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Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities

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Abstract

The presence of organic ligands in a solution containing metal ions modifies metal speciation, which in turn changes the sorption mechanism, optimum pH range and maximum sorption capacity. The present work investigates the sorption of copper by chitosan in the presence of citrate at different metal/ligand ratios. Copper uptake in acidic solution takes place through electrostatic attraction between the protonated amine groups of chitosan and anionic copper-citrate complexes (mainly $\text{Cu}(\text{OH})\text{L}^{2-}$ but also a small fraction of CuL^-). Sorption was negligible below pH 3 due to competition from dissociated anionic ligand and counter ions brought about by dissociation of the acid used for pH control. Actually, copper sorption begins to be significant when the fraction of anionic copper-complexes exceeds that of anionic copper-free ligand. So sorption capacity strongly increases up to pH 4.5–5.5. Above pH 5.5, the progressive decrease of amine protonation leads to a linear decrease in sorption capacity. An excess of ligand leads to an increase in the fraction of free dissociated (anionic) ligand that may compete for electrostatic attraction on protonated amine groups and therefore leads to a decrease in sorption capacities.

Keywords: Chitosan; Copper; Citrate; Metal speciation; pH effect; Sorption isotherms; Electrostatic attraction; Chelation; Polymer protonation

1. Introduction

The need for alternatives to precipitation or ion exchange processes for the treatment of metal containing wastewaters has led to the development of biosorption processes using bacterial or fungal biomass, algae and agricultural by-products [1,2]. Biopolymers have been extensively studied for the last 30 years because of their interactions with metal ions. Alginate extracted from algae [3], together with chitin and chitosan extracted from crustacean shells, are typical polymers with excellent properties for the uptake of metal ions [4]. The alginate and chitosan polymers are made up of carboxylic acids and amine groups, respectively. This composition explains their efficiency at interacting with metal ions. The uptake of metal ions on chitosan may proceed through different mechanisms including chelation of

metal cations on the free electronic doublet of amine groups [5–7], or ion exchange mechanisms [8–11]. At near-neutral pH, metal cations interact with nitrogen, while at acidic pH, competition from protons limits the possibility of interaction between cations and amine functions. The protonation of amine groups is controlled by the pK_a of chitosan. The acid–base properties of chitosan strongly depend on the degree of deacetylation of the polymer, which actually consists of glucosamine and acetylglucosamine units. The respective percentages and distribution (block-wise or random) of these units, together with the neutralization of the polymer may significantly affect their proton-exchange properties [12]. The protonation of amine groups is very useful for the uptake of anions. The counter ions bound to protonated amine groups can be exchanged with metal anions.

There is great diversity and many discrepancies in the sorption performances cited in the abundant literature about metal ion sorption on chitosan. Some of these differences may be explained by the differences in the characteristics of

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the biopolymer used for these studies. The conditioning of the polymer (i.e. control of particle size, control of sorbent crystallinity, expansion of the polymer network, the increase in the accessibility and availability of sorption sites) can strongly enhance uptake ability of the biopolymer [13–17]. Another important parameter that has been substantially underestimated in the understanding and interpretation of sorption mechanisms is the influence of metal ion speciation [18–21]. Lasko and Hurst compared the sorption performances of chitosan to those of four commercial resins: Amberlite IRA-67 (weakly basic, polyamine functional groups), IRA-458 (strongly basic, quaternary ammonium functional groups), IRC-718 (iminodiacetic acid functional groups) and Duolite GT-73 (thiol functional groups) [22]. In the presence of complexing agents, silver ions (Ag^+) appeared in the solution in a cationic form, $\text{Ag}(\text{NH}_3)_2^+$, with ammonia, and in anionic forms, $\text{Ag}(\text{CN})_2^-$, $\text{Ag}(\text{SCN})_3^{2-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ with cyanide, thiocyanate and thiosulfate, respectively. As expected, cationic forms were adsorbed at slightly acid to near-neutral pH (4–8), when the chitosan amine groups were unprotonated and the electron pair on the amine nitrogen was available for donation to silver. On the other hand, at low pH, the protonation of amine groups allowed metal anions to be sorbed: $\text{Ag}(\text{SCN})_3^{2-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ were efficiently sorbed at pH 2, while at pH 4, sorption was drastically reduced and null at neutral or alkaline pH. Chitosan was able to sorb silver species through different mechanisms (ion exchange and chelation), but compared to reference commercial resins (with similar functionalities) the biopolymer was more sensitive to pH.

Frequently, in the literature, experimental procedures do not take into account the change in pH due to chitosan addition and its effect on metal speciation, leading to inaccurate interpretation of sorption properties. Moreover, changing the experimental conditions (i.e. the pH, the concentration of the metal and the matrix of the solution) can considerably affect the distribution of metal species and consequently its ability to interact with chitosan. Recently, some investigations have focused on studying the influence of the speciation of metal ions on sorption capacity [11,21–24]. In the case of oxo-anion sorption (molybdate, vanadate) on chitosan it appears that the sorbent exhibits a marked preference for polynuclear species [11,21,23,25]. Juang et al. [26,27] highlighted the influence of the presence of ligands on the sorption of copper by ion-exchange resins and also on chitosan derivatives (poly(ethylenimine)-grafted chitosan beads). More detailed study appears to be necessary to show how the speciation of the metals may affect not only sorption capacities but also the mechanisms involved in the uptake of a given metal. In this study, we focus on investigating copper sorption by chitosan flakes in the presence of citrate. Since copper chelation by this ligand depends on the pH, sorption isotherms were determined at different pH values, selected for their impact on copper-ligand speciation.

