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## REVIEW

# Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan



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## KEYWORDS

Polymer assisted  
ultrafiltration;  
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Membrane;  
Metals;  
Wastewater

**Abstract** Polymer assisted ultrafiltration (PAUF) is a relatively new process in water and wastewater treatment and the subject of an increasing number of papers in the field of membrane science. Among the commercial polymers used, poly(ethyleneimine) and poly(acrylic acid) are the most popular to complex numerous metal ions. Recently, there is an increasing interest in the use of chitosan, a natural linear polymer, as chelating agent for complexing metals. Chitosan has a high potential in wastewater treatment mainly due to its polyelectrolyte properties at acidic pH. The objectives of this review are to present the PAUF process and to highlight the advantages gained from the use of chitosan in the process of complexation–ultrafiltration. For this, a PAUF-based literature survey has been compiled and is discussed. From these data, chitosan, a biopolymer that is non-toxic to humans and the environment, is found to be effective in removing metal ions and exhibits high selectivity. It might be a promising polyelectrolyte for PAUF purposes.

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## Nomenclature

### Acronyms

CA	cellulose acetate
CMC	carboxymethylcellulose
DA	degree of acetylation
DD	degree of deacetylation
EDTA	ethylenediaminetetraacetic acid
LPR	liquid-phase polymer retention
MW	molecular weight
MWCO	molecular weight cut-off
NF	nanofiltration
PA	poly(acrylic acid)
PAA	poly(allylamine)
PAN	poly(acrylonitrile)
PAUF	polymer-assisted ultrafiltration
PF	polymer filtration
PEI	poly(ethylenimine)
PES	poly(ether sulphone)

PEUF	polymer-enhanced ultrafiltration
PS	poly(sulphone)
PSA	poly(sulphonamide)
PSU	polymer-supported ultrafiltration
PVA <sub>1</sub>	poly(vinylalcohol)
RC	regenerated cellulose
SPA	sodium poly(acrylate)
UF	ultrafiltration
WFD	water framework directive

### Symbols

$J_p$	permeate volume flux
$J_w$	water flux
$R_M$	rejection rate
$m_p/m_M$	molar ratio between polymer and metal
$w_p/w_M$	mass ratio between polymer and metal
$m'_{fg}/m'_M$	molar ratio between functional groups and metal

## 1. Introduction

Industrial waste water and especially metal-containing effluent has, for twenty years or so, become a major environmental preoccupation. The main reason for this is the acknowledged toxicity of certain chemicals it can contain. Metalworking industries using or producing metals (metallurgy and hydro-metallurgy, surface treatment and finishing, the automobile and other mechanical industries, mining and associated activities, etc.) generate increasingly large volumes of polycontaminated and notably metal-containing effluents.

In order to respect current legislation, waste water is generally decontaminated by physico-chemical treatments. Yet, in spite of this, the discharge water still contains a significant pollutant load, which finishes up in the environment (Sancey et al., 2011). Current tightening of the regulations controlling the discharge of metals is making it necessary for industry to set up decontamination processes that are increasingly specific and efficient, the aim being to tend towards zero pollution outflow. In addition, the techniques used must, in a context of sustainable development and better water management, enable reuse of the treated water and also offer the possibility of recycling and/or recovery of the metal ions.

Conventional processes for the treatment of metal-containing effluent, such as for instance precipitation/decantation,

liquid–liquid extraction, but also pressure-driven membrane processes and electro-membrane processes, do not always simultaneously satisfy both legislative and economic criteria. In this context, coupling of processes can then be a promising alternative to the conventional approaches used by industry (Barakat, 2011; Fu and Wang, 2011). The aim of coupling processes is to finish off the conventional treatment. Possible configurations depend on the aim of the finishing step (better purification, recycling the water or zero pollution outflow). The pair complexation–ultrafiltration is one of these finishing treatments. In this case we speak of polymer-assisted ultrafiltration (PAUF) process which presents the advantages of (i) being able to separate ions or concentrate them, without affecting the other components in the solution, by bringing chemical affinity mechanisms into play, (ii) processing larger volumes of solution than with NF, liquid–liquid extraction and ion exchange, and (iii) allowing the regeneration of complexing agent for reuse.

The principle of complexation–ultrafiltration is based on a sequence of steps with complexation of metal ions by a complexing polymer (generally a synthetic polyelectrolyte or an exchanger of soluble ions) and a step involving the rejection of the complex formed by means of an UF membrane. Unlike free ions which cross the membrane, the macroligand/ion complex is held back. This hybrid process generates one solution

that is purified and one that has a high concentration of complexes. Two kinds of metal ions, both smaller than the membrane pore diameter, are defined: free metal ions in solution, whose movement across the membrane is not restricted and metals bound to polymer, which cannot cross the membrane. It is worth mentioning that in PAUF processes the retention of a species of interest mainly depends on its interaction with the macromolecular chains and is independent of its size (Rivas et al., 2011).

Natural polymers, and in particular polysaccharides, have attracted the attention of numerous researchers over the last decades, for use in water treatment, benefitting from the vast diversity of substances produced by living organisms (Varma et al., 2004; Kurita, 2006). Among them, we can mention chitosan, a modified biopolymer obtained from chitin. Chitin is a polysaccharide that is predominantly of marine origin, and is the most abundant natural polysaccharide after cellulose. Chitosan has been the focus of a large number of water treatment studies (Crini and Badot, 2008; Crini et al., 2009) as it is a biopolymer with excellent properties of complexation, flocculation, chelation, separation and adsorption of a whole range of pollutants, even when they are present as traces. The polycationic nature of chitosan in acid medium (no other natural polymers have this property) and its great versatility, open the way to numerous applications in water treatment. It is a material that can be used as a solid in processes of chelation and/or adsorption, or in the form of a solution in processes of coagulation/flocculation or PAUF. The aim of the current review is to present the state of the art of chitosan use in PAUF in the soluble state. We start the review with some general considerations. Then, we present the PAUF process and the use of chitosan as a complexing agent to decontaminate aqueous solutions polluted by metals, as illustrated by the numerous studies that have appeared in the literature. Finally, we report the reasons that have encouraged the use of chitosan and the mid-term perspectives.

