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Chitosan for wastewater treatment

Jacques Desbrières^{a*} and Eric Guibal^b

Abstract

Chitosan (an amino-polysaccharide obtained from deacetylation of chitin, the major constituent of crustacean shells and insect cuticles) presents a cationic character in acidic media allowing its dissolution, its shaping and possible ion-exchange interactions with anionic compounds (a property applied in adsorption and coagulation–flocculation processes). In neutral media, non-protonated amino groups allow complexation of metal cations or organic chemicals. These different properties explain the interest taken by the scientific community in using this biopolymer. In solution it contributes to complex metals and their recovery by complexation-assisted ultrafiltration. It can also be used to coagulate–flocculate organic compounds (as anionic dyes). In the solid state, it can be used for metal ion adsorption, as well as adsorption of organic compounds (dyes, pesticides, drugs, endocrine disruptors, etc.). The adsorption and coagulation–flocculation processes will be compared and examples considered. Moreover, it is noteworthy that the thermal degradation of this type of material is also more environmentally friendly than that of conventional synthetic resins (production of hazardous by-products, etc.), a supplementary advantage of these biopolymer-based sorbents. Combined with its ability to be chemically or physically modified improving the potential and phase separation of chitosan-based materials, all these properties mean it is an excellent candidate for wastewater treatment.

Keywords: chitosan; wastewater; adsorption; coagulation; flocculation

INTRODUCTION

The very marked development of environmental regulations in the last few decades has induced a strong impetus for developing alternative wastewater treatments. Processes for treating industrial or urban effluents (containing mineral as well as organic substances) involve various strategies depending on the nature of contaminants (metal ions, dyes, pharmaceutical compounds, etc.), the interest in recycling (and/or valorizing the by-products of the treatment) and toxicity. Precipitation processes are very often used but regularly encounter technical limitations and also produce large amounts of contaminated sludge. These alternative processes should reach discharge levels, be competitive and as far as possible be consistent with the requirements for sustainable growth. Additionally, in many countries the regulations concerning waste materials require proving that a waste cannot be recycled or valorized (under technical and economic constraints) before its discharge to landfill can be authorized. Membrane processes are very efficient but often expensive and limited to finishing treatments or for specific effluents. Liquid/liquid extraction processes are reserved for valorization of specific solutes (high added value, strategic or very toxic metals) with concentrated solutions (greater than 500 mg L⁻¹): losses of extracting matter by dispersion or dissolving are a great environmental drawback for these techniques. Electrochemical processes present similar drawbacks. Adsorption has received great attention in the last few decades as an alternative process for the recovery of metal ions or organic compounds from dilute solutions. Indeed, the conventional processes are not competitive when faced with dilute effluents. Many materials can be used (chelating or ion-exchange resins, mineral supports, active carbon, and residues from chemical industry, agriculture or fishing). In the case of biosorption processes, the sorbent is produced from a material of biological origin. Biosorption involves binding mechanisms similar to those used

with synthetic resins: complexation, chelation, ion exchange or electrostatic attraction.

Chitosan (a biopolymer constituted of glucosamine and acetylglucosamine monomers associated via $\beta(1 \rightarrow 4)$ linkages; Fig. 1) is obtained by the deacetylation of chitin (its fully acetylated form), present in the cell walls of most fungal biomass (chitosan being present in the cell wall of *Mucorales*), in the cuticles of insects and in the shells of crustaceans. Now shrimp shells are the main source for the industrial production of chitosan. This amino-polysaccharide presents unique properties among biopolymers being cationic in acidic solutions due to the presence of amine functions with a pK_a value in the range 6.0–6.7 (depending on the degree of deacetylation).¹ Chitosan is soluble in weak acids and low-concentration strong acid solutions but not sulfuric and phosphoric acids. This cationic property is the basis of its interesting ion-exchange properties and its solubility. The dissolution of the polymer in acidic solutions opens the route to ready physical modifications of the polymer that can be conditioned under different forms.^{2,3}

This material can be used directly in solid form for adsorption applications building on the presence of amino groups (complexation of cations or organic molecules, electrostatic attraction or ion exchange in acidic media to fix anions on protonated amine functions). It may be also used in the liquid state (dissolved in acidic media) to neutralize charges, for coagulation–flocculation

* Correspondence to: J Desbrières, University of Pau and Pays Adour, IPREM, UMR 5254, 64023 Pau cedex, France.
E-mail: jacques.desbrieres@univ-pau.fr

a University of Pau and Pays Adour, IPREM, UMR 5254, Pau, France

b Ecole des Mines d'Alès, Centre des Matériaux des Mines d'Alès, Alès, France

Jacques Desbrières is a professor at the University of Pau and Pays Adour (UPPA), engineer from ENSC Paris and doctor-engineer from Grenoble University. He has authored around 170 publications and 10 patents. After a position as research engineer with Dowell Schlumberger related to the application of polymers to oil well operations, he joined Grenoble University in 1990 and then UPPA in 2004. His research domain is concentrated on chemical modification of natural polymers and relations between their chemical structure, functional properties and applications.



Eric Guibal is lecturer and researcher at Ecole des Mines d'Alès (EMA). Engineer and doctor from Institut National des Sciences Appliquées, Lyon, he has contributed to more than 180 publications and associated with five patents. He prepared his thesis within Compagnie Française of Mokta (COGEMA group) and then joined EMA in 1990 as lecturer and researcher within Laboratoire Génie de l'Environnement Industriel (LGEI), before joining the Centre des Matériaux des Mines d'Alès (C2MA) in 2013. His developed research domains are about using biopolymers for effluent treatment (especially metal-bearing), generating these materials, their application to synthesis of advanced materials (supported catalysis, antimicrobial supports, etc.) and encapsulation of ionic exchangers (solids or liquids) to synthesize new adsorbents.



of anionic species (dissolved matter, colloids and particles in suspension) and for the complexation of metal ions. Various examples will be considered in this mini-review.