2. Material and methods

2.1. Materials

Chitosan was supplied by Aber Technologies (Plouvien, France). The deacetylation percentage (87%) and the molecular weight ($\text{MW}: 125,000 \text{ g mol}^{-1}$) were characterized beforehand by FTIR analysis and gel permeation chromatography (using a coupled multi-angle laser light scattering unit and a refractometer for analysis), respectively.

The chitosan was ground and sieved, and the fraction of particle diameter below $125 \mu\text{m}$ was used for sorption experiments. Apart from this treatment, the chitosan was used as delivered. Copper sulfate and citric acid were supplied by Fluka (Switzerland), while sulfuric acid and sodium hydroxide were supplied by Carlo Erba (Italy).

2.2. Procedures

Solutions were prepared by addition of known amounts of chitosan to a given volume of copper ion solution at known concentrations. The ligand was added at three different Cu/L molar ratios: 2, 1 and 0.5 (corresponding to excess of metal, equimolarity and ligand excess). Experiments were performed at controlled pH using sodium hydroxide and sulfuric acid (this acid was selected to avoid chitosan dissolving in acidic solutions). The pH of the solutions was regularly checked and the pH was controlled when the variation was equal to or higher than 0.1 U.

The solutions were continuously agitated for at least 3 days, which is the maximum contact time to reach equilibrium with this sorbent and particle size (according to previous studies with many other metals). Blank samples were also processed in the absence of sorbent to check for sorption on the experimental equipment (flasks, filtration units, etc.) and the absence of precipitation phenomena. Samples were finally collected and filtered using $1.2 \mu\text{m}$ pore size filter membranes. Metal content in the filtrate was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jobin-Yvon JY 2000, France). The mass balance equation was used to calculate the amount of copper bound to chitosan at equilibrium. Therefore, the sorption capacity q (mg Cu g^{-1}) was obtained from:

$$q = \frac{V(C_o - C_{eq})}{m}$$

where V is the volume of the solution (l), m is the amount of sorbent (g), C_o and C_{eq} are the initial and equilibrium concentration in the solution (mg Cu l^{-1}).

2.3. Metal ion speciation

The distribution of copper species in solution was calculated in function of total metal concentration, total ligand concentration and pH using the formation constants of

Table 1
Formation constants involved in the Cu/citrate system [28,29]

| Species | Reaction | log K |
|---|---|--------|
| Cu(OH) ⁺ | Cu ²⁺ + H ₂ O ↔ Cu(OH) ⁺ + H ⁺ | -8.22 |
| Cu(OH) ₂ | Cu ²⁺ + 2H ₂ O ↔ Cu(OH) ₂ + 2H ⁺ | -17.53 |
| Cu(OH) ₃ ⁻ | Cu ²⁺ + 3H ₂ O ↔ Cu(OH) ₃ ⁻ + 3H ⁺ | -27.8 |
| Cu(OH) ₄ ²⁻ | Cu ²⁺ + 4H ₂ O ↔ Cu(OH) ₄ ²⁻ + 4H ⁺ | -39.12 |
| Cu ₂ (OH) ₂ ²⁺ | 2Cu ²⁺ + 2H ₂ O ↔ Cu ₂ (OH) ₂ ²⁺ + 2H ⁺ | -10.6 |
| CuL ⁻ | Cu ²⁺ + L ³⁻ ↔ CuL ⁻ | 5.95 |
| CuL ₂ ⁴⁻ | Cu ²⁺ + 2L ³⁻ ↔ CuL ₂ ⁴⁻ | 8.09 |
| CuHL | Cu ²⁺ + H ⁺ + L ³⁻ ↔ CuHL | 8.68 |
| CuH ₂ L ⁺ | Cu ²⁺ + 2H ⁺ + L ³⁻ ↔ CuH ₂ L ⁺ | 11.34 |
| Cu(OH)L ²⁻ | Cu ²⁺ + H ₂ O + L ³⁻ ↔ Cu(OH)L ²⁻ + H ⁺ | 2.16 |
| HL ²⁻ | H ⁺ + L ³⁻ ↔ HL ²⁻ | 5.1 |
| H ₂ L ⁻ | 2H ⁺ + L ³⁻ ↔ H ₂ L ⁻ | 9.06 |
| H ₃ L | 3H ⁺ + L ³⁻ ↔ H ₃ L | 11.54 |

complexes listed in Table 1, collected from Baes and Mesmer [28], and Perrin [29].

3. Results and discussion

3.1. Case of equimolar concentrations of copper and citrate

In the absence of ligand, copper sorption proceeds by chelation on amine groups [5,6,30,31]. As a consequence, when the protonation of amine groups increases metal uptake diminishes due to competition from protons to react with amine groups. Copper sorption isotherms may be strongly influenced by pH in the presence of citrate since the organic ligand has a good chelating affinity for copper, which depends on the pH. Hence, chitosan and the ligand may compete for interaction with copper ions. However, there are some other possible effects of the presence of these competitor ligands, which depend on the pH of the solution: (a) a change in the sorption mechanism (electrostatic attraction versus chelation), (b) direct interaction of the ligand with chitosan (electrostatic attraction of anionic ligand to protonated amine groups).

