9.1 Structure of chitin, chitosan, and alginate (mannuronic [M] and guluronic [G] acid moieties).

distribution and the percentage of G and M residues. The molecular weight (MW) is another important parameter for characterizing the biopolymer.

The presence of carboxylic groups, as diuronate units, and their arrangement in the biopolymer chains may explain the strong interaction that may occur between alginate and metal cations and more specifically divalent cations (Agulhon et al. 2012a, Andersen et al. 2012). This is the basis of the affinity of the biopolymer for metal ions. This mechanism is frequently called “the egg-box” model (Christensen et al. 1990, Davis et al. 2003), though depending on the composition of alginate and the conditions selected for interacting with metal ions, other mechanisms could be involved (Agulhon et al. 2012b, Li et al. 2007, Sikorski et al. 2007). These interactions are responsible for the ionotropic gelation properties of alginate that can be used for preparing different stable conditionings of alginate under the form of beads, membranes, and scaffolds. Alginate is also gelling in HCl solutions. The acid–base properties of the biopolymer are conditioned by the presence of carboxylic groups, their G and M residues having pK_a of 3.65 and 3.38, respectively (Davis et al. 2003).

9.2.2 CHITOSAN

Chitin (2-acetamido-2-deoxy- β -D-glucose units bound by $\beta(1 \rightarrow 4)$ linkages) is the precursor of chitosan (partially or totally deacetylated form of chitin, Figure 9.1) (Roberts 1992). This biopolymer is present in the cell wall of fungi, the cuticle of insects, and the shell of crustacean. It is one of the most abundant polysaccharides in nature. It is commercially obtained from crustacean shells after grinding, acidic treatment (to remove carbonate-based materials), and alkaline treatment at ambient temperature (for protein and dye removal). The deacetylation of chitin proceeds with alkaline treatment at boiling temperature. Actually, it is quite difficult to elaborate a pure chitosan (i.e., totally deacetylated), and it results in the strong depolymerization of the biopolymer. Chitin and chitosan are thus, in most cases, heteropolymers with different levels of acetylation, and the difference between chitin and chitosan is generally correlated to dissolving properties in acidic solutions: chitin being less soluble than chitosan in acetic acid solutions, for example. The MW of the polymer and its deacetylation degree (DD) depend on the experimental conditions used for its extraction from raw material. These two parameters, in addition to the crystallinity of the biopolymer, strongly influence the properties of the biopolymer (Guibal 2004, Jaworska et al. 2003a,b, Varma et al. 2004). For example, the DD strongly affects the acid–base properties of the biopolymer (Sorlier et al. 2001): the pK_a of amine groups varies as a function of both DD and neutralization degree but for the most common samples of chitosan, its value ranges between 6.3 and 6.8. This property is important for electrostatic behavior of the polymer (critical for sorption properties) and also for its solubility (critical for polymer stability and conditioning process): polymer dissolving occurs in acidic solutions due to amine protonation.

9.2.3 CONDITIONING

One of the advantages of these materials (apart from their intrinsic sorption properties that will be explored in the next section) is the wide range of different conditionings that can be elaborated (Figure 9.2). The physical modification consists

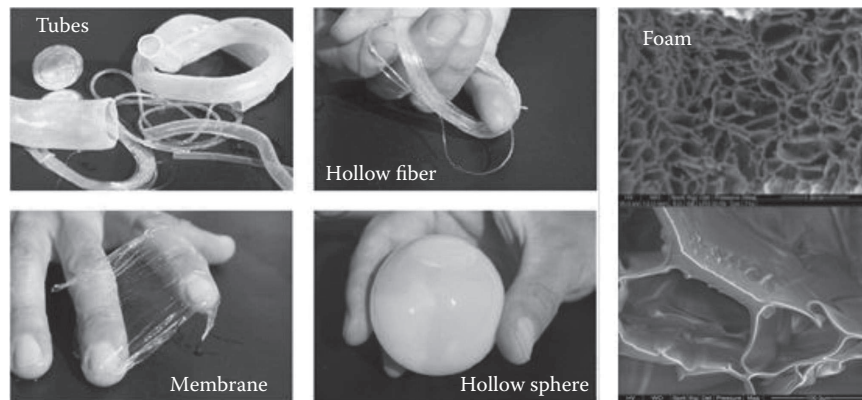


FIGURE 9.2 Examples of conditionings of chitosan.

in the dissolving of the biopolymer in a suitable solvent (water for alginate, acidic solutions for chitosan) followed by a shaping step and the gelling or neutralization step. Depending on the shape to elaborate, the sequence of treatment steps may vary.

9.2.3.1 Beads

The biopolymer solution is distributed through a thin nozzle into the neutralizing or gelling solution. Depending on the viscosity of the solution, the height of the nozzle must be adapted to produce spherical drops before they fall into the gelling/neutralization bath: the relaxation of the viscous solution influences the time necessary for restoring the spherical shape. Alternatively, some specific equipment can be used to produce well-calibrated (homogeneous in size) and well-dispersed (using electro-magnetic charging) beads: Encapsulator B-390 (Büchi, Switzerland), for example. The coagulating bath may be, for example, sodium hydroxide or hexametaphosphate for chitosan (Sicupira et al. 2010, Wu et al. 2013) and hydrochloric acid or metal cations for alginate (Agulhon et al. 2012a,b, Rodrigues and Lagoa 2006).

9.2.3.2 Membranes

The synthesis of membranes may basically follow two procedures. The casting procedure consists of the spreading of the viscous biopolymer solution in a plan holder support followed by the solvent evaporation (Modrzejewska and Kaminski 1999). The evaporation can be complete or partial (in this case, it is necessary to reach a sufficient evaporation, greater than 50%, to produce a self-supported membrane that can be manipulated) (Rabelo et al. 2012). The membrane is then neutralized (or treated with phosphate compounds, see Section 9.2.3.1, for chitosan), or gelled (with hydrochloric acid or metal cations). The second process consists of the direct extrusion of the viscous solution into the neutralization/gelling bath through a tailored extrusion module.

9.2.3.3 Fibers, Hollow Fibers, and Tubes

Fibers, hollow fibers, and tubes have been prepared using the wet spinning method (Cuadros et al. 2012, Dresvyanina et al. 2013, Modrzejewska and Eckstein 2004, Vikhoreva 2012, Vincent and Guibal 2001). Dry- and gel-spinning processes have

been also developed (Pillai et al. 2009, Tasselli et al. 2013): the viscous biopolymer solution (in acetic acid or acetic acid–alcohol solutions for chitosan) was spun using gaseous ammonia (Notin et al. 2006a,b) or in a dry air flow to remove alcohol and acetic acid solvent system) (Desorme et al. 2013). For hollow fibers, the viscous solution is extruded through a thin coaxial tube spinneret; a core liquid is pumped in the inner nozzle and the combined extruded hollow fiber is finally neutralized in the neutralizing bath (e.g., sodium hydroxide for chitosan and copper for alginate) (Mirmohseni et al. 2012, Modrzejewska and Eckstein 2004, Tasselli et al. 2013). For simple fibers, the viscous biopolymer solution is directly extruded through a simple thin nozzle.