## 2. General considerations

From the environmental point of view, the chemical compounds that are of greatest current concern are those which, either by their presence or their accumulation, can have a toxic or an inhibitory effect on living organisms. Among these compounds, metals have been largely investigated due to increasingly stringent standards worldwide. From 1976, the European Union included metals and their compounds in two lists of priority substances for surface waters: the first was known as 'The Black List', a list of high-priority hazardous substances (e.g. Cd, Hg, Pb), which must no longer be discharged, and the second 'The Grey List', or list of priority hazardous substances (e.g. Ni, Cr, As, Cu, Zn) whose levels in pollution must be reduced (Directive 76/464/EEC of 4 May 1976). Although considerable efforts have been made by the industrial sector over the last 20 years, water pollution remains a significant concern. The main environmental problem facing industrial plants is the high pollution load of the effluent they generate. It is known that industrial wastewaters containing metals, and in particular complexed metals, are difficult to process as they contain not only the metals but also a range of other organic and mineral pollutants, some of which can react with each other. In addition, a specific point that

should be born in mind is the extreme difficulty to remove metals present at very low concentrations from polycontaminated effluents that are heterogeneous and variable in nature. In Europe, as the industrial sector has to cope with an increasingly strict framework (Water Framework Directives WFD 2000/60/EC, 2000 and 2003/53/EC, 2003), it has to look towards new treatment methods to decrease the flow of pollution still present in discharge water, the aim being to tend towards zero pollution outflow. Among the emerging methods, PAUF processes, might be a promising alternative for the treatment of polycontaminated effluents containing metals.

## 3. Polymer assisted ultrafiltration processes

### 3.1. Ultrafiltration process

Ultrafiltration is based on the use of porous membranes with a MWCO in the range of 1–300 kDa (pore sizes between ~2 and 100 nm) and requires the application of transmembrane pressure differences of between 3 and 10 bars. UF is widely used to concentrate solutions of macromolecules by only letting the molecules of solvent and solutes of low MW through the membrane. Steric effects (dependent on the relative sizes of the pores and the molecular species) are central to the mechanisms of exclusion by the UF membrane. However, the effects of electric charge resulting from the chemical properties of the membrane material when the molecular species in solution are charged must also be taken into account. Indeed, most membranes, whether organic or inorganic acquire an electrical surface charge when brought into contact with a polar medium such as an aqueous solution. The origin of this surface charge can be the acidic or basic properties of the surface moieties, this is the case of organic membranes bearing, for instance, amide, carboxyl or sulphone groups, or amphoteric properties of the surface sites including hydroxyl functions at the surface of the metal oxides used to form ceramic membranes (Szymczyk and Fievet, 2007; Larchet and Pontié, 2008). These interactions can be put to good use to separate species of similar size but with different charges.

UF has become the norm in many industrial sectors such as water treatment (clarification–disinfection of drinking water) (Maurel, 1989), depollution of waste water by membrane bioreactors (Van Kaam et al., 2006; Hernandez, 2006), the dairy industry (standardisation of the level of proteins in milk (Nyström et al., 1998), concentration of whey proteins (Glover, 1985)), but also in the automotive industry (treatment of paint baths by electrophoresis (Maurel, 1989), treatment of degreasing baths (Li et al., 2006), destabilisation of machining oil emulsions). Note that applications involving the separation or concentration of ionic species are lacking – this can be understood by considering the size of the pores in UF membranes. However, the range of utilisation of UF can be enlarged towards solutes smaller than the pores in the membrane by means of pretreatments such as micellisation (Yurlova et al., 2002) or complexation (Kryvoruchko et al., 2002; Mimouné et al., 2007).

### 3.2. Complexation–ultrafiltration processes

The notion of complexation–ultrafiltration was first introduced in 1968 by Michaels (1968a,b). As an UF membrane

stops macromolecules but lets ions through easily, the novel idea was to “artificially” increase the size of the ions by complexing them onto a polymer that would be retained by the membrane. Thus, by adding macromolecular chains bearing ligand functions (called macroligands) to a metal-containing solution, the product of UF is a concentrated solution of complexed metal ions in the retentate and a metal-free permeate. This assumes that the macroligand–metal ion complexes are stable and rejected by the membrane, since cation rejection assumes not only rejection of the polymer but also stability of the complex. This technique appears under different names: PAUF, polymer or polyelectrolyte enhanced ultrafiltration (PEUF), polymer supported ultrafiltration (PSU), liquid-phase polymer-based retention (LPR), enhanced ultrafiltration, or simply polymer filtration (PF) (Geckeler et al., 1988; Canizares et al., 2002; Palencia et al., 2009; Rivas et al., 2009, 2011).

The main advantages of this hybrid process are that (i) the installations are compact with low operating costs since the energy consumption of the process is reduced compared to that of the alternatives (i.e. evaporation, NF, etc.), (ii) separation is efficient and selectivity good, (iii) the complexing agents are chosen so as to be easily regenerated. Table 1 reports other advantages and the main disadvantages. The performance of the double technique complexation–ultrafiltration depends on the rejection of both the macromolecules and the metal ions. In general, for a given MW, the retention of the flexible macromolecules in solution decreases as the pressure is increased. This can be explained by the fact that when the macromolecules are subjected to a transversal pressure gradient in the vicinity of the pore entrances, they are stretched out along the direction of flow and can then enter the pores. Sudareva et al. (1991) suggested that the existence of different conformations and/or the effect of the polarisation layer would contribute to this effect. Rejection is therefore not simply dependent

on MW. Staub et al. (1984) showed that the charge of the macromolecule strongly influences rejection and the closer the size of the macromolecule to the size of the pore, the greater the influence of the charge. Concerning metal ion binding, the stability of the complexes (at equilibrium) is closely linked to various parameters such as pH, ligand concentration, ionic strength of the solution (presence of salts or other ligands) and temperature. In particular, the pH is important since its increase can lead to the formation of metal hydroxides and this reaction will be in competition with the complexation of the cations by the polymer. In addition, the complexing properties of the polyelectrolytes depend on the pH. In general, an excess of ligand is used with respect to the metal cation since this improves binding. The limiting factors here are then the viscosity of the solution and the cost of the process as a whole.

### 3.3. Polymers used in PAUF processes

There are three main categories of water-soluble polymer able to form tight complexes with metal cations, namely (i) polyelectrolytes with amine functions [poly(ethyleneimine) (PEI), poly(allylamine) (PAA)], carboxyl functions [poly(acrylic acid) (PA), carboxymethylcellulose (CMC)] or hydroxyl functions [poly(vinylalcohol) (PVA<sub>i</sub>)] (Barron-Zambrano et al., 2002; Pastor et al., 2002; Islamoglu and Yilmaz, 2006; Petrov et al., 2002; Kryvoruchko et al., 2004; Molinari et al., 2004a,b, 2006a,b, 2008; Kuncoro et al., 2005; Cojocar and Zakrzewska-Trznadel, 2007), (ii) polyelectrolytes modified by complexing ligands [modified PEI, diethylaminoethylcellulose, etc.] (Trivunac and Stevanovic, 2006) and (iii) synthetic copolymers obtained by copolymerisation of vinyl monomers (Juang and Chiou, 2000a,b; Molinari et al., 2004b, 2006b). Additional novel natural macroligands such as pectin and chitosan have appeared in the last few years (Table 2).