3.1.1. Influence of pH on sorption isotherm

It is important to notice that with an equimolar initial concentration of citrate and copper the chelation of copper by citrate avoided the precipitation of copper even at metal concentration as high as 270 mg Cu l⁻¹. Fig. 1 shows copper sorption isotherms obtained in the presence of citrate at equimolar concentrations. At pH 3, the sorption capacity was below 10 mg Cu g⁻¹. The sorption capacity sharply increased when the pH increased to 4–5: the maximum sorption capacity hardly varied between pH 4.2 and 5.2. Further increasing the pH resulted in a progressive decrease in sorption capacities. Fig. 2 shows the maximum sorption capacities obtained at different pH values. Considering the deacetylation degree of chitosan, i.e. 87%, the pK_a may be close to 6.5. Though the polyelectrolyte behavior of chitosan would require that the Henderson–Hasselbach

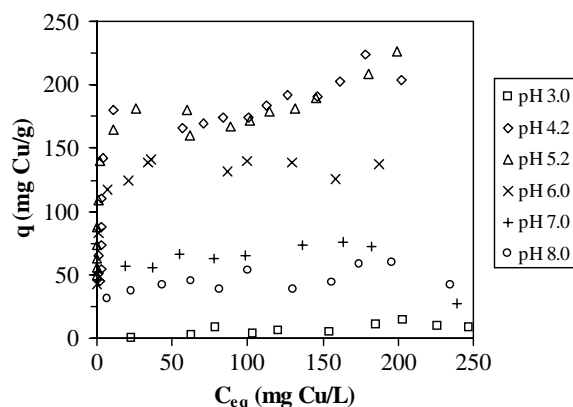


Fig. 1. Copper sorption isotherms in the presence of citrate at different pH values (Co/Cu): 20–270 mg l⁻¹ and equimolar concentration of citrate; sorbent dosage varying between 10 and 100 mg l⁻¹).

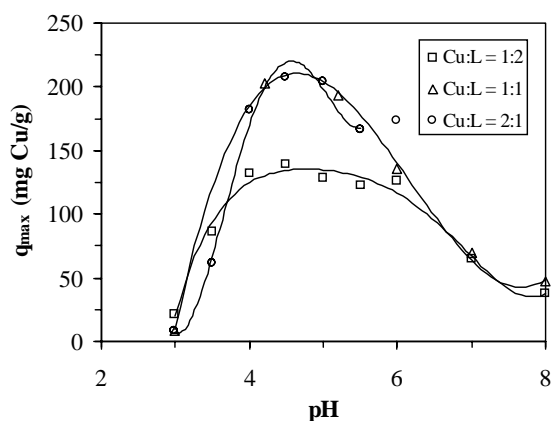


Fig. 2. Copper sorption in the presence of citrate. Influence of Cu/L ratio and pH on maximum sorption capacity.

equation should be taken into account in order to evaluate the protonation yield of the polymer, in a first approximation it was evaluated on the basis of the simple dissociation constant. At each experimental pH, the protonation yield can be calculated and compared to maximum sorption capacity (Fig. 3). For pH 3, the sorption capacity cannot be

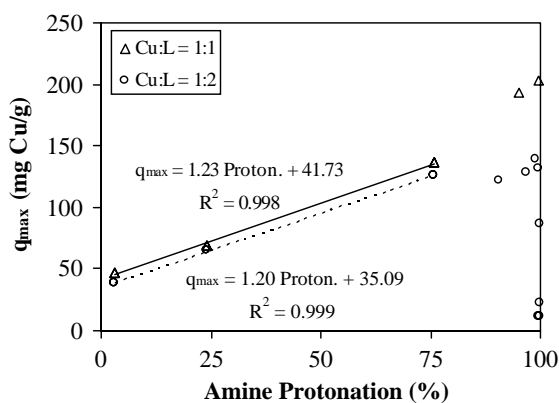


Fig. 3. Correlation of maximum copper sorption capacity with the protonation of amine groups in the presence of citrate.

correlated to the amine protonation yield: the polymer was fully protonated but other parameters have to be taken into account for the interpretation of copper–chitosan interactions, such as competition phenomena. For other pH values the sorption capacities increased linearly with amine protonation yield. The increase in sorption capacity with increasing polymer protonation and the decrease in sorption capacity with high concentrations of competitor anions (at low pH) clearly demonstrated that the sorption mechanism is not a simple chelation mechanism and is better described by a mechanism of electrostatic attraction. It appears to be necessary to consider metal speciation in the presence of the ligand for a more efficient interpretation of sorption data.

3.1.2. Influence of metal speciation on sorption performance and mechanism

Fig. 4 shows the distribution of copper and citrate species in solution as a function of pH for equimolar metal and ligand concentration (3 mM) (this concentration corresponds

to the equilibrium concentration of copper in the solution at maximum copper sorption capacity) using the formation constants summarized in Table 1. Below pH 3, copper in solution was mainly in the form of free copper (cationic form), which was electrostatically repelled by protonated amine groups. Moreover, the ligand was partially dissociated; and its anionic form H_2L^- may be attracted by protonated amine groups involving a supplementary competition. At pH 3, the predominant ligand species are H_2L^- and CuL^- forms, however, many other species may coexist: anionic forms (HL^{2-} , $Cu(OH)L^{2-}$), neutral forms (H_3L , $CuHL$) and cationic forms (CuH_2L^+). The only species that can interact with protonated amine groups are therefore H_2L^- , HL^{2-} , CuL^- , and $Cu(OH)L^{2-}$. Considering now the distribution of copper species at this pH, copper is mainly present in the form of anionic species (CuL^- and $Cu(OH)L^{2-}$), neutral species ($CuHL$) and cationic species (Cu^{2+} and $CuHL^+$). About 35% of total copper is present in the form of an anionic complex (CuL^- or $Cu(OH)L^{2-}$). These are the only

