

Influence of Physicochemical and Structural Characteristics of Chitosan Flakes on Molybdate Sorption

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ABSTRACT: This study investigates the effect of deacetylation degree and molecular weight of chitosan on molybdate sorption on both raw and glutaraldehyde crosslinked samples. It appears that the physicochemical parameters affect the crystallinity of the samples: a high crystallinity reduces the accessibility of both water and metal ions to the amine binding sites. Both equilibrium and kinetic performances are thus influenced. The crosslinking by glutaraldehyde decreases sorption performances for large size particles while it does not influence sorption for the smallest. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 571–580, 1998

Key words: molecular weight; deacetylation percentage; crystallinity; chitosan; molybdate; crosslinking; glutaraldehyde

INTRODUCTION

The ability of chitosan to recover metal ions from dilute wastewaters has been widely studied for the last 30 years. The high nitrogen content of this biopolymer extracted from chitin, the most abundant biopolymer in nature after cellulose, can explain such high collecting performances.^{1,2} However, the main part of this work was dedicated to the investigation of overall sorption performances of the most common and commercial available forms of chitosan^{3–6} or derived products.^{7–9} Several studies in the last 10 years have shown that metal uptake on chitosan is sometimes controlled by diffusion mechanisms.¹⁰ Both kinetic and equilibrium data are influenced by intraparticle mass transfer resistance. Such opinion is confirmed by the effect of particle size on sorp-

tion isotherms. Findon et al.¹¹ have shown that metal uptake capacity slightly depends on sorbent particle size for zinc, while this parameter has no significant effect on nickel, mercury, and copper removal. Guibal et al.¹⁰ have demonstrated that uranium recovery is influenced by chitosan particle size, with a maximum uptake capacity that is strongly decreased by increasing particle size. This conclusion is not valid for modified chitosan. Several processes have been proposed to modify raw chitosan flakes including dissolution/reprecipitation, grafting of new functional groups on polymer backbone,^{7,10} and gel formation.¹² These operations allow polymer porosity to be enhanced, and the uptake capacities to be increased. Sorption kinetics are also improved by these modifications. The structure of the polymer is thus an important criterion, which allows future sorption performances to be predicted. It appears necessary to investigate various types of chitosan with respect to their physicochemical characteristics: molecular weight and deacetylation percentage.

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These parameters play an important role in the distribution of sorption sites and on their accessibility. The greater the deacetylation percentage, the higher the number of free amine groups. The higher the molecular weight, the higher the viscosity. Both molecular weight and deacetylation percentage influence the dissolution of the polymer in acidic solution. The molybdate removal being optimum at around pH 3,¹³ it is necessary to increase the polymer resistance to dissolution. Various methods have been carried out to prevent chitosan dissolution: solvent casting;¹⁴ crosslinking is the technique most frequently used to reach a higher stability, using dialdehydes (such as glutaraldehyde), esters or ethers (EGDE), or epichlorhydrine.¹⁵ Moreover it has been shown by several groups that chitosan is less soluble in sulfuric acid than in chlorhydric and nitric or organic acids. The sulfuric acid changes the superficial structure of the polymer.¹⁶ Here the crosslinking was performed using glutaraldehyde, the dissolution being controlled on both acetic and sulfuric dilute acids.

This work investigates the effect of molecular weight, deacetylation percentage, crystallinity, particle size, and crosslinking on molybdate sorption, through sorption isotherms and a simple approach of sorption kinetics.

EXPERIMENTAL

To determine the uptake capacity of each type of chitosan, 20 mg of chitosan flakes were left in contact with 200 mL of molybdenum solutions at various concentrations (ammonium molybdate, RP Prolabo). Samples were withdrawn using a glass fiber filter (1.2 μm) and the molybdenum concentration of the solution at equilibrium was determined using a Jobin-Yvon AES-ICP spectrophotometer. The metal content (mg Mo/g) was determined by a mass balance on molybdate between liquid and solid phases. Solutions were initially controlled to pH 3, using sulfuric acid and sodium hydroxide molar solutions. The solutions were agitated with a reciprocal shaker for 72 h and pH was regularly controlled. Experiments were performed at room temperature.

