Adsorption of Chitosan and a Quaternized Derivative on Kaolin

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Synopsis

Adsorption of chitosan on kaolin was tested and a comparison was made with a fully quaternized derivative. The influence of pH, molecular weight, and acetyl content on the results was also studied. The adsorption isotherms and the flocculating properties as functions of the various parameters are discussed.

INTRODUCTION

Adsorption of water-soluble polymers on solids plays an important role in many applications requiring the dispersion or the agglomeration of particles. Generally, adsorbed polymers modify the electrokinetic potential of the solid. They can also cause interparticle linkage. Thus, they can be used to modify properties of colloidal suspensions.

Relatively little has been published on the adsorption of chitosan.[1-4] The work of Jiang et al. seems to be the only literature on the use of this polymer as a flocculating agent for suspensions of kaolinit, monmorillonit, and natural muds.[4]

The purpose of this work is to examine the adsorption of chitosan and its quaternized derivative on kaolin in a defined media.

EXPERIMENTAL

Materials

The kaolin used was a "kaolin des Charentes" with reference B-24 AGS. It has been the subject of numerous studies. Its principal characteristics were reported by Nabzar.[5] To reduce its ionic composition, we converted it into the homoionic Na-kaolin form by the procedure he described.

We used four commercial chitosan samples, purified as previously proposed[6] and a quaternized derivative prepared in our laboratory.[7] The characteristics of all these polymers are listed in Table I.

Methods

The solid concentration was chosen at 2%. The adsorption was performed in measuring tubes. Thus, 0.4 g of kaolin were dispersed in 10 cc of 5×10^{-2} M NaCl solution with moderate mechanical stirring for 1 minute. The resulting

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TABLE I
Characteristics and Origins of Polymers Studied

Chitosan	Acetyl content[a] τ (%)	$[\eta]$ (mL/g)	M_v ($\times 10^{-3}$)[b]
I. From Protan			
Lot 016.052.03	14.6	604	870
II. From Protan			
Lot 016.590.01	15.0	404	565
III. From Protan			
Lot 074.320.01	13.6	280	380
IV From Sigma			
Lot 44F-0795	5	434	610
100% quaternized			
sample[c]	5		$M_w = 74\,000$

[a] According to Miya et al. (8).
[b] Determined by means of Domszy and Roberts viscosity law (10).
[c] Obtained from sample IV (7).

suspension was adjusted to the chosen pH by addition of HCl or NaOH. After 24 hours of equilibration, 10 cc of a given polymer solution, with a known concentration, adjusted to the same pH, was added. The whole was homogenized by repeated reversals for 1 minute. After another 24 hours, the volume of sediment was measured. The supernatant was then isolated by centrifugation at 10,000 rpm for 5 minutes. To determine its polymer content, 1 mL of this solution was injected in a gel permeation chromatography column, 0.9 cm i.d. and 100 cm in length, filled with Biogel P4 (200–400 mesh). The eluent was a pH 4.2 buffer made from ammonium acetate ($5 \times 10^{-2}M$) and acetic acid (13 g/L). On-line refractive index detection was obtained by means of a Jota (Jobin-Yvon) differential refractometer. A standardization, established from several injections of polymer at various known concentrations, permitted the quantization of the polymer content in each supernatant and, therefore, the amount adsorbed per gram of kaolin. For the lowest concentrations, all supernatant was freeze-dried, redissolved in 1 mL of eluent, then injected. This method allows measurement of very low polymer concentrations at equilibrium. Thus, good precision was achieved in the range of 90–100% adsorption.

Electrokinetic potential was measured by electrophoresis, using a laser Zee-Meter 500 A (Pen-Kem Inc. USA). A potential of 100 volts was applied to the suspensions, which were diluted up to 0.05% (w/v) with the same solvent as was used to establish the isotherms of adsorption.