9.2.3.4 Foams and Sponges

The synthesis of scaffolds, sponges, or foams is a promising alternative since these materials can be used as filtration media due to their “hyperporosity.” Three typical procedures were developed for the synthesis of these materials based on the sequence of operation or temperature processing: (1) gelling followed by the conditioning/shaping (Hortigueela et al. 2011), (2) the conditioning/shaping followed by the gelling or coagulation/neutralization (Guibal et al. 2013, Li et al. 2011, Saravanan et al. 2011), or (3) the *in situ* generation of porosity during hydrogel formation (Andersen et al. 2012). For example, Hortigueela et al. (2011) reported the gelling of chitosan with HAuCl_4 through simultaneous formation of gold nanoparticles followed by the shaping of the hydrogels through a freezing step followed by a freeze-drying step. This process allows the shaping and the incorporation of metal ions in the same process. On the opposite hand, most of the processes that were developed consist of the synthesis of the biopolymer scaffold followed by metal binding (and possible *in situ* reduction). In most cases, the biopolymer solutions are frozen in a suitable mold (box, syringe, annular mold, etc.) before being gelled or freeze-dried: the temperature, the temperature ramp, and the biopolymer concentration are important criteria for setting the physical (porous microstructure: pore size and homogeneity of distribution of pores) and mechanical properties of the foams/sponges (Madhally and Matthew 1999). Andersen et al. (2012) reported the incorporation of (a) air bubbles by strong agitation and/or (b) bubbling agents (calcium carbonate associated with a slowly acidifying agent: glucono- δ -lactone) before the hydrogels were air-dried.

9.2.4 POST-TREATMENTS

Chitosan being soluble in most acidic solutions (with the remarkable exception of sulfuric acid), the material can thus be poorly stable for further application, for metal binding in slightly acidic solutions, etc. It is thus necessary to improve the chemical resistance of these materials by cross-linking with chemical agents (such as glutaraldehyde and epichlorhydrin in the case of chitosan) (Kolodynska 2012, Park et al. 2013, Rabelo et al. 2012, Ruiz et al. 2001, Webster et al. 2007) or sulfate anions (Peirano Blondet et al. 2008) or by reacetylation (using acetic anhydride in the case of chitosan, to be converted to chitin) (Lavertu et al. 2012, Portero et al. 2002, Sorlier et al. 2001, Vincent and Guibal 2001).

9.3 ALGINATE AND CHITOSAN AS SORBENTS

The mechanisms occurring in metal biosorption are similar to those involved in metal binding on synthetic resins, based on the specific reactivity of chemical groups hold on these biopolymers: carboxylic groups for alginate and amine groups for chitosan. Their performances are also driven by the same operating parameters.

9.3.1 MECHANISMS

The mechanisms involved in metal uptake depend on the metal, its speciation (and the composition of the solution), the pH, and the functional groups of the biosorbent. Basically, metal binding operates through (1) ion-exchange/electrostatic attraction mechanisms, (2) complexation/chelation, or (3) binding of ternary compounds (though much less frequent than other mechanisms and concerning very specific systems). Additional mechanisms may partly contribute to remove metal ions from solutions such as *in situ* precipitation and/or reduction.

In the case of alginate, it is generally agreed that metal sorption occurs through the ion exchange of protons (from alginic acid) or sodium/calcium cations (from alginate) with the divalent metal cations to be bound (Chen et al. 2002, Deze et al. 2012, Jodra and Mijangos 2001, Karagunduz and Unal 2006, Papageorgiou et al. 2006, Pielesz and Bak 2008). The bond between carboxylic groups and Ca(II) is much stronger than that with Na(I) leading to easier ion exchange with Na(I) (Khotimchenko et al. 2008); however, sodium alginate being soluble in water is generally preferred using calcium alginate gels (especially when prepared under the form of alginate hydrogel beads). Comparing Pb(II) and Cu(II) binding on calcium alginate resins, Chen et al. (2002) reported some differences in the binding mechanisms for Cu(II) (combination of ion exchange and coordinative complexation) and for Pb(II) (pure ion exchange) based on XPS and FTIR analyses. Similar ion-exchange mechanisms were identified by Raman spectroscopy and wide-angle x-ray spectroscopy (WAXS) in the case of dye sorption by alginate hydrogels (Pielesz and Bak 2008). These interactions can be also associated with the gelling mechanisms occurring between carboxylic groups of alginate and metal ions through the so-called egg-box model (divalent metal cations interact with vicinal carboxylic groups from different chains to form compact gel structures). Recently, Agulhon et al. (2012a,b) utilized both small-angle x-ray spectroscopy (SAXS) and quantum chemical density functional theory (DFT methods) for clarifying the kind of interactions existing between different metal ions and mannuronic/guluronic acid units of alginate. They conclude that with transition metals, the complexation with the disaccharides proceeds through strong coordination covalent bonds, while alkaline-earth cations form ionic bonds with uronate groups. While the alginate affinity for transition metals is correlated to the strength of the chemical interaction with uronate, in the case of alkaline-earth metal cations, the binding energy is not a critical parameter. However, the interaction mode of alginate-based materials with metal ions remains debatable (Plazinski 2013).

In the case of chitosan-based sorbents, the reactivity of functional groups may completely change with the metal and the pH of the solution: the amine groups may have different modes of interactions with metal ions (Guibal 2004). The free

electron doublet on nitrogen contributes to the binding of metal cation by complexation/chelation under near-neutral pH conditions. On the opposite hand, the acid–base properties of amine groups (weak base) may cause metal anion binding through ion exchange (with counteranions associated with protonated amine groups) and electrostatic attraction (to protonated amine groups) in acidic solutions. Metal binding on amine groups (and on chitosan derivatives; Varma et al. 2004) has been widely described and interpreted using different spectroscopic methods (Webster et al. 2007) and modeled using complexation concepts (Jeon and Holl 2004). The acid–base properties of amine groups of chitosan (pK_a in the range 6.3–6.8; Sorlier et al. 2001) may explain the strong competition of protons for the binding of metal cations in acidic solutions (Dzul Erosa et al. 2001) but also the possibility to bind metal anions by ion-exchange/electrostatic attraction mechanisms. Thus, metals that form anionic-hydrolyzed polynuclear species, such as molybdate (Guibal et al. 1999c, 2000a, Milot et al. 1998) or vanadate (Guzman et al. 2002) or metal chloro-anionic complexes in HCl solutions such as $PdCl_6^{2-}$, $PtCl_4^{2-}$, or $AuCl_4^{2-}$ (Arrascue et al. 2003, Guibal et al. 1999b, 2001, Ruiz et al. 2000) are bound on protonated amine groups in acidic solutions. A third mechanism of interaction of chitosan with metal ions has been identified. It consists of the formation of a ternary complex between the biopolymer, the metal (herein strontium), and a complexing agent (i.e., carbonate) (Piron and Domard 1998a). Under appropriate conditions (i.e., pH higher than 11 and carbonate concentration of 0.01 M) chitosan can bind the ion pair (Sr^{2+} , CO_3^{2-}) as a ternary complex. In the case of interactions of chitosan with polynuclear metal anions, ionotropic gelation mechanisms have been also identified (similar to those observed with alginate) (Dambies et al. 2001). These ionic interactions can be used for the conditioning and shaping of biopolymers and for the elaboration of new materials (similar to chitosan, Figure 9.2).

9.3.2 PARAMETERS INFLUENCING SORPTION PERFORMANCE

9.3.2.1 pH and Metal Speciation

The pH is a critical parameter for the binding of metal ions with alginate and chitosan. This parameter may control the interaction of the biopolymer with metal ions through different mechanisms: (1) competition of protons, (2) impact on chemical stability and reactivity of the sorbent, and (3) metal speciation. For example, chitosan (in its raw form) is soluble in acidic solutions by protonation of amine groups, while alginate is soluble in alkaline media (ion exchange of calcium, or other divalent metals, with sodium or potassium to give soluble forms of alginate). The stability (against dissolving) of the biopolymer is important for designing the optimum sorbent (selection of the acid to be used for pH control, cross-linking treatment, etc.). The acid–base properties of these biopolymers control the protonation of reactive groups, which, in turn, may influence the efficiency of the sorbent (competition effect, reactivity of functional groups) and up to the mechanisms involved in metal binding. The effect of pH on metal sorption on chitosan has been previously discussed in the section describing sorption mechanisms (see Section 9.3.1). Carboxylic groups on mannuronic and guluronic acid units of alginate have pK_a values in the range 3.4–3.7: the biopolymer will have different abilities to bind metal cations

depending on the predominance of carboxylic acid (acid solutions) or carboxylate (weak acid/neutral solutions) groups. The increase in the pH improves metal-binding efficacy (for metal cations) (Plazinski 2012, 2013).