**Table 1** Main advantages and disadvantages, and remarks for PAUF process.

Advantages	Disadvantages	Remarks
<ul style="list-style-type: none"> <li>• Removal or recovery of metal ions in a homogenous phase, even at low concentrations</li> <li>• A useful hybrid approach to concentrate valuable metals</li> <li>• Low energy consumption</li> <li>• High removal efficiency</li> <li>• High separation selectivity</li> <li>• Interesting kinetics due to rapid reactions</li> <li>• Various polymers commercially available</li> <li>• A large choice of membranes with excellent chemical, mechanical and thermal stabilities</li> <li>• A reversible process: possible regeneration and reuse of the chelating polymer</li> </ul>	<ul style="list-style-type: none"> <li>• An emerging process in wastewater purification</li> <li>• Choice of the proper water-soluble polymer</li> <li>• Requirement for a detailed prior technical study</li> <li>• Polymer dose variable</li> <li>• Price of membranes</li> <li>• Possible effect of other chemical species present in the solution to be treated</li> </ul>	<ul style="list-style-type: none"> <li>• Complexation–ultrafiltration not yet applied on an industrial scale</li> <li>• A hybrid process promises to be a suitable technique for the treatment of wastewater with the changes in legislation concerning priority hazardous substances such as metal ions and their compounds</li> <li>• Commercially available polymers are applied rather than tailored materials</li> <li>• Important role of the pH in the formation of chelates and precipitates</li> <li>• Need to define the role of the membrane in terms of hydrophobic or hydrophilic interactions</li> <li>• The numerous works in polymer chemistry (chemical derivatization of macromolecular chains, dendritic polymers, etc.) provide novel opportunities to develop chelating agents for environmental purposes</li> </ul>

**Table 2** Examples of polymers used for complexation-ultrafiltration coupling.

Characteristics of the polymer				Experimental conditions					Reference(s)	
Polymer	Origin	DD <sup>a</sup>	MW <sup>b</sup>	Membrane	MWCO <sup>c</sup>	Metal(s)	[Metal] <sup>d</sup>	[polymer] <sup>d</sup> or $m_p/m_M$ <sup>c</sup> or $w_p/w_M$ <sup>f</sup> or $m'_{fg}/m'_M$ <sup>g</sup>		pH
PEI	Synthetic		70,000	RC	10	Cd <sup>2+</sup>	112	300	3–9	Li et al. (2008)
PEI	Synthetic		60,000	PES	10, 30	Cu <sup>2+</sup> , Ni <sup>2+</sup>	50	150–300	3.5–9.5	Molinari et al. (2006a, 2008)
PEI	Synthetic		50,000	PES	30	Ni <sup>2+</sup>		$m_p/m_M = 2–10$	3–9	Shao et al. (2013)
PEI	Synthetic		750,000	RC	5	Co <sup>2+</sup>	40–80	36–414	4, 5.2, 6.4	Cojocar et al. (2009)
PEI	Synthetic		50,000		5	Hg <sup>2+</sup>	90.1–832.8	1802–186.7	5	Uludag et al. (1997)
PEI	Synthetic		25,000	Carbon-zirconia composite	10	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup>	200	5000	3–6	Canizares et al. (2002)
PEI	Synthetic		25,000	Carbon-zirconia composite	15	Cu <sup>2+</sup>	500	10,000	3–6	Canizares et al. (2002)
PAA	Synthetic		100,000	PES	3, 10, 100	Ni <sup>2+</sup>	21	0.05 M	5	Moreno-Villoslada and Rivas (2003)
PSS	Synthetic		100,000	PES	3,10,100	Cd <sup>2+</sup>	21	0.02 M	5	Moreno-Villoslada and Rivas (2003)
PA	Synthetic					Pb <sup>2+</sup>				Zhang and Xu (2003)
PA	Synthetic		100,000; 15,000	PES	10	Co <sup>2+</sup>	10	$m'_{fg}/m'_M = 1–10$	3–6	Dambies et al. (2010)
PA	Synthetic		250,000	PS	75	Mn <sup>2+</sup>	1	$m'_{fg}/m'_M = 0–100$	4–9	Han et al. (2007)
PA	Synthetic		240,000	Ceramic	10	Pb <sup>2+</sup> , Cd <sup>2+</sup>	25	$w_p/w_M = 0–6.9$	2–5	Canizares et al. (2004)
PA	Synthetic		250,000	Carbon-zirconia composite	10	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup>	500	5000–10,000	3–6	Canizares et al. (2002)
SPA	Synthetic		30,000,000	PES	30	Ni <sup>2+</sup>		$m_p/m_M = 2–10$	3–9	Shao et al. (2013)
SPA	Synthetic		30,000	PS		Ni <sup>2+</sup> , Zn <sup>2+</sup>		$m_p/m_M = 10–100$	2–10	Korus et al. (1999)
SPA	Synthetic		250,000	PS	6	Hg <sup>2+</sup> , Cd <sup>2+</sup>	10–1,500	40–5000	5–8	Zeng et al. (2009a,b)
PVA <sub>1</sub>	Synthetic		15,000; 49,000; 100,000	PES	50	Cu <sup>2+</sup>	6.3–63	500–2000	6.5–12.5	Mimoune and Amrani (2007)
PVA <sub>1</sub>	Synthetic		9000–10,000	RC	5	Co <sup>2+</sup>	10–50	$m_p/m_M = 2–12$	4.5–6.5	Uzal et al. (2011)
PVA <sub>1</sub>	Synthetic		15,000–100,000	PES	50	Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>3+</sup> , Ag <sup>+</sup>	$2.5 \times 10^{-4}$ – $5 \times 10^{-4}$ mol L <sup>-1</sup>	1500	7.1	Mimoune et al. (2007)
PDDAC	Synthetic		200,000–350,000	RC	10	Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	80–1,190	2000	2.0–10.5	Juang and Chiou (2001)
DEAEC	Synthetic			PSA	13	Zn <sup>2+</sup> , Cd <sup>2+</sup>	50	500	2–9	Trivunac and Stevanovic (2006)
CMC	Synthetic			PES	10	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>3+</sup>	10–100	0–1000	3–9	Barakat and Schmidt (2010)
CMC	Synthetic			PAN	10	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> , Ni <sup>2+</sup> , Fe <sup>2+</sup> , Mn <sup>2+</sup>	0.2–200	$m_p/m_M = 1, 2, 6$	2, 5, 8	Petrov and Nenov (2004)
Pectin	Citrus fruits			PS	500	Cr <sup>3+</sup> , Cr <sup>6+</sup>	10	$w_p/w_M = 0.01–0.25$	3–11	Aroua et al. (2007)
Alginate			294,000	PS	20	Cu <sup>2+</sup>	2, 4	50	2–6	Benbrahim et al. (1998)
Chitosan			170	CA	30, 100	Cu <sup>2+</sup>	5–30	50–300	3–8	Verbych et al. (2006)
Chitosan	Crab shells	79	70,000	Ceramic	50	Cd <sup>2+</sup>	10–54	0–500	2.5–8.5	Llorens et al. (2004)
Chitosan	Crab shells	79	70,000		50	Cd <sup>2+</sup>	2.2–56	$m_p/m_M = 35–250$	4–9	Sabaté et al. (2006)
Chitosan						Cu <sup>2+</sup> , Ni <sup>2+</sup>				Taha et al. (1996)
Chitosan			67,000	PES	3,10	Cu <sup>2+</sup> , Ni <sup>2+</sup>	32 (Cu <sup>2+</sup> ) and 29 (Ni <sup>2+</sup> )	0.01 mol L <sup>-1</sup>	3–12	Zamariotto et al. (2010)
Chitosan	Lobster shells		410,000	RC	10	Cu <sup>2+</sup> , Zn <sup>2+</sup>	260 (Cu <sup>2+</sup> ) and 1,000 (Zn <sup>2+</sup> )	150–2010	2–10.5	Juang and Chiou (2000a,b)