For kinetic investigations, two experimental procedures were used. In the first series, using the sorption isotherms, operating lines were drawn to determine the optimum sorbent mass, necessary to reach the plateau of the isotherm. Several masses (ranging from 60 to 130 mg) were used to

obtain kinetics in conditions such as when the saturation is reached: it corresponds to operating line slope ($-V/m$) between 0.0078 and 0.0167. The second series was obtained with a fixed sorbent/volume ratio corresponding to a sorbent concentration of 170 mg L⁻¹ (slope of the operating line: 0.0058). Experiments were performed in a tank reactor with a Floctest mixer at room temperature. Samples were taken at specified intervals and filtered through 1.2 μm glass fiber filters.

STRUCTURAL AND PHYSICO-CHEMICAL CHARACTERIZATION OF CHITOSAN SAMPLES

Chitosan Samples

Chitosan was supplied by France-Chitine (La Ciotat-France; Mahtani Chitosan Private Ltd., India). Using an IFA-Universalmühle M20 crusher, chitosan flakes (0–5 mm) were reduced to fine particles that were finally classified with a small shaken sieve, in three fractions:

$$0 < G1 < 125 \mu\text{m} < G2 \\ < 250 \mu\text{m} < G3 < 500 \mu\text{m}.$$

It was observed that for a similar crushing procedure (constant time and constant mass of material) the sieving of the crushed particles has given different weight proportions. Some of these samples were difficult to crush to fine particles. It was observed that the difficulty for the crushing of chitosan increases with the deacetylation percentage: this parameter seems to have a greater influence on crushing than molecular weight. However, it was observed that the greater the molecular weight, the higher is the difficulty in crushing.

Each fraction of each chitosan type was split into two fractions. One of them is used to investigate the effect of crosslinking, adding 12.5 g of glutaraldehyde (25% w/w aqueous solution) to 1 g of dry chitosan. The dry weight of chitosan flakes (before and after crosslinking) was obtained by placing each sample in an oven overnight and weighing it after 16 h of drying. The dry weight percentage varies between 87 and 88.5% for raw chitosan and between 86 and 86.5% for crosslinked chitosan.

Six chitosan samples were carried out with varying molecular weight and deacetylation per-

Table I Physicochemical Characteristics of Chitosan Samples

Sample Code	DD ^a (%)	DD ^b (%)	DD ^c (%)	Viscosity ^a (cP)	M_n 10^{-5}	M_w 10^{-5}	Polydispersity
2222	75–85	76	< 75	501–2000	3.59	4.95	1.37
2322	75–85	78	< 75	101–500	1.60	2.55	1.59
2332	93–97	95	94	101–500	1.37	2.68	1.94
2342	98–100	97	96	101–500	1.50	2.38	1.59
2524	75–85	81	< 75	5–20	0.49	1.12	2.30
2625	75–85	78	< 75	0–5	0.13	0.52	3.90

DD, deacetylation degree.

^a Commercial data.

^b Determination by the method of Baxter.

^c Determination by the method of Miya.

centage. The main characteristics (commercial and actual data) are reported in Table I. While other chitosan samples were deacetylated with a standard solid-state procedure (extraction in boiling sodium hydroxide solution), the 2625 sample was irradiated by a gamma ray source (Société GammaSter, Marseille, France) with a 13 kGy dose, to open β -1–4 linkages. This irradiation treatment involves a significant increase in the polydispersity, as observed in Table I. The size exclusion chromatography analysis has shown that the distribution of molecular weights is bimodal involving a high polydispersity compared to the other samples treated by standard physicochemical procedures.

Molecular Weight and Deacetylation Percentage

Deacetylation percentage was determined by FTIR spectrophotometry on chitosan films (chitosan in solution in acetic acid 1% w/w) using a Perkin-Elmer 1760 FTIR spectrophotometer. The spectra were treated by the methods of Baxter et

al.¹⁷ and Miya et al.¹⁸ The water content of the samples was obtained by weight loss in an oven for 24 h. The distribution of molecular weights was determined by size exclusion chromatography on TSK GW columns with an on-line double detection obtained with a Waters R410 differential refractometer and a Dawn-Wyatt multiangle laser light scattering photometer. In the case of an eluent at pH 4.3 (0.15M acetic acid/ammonium acetate buffer) the refractive index increment was fixed at 0.172 (cm³ g⁻¹).¹⁹