RESULTS AND DISCUSSION

Isotherms of Adsorption, Role of the Different Parameters

The chemical structure of the two types of polymer used in this work is given in Figure 1. The adsorption isotherms of chitosan [Fig. 1(a)] and of its 100% quaternized derivative [Fig. 1(b)] on kaolin are reported in Figure 2. The pH range of below 6 studied here was chosen intentionally to avoid precipitation of chitosan.[9]
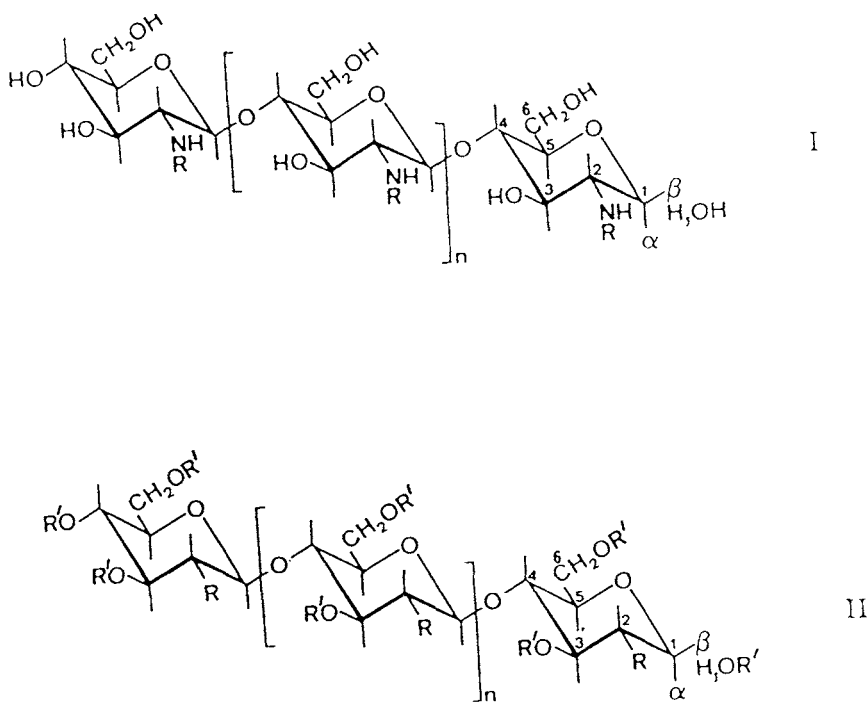
Fig. 1. Chemical structure of: (I) chitosan – R = H $(100 - \tau\%)$, $-\overset{\text{O}}{\underset{\|}{\text{C}}}-CH_3$ $(\tau\%)$ (see Table I); (II) N-trimethyl chitosan chloride – R = $-NH-\overset{\text{O}}{\underset{\|}{\text{C}}}-CH_3$ (5%), $-N^+$ $(CH_3)_3$, Cl^- (95%), R' = CH_3.

In the case of the quaternized derivative, there is a dependence on pH which corresponds to a gradual decrease of the level of the adsorption plateau as the H^+ concentration increases. The role of the pH is much more pronounced for the unmodified chitosan in that an adsorption plateau cannot be attained at pH 6. This dependence can be related to a modification of the charge of the kaolin when the pH varies, and, in the case of chitosan, to a large increase of the polymer net charge when pH values vary from 6 toward 4.

Three chitosans with nearly equal acetyl contents, but with different intrinsic viscosities, were used to test the influence of molecular weights on adsorption. Indeed, for all the samples, in the range of concentrations at equilibrium studied here (Fig. 3), the adsorption plateau is never attained, at pH 6, for any polymers. Moreover, the amount of adsorbed polymer increases with the molecular weight.