CHITOSAN AND ADSORPTION

Adsorption of metal ions and ionic dyes

Adsorption is the consequence of specific interactions between an adsorbent and a compound to be adsorbed (the adsorbate). These interactions are strongly correlated to the chemical structure of chitosan. The functional groups able to create such interactions are, for chitosan, hydroxyl and amine groups. Amine groups are susceptible to be ionized, as a function of pH (pK_a in the range 6.0–6.7). That allows chitosan to be polycationic and, hence, to interact by electrostatic interactions with anionic derivatives, such as some dyes. The protonated amine groups can bind anionic species by electrostatic attraction or ion exchange. Furthermore, when non-ionized, they possess a free electron pair on nitrogen atom, likely to interact with chemicals that are poor in electrons, such as cations. It will be possible to interact with hydrophilic chemicals, charged (anionic or cationic) or neutral. The basic structural parameter is the degree of acetylation.⁴ Finally, a certain amphiphilic character due to the presence of acetyl groups has been mentioned,⁵ adding the possibility of interaction with chemicals presenting a slight hydrophobic character.

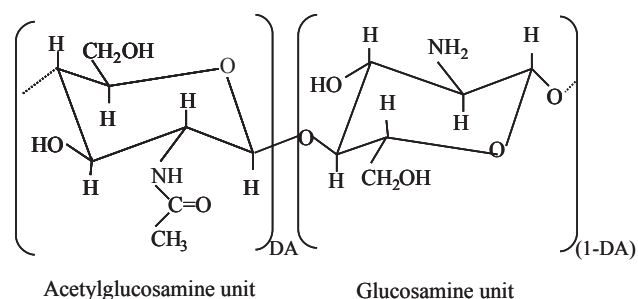


Figure 1. General structure of chitosan (DA: degree of acetylation).

Nevertheless, the adsorption mechanisms are not completely elucidated. Major works have been undertaken to study the mechanisms occurring during adsorption of metal ions. Though the contribution of —OH groups in metal binding was cited in some studies, it is now commonly accepted that metal binding takes place essentially on amine groups. Hydroxyl groups essentially contribute to stabilizing metal binding on amine groups. These reactive groups can bind metal ions through various mechanisms: (a) complexation on nitrogen (free electron pair), (b) formation of ternary complexes (one such case is the binding of the ion pair Sr(II)/carbonate on chitosan) and (c) ion exchange/electrostatic attraction. The acid–base properties of the amine groups of chitosan also allow proton binding. This protonation induces a competition for the binding of metal cations and for the formation of ternary complexes. These mechanisms are essentially active in near-neutral solutions. On the other hand, this protonation makes possible the binding of metal anions in acidic solutions through electrostatic attraction or ion exchange.

Different models were proposed to elucidate the mechanism of coordination implied in the formation of complexes. The first one is called the 'bridge model'. It is supposed that the metallic ion is bound to several nitrogen atoms from the same chain or from different chains.⁶ The second one, called the 'pendant model' considers that the metallic ion is bound to an amino group in a 'pendant' manner.⁷ Potentiometric, dichroic and spectroscopic experiments were carried out on chitosan–copper complexes to elucidate their structure.⁸ Observations during the variation of pH demonstrate that the fixation of copper ions on chitosan is negligible when the amino groups are in the protonated form. Two types of complex are present (Fig. 2):

- $[Cu(-NH_2)]^{2+}$ whose formation begins at a pH value of 5.3 (complex I)
- $[Cu(-NH_2)_2]^{2+}$ which is formed as soon as the pH is greater than 5.8 (complex II).

But the contribution of hydroxyl groups from glucosamine to cation binding remains debatable.⁹ It may be assumed that in complex I water molecules may be replaced by hydroxyl groups from glucosamine rings.

Moreover it was demonstrated that the degree of polymerization plays an important role in the interaction between oligomers and Cu(II) ions.⁸ A number-average degree of polymerization of 6.5 is the threshold for which complexation is efficient.

The electrostatic attraction mechanism can also be cited for the binding of a series of metals that form anionic complexes in acidic solutions. In acidic solutions (i.e. pH below 6) the protonation of amine groups is favourable for the attraction metal anions. At very low pH (below 2–3) the sorption of metal anions can be

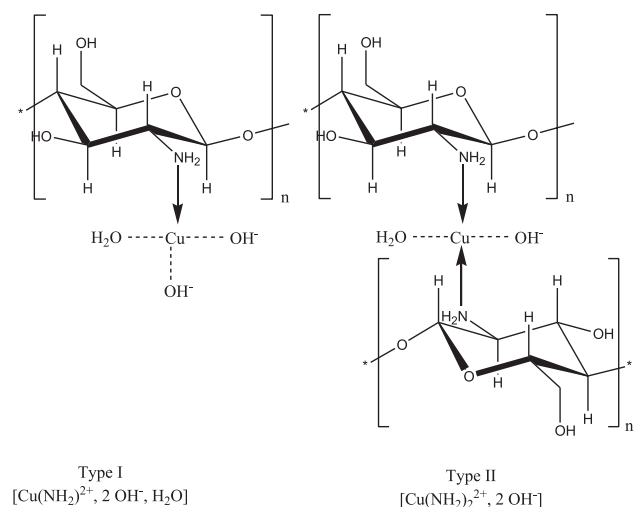


Figure 2. Structures of copper–chitosan complexes.