Table 2 (continued)

Characteristics of the polymer		Experimental conditions			Reference(s)					
Polymer	Origin	DD <sup>a</sup>	MW <sup>b</sup>	Membrane	MWCO <sup>c</sup>	Metal(s)	[Metal] <sup>d</sup>	[polymer] <sup>d</sup> or $m_p/m_M$ <sup>e</sup> or $w_p/w_M$ <sup>f</sup> or $m'_{fg}/m'_M$ <sup>g</sup>	pH	
Chitosan	Lobster shells		170,000	CA	30–100	Cu <sup>2+</sup> , Pb <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup>	10–100	50–300	5–9	Verbych et al. (2005)
Chitosan	Crab shells			PS	10	As <sup>3+</sup> , As <sup>5+</sup>	1.0–1.4	4800		Lin et al. (2008)
Chitosan	Lobster shells	87	41,000	PS	500	Cr <sup>3+</sup> , Cr <sup>6+</sup>	10	0.05%	3–11	Aroua et al. (2007)
Chitosan	Lobster shells			RC	10–30	Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	80–1190	2000	2.5–10.5	Juang and Chiou (2001)

<sup>a</sup> Degree of deacetylation.

<sup>b</sup> Molecular weight (Da).

<sup>c</sup> Molecular weight cut-off (kDa).

<sup>d</sup> Concentration expressed in mg L<sup>-1</sup> unless otherwise stated.

<sup>e</sup>  $m_p/m_M$ : molar ratio between polymer and metal.

<sup>f</sup>  $w_p/w_M$ : mass ratio between polymer and metal.

<sup>g</sup>  $m'_{fg}/m'_M$ : molar ratio between functional groups and metal.

### 3.4. Why use chitosan as polyelectrolyte?

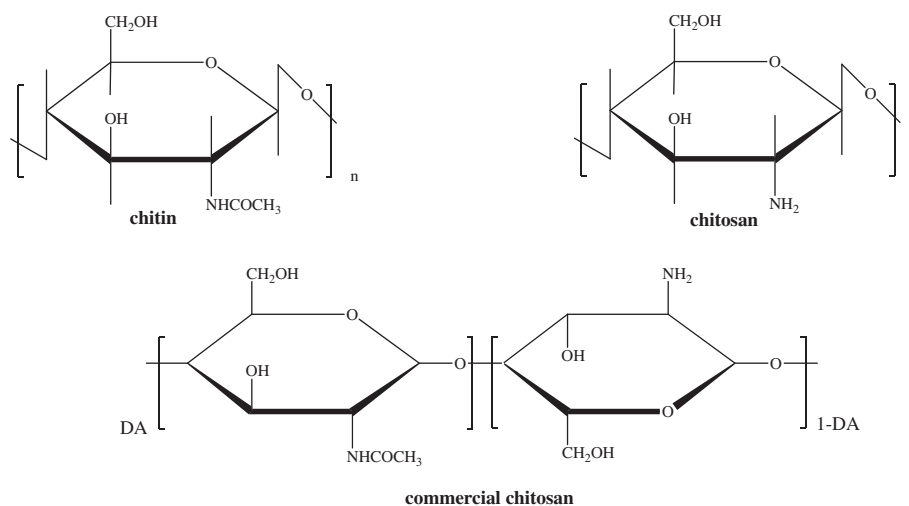
The majority of commercial water-soluble polymers are derived from petroleum-based raw materials synthesised using processing chemistry that is not always safe or environmentally friendly. Today, there is growing interest in developing natural low-cost alternatives to synthetic polymers. In addition, in a global context of seeking to reduce the mass of waste generated, recycling of manufacturing by-products is one of today's priorities in sustainable development.

Chitosan is obtained from chitin, a natural waste from shellfish (e.g. shrimp, crab, squid, lobster shells). It is cheap, abundant and ecologically relevant (Crini and Badot, 2008; Crini et al., 2009). Fig. 1 gives the stereochemical structure of commercial chitosan. Chitosan presents multiple physical-chemical and polyelectrolytic properties at acid pH (Table 3). Use is made of all these properties in PAUF.

Each commercial batch of chitosan is characterised by its molecular weight (MW), degree of acetylation (DA) or degree of deacetylation (DD), and crystallinity. As with PEI, the most suitable polymer is chosen for each separation. The structure of chitosan presents amine and acetamide moieties (Fig. 1) as well as, of course, numerous hydroxyl groups conferring a strong hydrophilic character. In acid media, the protonation of the amine functions makes the polymer soluble and thus it behaves as a polyelectrolyte (pKa ~6.3 depending on the DD). Note that it is the only cationic polymer known among all biopolymers. The advantages of using chitosan in its dissolved form arise from the availability and accessibility of the amine functions. Dissolving the polymer leads to the appearance of repulsion forces between the macromolecular chains, allowing them to unravel and make the internal sites accessible (Juang and Chiou, 2000a; Guibal, 2004; Crini and Badot, 2008). The intermolecular hydrogen bonding that occurs in the solid state is repressed in solution: this also enhances the availability of the internal amine moieties for interaction with metal cations.

