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Polycation adsorption on montmorillonite: pH and *T* as decisive factors for the kinetics and mode of chitosan adsorption

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ABSTRACT: Adsorption of the polycation chitosan on montmorillonite was studied at different pH values from 4.5 to 6.5 and at temperatures of 25, 50 and 75ºC. The amount of chitosan adsorbed increased with temperature, indicating that temperature is a decisive factor. At pH 5.0 and 25ºC the amount adsorbed was 1.18 $mol_c\ kg^{-1}$, whereas it was 1.5 times higher (1.79 $mol_c\ kg^{-1}$) at 75ºC. The uptake of chitosan increased significantly at higher pH. This can be attributed to the decrease in the degree of protonation. Surface charge and X-ray diffraction measurements indicate that most of the chitosan is adsorbed in the interlayer, where mono- and bilayer structures are formed.

The kinetics of chitosan adsorption also depend on temperature and pH. At $\geqslant$50ºC, the adsorption mechanism of chitosan on montmorillonite is closest to the intraparticle diffusion model, whereas at lower temperature (25ºC) the adsorption process is closer to the pseudo-second order model. The pH of the solution affects the protonation degree of chitosan and the mode of adsorption on montmorillonite, but not the adsorption rate.

For chitosan-montmorillonite prepared at pH 5.0 and 75ºC, the effective anion exchange capacity (AEC) was found to be 80% (0.36 $mol_c\ kg^{-1}$) of the calculated value. The relatively large AEC and the location of most of the anion exchange sites in the interlayer make chitosan-montmorillonite an interesting prospect as an adsorbent for water-purification procedures.

KEYWORDS: organo-clay mineral, chitosan, montmorillonite, adsorption kinetics, anion exchange capacity.

Clay minerals with negative layer-charge generally have a low adsorptive capability for neutral and anionic compounds. To improve the adsorption properties, clay minerals can be modified by certain organic cations (Beall, 2003; Gecol *et al*., 2005). The resulting organo-clays have the capability to adsorb neutral organic compounds (Mortland *et al.*, 1986) and, if the uptake of organic cations exceeds the cation exchange capacity (CEC), they exhibit adsorptive capability for anions. The latter is due to an ion exchange reaction. Montmorillonite modified with hexadecylpyridinium ($HDPy^+$) was suggested as an adsorbent for I^- and TcO_4^- (Bors *et al*., 2000), and in the case of modification with hexadecyltrimethylammonium ($HDTMA^+$) as an adsorbent for CrO_4^{2-} (Li & Bowman, 1998).

Polycation-exchanged clays are believed to be more stable adsorbents than clays modified with monovalent or bivalent organic cations, because a polycation is bound to the clay mineral at several sites (Döppers *et al*., 2004). Darder *et al*. (2003) reported that "the deintercalation of the biopolymer is very difficult". Despite the high charge and large molecular weight of polycations, they are not only adsorbed on the external surface but also in the interlayer of montmorillonite. Due to the long chain and the highly variable surface charge density of polycations, the adsorption on the surfaces of

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negatively charged clay minerals might be much less complete than in the case of mono- and bi-valent organic cations. The difference in the segment length between charged units in the polycation chain and the layer-charge density is thought to be the main reason for the formation of loops and trains on the external surface of montmorillonite (Breen, 1999), and these affect the surface properties and microstructure of polymer-clays. Negatively charged sites in the interlayer also attract polycation chains and increase the amount adsorbed. The amount adsorbed depends on the so-called cationicity (Denoyel *et al*., 1990) of the polycation. With decreasing cationicity, the amount adsorbed increases strongly. It is also known that the high uptake of polycations favours the delamination of montmorillonite (Döppers *et al*., 2004).