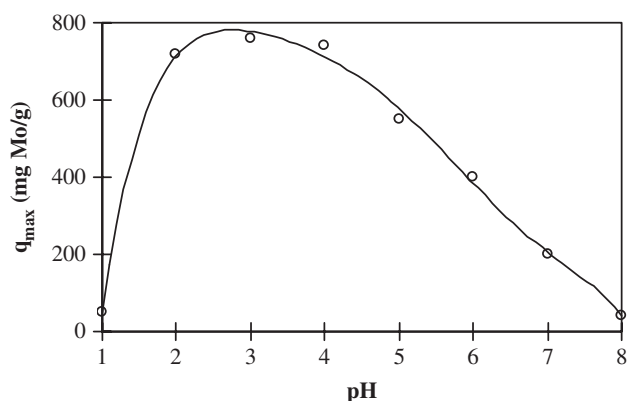


Figure 3. Effect of pH on sorption of Mo(VI) by ion exchange on glutaraldehyde-crosslinked chitosan beads. (From Guibal *et al.*¹²).

significantly decreased due to the competition of counter anions for binding on protonated amine groups. For these reasons, in most cases, the binding of metal anions (and anionic dyes) is generally optimal in a narrow pH range: between 2–3 and 5. Additionally, chitosan dissolves in acidic solution (except H₂SO₄) and it is necessary to crosslink it for improving its stability. Several processes have been described for chitosan crosslinking using, for example, epichlorohydrin. However, the crosslinking agent that is most used for chitosan stabilization is glutaraldehyde. A Schiff base reaction takes place between amine groups (on chitosan) and aldehyde groups of the crosslinker on both sides. These supplementary linkages between the chains of the polymer may explain the stability in acidic solutions. When increasing the extent of the crosslinking (using higher glutaraldehyde concentrations in the crosslinking bath) the amount of metal anions bound hardly decreased,¹⁰ while the crosslinking of amine groups completely inhibited metal cation binding by complexation.¹¹ In the case of a complexation/chelation mechanism the binding of protons does not allow a free electron pair to be available for interaction with metal cations. Figure 3 shows the effect of pH on Mo(VI) sorption.¹²

The sorption properties on chitosan are controlled by a series of experimental parameters related to the composition of the solution (pH, effect of the presence of competitor ions, metal speciation, metal concentration, etc.) or to the polymer (particle

size, sorbent dosage, conditioning of polymer, etc.). However, the effects of these parameters on metal adsorption are all involved with main criteria/mechanisms: (a) crystallinity and swelling behaviour, (b) diffusion properties and (c) metal speciation. The crystallinity of polymers affects their hydration and their swelling behaviour. This parameter, in turn, affects the accessibility to sorption sites. This accessibility can be controlled both at equilibrium and in terms of kinetic behaviour. The crystallinity can be affected by several parameters: (a) the origin of chitin (α -chitin, β -chitin or γ -chitin), (b) the treatment of the polymer during its extraction from biomass (tailoring polymer conformation: tendon form, annealing, etc.), (c) the post-treatment (dissolving and re-precipitation, freeze-drying, crosslinking, chemical grafting, etc.) and (d) the polymer conditioning (flakes, un-dried gel materials in the form of beads, membranes, fibres, etc.).

Hence, a comparison of chitosan samples with identical degree of acetylation (i.e. close to 90%) but produced from fungal, shrimp and squid sources showed considerable changes in Pt(IV) sorption isotherms and uptake kinetics. Shrimp- and fungal-based chitosan samples exhibited comparable performances, while sorption capacity and kinetic behaviour were significantly poorer for chitosan produced from squid material: (a) maximum sorption capacity decreased and (b) the time required for reaching equilibrium markedly increased. These differences were correlated with the crystallinity of the samples (analysed using XRD): squid chitosan was characterized by a greater crystallinity than the two other types (Fig. 4).^{13,14}

The contribution of diffusion mechanisms in the control of sorption performance can be easily explained by the poor porosity of the biopolymer. As a consequence, the sorption may be limited to external layers of the biopolymer and the accessibility to internal reactive groups may be markedly hindered, leading to very slow sorption kinetics. These restrictions to intra-particle diffusion are particularly important in the case of large-size diffusing molecules. An example is given in Fig. 5 for the sorption of molybdate anions on glutaraldehyde-crosslinked chitosan flakes (G1–G3).¹² Increasing the size of sorbent particles strongly reduced the maximum sorption capacity from 300 to 150 mg Mo g⁻¹. Metal ion removal is controlled by surface sorption or by sorption/diffusion restricted to an external thin layer. Under selected experimental conditions, molybdenum is present in the form of polynuclear molybdate species (MoO₇⁶⁻, and its hydrolysed forms). These large species face significant resistance to intra-particle diffusion through the compact porous network of the polymer (especially in the case of crosslinked material due to the supplementary bonds induced by heterogeneous crosslinking). This effect of diffusion limitations is concomitant with the effect of polymer crystallinity. A solution to reduce these limiting effects of diffusion may consist of manufacturing chitosan gel beads: this conditioning contributes to decreasing the crystallinity of the polymer and to expanding the porous network (more than 95% of water in the polymer hydrogel). Figure 5 shows the impact of the conditioning on particle size effects: the size of chitosan gel beads did not affect sorption capacity and the sorption isotherms superimposed with maximum sorption capacities close to 700–750 mg Mo g⁻¹ (this is about 2.5 times greater than the levels reached with chitosan flakes).

Concerning dyes, although hydroxyl groups may be involved in the adsorption of dye molecules, the amine groups remain the most active groups and influence polymer performances. Guibal and co-workers have observed that decreasing the degree of acetylation of chitosan implies an increase of the relative proportion of amine groups able to be protonated, favouring

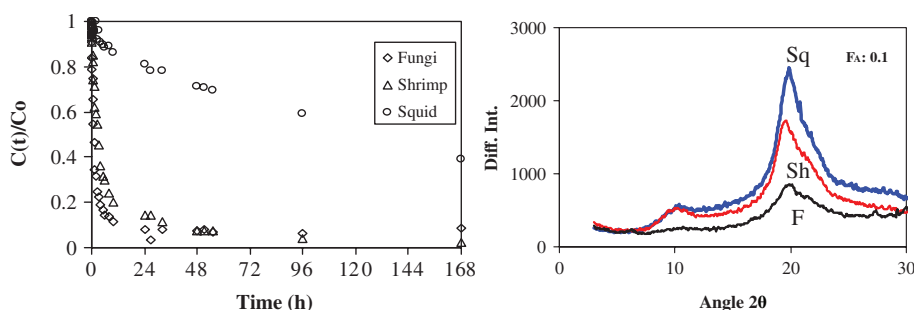


Figure 4. Influence of the origin of chitosan on Pt(IV) sorption uptake kinetics (left panel) and XRD patterns (right panel; F_A is the degree of acetylation). Glutaraldehyde-crosslinked chitosan beads used for Pt sorption. (From Jaworska *et al.*^{13,14}).