The affinity of chitosan for transition metal ions has been widely studied, and examples of selected affinity series are reported in Table 4. Irrespective of the type of material used, the results can mainly be explained by the interactions occurring between the amine functions of the chitosan and the metal ions. For instance, Krajewska (2001), studying the diffusive permeability coefficients of 15 metal ions through chitosan membranes, showed that the rank order of the coefficients (Cu<sup>2+</sup> < Ni<sup>2+</sup> < Zn<sup>2+</sup> < Mn<sup>2+</sup> < Pb<sup>2+</sup> < Co<sup>2+</sup> < Cd<sup>2+</sup> < Ag<sup>+</sup>) corresponds to the metal ion-polymer affinity sequence, confirming chelation of these ions by chitosan. Kaminski et al. (2008), studying interactions of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cr(VI) adsorbed onto chitosan beads, reported that at low concentrations the sequence of adsorption was Cu<sup>2+</sup> > Zn<sup>2+</sup> > Cr(VI), confirming that chitosan exhibited a strong selectivity towards copper, but at high concentrations the series of metal selectivity was different (Zn<sup>2+</sup> > Cu<sup>2+</sup> > Cr(VI)). Similar results were previously reported by Vold et al. (2003).

However, some issues do arise with the use of chitosan. In a PAUF process, its use requires addition of acid to enable complete dissolution in water because a minimum amount of -NH<sub>3</sub><sup>+</sup> groups is needed to prevent the formation of particles and/or flocculation. Thus, it is important to find the practical conditions needed to prepare solutions. Moreover, a further



**Figure 1** Chemical structure of chitin [poly(*N*-acetyl-β-D-glucosamine)], chitosan [poly(D-glucosamine)] and commercial chitosan (a copolymer characterised by its average degree of acetylation (DA)).

**Table 3** Intrinsic physical–chemical and polyelectrolyte properties of chitosan.

Physical–chemical properties	Polyelectrolyte (at acidic pH)
<ul style="list-style-type: none"> <li>• Linear amino-polysaccharide with high nitrogen content</li> <li>• Rigid D-glucosamine structure</li> <li>• Numerous reactive groups</li> <li>• High crystallinity</li> <li>• Hydrophilicity</li> <li>• Capacity to form hydrogen bonds</li> <li>• Weak base (powerful nucleophile, <math>pK_a \sim 6.3</math>)</li> <li>• Soluble in dilute acidic aqueous solutions</li> <li>• Insoluble in water and organic solvents</li> <li>• Ionic conductivity</li> </ul>	<ul style="list-style-type: none"> <li>• Cationic biopolymer with high charge density (one positive charge per glucosamine residue)</li> <li>• Chelating and complexing properties</li> <li>• Flocculating agent</li> <li>• Entrapment and adsorption properties</li> <li>• Filtration and separation</li> <li>• Film-forming ability</li> <li>• Adhesivity</li> </ul>

disadvantage is related to the difficulty of finding reproducible sources of chitosan, with a suitable MW (depending on the membrane MWCO).

#### 4. A brief review of the literature on metal removal by chitosan using PAUF processes

As with any PAUF process, the rejection of metals by complexing with chitosan depends on both the characteristics of the biopolymer (origin, DA, average molecular weight, polydispersity) and the ions to be separated (size and charge of the metal ion, type of counter ion), the experimental conditions (pH, ionic strength, nature of salts, temperature), behaviour of chitosan (solubility, crystallinity), and the characteristics of the filtration system (membrane cut-off threshold, membrane material, hydrodynamic conditions). This potentially broad experimental diversity makes any comparison between studies rather problematic. The reader is therefore encouraged to refer to the original papers for complete information on the experimental conditions in the filtration systems used.

Polymers which generally cover a whole range of molecular weights (polydispersity) must first be purified to remove the

molecular weight fraction that is below the MWCO of the membrane. In most cases, about 25% of a typical sample of chitosan with mean molecular weight of 410 kDa will in fact cross a membrane with a MWCO of 10 kDa (Juang and Chiou, 2000a). The removal of the low molecular weight chitosan fraction may be time consuming but it leads to substantial gains in metal rejection (Llorens et al., 2004).

Juang and Chiou (2000a) carried out a detailed study of 410 kDa chitosan. In acid medium,  $J_p/J_w$  was found to be fourfold higher for a 10 kDa MWCO membrane than for 30 kDa membrane even though 30% of the chitosan crossed both membranes. The sharp drop in the relative flux of permeate observed for the 30 kDa MWCO membrane can be explained by the polarisation concentration and the formation of a gel layer. The authors observed a well known reduction of  $J_p/J_w$ , which was halved, on raising the pH of the medium from acid to neutral. This drop of  $J_p/J_w$  can be observed for all polyamines as the solution pH changes from acid to one where the polymer is neutral. The neutralisation of the polyamines reduces their stability in solution owing to the reduction of their electrostatic repulsion – this results in reduced solubility and precipitation. The precipitation of chitosan



**Table 4** Examples of the binding strength of chitosan for different metals.

Metals	References
$\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$	Muzzarelli (1973)
$\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$	Mitani et al. (1992)
$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+}$	Yang and Zall (1984)
$\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$	Inoue et al. (1993)
$\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$	Ishii et al. (1995)
$\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}, \text{Ca}^{2+}$	Rhazi et al. (2002)
$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$	Kaminski et al. (2008)
$\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+}$	Huang et al. (1996)
$\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Ni}^{2+} > \text{Ag}^+ > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+}$	Koshijima et al. (1973)

can plug the membrane pores most effectively. In contrast, Juang and Chiou (2000a,b) observed a strong decrease of  $J_p/J_w$  tending towards 1 above pH 7. This was thought to be due to the deposition of insoluble polymer not on the membrane, but elsewhere.

#### 4.1. Free metal cations

Chitosan-based PAUF is currently in rapid expansion. The three main advantages often mentioned are (i) the good chelating capacity of the chitosan chains for numerous metal ions, especially those used in the surface treatment industry (the capacity is due to its high charge density) (ii) the excellent selectivity of the separations (Volchek et al., 1993; Taha et al., 1996; Chauffer and Deratani, 1998; Juang and Chiou, 2001; Rivas et al., 2003; Aroua et al., 2007), and (iii) the ability of the biopolymer to be regenerated without suffering degradation (Llorens et al., 2004).

Most transition metals can form complexes with chitosan albeit with differing binding strengths. Chitosan can separate numerous metals ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ , etc.) or recover them selectively from complex mixtures. Only alkali metals and alkali earths have no affinity for chitosan (Krajewska, 2001). This property is particularly useful for industrial applications involving decontamination of polycontaminated mixtures. It can also be noted that the selectivity can be related to the binding mechanisms and thus to the pH of the medium.