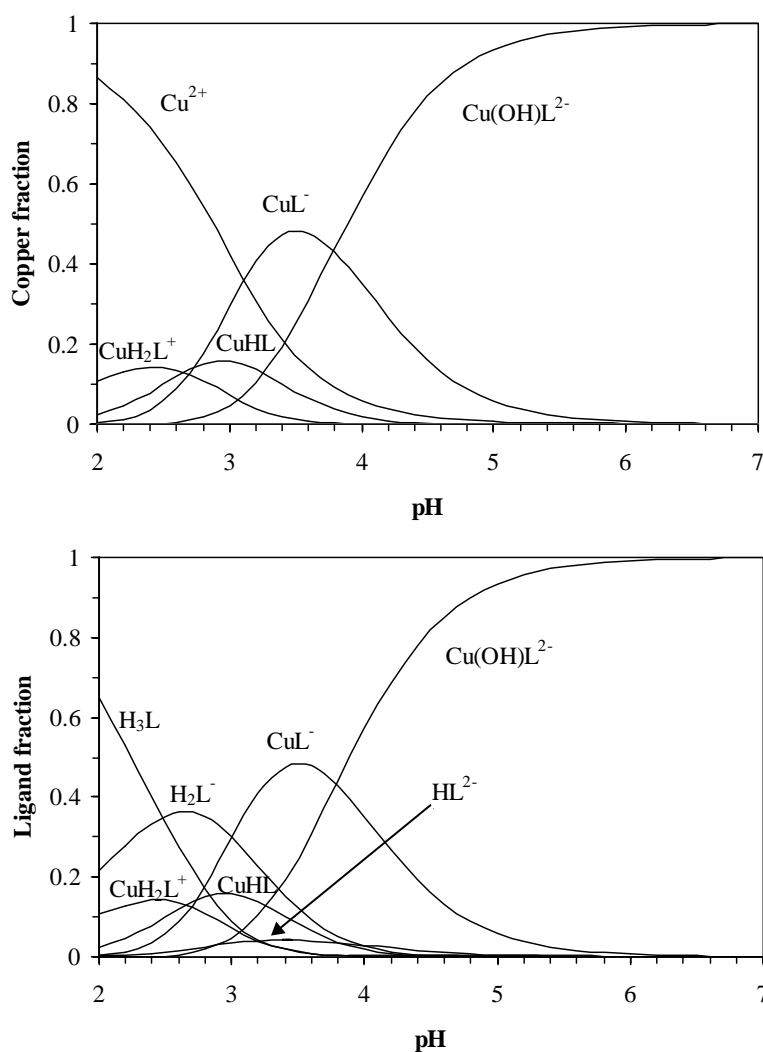


Fig. 4. Distribution of copper species (top) and citrate species (bottom) in solution in function of pH for total equimolar concentrations of copper and ligand of 3 mM.

copper species that can be electrostatically attracted to protonated amine functions; however, anionic forms of ligand (not bound to copper, i.e. HL^{2-} and H_2L^-) exist in the solution at a comparable molar fraction (concentration). These anionic forms of the ligand may compete with anionic forms of citrate-chelated copper. This may explain the low sorption capacity of copper at this pH (below 10 mg Cu g^{-1}). At increasing pH, the distribution of ligand species changes over to the formation of copper complexes. The competition of partially dissociated ligand for interaction with protonated amine groups thus decreases. Ligand species that are not complexed with copper represented less than 10% at pH 4. Moreover, the distribution of copper species gives way to the formation of copper complexes (mainly CuL^- at pH between 3 and 4, and then $\text{Cu}(\text{OH})\text{L}^{2-}$ at pH greater than 4), and free copper species progressively disappear. Thus, sorption capacity may be controlled by three parameters below pH 6: (a) protonation yield, (b) fraction of copper anionic forms (and in this case by the affinity of chitosan for selected copper-citrate complexes), and (c) fraction of copper-free citrate anionic forms (competition for sorption on protonated amine groups).

3.1.3. Identification of sorbed copper species

Fig. 5 shows the superimposition of the curves representing the maximum sorption capacities as a function of pH together with the molar fraction of copper-free anionic ligands (CuFAL: HL^{2-} and H_2L^-) and anionic copper complexes (ACuC: CuL^- and $\text{Cu}(\text{OH})\text{L}^{2-}$). It is interesting to note that at pH 3 CuFAL and ACuC species are present at the same molar fraction: copper-free anionic ligands compete with anionic copper complexes for electrostatic attraction on protonated amine groups. Above pH 3, ACuC species predominate over CuFAL species so the sorption of copper species is possible: sorption capacity progressively increased up to pH 4.5. In the pH range 4–5 the sorption capacity remained at a high value (about 200 mg Cu g^{-1}). Above pH 5, the sorption capacity decreased as did the protonation yield: copper is only present in the solution in the form $\text{Cu}(\text{OH})\text{L}^{2-}$; this form is highly adsorbable by the protonated amine groups; however, the number of protonated groups significantly decreased and the possibility for the sorbent to attract $\text{Cu}(\text{OH})\text{L}^{2-}$ decreased. This is consistent with the correlation between metal sorption and amine protonation shown in Fig. 3. Juang and Ju [26] have shown that, in the presence of chelating agents, copper can be sorbed on poly(ethylenimine)-grafted chitosan but at higher pH (5–6). The protonation of amine functions on the sorbent and on the PEI grafted on the polymer makes the material efficient at sorbing anionic copper species by electrostatic attraction. Indeed, in equimolar diluted solutions containing cupric ions and EDTA, for a wide range of pH (between pH 3 and 11.5), the predominant species is $\text{Cu}(\text{EDTA})^{2-}$, while at lower pH values, copper is present in solution in the form of $\text{CuH}(\text{EDTA})^-$ until pH 1.5. Juang and Ju observed that the sorption capacity was very