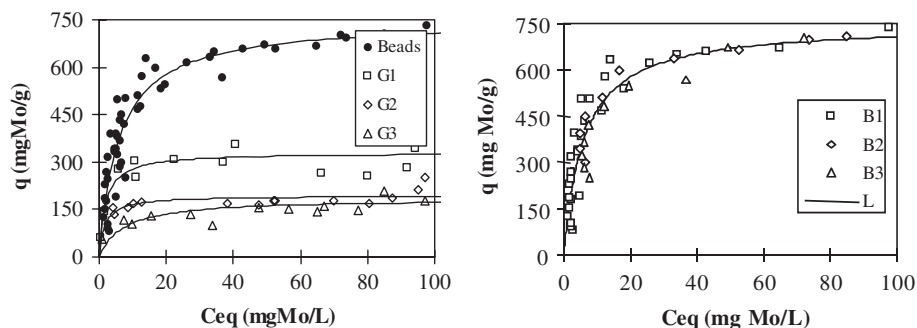


Figure 5. Influence of the size of chitosan particles and polymer conditioning (flakes: G1 < 125 μm < G2 < 250 μm < G3 < 500 μm ; beads: B1 = 0.95 mm, B2 = 1.6 mm, B3 = 2.3 mm) on Mo(VI) sorption isotherms at pH = 3 (glutaraldehyde-crosslinked chitosan). (From Guibal *et al.*¹²).

the adsorption of dyes.¹⁵ Nevertheless the variation in adsorption properties is not proportional to the degree of deacetylation, but it changes with the nature of the dye.¹⁶ More recently, it was reported that chitosan properties do not depend only on the degree of deacetylation but also on the repartition of acetyl groups along the macromolecular backbone.¹⁷

Dotto *et al.*¹⁸ have shown that, using food dyes such as amaranth (Table 1), the number of sulfate groups and the molar mass of the dye play an important role in adsorption properties; sulfate groups are more important than other ionic groups regarding the adsorption of food dyes on chitosan.

Adsorption of organic compounds by chitosan

Organic contaminants are nowadays some of the most serious environmental problems and the elimination of organic contaminants (dyes, pesticides, herbicides, drugs, etc.) from aqueous solutions is a major concern because they become persistent within the environment. The adsorption of organic substances depends on the size of these molecules, their chemical structure and their polarity. The nature of the functional groups on the organic compounds strongly influences their binding on the functional groups at the surface of the sorbent through several interactions that depend, for example, on the pH or the ionization of these groups.

Drugs

Active substances contained within a drug are characterized by very varied chemical structures. Once they have acted within an organism, they are excreted, mainly in faeces and urine, and then rejected within the network of wastewaters (human drugs) or in the ground (veterinary drugs). These residues end up somehow within the environment and potentially in sources of potable water. Once these pharmaceutical substances find themselves in

the environment, they may contaminate living organisms and potentially affect them, especially if they are bio-combinable. As a consequence it is very important to better treat wastewaters to eliminate such drug residues and not to reject them within aquatic media.

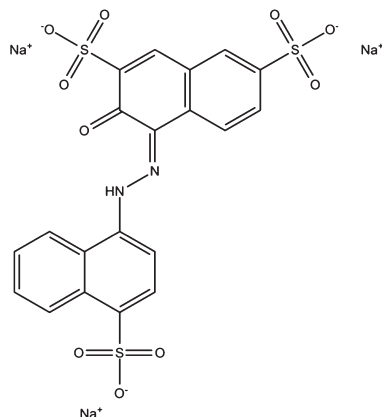
Pharmaceutical products may be eliminated by adsorption with synthetic or natural polymers. Chitosan presents hydroxyl and amino groups able to form hydrogen interactions with functional groups of antibiotics, as an example. In the case of cefoperazone (Table 1) sorption, chitosan allows elimination of 13% of the total amount during the first three hours.¹⁹ Compared with cellulose and sodium alginate, chitosan is the most efficient polymer considering that the amino groups have a larger activity compared with hydroxyl or carboxylic groups. The same observation was made for tetracycline (Table 1).²⁰ However, the solubility of chitosan in acidic media may decrease its stability for long-time use. Crosslinking allows one to overcome this problem and the porosity of hydrogels is an important parameter for this phenomenon. In the case of diclofenac or dipyron, non-steroidal anti-inflammatory drugs, the interactions between amino groups of chitosan and carboxylic ones of diclofenac and sulfoxide ones of dipyron are responsible for their adsorption.²¹ The chemical modification of chitosan with acetylacetone and ethylenediamine allows pH adjustment to optimize the recovery conditions of diclofenac²² and reduce the time necessary to its elimination to 45 minutes, compared with 80 minutes with non-modified chitosan.²³

Endocrine disruptors

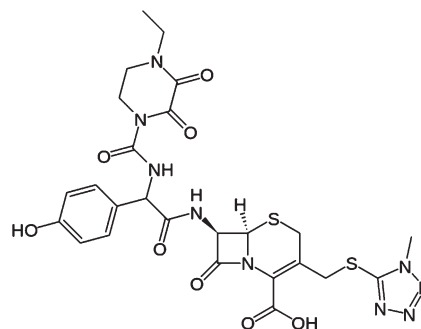
During the last few years, endocrine disruptors have become among the most studied molecules for their elimination because of their high potential to cause negative effects in human endocrine systems, and also in those of fauna and flora.^{24,25} Bisphenols, as well as chlorophenols (Table 1), are among the