Crystallinity

The crystallinity was studied by X-ray diffraction. The crystallinity index was obtained, after a baseline correction, by the ratio of the crystalline areas to the total area:

$$CrI = 100 \frac{(A_{tot} - A_{am})}{A_{tot}}$$

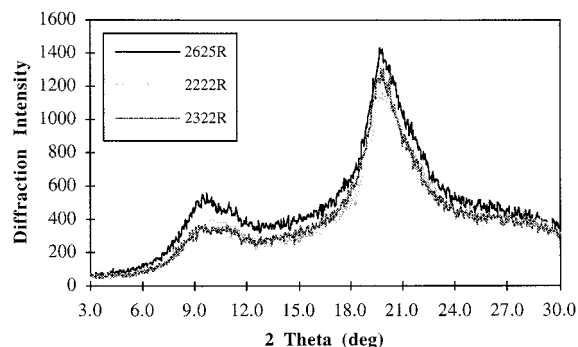


Figure 1 X-ray pattern for 2625, 2222, and 2322 raw chitosan samples.

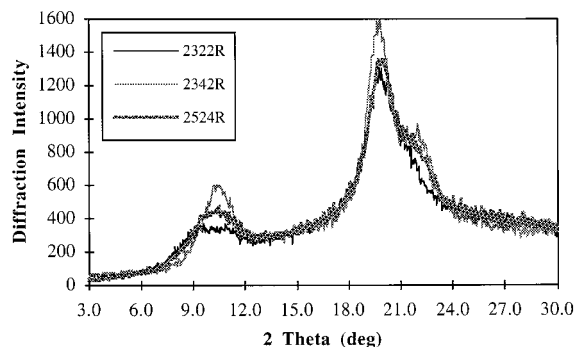


Figure 2 X-ray pattern for 2322, 2342, and 2524 raw chitosan samples.

Table II Crystallinity Index and Contribution of $2\theta \approx 10.4^\circ$, $2\theta \approx 20^\circ$, and $2\theta \approx 22^\circ$ Peaks

Sample Code	Crystallinity Index (%)	Contribution of $2\theta \approx 10.4^\circ$ Peak	Contribution of $2\theta \approx 20^\circ$ Peak	Contribution of $2\theta \approx 22^\circ$ Peak
2222 R	31.1	7.4	23.7	—
2322 R	26.9	5.4	21.5	—
2332 R	37.1	10.9	21.8	4.4
2342 R	36.8	7.8	23.3	5.6
2524 R	25.2	6.4	16.8	2.0
2625 R	25.0	7.2	17.8	—
2222 C	24.3	4.8	19.4	—
2322 C	27.2	5.8	21.3	—
2332 C	34.8	6.5	22.2	6.1
2342 C	28.2	4.9	18.3	5.0
2524 C	28.2	5.6	20.5	2.2
2625 C	24.8	5.6	19.2	—

The crystalline regions correspond to the peaks on the diffraction patterns at around $2\theta \approx 10.4^\circ$ and $2\theta \approx 20^\circ$. Figures 1 and 2 represent the diffraction patterns of the crude samples. It can be observed that the chitosan samples are separated in two classes regarding the general aspect of the pattern and the appearance of a shoulder at around $2\theta \approx 22^\circ$.

The X-ray reflection at the diffraction angle 10.4° is attributed to hydrated crystals of low crystallinity^{20,21} and corresponds to the form I cited by Samuels,²² while the reflection at $2\theta \approx 22^\circ$ is identified as representative of the crystallinity of the form II.

The presence of three peaks corresponds to the allomorphic crystalline form, also called "tendon" by Ogawa and coworkers:^{23,24} this is the hydrated form of the crude chitosan. Piron et al.¹⁹ reports that the dissolution of chitosan involves the progressive disappearance of the peak at $2\theta \approx 22^\circ$. Ogawa²⁵ has interpreted the loss in native crystallinity to the chitosan dissolving. Kurita et al.,²⁶ substituting nonaoyl groups on chitosan observe that the crystallinity decreases at low substitution degree while it increases again at high substitution levels. They explain the variation in copper sorption capacities to these grafting and to the variation in crystallinity.

Table II reports the main crystalline characteristics of the polymers, the contribution of $2\theta \approx 10.4^\circ$, $2\theta \approx 20^\circ$, $2\theta \approx 22^\circ$ peaks were separated, when possible, by measuring the area between the baseline of the region and the specific peak.

Resistance to Dissolution

Samples (before and after crosslinking) were put in contact for 48 h with pH 3 solutions containing

sulfuric or acetic acids. The dissolution was evaluated by weight loss. The sample being reacted with the solution was abundantly rinsed with demineralized water and the dry weight mass compared to the initial dry weight.