The speciation of metal ions is a critical parameter that is controlled by (1) the pH of the solution, (2) the concentration of the metal, and (3) the presence of ligands. Depending on the metal form, the affinity of the metal for the sorbent may change as well as the sorption mechanism. For example, the formation of polynuclear hydrolyzed species of uranium revealed favorable for metal binding on chitosan (Guibal et al. 1994). Similar conclusions were raised for molybdate and vanadate sorption on chitosan-based materials (Guibal et al. 1999c, 2000a, Guzman et al. 2002, Jansson-Charrier et al. 1996a): the sorption of target metal depends on the formation of polynuclear hydrolyzed species, which, in turn, was controlled by the pH of the solution and the concentration of the metal. Hence, for a given pH, the metal sorption began when the total concentration of the metal was sufficient (at this pH value) for forming polynuclear hydrolyzed species (Guibal et al. 2000a, Guzman et al. 2002) (Figure 9.3).

The presence of ligands may also interfere in the sorption of metal ions depending on the speciation of the metal (Guibal et al. 2000b, Guzman et al. 2003, Hernandez et al. 2007, Juang and Ju 1997, Juang et al. 1999, Nishad et al. 2012, Padala et al. 2011, Tseng et al. 1999, Wu et al. 1999). The concentration of chloride ions may displace the speciation of platinum or palladium to the formation of chloro-anionic species that can bind to protonated amine groups (Guibal et al. 2000b). To a certain extent, the presence of chloride ions may thus improve sorption performance, while an excess of chloride ions induces a strong competitor effect in the case of ion-exchange/electrostatic attraction mechanism. The presence of nitrilotriacetic acid changes the selectivity of chitosan for Co(II) and Cu(II), depending on the pH (Padala et al. 2011). While Cu(II) is bound to chitosan through chelation of amine

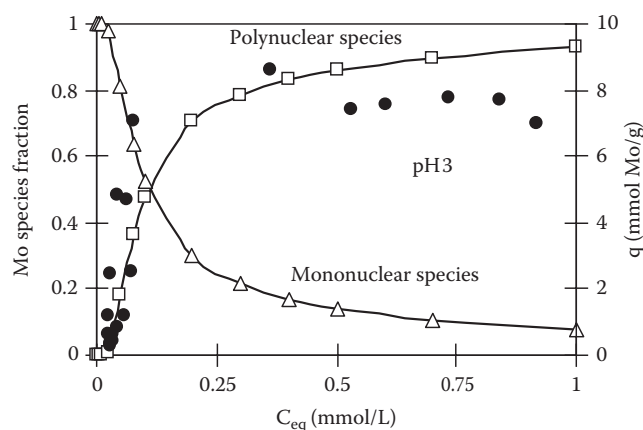


FIGURE 9.3 Example of correlation between the speciation of the metal ions (concentration of polynuclear species, \square , and mononuclear species, Δ) and molybdate sorption capacity (sorption isotherms points: bold circles) using chitosan at pH 3. (From Guibal, E. et al., *Sep. Sci. Technol.*, 35, 1021, 2000a. With permission.)

groups under near-neutral pH conditions, the presence of citrate anions leads to the formation of anionic citrate–Cu anionic species that can bind to chitosan in acidic solutions: there is a change in the optimum pH range and in the binding mechanism (Guzman et al. 2003). Actually, a correlation was found between the predominance of copper–citrate complex anions over free anionic citrate species and the beginning of copper sorption by electrostatic attraction. In addition, the speciation diagram of Cu(II) in the presence of citrate was also correlated to the curve showing the maximum sorption capacity at different pHs.

9.3.2.2 Intrinsic Polymer Characteristics: Crystallinity and Structure

The crystallinity of materials may affect their hydration, which, in turn, may impact the accessibility of water and target metal ions to reactive groups in the core of sorbent particles (Piron and Domard 1998b, Piron et al. 1997). The sorption of uranyl ions on chitosan proceeds by coordination with amino groups (Piron and Domard 1997, 1998b), the stoichiometric ratio being close to two $-\text{NH}_2$ units present on the amorphous domain of the biopolymer with one uranyl ion. The impact of crystallinity properties of chitosan on molybdate and hexachloroplatinate sorption has been abundantly discussed (Guibal et al. 1999a, Jaworska et al. 2003a,b, Milot et al. 1998). It was found that the residual crystallinity of the biopolymer (and the origin of the material: squid vs. fungal or shrimp origin) strongly influences both the accessibility and the availability of reactive groups (protonated amine groups) for metal binding. For example, chitosan issued from β -chitin (squid chitosan) revealed much less efficient for Pt(IV) sorption than the material produced from α -chitin (shrimp, fungal biomass) (Jaworska et al. 2003a,b). X-ray diffraction patterns can be used for differentiating the different materials and the presence of specific peaks (shoulder at $2\theta \approx 22^\circ$) can be correlated to worst sorption performance (equilibrium and kinetics) (Milot et al. 1998). A high crystallinity index can be correlated to less efficient sorption (Jaworska et al. 2003a,b), consistently with previous studies on sorption of uranyl ions (Piron and Domard 1998b, Piron et al. 1997). As a direct consequence of crystallinity effect, the uptake kinetics is controlled by the size of sorbent particles, the accessibility being reduced in the crystalline regions the mass transfer properties (especially intraparticle diffusion) are hindered. It is thus necessary reducing the size of the sorbent for decreasing the equilibrium time (Dzul Erosa et al. 2001, Ruiz et al. 2000). The main drawback of reducing the size of sorbent particles consists of either making more complex the solid/liquid separation in batch systems or decreasing hydrodynamic properties (head loss pressure, blocking) in fixed-bed columns (Jansson-Charrier et al. 1996b). An alternative may consist of changing the conditioning of the biopolymer, the best example being shown by the manufacturing of chitosan gel beads (Guibal et al. 1999d, 1998, Sicupira et al. 2010). The synthesis procedure includes a dissolving state that contributes to (at least partially) destroy the initial crystallinity of the material before being neutralized, coagulated, or ionotropically gelled. This method significantly improves the accessibility and availability of reactive groups by expansion of the structure of the material and decreases the crystallinity. However, at the end of the process, it is necessary to carefully control the drying process (water content being initially higher than 95%). Indeed, uncontrolled drying produces xerogels with collapse of the porous structure

of the material increasing the resistance to intraparticle diffusion (Ruiz et al. 2002, Sicupira et al. 2010). Among the processes that can be used for controlled drying are freeze-drying (Ruiz et al. 2002), drying in the presence of spacer molecules (Ruiz et al. 2002), and drying under CO₂ supercritical conditions (Agulhon et al. 2012b, Deze et al. 2012, Quignard et al. 2010).