Table 1. Structures of various organic compounds cited in this article

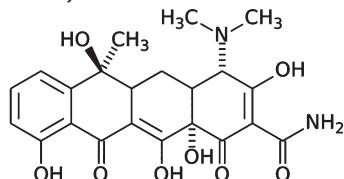
Amaranth



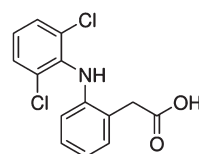
Cefoperazone



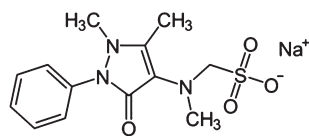
Tetracycline



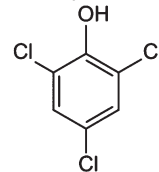
Diclofenac



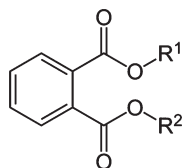
Dipyrrone



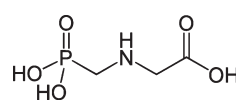
Chlorophenols



Phthalic esters



Glyphosate



most used in industrial or agricultural activities. Generally the adsorption process is efficient and economically feasible for eliminating bisphenols and chlorophenols.²⁶ Active carbon is the most used material but clays or clay-based composites were recently developed.^{27,28} Pan *et al.* have formulated composite sorbents based on chitosan and iron oxide nanoparticles or by incorporation of ash particles.²⁹ The presence of magnetite allows easy separation of these particles after adsorption using an external magnetic field. Adsorbed quantities are 31.92 mg g⁻¹ for bisphenol A and 68.89 mg g⁻¹ for 2,4,6-trichlorophenol.

Phthalates and phthalic acid esters represent another important class of contaminants. They are used as plasticizers to improve the flexibility of plastics such as poly(vinyl chloride).³⁰ Although phthalates are quickly excreted by organisms, some of them, due to their lipophilic properties, build up within the adipose

tissues. Most phthalates present a weak acute toxicity but chronic exposure to these esters may result in serious toxic effects towards rodent animals, and even humans. Adsorption by active carbon is non-selective and expensive, its performances depending a lot on the type of carbon used.³¹ Moreover, these technologies are able to remove their metabolites such as phthalate monoesters and phthalic acid during their hydrolysis. Chitosan beads were shown to efficiently remove some phthalate esters from aqueous solutions.³² Amine groups of chitosan can interact with carbonyl groups of monoesters and phthalic acid, and these beads may be able to remove these metabolites.³³ Chitosan adsorbs diesters principally by hydrophobic interactions and by polar interactions with phthalic acid.

To improve the adsorption of phthalates, α -cyclodextrins were grafted on chitosan.³² Molybdenum-impregnated chitosan beads

were also tested³⁴ and in these cases phthalate adsorption was improved and the influence of pH, salinity and calcium ions was decreased.

Herbicides

Herbicides are biologically active when applied to plants and they are further carried towards soils and aquatic systems. Excessive use of pesticides and herbicides leads to short- and long-term harmful effects on human health, such as reproduction abnormalities, cancers, hormonal perturbations, etc. Chitosan membranes are very efficient in adsorption of glyphosate (Table 1), a non-selective herbicide that is widely used.³⁵ The maximal value of adsorbed glyphosate is 10.9 mg g⁻¹, and adsorption is due to the attractive electrostatic interaction between positive charges of chitosan and anionic ones of the herbicide (as a function of pH).

CHITOSAN AND COAGULATION – ADSORPTION

Principle

Protonation of amino groups imparts to chitosan a potential for electrostatic attraction of anionic compounds as observed in the adsorption of metal anions. Anionic derivatives can then interact with amino functions to cause the neutralization of charges. This interaction is the basis of the coagulation phenomenon, which can be set up to eliminate dissolved anionic derivatives or anionic colloids when sedimentation is too slow to allow a competitive process. The principle of coagulation–flocculation is as follows. Colloidal suspensions are characterized by the presence of well-dispersed small particles bearing ionic charges of the same nature that contribute to stabilize these suspensions. The repulsion forces hinder their aggregation under stirring. The objective of coagulation is to neutralize the surface charges of these colloids in order to limit the repulsion forces and allow their aggregation (under stirring). By increasing the density and size of these neutralized particles, their capacity to settle is significantly increased. Among frequently used reagents are metal ions (iron or aluminium salts), poly(aluminium chloride) or poly(diallyldimethyl)ammonium chloride. Some of these chemicals present technical or environmental drawbacks. There is a need to develop alternative systems based on eco-compatible chemicals from renewable raw materials (e.g. tannins, chitosan or alginate, and/or their combination). The second step of this process involves flocculating the aggregated matter in suspension. Aggregation can be improved using a flocculant (high-molecular-weight polymer), in which the network contributes to entrap the particles, to favour their agglomeration, playing the role of a net that makes easier the sedimentation of aggregates. Chitosan, being of high molecular weight, may play the role of both coagulant and flocculant. Its efficiency is directly affected by its characteristics, the degree of deacetylation (influence on acid–base properties and charge neutralization) and the molecular weight (influence on flocculating properties). Its major additional advantages are the reduced noxiousness of wastes obtained at the end of the treatment (by comparison with other coagulants and flocculants, which may deliver metals and potentially toxic compounds such as acrylamide monomers) and the significant reduction in produced sludge (when compared with conventional mineral coagulants).

Treatment of mineral suspensions

In industrial units, pre-conditioned process water is collected from surface water; these water bodies frequently contain high

levels of suspended matter such as humic and inorganic colloids. This content may influence the quality of manufacturing processes, and a pretreatment is generally required to clarify these waters. The ionic charge carried by these mineral matters in suspension (clays) at natural pH is generally negative. Using chitosan is obviously justified to allow neutralization of surface charges of these mineral colloids and make easier their aggregation. The coagulation–flocculation performance for clay suspensions is strongly affected by parameters such as pH, charge of the matter in suspension, chitosan concentration and ionic charge of the solution (presence of salts *versus* pure water).^{36,37} These parameters have to be very accurately adjusted: indeed adding an excess of positive charge may lead to a ‘re-stabilization’ of the suspension. An excess of chitosan may lead to a positive charge being imparted to the colloidal particles in suspension, provoking again their repulsion. The presence of salts (salinity of solution, water hardness) may also impact the performance in coagulation–flocculation, by a charge screening effect. The quantities of coagulation–flocculation agent to be introduced within the suspensions are particularly low: Roussy *et al.* have observed that for slightly acid suspensions (pH of *ca* 5), chitosan concentrations of 0.1 mg L⁻¹ are enough to decrease the turbidity of suspensions prepared with initial bentonite contents of a few grams per litre below the required turbidity threshold (i.e. 5 FTU, formazine turbidity unit).³⁷