It appears that dissolution depends, as expected, on chitosan characteristics²⁷ and crosslinking increases chitosan resistance. It might be noticed that the weight of crosslinked chitosan particles increased after being reacted with sulfuric acid. This has been observed earlier by Muzarelli.¹⁶ Except for this case, all other experiments show that 49 to 73% of crosslinked chitosan flakes dissolve in acetic acid, while raw chitosan flakes are entirely dissolved. In sulfuric acid, raw chitosan flakes dissolution rate ranges between 29 and 63%. Taking into account the reaction of sulfate groups on chitosan, which has been observed with crosslinked particles, the actual dissolution rate might be higher, proving the effectiveness of the crosslinking step in the resistance to dissolution.

RESULTS AND DISCUSSION

Crosslinking Effect

Figure 4 and 5 show for the series of samples the molybdate sorption isotherms on chitosan and crosslinked chitosan flakes. Obviously, the crosslinking of chitosan flakes (G3: 250–500 μm) involves a significant reduction of uptake capacity: the maximum uptake capacity is about two times lower than that of the original raw material. This reduction seems to be indifferent to the type of chitosan: the molecular weight as well as the

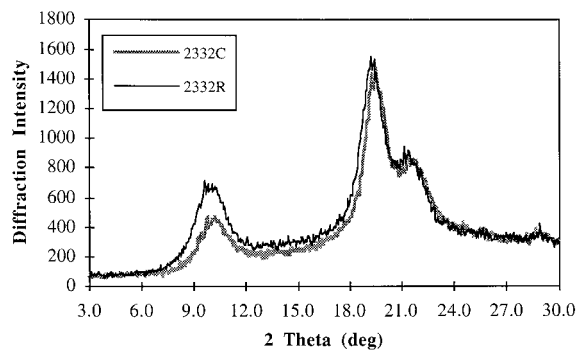


Figure 3 Effect of crosslinking on X-ray pattern for 2332 chitosan samples (R, raw; C, crosslinked).

deacetylation percentage do not affect the effect of glutaraldehyde crosslinking on sorption performances. The ranking of chitosan samples with respect to maximum sorption capacity is maintained before and after crosslinking. The effect of crosslinking may be related to two possible explanations: the crosslinking step blocks a significant number of sorption sites, or the crosslinking operation restricts the access of metal ions to internal sites by establishing physical bridges between the polymer chains and reducing free accessible volume.

The reaction of chitosan with glutaraldehyde has been widely discussed: two theories are proposed to explain the linkage between chitosan and aldehyde moieties. Muzzarelli et al.²⁸ have proposed that the unsaturated aldehyde groups give Mickael-type adducts on reaction with amino groups that involve the existence of two free aldehyde groups. On the opposite hand, Roberts and Taylor²⁹ have proposed the formation of an imine linkage between glutaraldehyde and amino groups via a Schiff's base reaction. The linkage between amine and aldehyde moieties could thus involve 1/1 or 1/2 relations (i.e., glutaraldehyde can be linked to one or two amine groups, some aldehyde groups can thus be free) involving a possible phenomenon of reduction.

The reaction of chitosan with glutaraldehyde produces a change in the crystallinity of the sorbent samples as shown in Table II. The grafting of the dialdehyde is expected to change the arrangement of the polymer and to increase the disorder of the polymer network. This rearrangement may decrease its crystallinity. This trend is not homogeneous in these experimental results. For some samples, the crystallinity is increased by the treatment, or almost unchanged (as seen in Fig. 3 and Table II). The difference in the be-

havior could be attributed to heterogeneous crosslinking. The difference in the crystallinity of the original material affects the hydration treatment of the polymer and the accessibility of glutaraldehyde to amine sites, inducing a varying crosslinking efficiency.

Chitosan samples being partially soluble in dilute sulfuric acid solutions (pH 3) it is unexpected to obtain such high uptake capacities with raw samples. Molybdate analysis, in the solution, takes into account both free and possible complexed forms. The organic content analysis in the filtrate is nonsignificant (measured by TOC meter). This behavior can be explained by a molybdate precipitation phenomenon previously described by Muzzarelli.¹⁶ Chitosan, dissolved in acetic acid, precipitates polymolybdate quantitatively. We can then imagine that the molybdate ions are recovered by a precipitation of chitosan molybdate (an instantaneous phenomenon) at the surface of the polymer allowing both metal recovery and polymer stability. Thus, we confirm that the high values reached for the sorption capacity are really due to metal ion recovery, even if the mechanism is rendered complex by the coexistence of sorption and dissolution/precipitation steps. This mechanism of gelling was also observed by Draget et al.,³⁰ molybdate being used for preparing homogeneous chitosan gels by *in situ* metal to polymer crosslinking.