Another important criterion for metal-binding affinity is the structure of the material and the distribution of functional groups. Indeed, both chitosan and alginate are heteropolymers made of glucosamine/acetylglucosamine units and mannuronic/guluronic acid groups for chitosan and alginate, respectively. Acetylglucosamine being poorly reactive for metal binding, the degree of acetylation is a critical parameter for the efficiency of chitosan (Guibal et al. 1999a, Milot et al. 1998). Similar differences in the sorption performance are reported when varying the M/G ratio in alginate materials (Agulhon et al. 2012a,b, Papageorgiou et al. 2006). Depending on the repartition of the different groups and their organization in the polymer (blockwise, random, alternated), the spatial arrangement (which needs to be compatible with the steric organization of metal ions), and the type of metal ion, the affinity will be favored by the presence of mannuronic or guluronic acid groups (Agulhon et al. 2012a,b).

9.3.3 SELECTIVITY ISSUES

Due to the proper reactivity of functional groups, the sorbents are expected to have a selectivity for given metal ions (Vold et al. 2003), according, for example, to the principle of Pearson (hard and soft acid and base theory) (Ayers et al. 2006, Pearson 1966): “hard acids” (low polarizability and hard sphere type metals such as Mg(II), La(III), Fe(III), Cr(III), U(VI), V(IV)...) prefer to associate with “hard” bases ($N \gg P, O \gg S, F \gg Cl$), and “soft” acids (Ag(I), Cd(II), Hg(II), Au(III), and Sn(II)) prefer to associate with “soft” bases ($P \gg N, S \gg O, I \gg F$). Borderline metal cations (Fe(II), Pb(II), Zn(II), Co(II), Ni(II), V(V), Cu(II) ...) have intermediary binding properties and are generally classified according to the Irving–Williams series in terms of stability constants ($Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$). Hence, for alginate the following series was cited in terms of decreasing affinity: $Pb(II) > Cu(II) > Zn(II) > Co(II) > Ni(II) > Mn(II) > Fe(II)$ (Chen et al. 2002, Karagunduz and Unal 2006). Selectivity for chitosan does not appear to depend on the ionic size and the hardness of metal cations (Rhazi et al. 2002). Alkaline and alkaline-earth metal ions are not bound to chitosan: transition metal ions can thus be efficiently recovered from brines and industrial effluents. The speciation of metal (formation of polynuclear species, chloro complexes) may affect the selectivity of the sorbent for target metals through speciation effects and change in the sorption mechanism (as discussed earlier).

The selectivity is generally difficult to reach for the effective separation of metals with similar chemistry. For example, in the case of the binding of precious metals (e.g., Pd(II), Pt(IV)) on chitosan, it is generally not possible to completely separate the two metals, despite the marked preference of the material for Pd(II), as shown by the Pd(II) overshoot observed on breakthrough curves from bicomponent solutions (in fixed-bed reactors, Figure 9.4) (Chassary et al. 2005). The desorption step can be used to increase the selectivity of the process but it remains difficult to reach the complete separation of the metals.

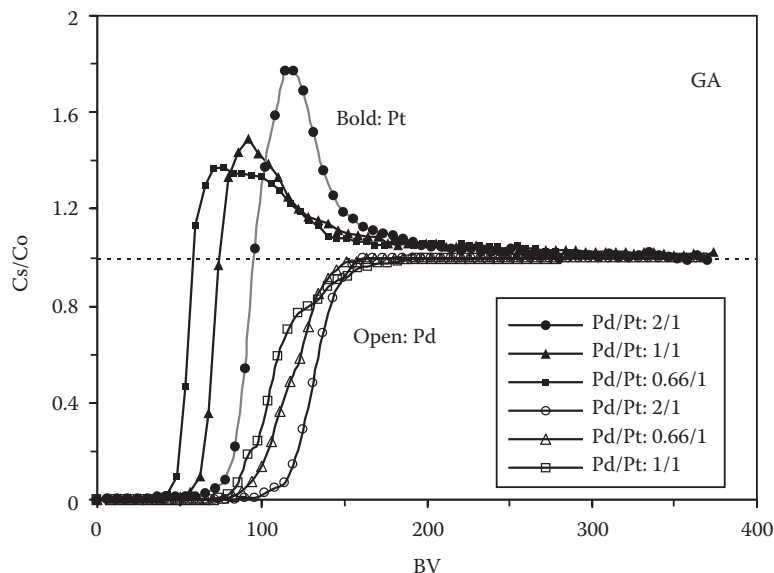


FIGURE 9.4 Example of breakthrough curves for the simultaneous sorption of Pd(II) and Pt(IV) in fixed-bed columns for glutaraldehyde cross-linked chitosan (different Pd/Pt ratio: the overshoot on Pt(IV) profiles shows the preference of the sorbent for Pd(II)). (Reprinted from *Hydrometallurgy*, 76, Chassary, P., Vincent, T., Marcano, J.S., Macaskie, L.E., and Guibal, E., Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, 131–147, Copyright 2005, with permission from Elsevier.)

9.3.4 RECYCLING

The recycling of the sorbent (and the possible valorization) of sorbed metals is a key parameter for the competitiveness of the sorption process. The possibility to desorb bound metal ions strongly depends on the type of metal, sorbent and mechanism involved in metal binding. A change in the pH is generally sufficient for achieving metal desorption, especially for metal cations. Metal cations being generally bound to chitosan at near-neutral pH can be readily desorbed when decreasing the pH: the protons contribute to the protonation of amine groups and compete with metal cations (Kamari and Ngah 2009, Kannamba et al. 2010, Osifo et al. 2009, Vieira et al. 2007). Since chitosan is soluble in acidic solutions (except in sulfuric acid solutions), this process is generally not applicable or requires the cross-linking of the material to prevent its dissolving during the desorption step. Glutaraldehyde can be used but at the expense of a loss of sorption efficiency in the case of metal cation binding by chelation (Dzul Erosa et al. 2001), because the amine groups bound to aldehyde groups do not react with metal cations. Metal binding can, in some cases, react with other reactive groups such as imino bonds (Vieira and Beppu 2006). Alternatively, metal ions can be desorbed using complexing agents such as EDTA (Chen et al. 2012, Kamari and Ngah 2009, Kannamba et al. 2010, Vieira and Beppu 2006). In the case of the desorption of metal anions loaded on chitosan, though some positive results were obtained changing the pH (using NaOH or NH_4OH , which can have a dual

effect associating pH change and complexing effect) for molybdate, for example, the strength of the interaction is strong enough to maintain a significant amount of the metal (especially Pt(IV) and Pd(II)) on the sorbent (Chassary et al. 2005, Sicupira et al. 2010). Strong complexing agents are generally necessary for removing these metal ions such as thiourea (alone or associated with HCl), which can be efficiently used for removing precious metals from loaded sorbents (Chassary et al. 2005, Park et al. 2013, Santos Sopena et al. 2011, Sicupira et al. 2010, Zhou et al. 2010).

9.3.5 MODE OF OPERATION

The mode of operation for these materials will strongly depend on their conditioning. Indeed, previous sections have identified the drastic effect of particle size of biopolymer powder on the mass transfer properties. The resistance to intraparticle diffusion requires selecting small particles that cannot be used at large scale for filling fixed-bed columns (due to pressure drop and clogging effects, hydrodynamic behavior) (Jansson-Charrier et al. 1996b). For short analytical-like columns, this parameter is less significant and microparticles can be used (Chassary et al. 2005, Ruiz et al. 2001, Singh et al. 2011). Small particles can then be only operated through batch reactor at the expense of the optimization of solid/liquid separation. The main parameters to be considered are the size of sorbent particle, the agitation speed, and the sorbent dosage (in relation with the metal concentration, and, more generally, the composition of the effluent). These reasons (combined with the analysis of diffusion properties) led to developing alternative conditionings of biopolymer to operate fixed-bed systems. Under the form of spherical particles with expanded structure (due to gelling procedure and decrease in material crystallinity) both the mass transfer performance and the hydrodynamic characteristics are favorable to the use in fixed-bed columns (Guibal et al. 1999d, Osifo et al. 2009). The main parameters to be optimized are thus the size of particles and the flow rate (superficial flow velocity and average contact time in the column).