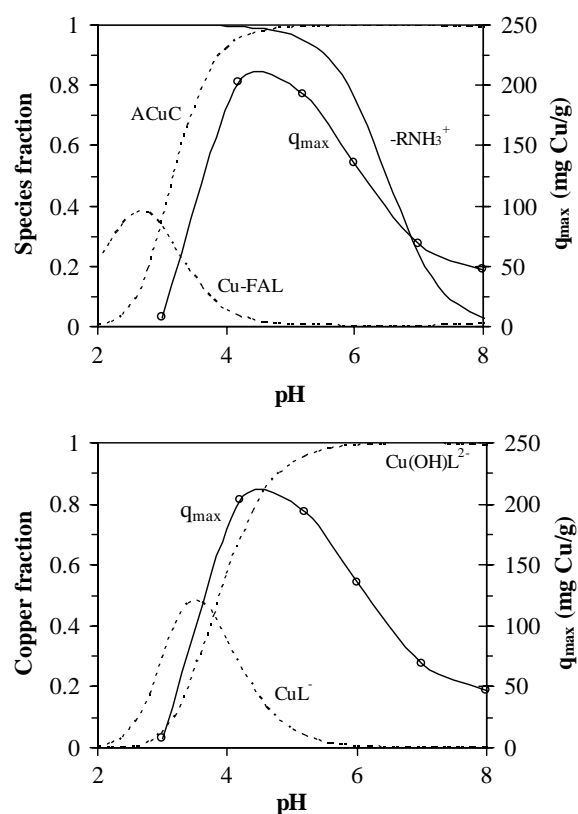


Fig. 5. Maximum copper sorption capacities in function of pH in the presence of citrate. Comparison with the diagrams of species distribution (ACuC: anionic copper complexes; CuFAL: copper-free anionic ligand; $-\text{RNH}_3^+$: protonated amine groups) (top); and correlation of the distribution of anionic copper complexes with maximum sorption capacities (bottom). Equimolar concentrations of copper and citric acid (3 mM).

low below pH 3 due to the weaker electrostatic attraction of monocharged species by the ammonium groups of PEI immobilized on the sorbent. Finally, they observed that the sorption capacity increased again with increasing pH. They suggested that this might be caused by competitive reactions of protonation and complex binding. Similar conclusions were given by Wu et al. [24] for the sorption of copper on chitosan in the presence of ligands at different pH values.

Fig. 5 (bottom) shows the superimposition of sorption capacities at given pH to the distribution of anionic copper complexes in function of pH. This figure also enables the copper species that were preferentially sorbed to be identified. Indeed, the curve plotting maximum sorption capacity versus pH was very close to that of $\text{Cu}(\text{OH})\text{L}^{2-}$.

Taking into account the degree of acetylation of the polymer (about 13%), the molecular weight of the equivalent monomer unit is approximately 166 g mol^{-1} . One gram of polymer was thus equivalent to 6 mmol of nitrogen, i.e. 5.2 mmol of free amine groups. The maximum sorption capacity was close to 210 mg Cu g^{-1} (about $3.3 \text{ mmol Cu g}^{-1}$). This corresponded to a $\text{Cu}/-\text{RNH}_3^+$ molar ratio of 0.63, consistent with the anionic charge of $\text{Cu}(\text{OH})\text{L}^{2-}$,

suspected to be sorbed by electrostatic attraction on protonated amine groups (1/2). This ratio is consistent with those obtained for platinum and palladium sorption on glutaraldehyde cross-linked chitosan [23,32], but significantly lower than those obtained with oxo-anions, for which the sorption capacities were 8–9 mmol metal g⁻¹ (i.e. a ratio metal/-RNH₃⁺: 1.5–1.7). Oxo-anions were sorbed in the form of polynuclear species, which may explain this high molar ratio between metal and amine groups [21,25]. However, this ratio is only indicative. Indeed, the amount of 5.2 mmol of amine groups per g of chitosan is the total amount of amine groups present on the biopolymer. Hence, this molar ratio (Cu/RNH₃⁺, which tended to 1:2) remains debatable since the total number of amine groups is not necessarily the number of amine groups really available and accessible for uptake. Due to the residual crystallinity of the polymer, it is recognized that all the amine groups are not fully accessible [13,33,34]. Piron et al. showed that only a fraction of these amine groups remained available for sorp-

tion on raw chitosan due to the residual crystallinity of the polymer. They also showed that dissolving the biopolymer followed by freeze-drying the resulting solution reduced polymer crystallinity and thus increased accessibility to sorption sites (both kinetics and sorption capacities were enhanced) [33]. According to this hypothesis, the ratio of copper to accessible protonated amine groups would be greater and tend to 1. In this case it would indicate that protonated amine groups react mole to mole with copper anions.

These results suggest that in the presence of equimolar concentrations of copper and citrate ligand, copper sorption begins when the fraction of anionic copper complexes begins to predominate compared to the copper-free anionic ligand molar fraction. This also corresponds to the appearance of Cu(OH)L²⁻, which seemed to be the preferred copper complex for adsorption on protonated amine groups. Sorption capacity increases with increasing concentration of this adsorbable species. However, above a limit pH value, sorption capacity decreases with the decrease in protonation yield.