The maximum capacity with these samples (2222/2322/2625) reached 700–750 mg Mo g⁻¹, corresponding to the uptake capacity of an equimolar ratio between molybdate and amine sites (Fig. 4). This interpretation of this molar ratio in terms of molecular mechanism is complicated due to the uncertainty on the molybdate species actually binded. Baes and Mesmer³¹ discuss the distri-

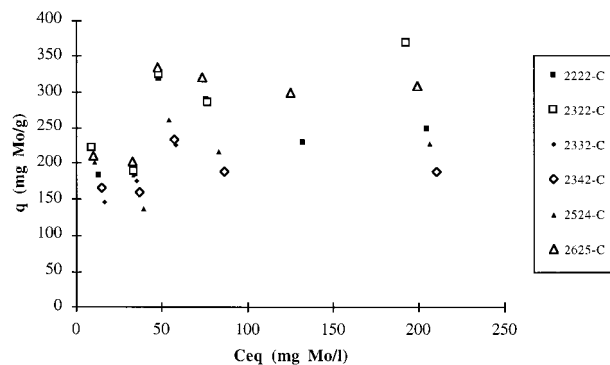


Figure 4 Molybdate sorption isotherms for 6 crosslinked chitosan samples (pH 3).

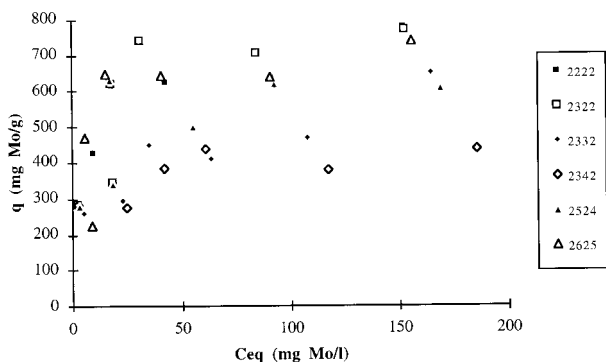


Figure 5 Molybdate sorption isotherms for 6 chitosan samples (pH 3).

bution of molybdate between several hydrolyzed polynuclear forms in the function of pH and total concentration. Milot et al.¹³ report the predominance of polymolybdate species of high anionic charge at pH 3. Then the identification of the effective sorbed species and following the comprehension of uptake mechanisms is not obvious.

With crosslinked chitosan the sorption performances are two times lower than those of raw chitosan, independent of chitosan sample (Fig. 5). The interpretation of sorption mechanisms is also complicated and studies using FTIR, ¹³C-NMR, and reflectance spectroscopy methods have shown that crosslinked chitosan involves a reduction of molybdate to molybdenum with a lower (but uncertain) oxidation state (Milot et al., unpublished results).

The reduction of sorption capacity by crosslinking can be attributed to several causes: the grafting of glutaraldehyde induces the saturation of a significant number of amine sites not available for a further molybdate sorption, and the change in the accessibility of sorption sites due to a modification of the crystallinity of the polymer. Kurita et al.²⁶ verify that the introduction of nonaoyl groups improves copper sorption on chitosan until an optimum substitution degree, while for higher substitution yield the sorption capacities decreases again, with respect to the crystallinity of the resulting polymer.

Molecular Weight and Deacetylation Percentage

Molecular weight and deacetylation percentage play an important part on dissolution procedure but can affect other important characteristics such as the density of available sorbent sites. The higher the acetylation rate, the lower the number

of free amine groups. The steric hindrance due to acetylation of amine involves a restriction of the accessibility to the free nitrogen doublet, a reduction of sorption performances may be expected with increasing the acetylation degree, as observed on several different samples of chitosan produced from shrimp or crab shells³² or fungal cell walls.³³ The distribution of molecular weights for 2322, 2332, and 2342 samples is almost identical ($1.5 \cdot 10^5 \pm 10\%$), ranking chitosan samples with respect to deacetylation degree shows that maximum uptake capacities are almost inversely proportional to this parameter. The previous hypothesis is not confirmed. Molybdate is not adsorbed on chitin (deacetylation degree < 15%); then the interpretation of the effect of this parameter is not clear.