The comparison between the results obtained with two chitosans of nearly equal molecular weights, but with two different acetyl contents namely 5 and 14.6% (Fig. 3), shows the importance of the latter parameter. It appears particularly that the presence of N-acetylated residues is an unfavorable factor for the adsorption process.
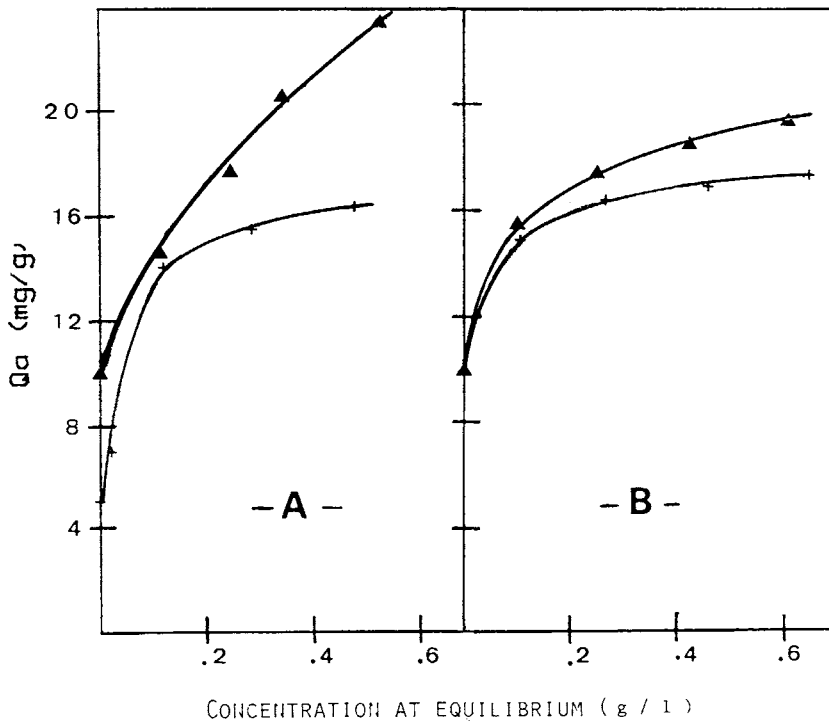
Fig. 2. Influence of pH on the adsorption isotherms in $5 \times 10^{-2} M$. NaCl: A, for chitosan IV (see Table I) and B, for the 100% quaternized derivative, at pH 4 (+ + +) and 6 (▲▲▲). Q_a is the adsorbed amount of polymer per gram of kaolin.

Adsorption results can be interpreted by means of the Langmuir equation

$$C_{eq}/Q_a = 1/Q_s \times b + C_{eq}/Q_s$$

in which Q_a and Q_s are the experimental adsorbed and limit adsorbed amounts, respectively, for a C_{eq} polymer concentration at equilibrium and b is the adsorption intensity. Q_s, thus determined, can be compared with the theoretical limit adsorbed amount $Q_{max} = S \times mo/S_m$ with S_{m_0} the space occupied by a glucosamine residue (assumed to be equal to 25 Å^2), m_o its molecular weight, and S the specific area of kaolin. The quantity $\theta = Q_s/Q_{max}$, expresses the coverage ratio, corresponding to the maximal fraction of surface area covered, under the hypothesis of a flat binding. Table II gives the values obtained for the various conditions studied. Particularly noticeable is an increase of θ and Q_s with pH as b decreases.