Treatment of coloured effluents

Coloured effluents (or tincture agents, pigments and dyes) are encountered often in the dissolved form (and not as colloids) and can present an affinity with chitosan. The most classical process to treat coloured effluents using chitosan is the adsorption of anionic compounds (typically those bearing sulfonic groups) on amine groups that are protonated in acidic medium using an electrostatic attraction or ion-exchange mechanism.^{38–41} This ion-exchange or electrostatic attraction mechanism may occur directly in solution between the dye and dissolved chitosan, this interaction resulting in the coagulation–flocculation of the dye. These mechanisms are at the basis of the coagulation and flocculation processes of dyes using chitosan.^{42–44} The influence of chitosan concentration is important (Fig. 6).

When the quantity of coagulant (therefore of cationic charges) reaches the stoichiometric ratio of anionic charges present on the dye, the residual dye concentration reaches a minimum. As soon as a supplementary addition of coagulant is introduced, the suspension re-stabilizes (excess of cationic charges) and the coagulant efficiency decreases. The optimum concentration (threshold concentration) is very accurate and the slope of the re-stabilization curve is sharper than that of the stabilization curve. As a consequence the optimization of the coagulant quantity is quite delicate. However, knowing the composition of the solution allows anticipation of polymer dosage.

Other tests performed on industrial effluents containing inks confirmed the usefulness of chitosan, and a combination with tannins proves very beneficial to improve the efficiency of the treatment.⁴⁵

Treatment of effluents containing organic suspensions

Chitosan may also be used to treat suspensions containing organic matter (in the food-processing domain as an example).³⁷ Using a biopolymer to treat organic suspensions leads naturally to the production of less toxic sludge than when using metal

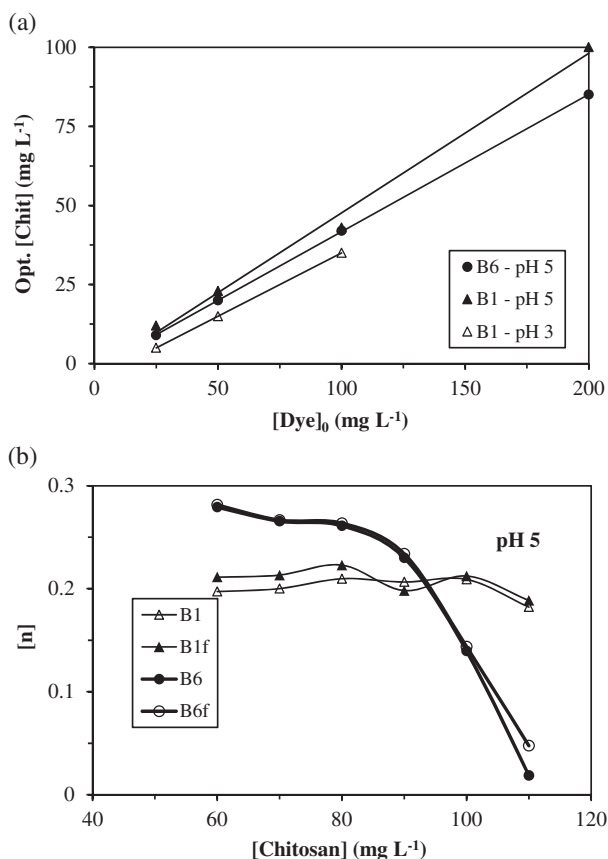


Figure 6. Effect of chitosan concentration on efficiency of coagulation–flocculation of reactive black 5 at pH=5 for two types of chitosan (DA: 89.5%; M_w : 308 300 g mol⁻¹ for B1 and 80 100 g mol⁻¹ for B6). The profiles are compared for water treatment without and with supernatant filtration (‘f’). (a) Variation in optimal concentration; (b) variation in stoichiometric ratio ($[n]$) between dye and amine groups at optimal dosage. (From Guibal and Roussy.⁴²).

salts or polyacrylamide. Consequently, the sludge produced using this process might be valorized. Considering mixtures of food-processing industry wastes (production of food flavours, wastes of mushrooms), the coagulation–flocculation process using chitosan was studied.^{46–48} The pH value has a strong effect on the efficiency of the treatment. Decreasing the pH down to 5 allows a decrease by half of the quantity of chitosan to be introduced. The effects of degree of deacetylation and molar mass depend on pH and chitosan concentration. Usual concentrations of chitosan close to 5 mg L⁻¹, in slightly acidic solutions, allow limiting the impact of chitosan characteristics. Chitosan has, naturally, an antimicrobial and bacteriostatic effect, due to the presence of protonated amine groups. This effect may be improved by imparting a quaternary amine function by grafting reagents. This property was used to synthesize a derivative of chitosan having both coagulation–flocculation and antimicrobial effects: a quaternary amine was grafted on carboxymethylchitosan.⁴⁹