The ranking of sorption capacities with respect to molecular weight does not obey a significant and continuous trend. Relative to sorption capacities, the six samples can be separated in two classes:

Best sorbents: 2322/2625/2222/2524

Worst sorbents: 2332/2342

In the class of the best sorbents, it appears that chitosan samples exhibit indifferently high or low molecular weights, this parameter cannot directly influence metal uptake rate. This is consistent with the results cited by Miyoshi et al.³³ on copper sorption on chitosan. Comparing maximum uptake capacities, it appears that for the best sorbents, the sorption level is almost the double of the level reached for the poorest sorbents. It seems that the differences in sorption performances and the unexpected effect of deacetylation percentage are not directly due to these parameters but to physical and physicochemical properties of the material, more specifically to the porosity and the crystallinity of the sorbent. These parameters are influenced by the production techniques used to reach chitosan specifications (molecular weight, deacetylation degree). Piron et al.¹⁹ show that uranyl sorption by chitosan flakes is affected by polymer hydration kinetics and by crystallinity of the material. The crystalline part of the polymer being not accessible to metal ions, inside the particle, decreasing the crystallinity of the sorbent allows a greater part of the particle to be used for metal recovery.

Ogawa and Yui²⁴ have observed that *N*-acetylated chitosan is less crystalline than pure chi-

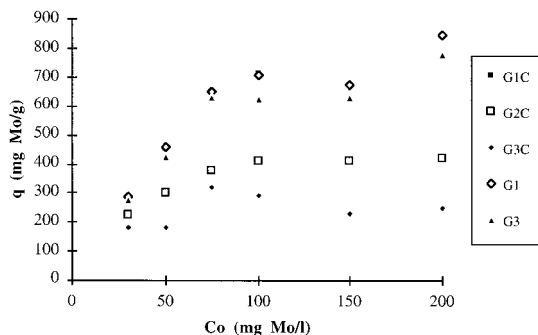


Figure 6 Particle size and initial concentration effects on molybdate sorption on chitosan 2222 (pH 3).

tosan, and that the molecular weight has a stronger effect on the sample crystallinity than the deacetylation percentage. Mochizuki et al.³⁴ have shown on chitosan membranes that the permeability is restricted to the amorphous regions of the film. Such conclusions are consistent with the actual observations.

Upon exposure to hydration, H₂O diffuses into the amorphous regions of the polymer, being below its glass transition temperature. The water diffusion obeys the same trend as metal ions diffusion. This hydration decreases the glass transition temperature T_g and water acts as a plasticizer.¹⁹ A similar trend is described by Murthy et al.^{35,36} for nylon 6: the decrease in glass transition temperature is attributed to the disruption of the hydrogen bonds between polymer chains and the mobility of the amorphous regions is increased. Piron et al.¹⁹ suggest that the polymer swelling destroys the residual crystallinity, increasing the accessibility of solute to sorption sites. Murthy et al.^{35,36} discuss and compare the effect of hydration on both crystalline and amorphous regions, and show that water diffuses preferentially into amorphous regions in which the humidity increases interlamellar spaces and decreases the plane spacing in the crystal lattice. In contradiction with the suggestions of Piron et al.,¹⁹ they also observe that the hydration increases the crystallinity of the samples; however, this increase in the crystallinity is attributed to the partial hydrolysis of the amide polymer at elevated temperatures.

For semi-IPN chitosan network, Yao et al.³⁷ show that the swelling for two chitosan deacetylated degrees, obeys the same trend for the first 7 min, while above this delay, the swelling degree increases in both rate and kinetics with the deacetylation degree. The increase in the glutaralde-

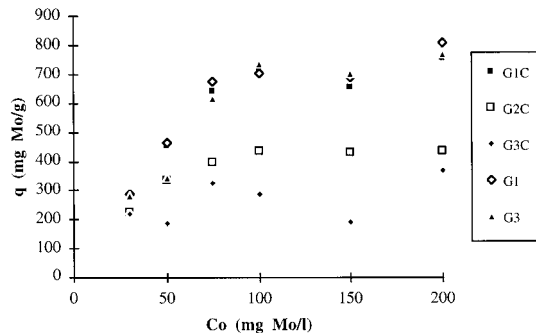


Figure 7 Particle size and initial concentration effects on molybdate sorption on chitosan 2322 (pH 3).

hyde crosslinking rate decreases the swelling degree. They show also that the swelling degree increases with a pH decrease.