Study of Sediment Volumes and Electrokinetic Potential

Flocculation was studied by measuring the sediment volume after 24 h of equilibration. The results are given in Figure 4. For the 100% quaternized derivative, the variation of the sediment volume as a function of the polymer concentration is similar for pH 4 and 6, but more pronounced at pH 4. This
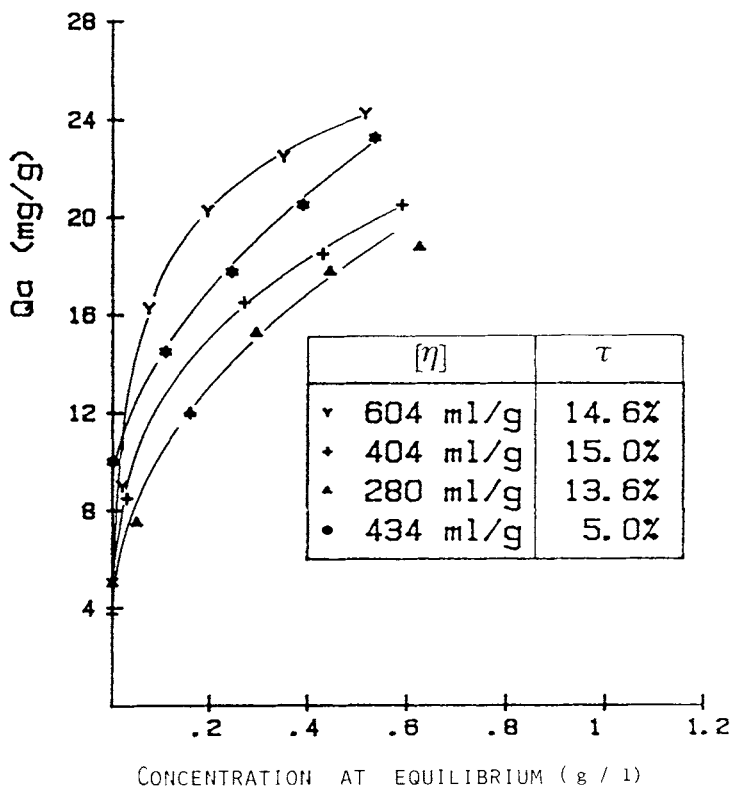
Fig. 3.   Influence of molecular weight (characterized by $[\eta]$) and of the N-acetyl content ($\tau\%$) on the adsorption isotherms at pH 6, in $5 \times 10^{-2}M$ NaCl.

corresponds to a progressive evolution from partially flocculated suspension, in the absence of polymer, to a highly flocculated media, then to a stabilization of the dispersion for the highest polymer concentrations. The measurements of light transmission through the supernatants show an analogous evolution: from partially clear, they become quite transparent at the maximum of flocculation, and then become fully opaque at high polymer concen-

TABLE II
Parameters Calculated from Langmuir Equation for the Various Polymer Samples Studied

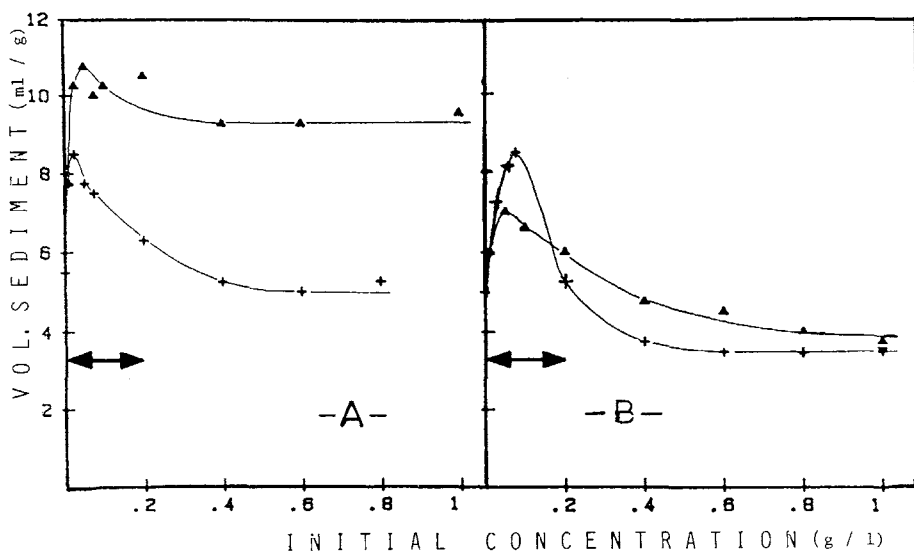| Samples	100% Quaternized derivative		I	II	III	IV	
Q_{max} theoretical (mg/g)	48.0		37	37	37	35.8	
pH	4	6	6	6	6	4	6
Q_s (mg/g)	18.2	21.0	27.0	24.3	23.0	17.0	25.0
b	31.3	27.1	16.5	8.2	7.2	58.8	12.3
θ	0.38	0.44	0.73	0.65	0.62	0.47	0.70

Fig. 4. Influence of pH on the variation of sediment volume as a function of the initial concentration of polymer in $5 \times 10^{-2}M$ NaCl: A, for chitosan IV and B, for the 100% quaternized derivative, at pH 4 (+ + +) and 6 (▲▲▲). ↔ range of total polymer adsorption.

tration. Also of note is an increase of the sediment volume at the maximum of flocculation when pH decreases. This maximum takes place for relatively low initial polymer concentrations between 5×10^{-2} and 7.5×10^{-2} g/L (2.5 to 3.75 mg of chitosan per gram of solid) in the range of total adsorption.