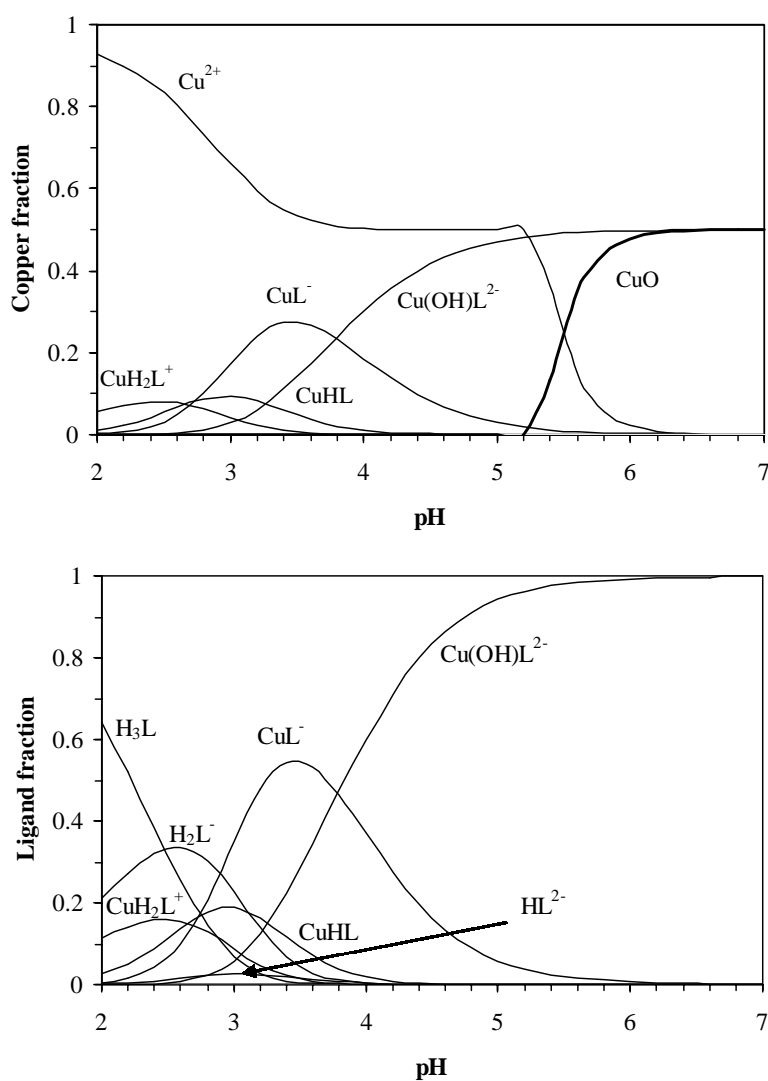


Fig. 6. Distribution of copper species (top) and citrate species (bottom) in function of pH for copper/citrate molar ratio 2:1 (Cu: 3 mM).

In order to verify these hypotheses, experiments were performed with different Cu/L molar ratios (2:1 and 1:2) (Fig. 2). Changing from excess to deficit of metal over ligand allows the influence of copper-free anionic ligand competition on the sorption capacity and uptake mechanism to be evaluated, together with the influence of metal speciation (fraction of anionic copper species).

3.2. Case of copper excess (Cu/citrate molar ratio: 2:1)

Fig. 6 shows the distribution of copper and ligand species in function of pH for Cu/citrate molar ratio 2:1. The excess of metal (compared to organic ligand) resulted in a partial precipitation of copper above pH 5.2. This is important for the interpretation of copper removal: above pH 5.5, a considerable percentage of the copper eliminated from the solution can be attributed to copper precipitation rather than sorption. It is also important to notice that copper may co-exist below pH 5 in the form of ligand-free cationic species (above 50%, up to 93% at pH 2). Between pH 3.5 and pH 5, less than 40–45% of total copper was present in the form of anionic copper complexes. It is to be expected that this could control the shape of the sorption isotherms and lead to a decrease in the initial slope of the curve, since only a fraction of the total concentration of metal in the solution is in the form of an adsorbable species. However, if we consider only the maximum sorption capacity (corresponding to the saturation of sorption sites), as in the present case, this value is not expected to change. The distribution of ligand species was not significantly different to that observed in the preceding case (Cu/L molar ratio 1:1). The curves for CuH_2L^+ and CuHL were only shifted to higher pH; however, these species are not adsorbable and do not interfere in the control of sorption performances. For these reasons the maximum sorption capacity at the optimum pH (in the range pH 4–5) was not significantly changed.

Fig. 7 (top) confirms that in this case copper sorption also began to increase at a pH corresponding to the predominance of anionic copper complexes over copper-free anionic ligand, while sorption began to decrease when protonation decreased, as the result of a decrease in electrostatic attraction. Fig. 7 (bottom) shows that sorption capacity correlated well with the fraction of $\text{Cu}(\text{OH})\text{L}^{2-}$ in the solution. This is consistent with the results obtained at equimolar concentration of copper and citrate (Fig. 5). Additionally, it is not possible to reject the hypothesis of a possible contribution of chelation mechanism in the sorption of free copper cations. Hence, at pH close to pH 5, for which several authors have shown that copper begins to be complexed by chitosan, copper co-exists in the solution as both free Cu^{2+} and the copper-citrate complex ($\text{Cu}(\text{OH})\text{L}^{2-}$). In this case copper could be bound by two simultaneous mechanisms: (a) electrostatic attraction of copper-citrate complexes on protonated amine groups, and (b) the chelation of free copper cations on free amine groups. This could explain that despite the presence of the ligand, which controls the avail-