COMPARISON BETWEEN ADSORPTION AND COAGULATION–FLOCCULATION

The principles of the interaction between biopolymer and solute are more or less analogous for the two processes or polymer uses: solid (adsorption) *versus* liquid (coagulation–flocculation). This analogy does not lead yet to similar performances as well

in terms of yield in using reactive groups as of kinetics.^{50,51} Maximal adsorption capacities (q_m , milligrams of solute per gram) can be converted (as a function of the number of reactive groups of solute) taking into account the ‘concentration’ of amine groups in the biopolymer in the form of a coefficient, $[n]$ (moles of function in solute per mole of amine), which can be compared to the optimal molar ratio between solute and amine groups in coagulation–flocculation. In a systematic way a comparison between $[n]_{\text{liquid}}$ and $[n]_{\text{solid}}$ shows a better use of amine groups when the chitosan is used in dissolved form. This may be correlated with the differences in availability and accessibility of amine groups in the two forms. Solid structure of chitosan is a compact one associated with the presence of hydrogen interactions between amine groups. There are both diffusional limits (due to structure compactness) and reactivity constraints (amine groups within inter-chain interactions). In contrast, when chitosan is used in dissolved form (liquid) in coagulation–flocculation, the protonated amine groups are accessible and available to interact with dyes or for metal ion complexation (Hg(II)).⁵⁰ Considering the kinetics, using the biopolymer in dissolved form also improves the reaction rate: for coagulation–flocculation, the process time unit is related to the fast stirring step (dispersion phase of a few minutes), the slow stirring step (around 20 minutes) and the sedimentation step (1–2 hours). On the whole, it is much shorter than the contact time necessary to reach equilibrium in the case of adsorption on solid chitosan (24–48 hours).

MODES OF APPLICATION

The preceding sections have pointed out the different parameters and mechanisms that can control sorption performance. This section also identifies some solutions for limiting their impact. These solutions involve chemical and/or physical modifications. Indeed, chitosan is a very versatile material. It is readily modified by grafting new functional groups to the hydroxyl or amine groups.⁵² Regarding physical versatility, the solubility properties of chitosan (due to the protonation of amine groups in acid solutions) make possible the synthesis of various forms of chitosan that can find specific applications in metal sorption. Figure 7 shows some examples of chitosan conditionings. Chitosan being dissolved in an acetic acid solution can be extruded, dropped into an alkaline solution to neutralize the acid and stabilize the biopolymer in an appropriate form: beads,⁵³ membranes,⁵⁴ fibres,⁵⁵ hollow fibres.^{56,57} These various conditionings allow the design of different systems for metal ion recovery.

Recently, new materials (highly macroporous foams/sponges) have been designed using chitosan or chitin foams for reactive filtration of metal-bearing solutions using chitosan alone,⁵⁸ or after incorporation of a specific ion-exchanger.² The sponge can also be used for treating accidental dumping of contaminated water: the water is absorbed by the sponge, the contaminant (radioactive caesium) is transferred to the ion-exchanger before the wringing of the sponge releases decontaminated water (with confinement of the radioelement into the ion-exchanger).

CONCLUSIONS

Chitosan is a biopolymer which may be more often used for treating wastewaters and removing pollutants, whatever their nature. Different processes are considered. Adsorption is very developed and much progress has been made during the last few years, allowing the planning of an industrial development in coming years

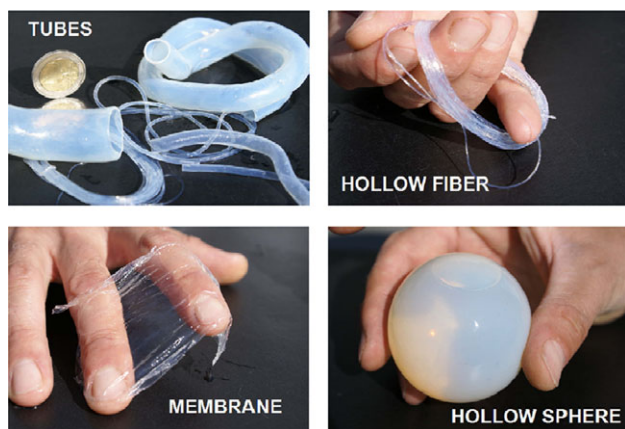


Figure 7. Examples of chitosan conditionings elaborated at Alès School of Mines.

as soon as the supply conditions and characterization of chitosan samples are ensured.

Coagulation–flocculation of substances in suspension (whether mineral or organic in nature) or dissolved substances (dyes) by chitosan is a very promising technique. At the same time it builds on (a) the acid–base characteristics of this biopolymer (unique due to its cationic properties in acidic media) to ensure the neutralization of ionic charges of anionic colloids (coagulation) and (b) the flocculating properties of this material (related to its high molecular weight). The dissolution of chitosan allows ‘opening’ the compact structure of the polymer, to make easier the availability and accessibility of the reactive amino groups and to improve their use as well in terms of equilibrium performances and in terms of kinetics of transfer or reaction time. Performances, in relation to process conditions, can significantly vary as a function of intrinsic characteristics of the biopolymer (degree of acetylation and molar mass). There are likely obstacles to its industrial use: material variability; difficulty of having reproducible and constant sources of chitosan may trouble industrial operators when it is time to substitute usual techniques with this new process. Moreover, although coming from abundant and renewable sources, the cost of this biopolymer limits its potential application to particular niches.

REFERENCES

- Sorlier P, Denuziere A, Viton C and Domard A, *Biomacromolecules* **2**:765–772 (2001).
- Vincent C, Barre Y, Vincent T, Taulemesse JM, Robitzer M and Guibal E, *J Hazard Mater* **287**:171–179 (2015).
- Perrano F, Vincent T, Robitzer M, Quignard F and Guibal E, *J Membr Sci* **329**:30–45 (2009).
- Kurita K, Sannan T and Iwakura Y, *J Appl Polym Sci* **23**:511–515 (1979).
- Philippova OE, Volkov EV, Sitnikova NL, Khokhlov AR, Desbrieres J and Rinaudo M, *Biomacromolecules* **2**:483–490 (2001).
- Schlick S, *Macromolecules* **19**:192–195 (1986).
- Ogawa K, Oka K and Yui T, *Chem Mater* **5**:726–728 (1993).
- Rhazi M, Desbrieres J, Tolaimate A, Rinaudo M, Vottero P and Alagui M, *Polymer* **43**:1267–1276 (2002).
- Wang X, Du Y, Fan L, Liu H and Hu Y, *Polym Bull* **55**:105–113 (2005).
- Ruiz M, Sastre AM and Guibal E, *React Funct Polym* **45**:155–173 (2000).
- Dzul Erosa MS, Saucedo Medina TI, Navarro Mendoza R, Avila Rodriguez M and Guibal E, *Hydrometallurgy* **61**:155–167 (2001).
- Guibal E, Milot C and Tobin JM, *Ind Eng Chem Res* **37**:1454–1463 (1998).
- Jaworska M, Sakurai K, Gaudon P and Guibal E, *Polym Int* **52**:198–205 (2003).
- Jaworska M, Kula K, Chassary P and Guibal E, *Polym Int* **52**:206–212 (2003).