An alternative application may consist of using chitosan hollow fibers: the concept is based on (1) the reactivity of the chitosan material (at the outer side of the fiber, shell side) to bind metal ions and (2) the morphology of the material that allows circulating the eluent (at the inner side of the fiber, core side). This makes possible the simultaneous sorption and desorption of the metal. For example, this concept was used for the recovery of chromate anions in acidic solutions (ion exchange/electrostatic attraction of chromate anions on protonated amine groups) and its elution/concentration using Aliquat 336 (a quaternary ammonium salt) (Vincent and Guibal 2000, 2001). The hollow fiber served as both a reactive support and a phase separation (aqueous/organic) barrier.

Ultrafiltration assisted by complexation (UFAC) is another way to use the biopolymer for metal binding, the concept being completely different. The principle used in the other systems consists of the transfer of the metal from the liquid phase to the solid phase. In UFAC, the biopolymer is dissolved and mixed with the metal solution: the biopolymer forms soluble complexes with metal ions and an ultrafiltration membrane is used for retaining the metal-bearing macromolecules (Fatin-Rouge et al. 2006, Rivas et al. 2005). The retentate concentrates the target metal ions, while the metal ions that do not react with the biopolymer can pass the membrane and are collected in the filtrate (Kuncoro et al. 2005). The main disadvantage of the process is related to the operating

pH range that should conciliate both the reactivity of amine groups (in the case of chitosan) and the stability of the biopolymer (in this case, the biopolymer should remain in the dissolved state in the solution). To overcome this problem it is possible to modify the biopolymer to improve its dissolution in a wider range of pH. For example, the regioselective grafting of sulfonic groups on chitosan (grafting on C–OH groups) lets free amine groups for interacting with metal ions while maintaining the solubility of the biopolymer even in alkaline solutions (Carreon et al. 2010).

9.4 ALGINATE AND CHITOSAN AS ENCAPSULATING MATERIALS FOR THE ELABORATION OF NEW SORBENTS

Though this application is not directly connected to the affinity of the biopolymer for metal ions, the properties of these biopolymers for encapsulating microorganisms, enzymes, solid particles and liquids (oils, etc.) are well documented, and open the route for developing new sorbents. The potential of these materials to be elaborated under different forms (see Section 9.2.3) also justifies the interest for using these biopolymers for the design of new sorbing materials and new modes of application. The challenge in the synthesis of these materials is to manage and optimize both the accessibility and reactivity of the incorporated material (management of mass transfer properties) and the retention properties of the biopolymer matrix (confinement of micro- or nanoparticles, or retention of organic extractants).

9.4.1 ENCAPSULATION OF EXTRACTANTS AND IONIC LIQUIDS

Several recent studies have shown the possibility to incorporate extractants and/or ionic liquids into biopolymer capsules. The principle consists of the addition of the organic liquid phase into the biopolymer solution and the distribution of the viscous solution into neutralization, coagulation, or ionotropic gelation solution through a thin nozzle (Ngomsik et al. 2009, Wu et al. 2009). The main problem deals with the compatibility of the two phases: the organic (hydrophobic) and aqueous (hydrophilic) phases tend to segregate. The “compatibilization” of the two phases can be operated using an alkaline solution of gelatin (Campos et al. 2008a,b, Guibal and Vincent 2006, Guibal et al. 2008, 2009, 2010). In this case, the extractant is dispersed in the core of the alginate matrix under the form of small vesicles that are not necessarily interconnected (Figure 9.5).

The sorption properties in both terms of thermodynamics (equilibrium) and kinetics are controlled by the porosity of the matrix (drying method, characteristics of the biopolymer) and the properties of the extractant (in relation with the target metal). Though beads are the encapsulated materials most commonly prepared, it is also possible to elaborate composite materials under the form of foams using the same method for extractant immobilization (Guibal et al. 2010). The extractant is “compatibilized” with the biopolymer and poured into a mold before being frozen, reacted with the neutralizing or gelling agent and finally freeze-dried (see Section 9.2.3.4: the same procedure as for the preparation of biopolymer sponges and foams). These materials have been used for immobilizing ionic liquids for the binding of palladium, and they were finally used for supported catalysis applications (Jouannin et al. 2013, Vincent et al. 2013).

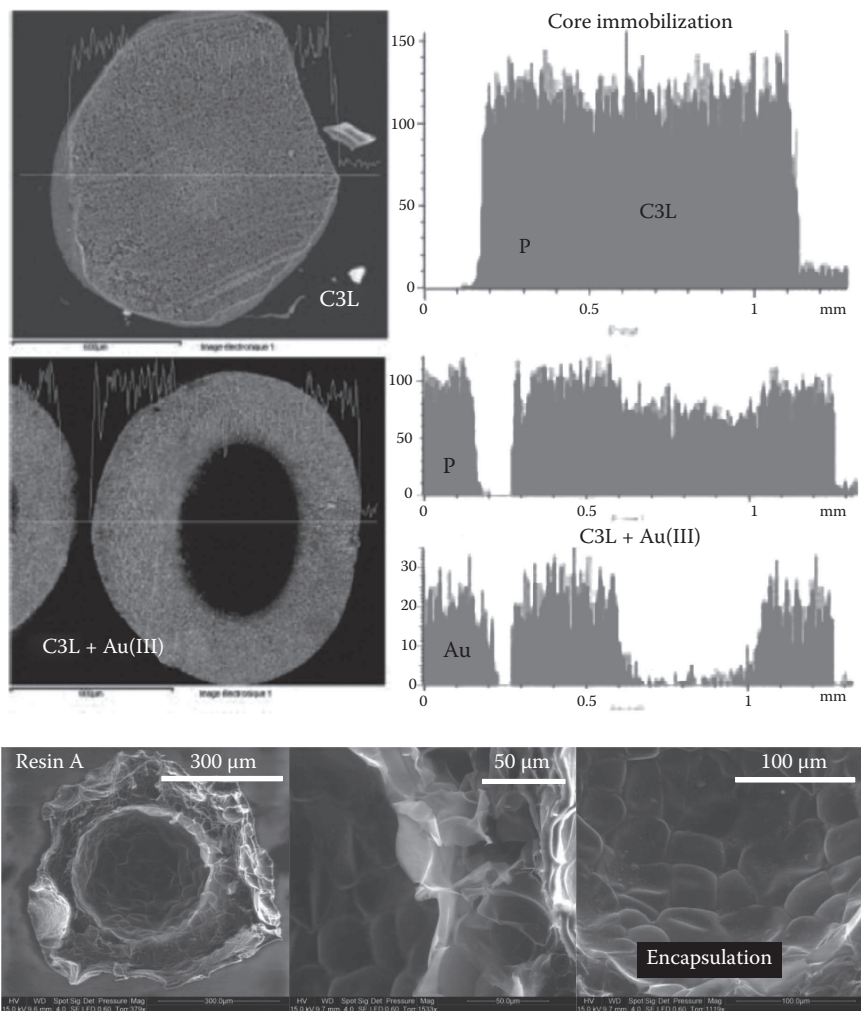


FIGURE 9.5 Examples of tetraalkylphosphonium ionic liquid encapsulation using alginate (core immobilization: dispersion in the whole mass of the biopolymer matrix [before and after Au(III) sorption]; encapsulation: liquid core and solid envelope, SEM photographs and SEM-EDX analysis). (Core immobilization: Reprinted from Campos, K. et al., *Solvent Extr. Ion Exch.*, 26, 270-601, 2008. With permission. Encapsulation: Reprinted from Kica, M. et al., *Solvent Extr. Ion Exch.*, 32, 543, 2014. With permission.)