Not only must the pH be taken into account but also other parameters such as the quantity of amine present on the macromolecular chains and thus DD, MW and crystallinity. DD and MW are important characteristics since they control a lot of the properties of chitosan including its behaviour in water and hence its binding capacity. The degree of crystallinity controls the properties of hydration and swelling of the chitosan in solution which in turn influence the diffusion properties (Guibal, 2004; Crini and Badot, 2008). Chitosan is often considered as a flexible linear cationic copolymer with a higher binding capacity than PEI. However, the flexibility is dependent on the conformation of the macromolecule in solution. Likewise, the conformation and thus also the viscosity of the solutions also depend on the DD and on the pH which both alter the charge density of the polymer chain. When the charge density is high, the macromolecules are unrolled (owing to charge repulsion phenomena) and the viscosity is high. In contrast, when the polymer charge is low, the macromolecule chains are rolled up into statistical bundles which implies low viscosity (owing to lack of chain interaction phenomena).

Hence, the lower the pH, the higher the viscosity. Viscosity also increases with DD as the more the polymer is deacetylated, the more the free amine groups can become protonated and the greater its solubility. Viscosity rises too with concentration and it is also dependent on the molecular weight of the polymer chains, but it falls as the temperature rises.

Generally high-molecular-weight biopolymers are preferred as they prevent losses of material in the form of low MW chains but also because they enable the use of UF membranes with higher MWCO values which leads to higher permeate flow rates (Juang and Chiou, 2001; Tabatabai et al., 1995). The main advantage of chitosan nevertheless remains its high binding capacity – but even this point has been a subject of debate. Indeed, while several studies report the good retention of bivalent metal cations by chitosan (Juang and Chiou, 2000a,b; Llorens et al. 2004; Bal et al., 2006; Verbych et al., 2006; Miretzky and Fernandez, 2009), the binding constant of chitosan with metal cations remains low. We can recall that its affinity for metal cations is variable and particularly dependent on the pH.

Juang and Chiou (2000b) demonstrated the selectivity of chitosan for  $\text{Cu}^{2+}$  in a  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  mixture. The presence of chitosan at a concentration twice as high as that of  $\text{Cu}^{2+}$  improves copper retention 6- to 10-fold at  $\text{pH} < 6$  (pH of  $\text{Cu}^{2+}$  precipitation). On filtration of a solution of  $\text{Cu}^{2+}$  in the presence of 2 eq. of chitosan, metal retention is seen to be around 50–75% in slightly acid medium (pH 3–6) and reaches 100% for pH values over 8 (Juang and Chiou, 2000b). These authors also reported the ability of chitosan to separate  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions unlike PEI. In another article, the same authors Juang and Chiou (2001) showed that chitosan is much more efficient than PEI at extracting and concentrating the ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

It is therefore in alkaline medium that divalent metal-ion containing solutions are best processed by metal complexation with the polymer and precipitation of the metal hydroxides and secondly optimum permeate fluxes. The downside is that chitosan is hydrolysed in alkaline media.  $\text{Ni}^{2+}$  was found to present characteristics similar to  $\text{Cu}^{2+}$  whereas for  $\text{Zn}^{2+}$ , retention only became total at around pH 10 owing to the formation of hydroxides. The presence of the cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , even at high concentrations, had very little influence on  $\text{Cu}^{2+}$  uptake by chitosan in acid media. This suggests that the metal–polymer interaction likely takes the form of a coordination bond. For instance Verbych et al. (2006) showed that the introduction of NaCl into the solution did not influence copper uptake but that high concentrations of  $\text{CaCl}_2$  can hinder chitosan-metal exchanges. Moreover, increasing the

salinity causes a sharp drop in permeate flux, probably due to a reduction in the electrostatic repulsion between polycations.

Taha et al. (1996), Juang and Chiou (2000a,b), Llorens et al. (2004) and Kuncoro et al. (2005) demonstrated that chitosan's efficiency varies with its concentration (there are also contradictory reports on this point) and the pH of the medium. The viscosity of chitosan solutions can affect their UF performance as they alter the hydrodynamics of the system. Kuncoro et al. (2005) reported that the performance of the process mainly depends on the pH of the solution. They showed that recovery of mercury increases with the pH to stabilise at about pH 5.5. Mercury uptake was also found to increase with the excess of polymer before it reached a plateau over a molar ratio of 5–7 (amine/mercury). The excess does not have to be too large before binding is optimal. Problems of fouling also occur in conditions that favour aggregation (Juang and Chiou, 2001) or when the polymer starts to degrade in basic medium (Juang and Chiou, 2000a,b).

The studies of Verbych et al. (2006) indicate that chitosan/metal complexes are very stable and can easily form deposits at the surface of membranes and in the pores. In addition, it is not necessary to use high concentrations of polymer. The authors demonstrate the high exchange capacity of chitosan in neutral medium. Similar results had been published earlier for  $\text{Cd}^{2+}$  (Llorens et al., 2004).

Two metal cations that bind very easily to chitosan are  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  (Guibal, 2004). However, the binding/uptake capacity also varies with the authors. For  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{UO}_2^{2+}$  a binding capacity of up to 2 mmol metal  $\text{g}^{-1}$  has been reported. It is 0.5–1 mmol metal  $\text{g}^{-1}$  for ions  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  and under 0.5 mmol metal  $\text{g}^{-1}$  for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . For metal anions (e.g. vanadate or molybdate), the uptake is higher, reaching 7–8 mmol metal  $\text{g}^{-1}$  (Guibal, 2004). These differences in uptake capacity suggest that in complex mixtures some ions will be retained preferentially. The process will be dependent on the pH but in general will not depend on the ionic strength of the solution, unlike with PEI.

Monovalent cations, especially ions of alkali metals, generally show a low binding affinity for chitosan. Trivalent ions are particularly well eliminated since they generally hydrolyse at acid pH. They also have a higher affinity for oxygen-rich polymers, such as pectin, which are better chelators (Aroua et al., 2007). Uptake of gold III by cheap biopolymers such as chitosan and sericin has been studied (Chen et al., 2011), and it is sericin, which presents amide functions, that proved to be the more efficient.