In the case of the unmodified chitosan, flocculation occurs for a slightly lower range of initial concentration, between 2.5 and 5×10^{-2} g/L. These values depend on pH. Unlike the above case, the sediment volumes increase with pH on a relatively wide scale. A correlation between increased flocculation and polymer molecular weight is also observed.

After the maximum, attributed to the formation of interparticular bridges, the values of the sediment volume decrease and attain values lower than the initial measurements in absence of polymer. This is obtained with chitosan under $-NH_3^+$ form (pH 4) and for the quaternized derivative mainly at pH 4. This phenomenon corresponds to a dispersing effect based on electrostatic repulsion between positively charged adsorbed layers.

Simultaneously, the evolution of the electrokinetic potential was also measured. In absence of polymer, the zeta potential (ZP), according to the pH, varies between -18 and -35 mv for the solid (Fig. 5). The lower value obtained at pH 6 corresponds, in this case, to a better stabilization of kaolin. Whatever the studied parameter, the ZP does not vary much in the range of concentrations below that initial polymer concentration (0.1 g/L) for which a high polymer adsorption and maximum flocculation were observed. The crossover, present in each case, seems to indicate that adsorption of cationic polymers reverses the net charge of the solid. This becomes a positive particle with a high ZP, producing, then, a stabilization of the dispersion. The values of ZP are also higher at pH 4 and confirm the previous data.
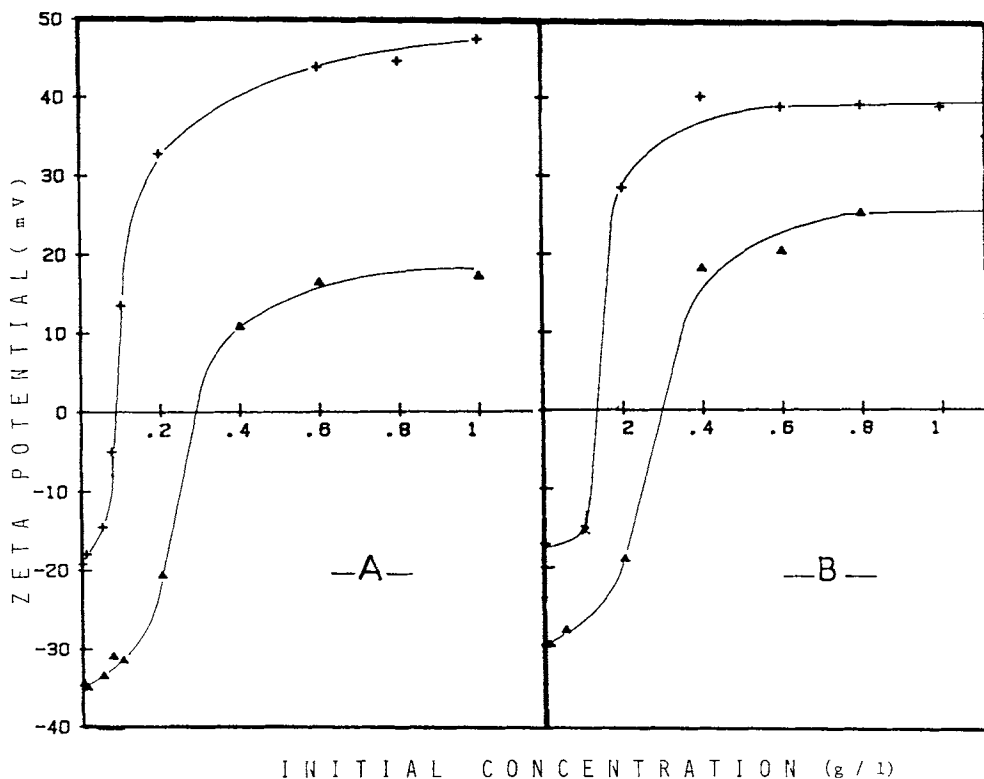
Fig. 5. Influence of pH on the variation of the zeta potential as a function of initial concentrations of polymers for: A, chitosan IV and B, the quaternized derivative, at pH 4 (+ + +) and 6 (▲▲▲) in NaCl 5×10^{-2} M.