Another concept has been recently tested for the immobilization of ionic liquid into biopolymer: the extractant phase is injected through a concentric nozzle into the coagulation/ionotropic gelation solution. The extractant forms the core of the spherical particle, while the biopolymer entraps the ionic liquid in a shell. In this case, the ionic liquid phase forms a unique internal vesicle and the challenge is the control of diffusion properties of the shell layer (Figure 9.5): this is especially important if the capsules need to be dried (Kica et al. 2014). The drying of the material has to be controlled,

taking into account the mechanical behavior of the capsules, the retention of the ionic liquid, and the mass transfer properties. The stability of the material in terms of extractant retention depends on the loading of the composite material, the dry mass percentage for the encapsulated extractant being generally less than 30% (at the maximum less than 50%) to prevent disruption of the hybrid material, and the release of the extractant.

9.4.2 ENCAPSULATION OF SOLID ION EXCHANGERS

The same concepts can be used for the immobilization of solid particles into biopolymer matrices. A great diversity of solid particles having ion-exchange properties have been tested for the elaboration of composite adsorbents: ferrocyanide compounds (Prussian blue and analogues) (Lian et al. 2012, Lim and Kang 2013), mineral ion exchangers (ammonium molybdophosphate, zirconium phosphate, Figure 9.6) (Krys et al. 2013, Mimura et al. 2001, 2011, Ye et al. 2009), clays, and metal oxides and hydroxides (Boddu et al. 2008, Escudero et al. 2009, Lezehari et al. 2010, Sarkar et al. 2012, Yamani et al. 2012). The choice of the encapsulating agent depends on the solid compound to be incorporated and, more specifically, on its pH range of stability. Indeed, chitosan being soluble in acidic solutions and being gelled in alkaline solution, the ion exchanger needs to be resistant to these drastic conditions (to prevent material dissolving or acid–base degradation). On the other hand, alginate is stable in acidic solution and can dissolve in mild pH conditions. Chitosan and alginate are thus complementary in terms of dissolving and acid–base stability. It is noteworthy that chitosan can be reacylated to reinforce the chemical stability of the biopolymer but at the expense of a procedure that could interfere with (or degrade) the encapsulated material. It is also possible in the case of the encapsulation of solid particles to

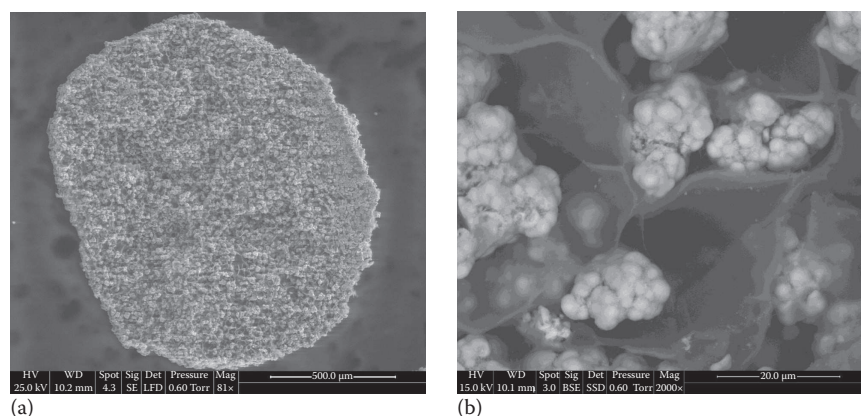


FIGURE 9.6 Encapsulation of zirconium phosphate (solid ion exchanger) in alginate matrix (SEM photographs): (a) general view of the cross-section of composite capsule; (b) focus on ion-exchanger particles in the alveoles of the bead. (Reprinted from *J. Colloid Interf. Sci.*, 409, Krys, P., Testa, F., Trochimczuk, A., Pin, C., Taulemesse, J.M., Vincent, T., and Guibal, E., Encapsulation of ammonium molybdophosphate and zirconium phosphate in alginate matrix for the sorption of rubidium(I), 141–150, Copyright 2013, with permission from Elsevier.)

elaborate alternative conditioning of hybrid supports: foams versus gel beads (Vincent et al. 2014). These systems can be used in fixed-bed columns using the foams as a reactive filtration unit.

9.5 IS THERE “ANOTHER LIFE” FOR METAL–BIOPOLYMER COMPOSITES AFTER METAL BINDING?

The interactions of the biopolymers with metal ions can serve not only for the recovery of metal ions but also for the elaboration of new hybrid materials and the design of new applications. Some examples are listed in the following as an illustration of the broad range of new materials that can be manufactured associating chitosan or alginate with metal ions.

9.5.1 NEW MATERIALS FOR ENVIRONMENTAL APPLICATIONS

The affinity of a pollutant (metal ion, organic compound, etc.) for a given metal can be used for elaborating new sorbents making profit of the proper affinity of the metal ions for the biopolymers. For example, sulfur-bearing pesticides have affinity for silver (strong interaction between silver cation and sulfur groups) (Yoshizuka et al. 2000): binding silver ions on chitosan offers the possibility to recover methyl parathion from pH 5 to 6 solutions. The pesticide can be selectively desorbed from loaded supports using ammonium thiocyanide or ammonia, silver remaining bound to the biopolymer. Ammonia sorbents were prepared by immobilizing Cu(II) metal ions onto chitosan support (Li et al. 2012a). Chromate and vanadate were sorbed by hybrid Cu/chitosan membranes: Cu(II) is sorbed on chitosan membranes before being chemically reduced (using sodium borohydride). Copper nanoparticles bind metal anions by a combination of adsorption and reduction mechanisms (Condi de Godoi et al. 2013): chromate is mainly bound by reduction (copper being oxidized on the support), while the part of direct binding is more important for vanadate sorption. A number of studies have focused on the sorption of arsenic species (arsenate, arsenite, or organic species) using metal–chitosan hybrid materials. Molybdate anions are capable of reacting with arsenic to form a colored complex: the method is used for spectrophotometric determination of arsenic in solution. On the other side, molybdate is strongly bound to chitosan (with sorption capacities that can reach up to 800 mg Mo g⁻¹). Molybdate-impregnated chitosan beads are very efficient for removing As(III) and As(V) from slightly acidic solutions (Dambies et al. 2000, 2002). The reactivity and the selectivity are reinforced by the specific reaction of As(V) with molybdate and the sorbent can be regenerated and recycled using phosphoric acid (at fixed values of concentration and pH for preventing molybdate desorption). Iron-coated chitosan flakes and iron-doped chitosan granules were prepared by deposition of iron hydroxide at the surface of biopolymer particles or by alkaline coprecipitation (Gupta et al. 2009). These materials were efficiently tested for binding As(III) and As(V) from neutral solutions. The incorporation of zero-valent nanoparticles at the surface of chitosan fibers was obtained by impregnation of the biopolymer material with iron(III) chloride ions followed

by their *in situ* reduction (using sodium borohydride) (Horzum et al. 2013): the composite material directly bound As(V) while As(III) was sorbed by a combined oxidation–sorption mechanism. As(V) was also recovered from aqueous solutions using chitosan complexed with different metal ions (Cu(II), Fe(III), La(III), Mo(VI) and Zr(IV)) (Shinde et al. 2013).