Chitosan, a natural non-toxic biopolymeric cation, was recently found to adsorb on external surfaces and in the interlayer of montmorillonite in amounts of 157% of the CEC (Darder *et al*., 2003). As a consequence of this high uptake, chitosan-montmorillonite is an adsorbent for anions and has an anion exchange capacity (AEC) which is greater than half the CEC. It was shown that certain anions are preferentially adsorbed on chitosan-montmorillonite. Gecol *et al*. (2005) reported that chitosan-coated montmorillonite exhibits selectivity for anionic tungsten species.

From the economic point of view, chitosan obtained from chitin is a relatively cheap material because chitin is the second most abundant polymer in nature, next to cellulose (Chang & Juang, 2004). The unfavourable mechanical property (pronounced swelling in water) and the low specific gravity of chitosan, however, makes it rather inconvenient for use as an adsorbent in either batch or column experiments. The physical nature of chitosan improves when it is adsorbed onto clay minerals. Chitosan may have a high surface charge-density due to amine groups in its chain, which can be protonated in weak acidic solutions (Dambies *et al*., 2001). An extensive study on the determination of the protonation degree of chitosan was recently performed by An & Dultz (2007). Due to the protonation of amine groups, the pH of the solution governs the adsorption mode of chitosan on montmorillonite. As most of the adsorption sites for chitosan-montmorillonite are located on the internal surfaces of montmorillonite, the diffusion of chitosan into the interlayer is a very important process. In general, temperature affects such adsorption processes.

Several kinetic models such as mass transfer and chemical reaction can be used as controlling mechanisms of the adsorption processes. It is doubtful that the adsorption process of a polycation with different functional groups such as chitosan, which contains different amounts of protonated and non-protonated amine and hydroxyl groups, can be explained by only one kinetic model (Wu *et al*., 2000). To date, only a few studies exist on the adsorption of chitosan on montmorillonite (e.g. Darder *et al*., 2003), and there is little knowledge about the factors which favour the uptake of chitosan in the interlayer.

In this paper we explain the effect of the two main factors, temperature and pH of the solution, on the adsorption of chitosan on montmorillonite, considering the kinetics and mode of the adsorption process and structural and chemical properties of the resulting chitosan-montmorillonites.

MATERIALS AND METHODS

Preparation of chitosan-montmorillonite

For the preparation of chitosan-montmorillonite, MX-80 Wyoming-bentonite (Volclay) was used. The CEC, determined with the Cu-triene-complex, is 0.822 $\mathrm{mol_c\ kg^{-1}}$. The exchangeable cations are Na^+ (~65%) and Ca^{2+} (~35%). Chitosan of high molecular weight (MW average = 342500 g $\mathrm{mol^{-1}}$) containing an average number of 2130 glucosamine units with a MW of 161 g $\mathrm{mol^{-1}}$ (Darder *et al*., 2003), was purchased from Kraeber GmbH&Co (Germany). The deacetylation degree, determined by polyelectrolyte titration in combination with a particle charge detector (PCD 03, Mütek), is 74.5% (4.6 $\mathrm{mol_c\ kg^{-1}}$). The solubility properties of chitosan as a function of pH and *T* were determined by measuring the turbidity of the chitosan solution by a UV-visible spectrophotometer (VARIAN Cary 50 Scan).

The method described by Darder *et al.* (2003) was used for the preparation of chitosan-montmorillonite. Chitosan solutions were prepared by addition of corresponding amounts of poly-saccharide to 1% (v/v) acetic acid. To determine the effect of the solution pH on the uptake of chitosan, the pH of the biopolymer solution was adjusted to 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5 using 1 M NaOH before mixing with the montmorillonite suspension (2%). In each case, chitosan was applied in amounts corresponding to 500% of the CEC (200 mg clay and 175 mg chitosan). When chitosan was applied in concentrations >500% of the CEC, the amounts adsorbed were found to be more or less constant (An & Dultz, 2007). The suspensions were placed in 60 ml centrifuge tubes and shaken in a temperature-controlled water bath for time periods of 0.5, 1, 2, 4, 6, 12, 24, 48, 72 and 168 h at 25, 50 and 75ºC. As flocculation of chitosan was observed at pH 6.0 at >60ºC and pH 6.5 at >50ºC, no chitosan-montmorillonites were prepared under these conditions. The shaking frequency was 200 rpm. The resulting organo-clays were separated by centrifugation and washed three times with water to remove the free salt. Finally, the samples were freeze-dried. In order to characterize the uptake of chitosan, the C-content of the samples was determined by a CNS analyser (LECO 2000).