Mechanism of Adsorption Proposed

Kaolin possesses a negative net charge for all pH > 4[5] that increases between pH 4 and 6. Chitosan exhibits an $-NH_3^+$ sites fraction near 0.9 and 0.5 at pH 4 and 6, respectively.[9] Thus, the electrostatic attractions kaolin-polymer will be favored on acidic pH in agreement with a faster inversion of the electrokinetic potential at pH 4 [Fig. 5(A)]. The large value of the adsorption intensity obtained on pH 4 (Table II) can be explained, assuming that, although the solid has, at this pH, a lower negative charge (compared to pH 6), the polymer bears a very important positive charge. At pH 6, the electrostatic mechanism is weakened ($-NH_2/$ $-NH_3^+$).[1] It is then possible to consider a fixation of chitosan on kaolin by means of hydrogen bonds with the oxygen atoms of the silicic basal faces or with the aluminol and silanol groups of the lateral faces. The presence of these low energy interactions agrees with the fact that the adsorption plateau is never attained (for our conditions) at pH 6 [Fig. 2(A)]. The influence of pH on the adsorption of the quaternized derivative is much less important because, in this case, only the net charge of kaolin varies with pH. The electrostatic attractions are then less important at pH 4, which corresponds to a lower adsorption [Fig. 2(B)]. A certain analogy between chitosan under its cationic form and its quaternized

derivative is noticeable. As concerns the influence of the molecular weights, the results reported in Table II for the three polymers of near acetyl contents show an increase of Q_s with $\overline{Mv}$. One can consider that an increase of molecular weight favors the formation of loops during the fixation.

CONCLUSION

Chitosan can be considered as a good flocculating agent for mineral particles. The best conditions can be obtained with a polymer fully deacetylated and of high molecular weight. The quaternized derivative can also be considered interesting, but its low molecular weight caused by degradations during its synthesis, limits its applications. On the contrary, it becomes a good dispersing polymer to stabilize kaolin suspensions mainly for pH 4.

References

1. A. Suzuki and I. Kashiki, *Kagaku Kogaku Robumshu*, **8**, 728 (1982).
2. J. Rouger and P. Mutje, *Br. Polym. J.*, **16**, 83 (1984).
3. J. G. Domszy, G. K. Moore, and G. A. F. Roberts, in *Cellul. Its Derivatives*, J. F. Kennedy, Ed., Horwood, Chichester U.K., 1985, p. 463.
4. T. Jiang, E. Luan, E. Wu, M. Suping, and L. U. Depei, *Huanjing Huaxue*, **3**, 31 (1984).
5. L. Nabzar, Thesis, Strasbourg, France, 1985.
6. A. Domard, *Int. J. Biol. Macromol.*, **9**, 98 (1987).
7. A. Domard, M. Rinaudo, and C. Terrassin, *Int. J. Biol. Macromol.*, **8**, 105 (1986).
8. M. Miya, R. Iwamoto, S. Yoshikawa, and S. Mima, *Int. J. Biol. Macromol.*, **2**, 323 (1980).
9. A. Domard, *Int. J. Biol. Macromol.* **9**, 98–104 (1987).
10. G. A. F. Roberts and J. G. Domszy, *Int. J. Biol. Macromol.*, **4**, 374–377 (1982).