The interactions of chitosan with Ni(II) were used for the synthesis of affinity membranes (Ahmed et al. 2006). Histidine-tagged molecules are immobilized on a hybrid membrane (Ni(II) is sorbed on chitosan supported on polymeric support) for binding specific antibodies. This composite material allowed significant improvement in both the amount of bound protein and the affinity constant for the antibody. This enhancement is explained by the positive effect of Ni(II) that contributes to give to the protein a proper orientation (which increases its reactivity).

Another beneficial effect of the binding of metal ions on chitosan support is reported for the immobilization of trypsin (Wu et al. 2006). Chitosan was deposited on silica gel by impregnation and precipitation before binding metal cations by chelation at near-neutral pH (Cu(II), Zn(II), and Ni(II)). Trypsin is bound to the hybrid material at pH close to 7. The presence of the metal ions allows the reversible immobilization of the enzyme (by pH decrease); in addition, the immobilization is less inhibitory to enzyme activity compared to covalent immobilization. The stability of immobilized trypsin follows the sequence, Zn(II) > Ni(II) > Native > Cu(II).

9.5.2 NEW MATERIALS FOR SUPPORTED CATALYSIS

An abundant literature exists on the use of hybrid chitosan or alginate/metal materials for catalytic applications (Ai and Jiang 2013, Chtchigrovsky et al. 2012, Guibal 2005, Guibal et al. 2007, Macquarrie and Hardy 2005). In most cases, palladium or copper is used as the catalytic metal. Several procedures have been identified for the preparation of chitosan-supported Pd catalysts including (1) sorption followed by metal reduction (for hydrogenation reactions), (2) incorporation of metal precipitate (encapsulation), and (3) coprecipitation of metal and biopolymer (Kramareva et al. 2004, Leonhardt et al. 2010). These materials were used for hydrogenation (Guibal and Vincent 2004, Kramareva et al. 2003, Peirano Blondet et al. 2008, Schuessler et al. 2012, Vincent and Guibal 2002, 2003, 2004, Vincent et al. 2003), oxidation (Guibal et al. 2006, Kramareva et al. 2003, Kucherov et al. 2003), dehalogenation (Vincent et al. 2003), hydroamination (Corma et al. 2007), cycloaddition (Chtchigrovsky et al. 2009), and Suzuki cross-coupling reactions (Martina et al. 2011), depending on the catalytic metal and its oxidation state.

These materials have been manufactured under different forms: powder/flakes (Guibal et al. 2006, Vincent and Guibal 2002), gel beads (Guibal 2005), membranes, and hollow fibers (Guibal et al. 2005, Peirano et al. 2009) (Figure 9.7). It is noteworthy that the possibility to encapsulate ionic liquids (or incorporate these ionic liquids in the opened porosity of the support) for the binding of some catalytic metals (especially palladium) opens the route for elaborating new catalysts (called supported ionic liquid catalysts [SILC] or supported ionic liquid-phase catalysts [SILP]) under the form of gel beads or sponges/foams (Czulak et al. 2012, Jouannin et al. 2011, 2013, Moucel et al. 2010, Vincent et al. 2013).

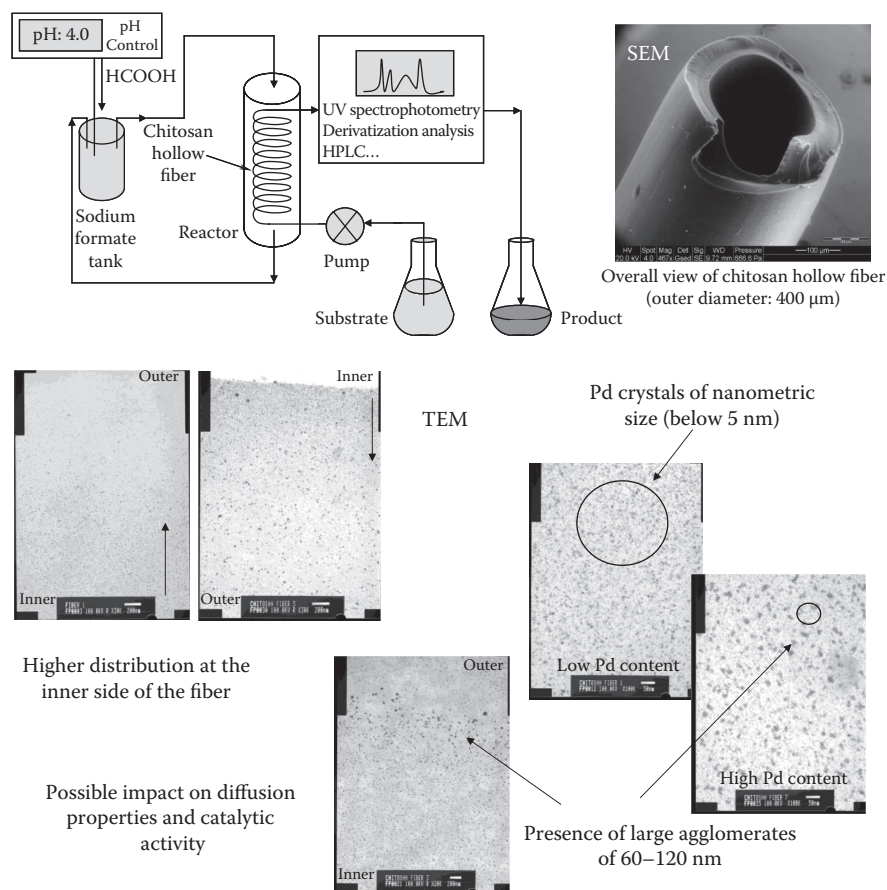


FIGURE 9.7 Experimental setup for the testing of Pd supported catalyst on chitosan hollow fiber—SEM image of the fiber and TEM analysis of catalytic hollow fibers (impact of metal loading on the size and distribution of the metal nanoparticles). (Reprinted from *J. Membr. Sci.*, 329, Peirano, F., Vincent, T., Quignard, F., Robitzer, M., and Guibal, E., Palladium supported on chitosan hollow fiber for nitrotoluene hydrogenation, 30–45, Copyright 2009; *Int. J. Biol. Macromol.*, 43, Peirano Blondet, F., Vincent, T., and Guibal, E., Hydrogenation of nitrotoluene using palladium supported on chitosan hollow fiber: Catalyst characterization and influence of operative parameters studied by experimental design methodology, 69–78, Copyright 2008, with permission from Elsevier.)

9.5.3 NEW MATERIALS FOR ANTIMICROBIAL/ANTIVIRAL EFFECTS

The affinity of biopolymers for metal ions that have a bactericidal effect can be used for elaborating antibacterial materials or antiviral materials (Mori et al. 2013). Chitosan, by itself, has a weak bacteriostatic effect that can be improved by binding metal ions such as Ag(I) (Hoang Vinh et al. 2010, Jena et al. 2012, Saravanan et al. 2011, Thomas et al. 2009), Zn(II) (Patale and Patravale 2011, Wang et al. 2004), and Cu(II) (Patale and Patravale 2011, Qin et al. 2007). The challenge is to maintain a good stability of the

metal both on the support and under its active forms. Indeed, some metals, like silver, are readily subject to redox reactions that may contribute to metal release and loss of activity. The choice of the metal and the loading of the biopolymer are controlled by the target microorganisms (Gram+/Gram- bacteria, yeast, fungi), the objective (food, agriculture products, health applications), and the mode of application (water, contact with healing parts, burn parts, etc.). The release of metals such as silver may have a crippling effect for health applications, for example. The release of metals may be enhanced when the material comes in contact with human fluids (Qin et al. 2007). The stoichiometric ratio between the metal and the biopolymer controls the speciation of the metal in the composite, which, in turn, controls its antibacterial activity (Wang et al. 2004). The antimicrobial metals can be immobilized on self-supported biopolymer or on textile fiber-coated biopolymers. Playing with the conditioning of the biopolymer makes possible the design of new depurating materials: for example, the binding of silver on chitosan foams allowed developing antimicrobial filtration systems (Guibal et al. 2013) (Figure 9.8),