Ogawa and Yui,²⁴ comparing partially *N*-deacetylated chitin and partially *N*-acetylated chitosan, observe that these modified forms of chitosan are less crystalline than a pure deacetylated chitosan and that the *N*-acetylation of pure chitosan involves the production of a less crystalline sample than the solid-state deacetylation of chitin. The transition metal chelation being favored by the hydrated crystal or noncrystalline form of chitosan, they propose to process the deacetylation on higher molecular weight chitosan samples. They demonstrate that the acetylation degree has a lower influence on the crystallinity of the produced samples than the molecular weight of the crude material.

Moreover, we can observe that the best sorbent are characterized by the absence of diffraction peak at $2\theta \approx 22^\circ$, showing that the crystallinity affects the polymer ability to sorb efficiently molybdate (Table II).

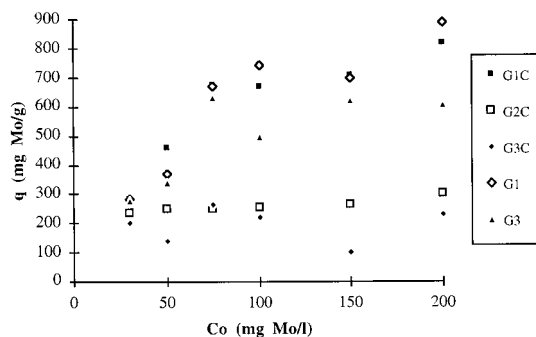


Figure 8 Particle size and initial concentration effects on molybdate sorption on chitosan 2524 (pH 3).

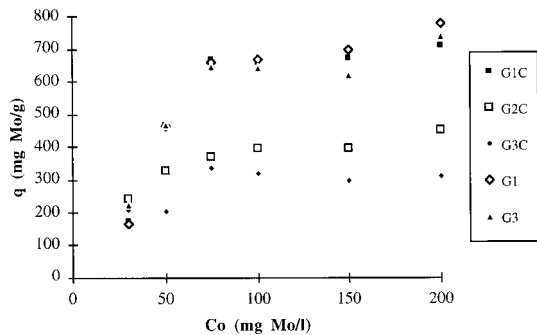


Figure 9 Particle size and initial concentration effects on molybdate sorption on chitosan 2625 (pH 3).

Effect of Particle Size

Figures 6–9 report for the four best sorbents (2322/2625/2222/2524), respectively, the molybdate sorption for several particle sizes of chitosan in both raw and crosslinked forms at several initial concentrations. These figures confirm, whatever the type of chitosan, that sorption performances are comparable for G1 and G3 particle size in the raw form, while a strong and continuous restriction is obtained with crosslinked chitosan particles between G1, G2, and G3 classes.

It should be noticed that the sorption performances of G1 crosslinked chitosan flakes are quite similar to those obtained with raw flakes. This observation allows the effect of glutaraldehyde crosslinking to be highlighted. Two hypotheses have been previously proposed: blockage of sorption sites by aldehyde moieties, and restriction of the accessibility to internal sites by formation of linkage between polymer neighboring chains. The capacity being quasi-identical for G1 sorbent size in both raw and crosslinked flakes, it indicates that the grafting of glutaraldehyde moieties on amine sites does not affect the accessibility of sorption sites.

The restriction in sorption observed for greater particle sizes, which was already observed with raw chitosan and uranyl ions, is more conveniently attributed to a restriction of the access to the diffusion network over the first external layers of the polymer.¹⁰ This restriction is not effective for the lowest particle sizes: the diffusion layer thickness being of the same order of magnitude of the corresponding particle radius (0–60 μm).