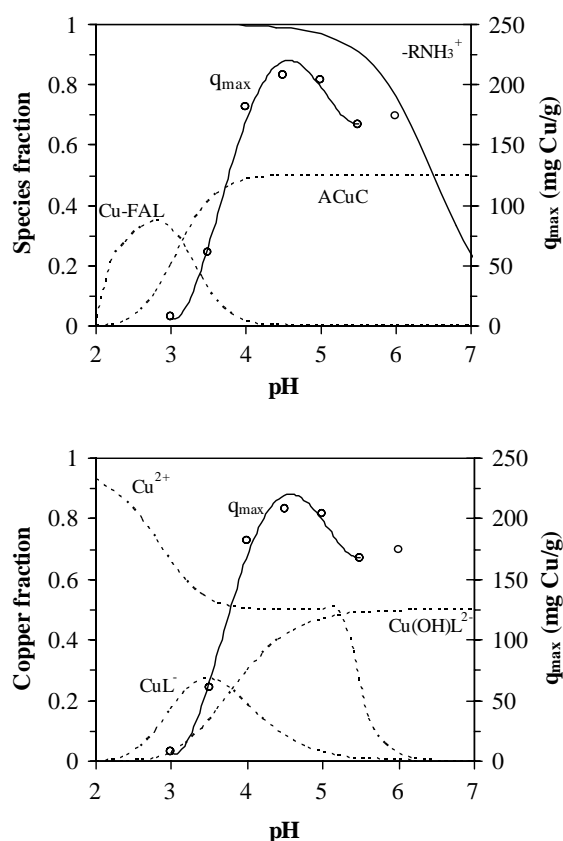


Fig. 7. Copper sorption capacities in function of pH in the presence of citrate. Comparison of predominance diagrams (ACuC: anionic copper complexes; CuFAL: copper-free anionic ligand; and $-\text{RNH}_3^+$: protonated amine groups) (top); and correlation of the distribution of anionic copper complexes with maximum sorption capacities (bottom) for copper/citrate 2:1 molar ratio (Cu: 3 mM).

ability of free copper ions for chelation, the sorption capacity remained high. Above pH 5.5 the high sorption capacities were attributable to precipitation.

3.3. Case of citrate excess (Cu/citrate: 1:2)

In the case of ligand excess (Fig. 8), the trends are significantly different. Indeed, the distribution of copper is similar to that observed with equimolar concentrations of copper and ligand: anionic forms of copper predominate above pH 2.8. The main differences appeared in the distribution of ligand species. There was a large excess of ligand, and copper-free anionic ligands represented at least the same molar fraction as anionic copper complexes. These anionic ligands may strongly compete for electrostatic attraction on protonated amine groups and thus, the sorption capacity is expected to decrease significantly (more or less halved).

Fig. 9 (left) confirms this significant decrease in the sorption capacity: at the optimum pH the maximum sorption capacity did not exceed 140 mg Cu g^{-1} (i.e. $2.2 \text{ mmol Cu g}^{-1}$). This means a 30% decrease of maximum sorption capacity compared to other experiments with different Cu/L ratios.

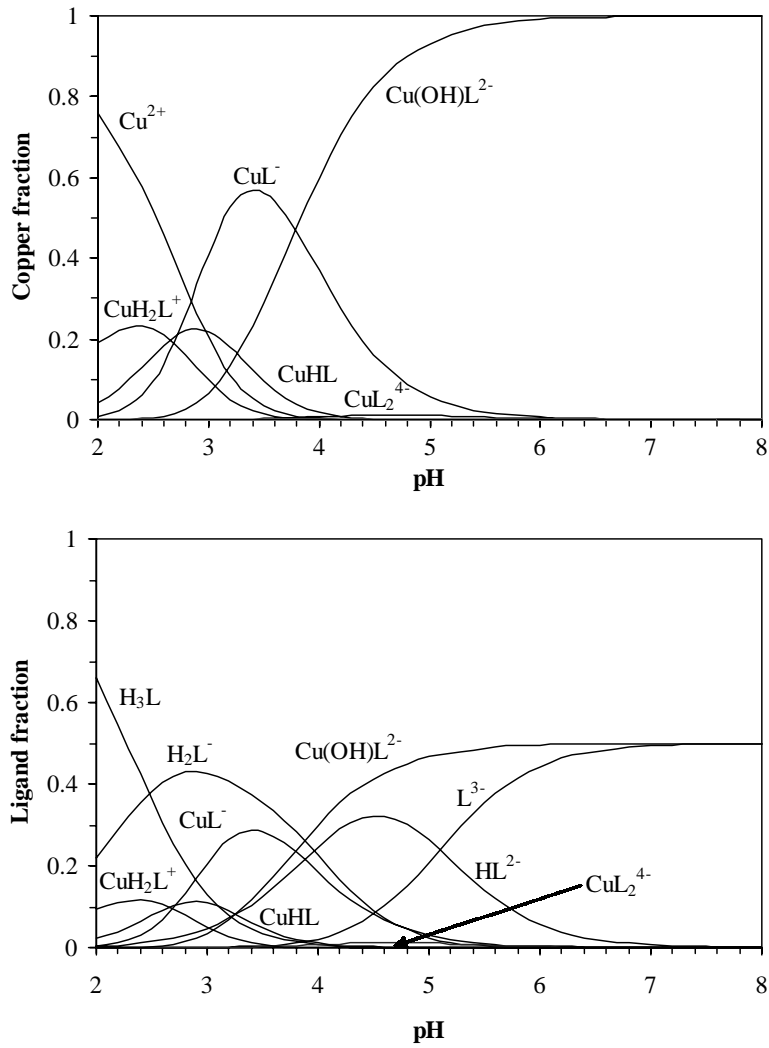


Fig. 8. Distribution of copper species (top) and citrate species (bottom) in function of pH for copper/citrate molar ratio 1:2 (Cu: 3 mM).