- Gibbs G, Tobin JM and Guibal E, *J Appl Polym Sci* **90**:1073–1080 (2003).
- Saha TK, Ichikawa H and Fukumori Y, *Carbohydr Res* **341**:2835–2841 (2006).
- Rinaudo M, *Prog Polym Sci* **31**:603–632 (2006).
- Dotto GL, Pinto LAA, Hachika MA and Knani S, *Food Chem* **171**:1–7 (2015).
- El-Shafey AIA, Moustafa HY, El-Masry AM and Hassan SA, *J Appl Polym Sci* **131**:40458 (2014).
- Caroni ALPF, de Lima CRM, Pereira MR and Fonseca JLC, *J Colloid Interface Sci* **340**:182–191 (2009).
- Carvalho TO, Matras AEB, Braga LR, Evangelista SM and Prado AGS, *J Therm Anal Calorim* **106**:475–481 (2011).
- Pereira KAA, Osorio LR, Pereira Silva M, Soares Sousa K and da Silva Filho EC, *Mater Res* **17**:141–145 (2014).
- Antunes M, Esteves VI, Guegan R, Crespo JS, Fernandes AN and Giovanella M, *Chem Eng J* **192**:114–121 (2012).
- Liu ZH, Kanjo Y and Mizutani S, *Sci Total Environ* **407**:731–748 (2009).
- Bicchi C, Schilirò T, Pignata C, Fea E, Cordero C, Canale F *et al.*, *Sci Total Environ* **407**:1842–1851 (2009).
- Sun K, Gao B, Zhang ZY, Zhang GX, Liu XT, Zhao Y *et al.*, *Chemosphere* **80**:709–715 (2010).
- Tsai WT, Hsu HC, Su TY, Lin KY and Lin CM, *J Colloid Interface Sci* **299**:513–519 (2006).
- Hameed BH, *Colloids Surf A* **307**:45–52 (2007).
- Pan J, Yao H, Li XX, Wang B, Huo P, Xu W *et al.*, *J Hazard Mater* **190**:276–284 (2011).
- Julinova M and Slavik R, *J Environ Manage* **94**:276–284 (2012).
- Crini G, *Prog Polym Sci* **30**:38–70 (2005).
- Chen CY and Chung YC, *J Environ Sci Health A* **41**:235–248 (2006).
- Salim CJ, Liu H and Kennedy JF, *Carbohydr Polym* **81**:640–644 (2010).
- Chen CY and Chung YC, *Environ Eng Sci* **24**:834–841 (2007).
- Carneiro RTA, Taketa TB, Gomes Neto RJ, Oliveira JL, Campos EVR, de Moraes MA *et al.*, *J Environ Manage* **151**:353–360 (2015).
- Guibal E, Dempsey BA, Van Vooren M and Roussy J, *Sep Sci Technol* **41**:2487–2514 (2006).
- Roussy J, Van Vooren M, Dempsey BA and Guibal E, *Water Res* **39**:3247–3258 (2005).
- Szygula A, Guibal E, Ruiz M and Sastre AM, *Colloids Surf A* **330**:219–226 (2008).
- Szygula A, Guibal E, Ruiz M and Sastre AM, *Int J Chem Eng* **1**:183–202 (2008).
- Szygula A, Guibal E, Palacin MA, Ruiz M and Sastre AM, *J Environ Manage* **90**:2979–2986 (2009).
- Barron-Zambrano J, Szygula A, Ruiz M, Sastre AM and Guibal E, *J Environ Manage* **91**:2669–2675 (2010).
- Guibal E and Roussy J, *React Funct Polym* **67**:33–42 (2007).
- Jiang X, Cai K, Zhang J, Shen Y, Wang S and Tian X, *J Hazard Mater* **185**:1482–1488 (2011).
- Wang YF, Gao BY, Yue QY, Wang Y and Yang ZL, *Bioresour Technol* **113**:265–271 (2012).
- Roussy J, Chastellan P, Van Vooren M and Guibal E, *Water SA* **31**:369–376 (2005).
- Dong C, Chen W and Liu C, *Bioresour Technol* **170**:239–247 (2014).
- Fast SA and Gude VG, *J Ind Eng Chem* **24**:153–160 (2015).
- Roussy J, Van Vooren M and Guibal E, *J Appl Polym Sci* **98**:2070–2079 (2005).
- Yang Z, Degorce-Dumas JR, Yang H, Guibal E, Li A and Cheng R, *Environ Sci Technol* **48**:6867–6873 (2014).
- Guibal E, Touraud E and Roussy J, *World J Microbiol Biotechnol* **21**:913–920 (2005).
- Guibal E, Dempsey BA, Van Vooren M and Roussy J, *Sep Sci Technol* **41**:2487–2514 (2006).
- Varma AJ, Deshpande SV and Kennedy JF, *Carbohydr Polym* **55**:77–93 (2004).
- Guibal E, Milot C and Roussy J, *Water Environ Res* **71**:10–17 (1999).
- Modrzejewska Z and Kaminski W, *Ind Eng Chem Res* **38**:4946–4950 (1999).
- Agboh QC and Qin Y, *Polym Adv Technol* **8**:355–365 (1997).
- Vincent T and Guibal E, *Solvent Extr Ion Exch* **18**:1241–1260 (2000).
- Vincent T and Guibal E, *Ind Eng Chem Res* **40**:1406–1411 (2001).
- Allouche FN, Guibal E and Nameri N, *Colloids Surf A* **446**:224–232 (2014).