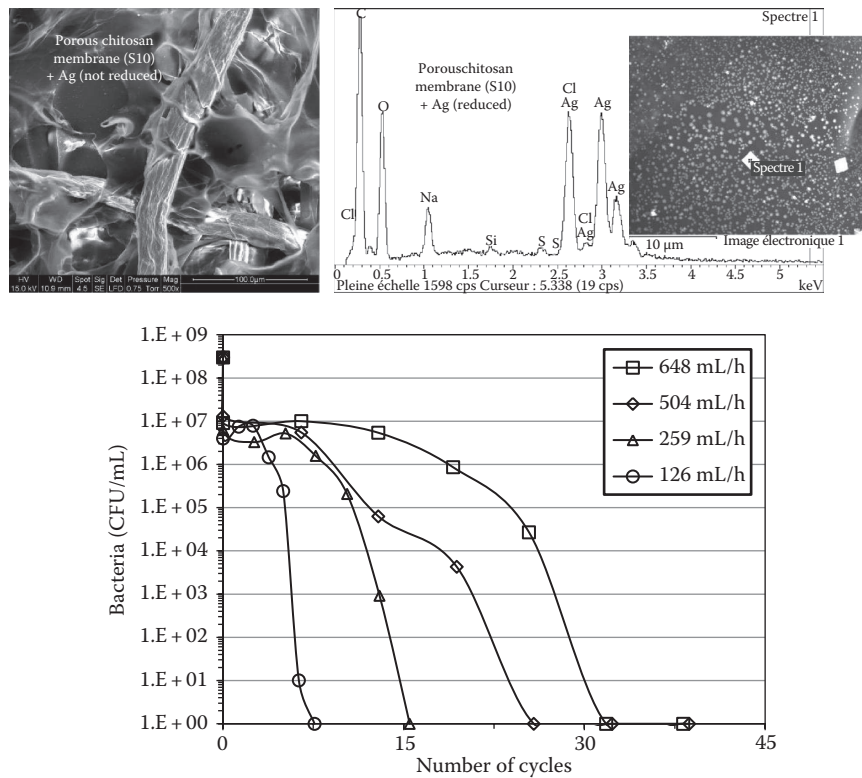


FIGURE 9.8 SEM photograph of silver/cellulose/chitosan foam, SEM-EDX analysis of silver micro-crystals on composite material, and effect of flow rate (with recirculation) on the abatement of *Escherichia coli* population through composite antibacterial foams. (Reprinted from *J. Colloid Interf. Sci.*, 393, Guibal, E., Cambe, S., Bayle, S., Taulemesse, J.-M., and Vincent, T., Silver/chitosan/cellulose fibers foam composites: From synthesis to antibacterial properties, 411–420, Copyright 2013, with permission from Elsevier.)

or manufacturing highly efficient wound dressings (Vimala et al. 2010). Combined with hydroxyapatite, silver/chitosan scaffolds were tested for controlling implant during reconstructive surgery of bones (with complementary antibacterial effects) (Saravanan et al. 2011). The association of chitosan with copper showed a very interesting synergistic effect in the protection of cucumber seedlings against *Botrytis cinerea* (Ben-Shalom and Fallik 2003): the presence of copper prevents chitosan degradation and enhances the elicitor effect of the biopolymer.

9.5.4 NEW MATERIALS FOR SENSORS

Chitosan has retained a great attention for the last decades in the field of the elaboration of sensors. Indeed, the sensors are requiring in many cases gold (or other metals) nanoparticles at the surface of electrodes. Gold nanoparticles have a strong tendency to agglomerate/aggregate, which, in turn, reduces the activity of these nanoparticles. Citrate anions are frequently used for stabilizing these nanoparticles, but chitosan is also a promising substrate for achieving gold stabilization (Lim and Kang 2013, Sugunan et al. 2005). Chitosan has different modes of action in the synthesis of these materials: encapsulating the metal nanoparticles (with stabilization), binding of metals (with subsequent reduction), and encapsulating other supports that immobilize metal nanoparticles (Khun et al. 2012, Lian et al. 2012, Lim and Kang 2013, Mathew et al. 2012). These materials can be used for the detection of metal ions (Mathew et al. 2012, Sugunan et al. 2005), glucose (Khun et al. 2012, Li et al. 2012b), organic compounds (Lian et al. 2012, Lim and Kang 2013), and humidity (Condi de Godoi et al. 2011). A similar stabilizing effect is reported on the synthesis and immobilization of silver nanoparticles for hydrogen peroxide detection (Tian et al. 2012, Zhang et al. 2012), and trichloroacetic acid analysis (Liu et al. 2012).

Chitosan can be also used in sensor manufacturing through electrodeposition mechanism for immobilization of analytical nanoparticles and nanocomposites (Liu et al. 2012, Payne 2007, Yang et al. 2013). When applying a cathodic potential, protons in the acidic solution are consumed at the surface of the electrode. This causes a localized strong increase in the pH; as a result, the chitosan chains become insoluble at the surface of the electrode with entrapment of materials in suspension (in the chitosan solution: enzymes, cells, nanoparticles, etc.). Alginate can be also deposited on chips (Cheng et al. 2011): in this case, the sol-gel transition is driven by anodic electrodeposition.

9.6 CONCLUSION

Chitosan and alginate are promising renewable resources for the binding of metal ions. Sorption mechanisms and performances are mainly controlled by the type of functional groups, the pH and the composition of the solution (metal speciation, protonation of reactive groups, etc.), and the conditioning of the biopolymers (size of particles, morphology, arrangement, etc.). Sorption may proceed through chelation/complexation, ion exchange/electrostatic attraction,

and formation of ternary complex. The choice of the biopolymer depends on the target metal and the metal speciation. The great versatility of this material (both in terms of chemical modifications, not discussed in this chapter, and physical modifications) is a great interest for developing materials with improved diffusion properties, enhanced hydrodynamic behavior, and innovative application modes. Depending on the type of metal, the sorbent can be recycled (taking into account the strength of the interaction but also the cost of the metal compared to the cost of the sorbent: thermal degradation makes sense in the case of precious metals). In addition, these biopolymers can be used for encapsulating reactive compounds (ionic liquids, extractants, ion exchangers) in order to improve the reactivity, the selectivity, or the sorption efficiency of these materials, making also profit of the possibility to condition these composite sorbents under different forms (beads, membranes, foams, etc.).

The hybrid materials (i.e., metal-loaded biopolymers) can be also used to design new materials and new applications. Some examples have been reported to show how a second life can be offered to the biopolymers after metal binding. These composite materials are specially designed for high-added-value applications.

Despite the great potential of these biopolymers, the transfer to “true life” remains difficult. This is probably due to a lack of standardization in the characterization and production of these materials. Their variability in composition (degree of acetylation for chitosan, percentage and distribution of guluronic and mannuronic acid groups, MW, crystallinity, etc.) may explain that the final industrial users could be reluctant to use these materials. A great effort is thus necessary to convert these promising properties to successful applications.

ACKNOWLEDGMENTS

E.G. acknowledges the support of all PhD and master-level students and academic partners that collaborated with the research group over the last two decades for the development of biopolymer-based materials.

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