The presence of large concentrations of anionic ligands (HL^{2-} , and to a lesser extent L^{3-} and H_2L^-) may lead to their sorption and thus to a decrease in the number of sorption sites available for the electrostatic attraction of

copper-citrate complexes. As in the case of Cu/L ratios 2:1 and 1:1, sorption increased from pH 3 to 4 and sorption capacity began to decrease above pH 5 and strongly decreased above pH 6, consistently with the decrease in amine

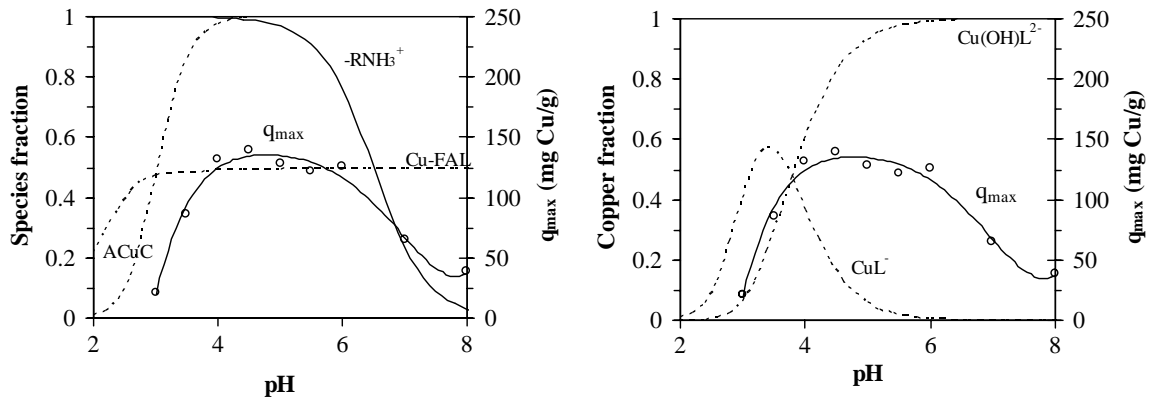


Fig. 9. Sorption capacities in function of pH and comparison of predominance diagrams (ACuC: anionic copper complexes; CuFAL: copper-free anionic ligand; -RNH_3^+ : protonated amine groups) (left); and correlation of the distribution of anionic copper complexes with maximum sorption capacities (right) for copper/citrate molar ratio 1:2 (Cu: 3 mM).

protonation. Fig. 9 (right) compares sorption capacity versus pH to the distribution curve for different copper complexes. In contrast with the other cases, the correlation did not match perfectly at pH below 5. This difference may be due to (a) the simultaneous sorption of CuL^- and Cu(OH)L^{2-} , and/or (b) the competitor effect of copper-free anionic ligands competing for electrostatic attraction on protonated amine groups. Above pH 6, sorption capacities were comparable for both Cu/L: 1:1 and Cu/L: 1:2 (Fig. 2).

4. Conclusion

Complexation of copper by organic ligands present in the solution strongly affects sorption performance. The chelation of copper by soluble ligands may also change the uptake mechanism and contributes to reducing the precipitation phenomena that may occur in near-neutral solutions. The distribution of metal species varies with total metal concentration, pH and ligand concentration. The predominance of anionic species in acidic solutions (above pH 3) may explain the fact that below pH 6, protonated amine groups electrostatically attract anionic copper-complexes, while in the absence of ligand, copper is sorbed by direct chelation on free amine groups. The presence of the organic ligand causes strong competition (especially when the ligand is in excess compared to the metal), which may result in a significant decrease in sorption capacities for copper: protonated amine groups are saturated by dissociated ligands (competitor anions). The influence of pH on sorption capacity was more specifically controlled by the predominance of anionic copper complexes over anionic copper-free ligands. For example, in the case of copper sorption in the presence of citrate, above pH 3 anionic copper complexes predominate and sorption capacity begins to increase until pH 4.5–5.5 due to the decreasing competitor effect of free dissociated ligand species. Above pH 5.5, there is a significant decrease in the protonation of amine groups and the sorption capacities therefore decrease linearly (with protonation yield, at increasing pH). At equimolar concentrations of copper and citrate, and with an excess of copper, there is a good correlation between the curves plotting the sorption capacity versus the pH and the distribution curve of Cu(OH)L^{2-} . This may be indicative of a preference of the sorbent for this copper species. With an excess of ligand, the conclusion was not so obvious and it appeared that CuL^- could be simultaneously adsorbed.

Maximum sorption capacity at the optimum pH tended to 3–3.3 mmol Cu g^{-1} , which is a molar ratio $\text{Cu}/\text{-NH}_3^+$ of approximately 0.63. Considering that all amine groups are not necessarily accessible (due to residual polymer crystallinity), we can assume that the stoichiometric $\text{Cu}/\text{-NH}_3^+$ ratio could be greater. A stoichiometric ratio close to 1 would be indicative of an interaction of chitosan with a monocharged copper species. However, a more complete study of the simultaneous sorption of the anionic ligand

would be necessary to draw any conclusion regarding the species of copper that are actually sorbed on the polymer.

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