Influence of Chitosan Physicochemical Properties on Molybdate Sorption Kinetics

Figures 10–11 show that the kinetic behavior changes significantly with the physicochemical

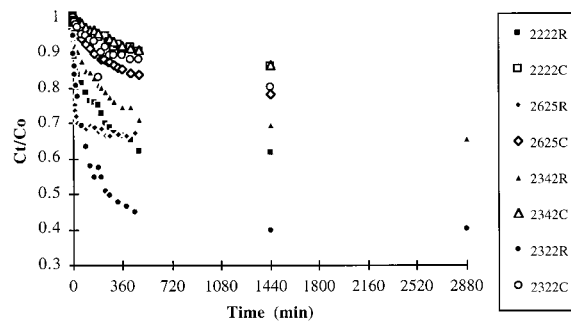


Figure 10 Effect of physicochemical characteristics of chitosan and crosslinking on molybdate sorption (pH 3, variable volumetric charge; R, raw chitosan; C, crosslinked chitosan).

characteristics of the sorbent and its crosslinking. With a varying volumetric charge, giving a saturation rate equivalent for each sorbent, it appears that the sorption kinetics are significantly reduced for crosslinked particles, while raw chitosan exhibits both high uptake capacity and sorption rate. Among raw chitosan, samples (2322/2222/2342/2625) present fast molybdate sorption. However, one of them (2625) exhibits an unexpected kinetic trend with a quasi-instantaneous sorption giving equilibrium in the first minutes of contact time, while for other experimental conditions, about 6 h of mixing are required to reach about 80% of the total uptake. This sample is characterized by one of the lowest deacetylation degrees and a low viscosity and molecular weight.

These observations are also valid when the volumetric charge is constant: kinetic curves are quite well superimposed for 2222/2322/2625 crosslinked flakes, with low uptake capacities. 2322 and 2222 are also superimposed for raw chitosan flakes, while the sample 2625 differs sig-

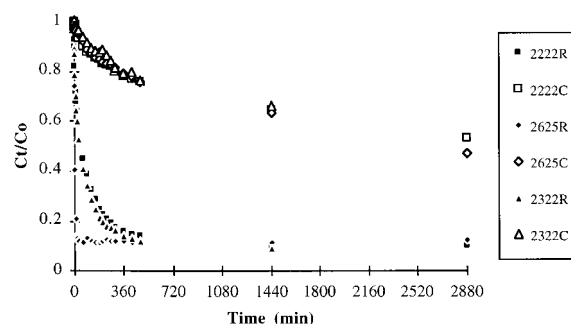


Figure 11 Effect of physicochemical characteristics of chitosan and crosslinking on molybdate sorption (pH 3, constant volumetric charge; R, raw chitosan; C, crosslinked chitosan).

nificantly from them, with the same instantaneous trend in sorption kinetics as observed with variable volumetric charge.

The behavior of the 2625 sample can be explained by two possible phenomenons related to an increased solubility of the polymer and by a low crystallinity. The former favors the contact between each binding/complexing site with metal ions followed by a fast gel formation; the latter induces an increase in the water diffusion and hydration that favors metal diffusion. However, the trend followed by the other samples is not directly related to the molecular weights or deacetylation percentage. The crosslinking step uniformly reduces the sorption kinetics, with an initial slope less favorable for crosslinked samples and an equilibrium reached after a longer contact time.

The study of sorption isotherms has shown that among the six chitosan samples, 2625 and 2322 samples exhibit the highest uptake capacity; we observe, in this part, that the 2625-type chitosan is much more adapted to molybdate recovery in acid medium than the 2322 type, due to the faster sorption reaction.

CONCLUSION

These experiments show that molybdate sorption is strongly influenced by several physicochemical parameters. Varying deacetylation degrees and molecular weight demonstrates that the maximum uptake capacity can be easily doubled, with an appropriate choice of the physicochemical characteristics of the sorbent.

The trends followed by the uptake capacities against molecular weight and deacetylation degree are not easy to interpret directly. However, the experimental procedures employed to reach these technical specifications affect the crystallinity of the polymer samples, and we show that a correlation exists between the best sorbents and the lowest crystallinities. These conclusions are consistent with previous results exposed by Kurita et al.^{26,32} and Piron et al.¹⁹ The sorption occurs in the amorphous regions and the crystallites are not accessible for water and metal ions (excepted at their external surface). These parameters also affect the sorption kinetics, due to the influence of crystallinity on the hydration kinetics.

This study has been performed on commercial samples issued from several lots. This prelimi-

nary study, showing the necessity to improve the understanding of the sorption control by physicochemical characteristics of the polymer might be completed by a complementary work using a standard chitosan on which several samples will be produced with different deacetylation degree and molecular weight.

The glutaraldehyde crosslinking reduces the sorption performances for high particle sizes (G3: 250–500 μm), mainly due to a restriction of the accessibility to internal sites. The blockage of sorption amine sites by aldehyde moieties does not affect the sorption yield for the lowest particle sizes (G1: 0–125 μm).

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