All these data on chelation can be mainly explained by the behaviour of chitosan in solution. As with other water-soluble polymers, its complexing capacity for numerous metals is higher when the polymers are dissolved because the macromolecular chains are better deployed and thus their surface of interaction increases (Guibal, 2004). Metal uptake increases with the polymer concentration following the law of mass action. However, increasing the chitosan/metal ratio rapidly affects the flow of permeate in acid and neutral media, following a hyperbolic law in acid medium and extremely abruptly at pH 6 (Verbych et al., 2005, 2006). In general, the polymer concentration increases exponentially in the vicinity of the membrane/solution interface over a thickness of a few tens of microns (concentration polarisation phenomenon). A simple 2-phase model provided a satisfactory description of the experimentally observed rejection (Llorens et al., 2004).

In most cases, the interaction of metal cations with a polymer (especially with a polycationic polymer like chitosan) does not lead to the formation of flocs and sedimentation, the metals thus remain in suspension. Ultrafiltration thus offers a physical barrier suited to the size of the polymers, enabling filtration at lower pressures and with higher permeate flows than nanofiltration. This also offers the possibility to recycle the polymer, releasing the metals in acid medium to then precipitate them by electrolysis. Another advantage that is often mentioned when using chitosan concerns this regeneration step (Llorens et al., 2004; Juang and Chiou, 2000a). Once complexed on the chitosan chains, the metals can be easily “decomplexed” after their separation. The metals can then be concentrated justifying their recovery by conventional processes (e.g. precipitation) which cannot be economically applied to the initial low-concentration solutions. Rivas et al. (2003) reported that the pollutants can be concentrated 100-fold. After elimination of the metal from the concentrate, the polymer can be regenerated to its active form by addition of base. This technique also enables the separation of metals of the same valency on the basis of the chemical affinity for the polymer. It can therefore compete with electro dialysis or ion exchange resins, especially when the solution to be treated requires a disinfection step. Molinari et al. (2008) reported the successful separation of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions by UF in the presence of PEI while Verbych et al. (2006) described the separation of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions using chitosan. This chemical selectivity is complementary to that of NF (selectivity achieved by charge effects).

For metal cations, regeneration is often performed by acidification or electrolysis, which reverses the complexation of the metal. The risk is the degradation of the polymer although this point is still unclear. While Llorens et al. (2004) reported easy regeneration of the polymer without degradation, the ability to undergo numerous regeneration cycles was a critical point of the process (especially reduction of the polymer's molecular weight) for other authors (Volchek et al., 1993; Geckeler and Volchek, 1996; Juang and Chiou, 2001). Some metals such as palladium (Guibal, 2004) and cadmium (Llorens et al., 2004) are more easily desorbed than others such as platinum. Optimising the binding and regenerations steps can also significantly enrich the solution with respect to one of the metals (Llorens et al., 2004).

Modification of the chitosan chains is also possible and has been proposed to improve the capture of cations (Emara et al., 2011). The chelation properties (binding and selectivity) can indeed be improved by chemically altering the polymer, grafting specific functional groups onto the amine functions. Chitosan is a highly reactive polyamine and its chemical alteration can (i) increase the number of chelation/complexation sites (and hence the uptake capacity of the polymer chains), (ii) improve the intrinsic binding selectivity by grafting functions that can change the mechanism of binding, broadening the range of action of the polymer by shifting its workable pH range. Numerous ligands can thus be grafted onto the glucose units of chitosan such as derivatives with carboxylic acid functions, phosphates, or sulphur-containing moieties (Varma et al., 2004; Wu et al., 2010; Emara et al., 2011). For instance, the selective recovery of precious metals or of very toxic substances requires a modification of the amine functions of chitosan giving rise to elaborated structures with easily accessible sites (Arrascue et al., 2003; Chang and Chen, 2006).

The choice of the MWCO threshold of the membrane is extremely important, and severe permeate flux reductions are observed for higher MWCO thresholds which can allow a significant fraction of the polymer to enter the pores. It has been reported that the most suitable MWCOs are situated around 10–30 kDa (Verbych et al., 2005, 2006).

The same group (Verbych et al., 2005) studied the effect of humic and fulvic acids in water containing divalent cations during UF treatment. They noted that the presence of humic acids did not reduce the rejection of metal cations and that it increased their rejection when the concentrations of chitosan and humic acid increased together. However, increasing the concentrations of the macromolecules (chitosan and humic acid) leads to a sharp reduction of the permeate flow due to the formation of chitosan-humic acid complexes, with accumulation on the membrane leading to charge neutralisation and concentration polarisation.

In conclusion, numerous metal cations can bind to chitosan, although the affinity varies. However, the fact that the formation constants are relatively weak is an advantage, facilitating polymer regeneration after complexation (Llorens et al., 2004). In some cases, chemical modification of the polymer is necessary, especially to increase the binding capacity or the selectivity. The modifications can also obviate the need for chemical reagents to release the concentrated metal. To avoid serious and rapid loss of permeate flow, it is important to be able to run the filtration at a low trans-membrane pressure and high tangential velocity. Filtration is more efficient in alkaline media but there is a risk of chitosan degradation. In spite of the advantages that chitosan presents for the chelation of metals, it has not yet been used at an industrial scale. The following reasons for this were given by Guibal (2004). Firstly, the chemical stability of the polymer is low when in solution. It is easily degraded by microorganisms (bacteria, fungi) which can also lead to biological contamination of the solution being processed. In addition, it becomes hydrolysed in strongly acid or alkaline media, decreasing its mean molecular mass and adversely affecting its rejection by the PAUF membrane. Currently, the absence of large units of production and the lack of standardisation of the production processes lead to a high variability in the properties of the polymer obtained. Finally, the raw material is still quite costly, 10–15 Euros/kg for environmental applications, owing to the very limited market. Moreover, when the affinity of the metal cation for the chitosan remains moderate, as is the case for  $\text{Cd}^{2+}$ , competition with the proton is not favourable and the cost of acid and base to regenerate the polymer remain dissuasively high (Sabaté et al., 2006).

#### 4.2. Anionic species

As a polycation, at  $\text{pH} \leq 6$  chitosan is associated to polyanions including humic and fulvic acids (Verbych et al., 2005), tartrate, citrate and polyaminocarboxylates such as ethylenediaminetetraacetic acid (EDTA) (Gyliené et al., 2006, 2008). The stability of these complexes is strongly dependent on the polymer concentration and the pH. The interactions involve electrostatic attraction but the presence of numerous hydrogen bonds can also stabilise the associations. Metals with a high valency, which become hydrolysed when present as anions, can be captured by the chitosan in acid medium. Aroua

et al. (2007) reported for instance that at acid pH filtration with a PES membrane led to a 70% abatement of Cr(VI) with chitosan, and almost 100% elimination with PEI.

#### 4.3. Metal-based complexes

Several associations of anionic complexes with chitosan have been reported. For instance UF of As(V) in water that contains humic acids at pH 7.6 showed extensive fouling of the cellulose membrane due to the formation of a gel, which is greatly reduced upon addition of chitosan (Lin et al., 2008). It appeared that the humic acids bind preferentially to chitosan and are then more soluble. At pH 7.6 the chitosan is unable to take up anionic As(V) directly but becomes associated to the arsenic-humic acid complex. In addition, chitosan is able to retain numerous anionic complexes in which the metal cation is stabilised by a ligand. Thus, the Cu-citrate (Guzman et al., 2003) and the Cu-EDTA (Gyliené et al., 2006) complexes bind to chitosan in slightly acid medium. The driving forces underlying the binding are electrostatic interactions between polyions of opposite charges, direct interactions between the metal and the chitosan, and numerous hydrogen bonds. These observations were confirmed by Zamariotto et al. (2010) with PEI on copper and nickel chelated with nitrilotriacetic acid (NTA) and EDTA. An apparent rejection rate of 98% was noted between pH 4 and 9. However, the more the metal is enveloped in the chelating agent, the less it is retained by the membrane. This is because the number of coordination bonds between the polymer and the metal decreases. The excess of free anionic ligand bound by the polycation is little by little displaced by the metal, which forms a more stable coordination complex (Zamariotto et al., 2010).

#### 4.4. Mechanisms

In UF processes, metal cations cannot be retained by the membrane since the average ion size is smaller than the membrane pore diameter. With the PAUF process, separation is dependent on the interaction strength between metal ions and the polymer functional groups. When these interactions are strong and when the complex generated is sufficiently large, it is retained by the membrane. Those metal ions that are not fixed to polymer cross through the membrane. Data on the general principles and fundamental concepts of the PAUF process using different water-soluble functional polymers have been discussed in detail by Rivas et al. (2011).

Chitosan-based PAUF also associates the two mechanisms for the recovery of metals, i.e. complexation in solution and separation by the membrane (Verbych et al., 2006; Aroua et al., 2007). The water-soluble chitosan polymer and metal ion solution are contacted on the feed-side in the filtration system. The macromolecular chains interact with metal ions which are bound to the polymer resulting in polymer-metal chains, which are then retained by a size exclusion mechanism; whereas unbound species, smaller than the pores, pass through the membrane into the permeate stream. The principle of the process is to increase the size of the target solute by complexation with the macromolecular chains of chitosan. This step corresponds to the binding of the metal onto the macromolecular chain in specific conditions. The reaction is pushed to the right owing to the high affinity of metal ions for chitosan.

Two mechanisms are clearly established for the interpretation of metal complexation on chitosan, i.e. electrostatic interactions in acid media and metal chelation (coordination), although the formation of ion pairs has also been reported (Guibal, 2004; Crini and Badot, 2008). Metal ion adsorption is assumed to occur through single or mixed mechanisms including coordination on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups, and ion-exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal anion. Other interactions are also involved such as hydrogen bonding, hydrophobic interactions and physical interactions due to the structure of the network of macromolecular chains.

The nature of the reaction depends upon several parameters related to the polymer (ionic charge, DA, MW, chemical modification), to the solution (pH, ionic strength, polymer dose, metal concentration) and to the chemistry of the metal ion (ionic charge, ability to be hydrolysed and to form polynuclear species).

In spite of the numerous studies focusing on the uptake of metal ions by chitosan, there is still debate as to the actual mechanisms involved (Monteiro and Airoidi, 1999; Rhazi et al., 2002; Llorens et al., 2004; Debbaudt et al., 2004; Verbych et al., 2006). Depending on the interactions between the metal species and the chitosan, processes observed include rejection of metal anions (e.g. Cr(VI), As(V)) in acid medium involving the polycation and rejection of metal cations at  $\text{pH} \geq 3$ . As UF is also able to eliminate colloidal metal hydroxides very efficiently (Juang and Chiou, 2000a,b), sorting out exactly what happens in neutral and alkaline media with respect to the chitosan is often difficult and few studies provide enlightenment on this subject (Llorens et al., 2004).

Studying the chelation of copper by chitosan, Domard (1987) was the first to propose a mechanism known as the “pendent model” which considers that the metal is bound to an amine function just like a pendent jewel (the rest of copper’s coordination shell is occupied by hydroxyl functions of chitosan or of the hydration shell). Other authors (Muzzarelli et al., 1980; Schlick, 1986; Rhazi et al., 2002) propose a bridging model involving two amine functions, either from two different chains or from a single chain (the coordination shell being completed by the contribution of two hydroxyl groups from the chitosan or from the hydration shell (Guibal, 2004)). It is still today difficult to make a decision in favour of either of the models (Monteiro and Airoidi, 1999; Debbaudt et al., 2004). By means of molecular modelling Sabaté and co-workers (Llorens et al., 2004; Sabaté et al., 2006) proposed two complexes for cadmium involving the metal ion and the amine group of the chitosan chains ( $\text{R-NH}_2$ ) as follows:  $\text{Cd}(\text{R-NH}_2)^{2+}$  and  $\text{Cd}(\text{R-NH}_2)_2^{2+}$ .

## 5. Conclusions

In this review, we describe the recent use of chitosan in the process of UF assisted by complexation to extract, concentrate and separate metals present in solution.

The conclusions can be summed up as follows;

- Uptake of a large variety of metal ions;
- Concentration of solutions (even weakly concentrated);

- Selective separation of metal cations (solutions containing a single metal or mixtures);
- Data can be obtained on kinetics and thermodynamics (equilibrium constants, maximum retention capacity, etc.) which leads to a better understanding of metal ion uptake mechanisms.

Its high binding capacity for metals, in addition to its non-toxicity, its recyclability and its price, make chitosan a good candidate substitute for conventional synthetic polyelectrolytes currently in use. Significant results have been obtained on a laboratory scale. However, the challenge will be to adapt the physical-chemical properties of chitosan to the resolution of new problems (for instance cleaning up novel complex industrial mixtures). This challenge is now the driving force behind active research in numerous laboratories.

Although important work has already been done, future research needs to look into some of the following aspects:

- Metal complexation from real wastewaters with differing pH: for example, Zeng et al. (2009a) showed that, compared to mercury, cadmium complexation was more sensitive to changing pH;
- Influence of salts and ligands on PAUF performance: metal-loaded wastewaters usually contain large amounts of salts and also (organic) ligands;
- Influence of the molecular weight and DA (amino group content) on chitosan-based PAUF performance: few reports can be found on how these factors affect chitosan’s behaviour.

Chitosan is therefore a very promising candidate for a vast range of complexation-based UF applications presenting clear advantages on numerous accounts.

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