Surface-charge determination

A particle charge detector (PCD 03, Mütek) was used in combination with titration with charge-compensating polyelectrolytes (Müller, 1996; Böckenhoff & Fischer 2001). The end-point of titration was defined at zero potential. For negative surface-charge, the cationic polyelectrolyte poly-DADMAC (poly-diallyl-dimethyl-ammonium chloride) and for positive surface-charge, the anionic polyelectrolyte PES-Na (sodium-polyethylene-sulphonate) was used. For each titration, 20 mg of the organo-clay sample were mixed with 10 ml of distilled water, which was adjusted to pH 4.5 with 0.01 N HCl. At this pH, free amine groups in chitosan-montmorillonite can be protonated, and those on the external surface can be quantified by polyelectrolyte titration. After dispersion by ultrasonic treatment for 15 s, the sample was transferred into the titration cell.

Determination of the anion exchange capacity

The AEC was calculated from the amount of chitosan adsorbed on montmorillonite, from the C content and the protonation degree. For the chitosan under investigation, 74.5% of the amine groups can be protonated. Based on the CEC of MX-80 bentonite, the positively charged amine groups required for neutralization of the layer charge amount to 0.822 $\text{mol}_c\ \text{kg}^{-1}$. The AEC of chitosan-montmorillonite is calculated according to:

$$\text{AEC} = 0.745*q - 0.822 \tag{1}$$

where the unit of AEC is $\text{mol}_c\ \text{kg}^{-1}$ clay and q is the amount of chitosan adsorbed ($\text{mol}_c\ \text{kg}^{-1}$ clay). For chitosan-montmorillonite, which is the reference in this study, the AEC is therefore given as $\text{mol}_c\ \text{kg}^{-1}$ chitosan-clay.

The calculated protonation degree (P_c) can be estimated using the following equations:

$$P_c = C_{\text{NH}_3^+-\text{R}}/C \tag{2}$$

$$\text{pK} = \text{pH} - \lg((1 - P_c)/P_c) \tag{3}$$

where K is the equilibrium constant in the protonation reaction of the amine group in chitosan, pK is 6.3 (Darder *et al.*, 2003), C is the total concentration of the amine group in chitosan and $C_{\text{NH}_3^+-\text{R}}$ the concentration of the protonated amine group at a given pH. The protonation degree was determined experimentally using the PCD combined with polyelectrolyte titration. The measured protonation degree (P_m) is given by:

$$P_m = S_{\text{pH}}/S_{\text{total}} \tag{4}$$

where S_{pH} and S_{total} are the surface charges of chitosan at a given pH and for completely protonated chitosan, respectively. The calculated protonation degree of chitosan (P_c) was found to be in good agreement with the measured value, P_m (An & Dultz, 2007).

For comparison, the AEC was also determined experimentally for chitosan-montmorillonite prepared at pH 5.0 and 75ºC. 50 mg were added to 50 ml of a 0.1 N NaI solution. The pH of the suspensions was adjusted to pH 4.5 with 0.1 N HCl. After shaking at 200 rpm for 5 h at room temperature, the samples were separated and washed until free of salt. Then 50 ml of a 0.05 M NaCl solution adjusted to pH 4.5 were added and the samples were shaken for 5 h at room temperature to desorb I^- from the exchange sites. After separating the sample from the solution by centrifugation and decantation, this procedure was repeated twice. The amount of I^- in the exchange solution was analysed by anion chromatography (DIONEX ICS-90).

X-ray diffraction analysis

The basal spacings of the original clay and the chitosan-montmorillonite samples were determined using a Philips PW1390 X-ray diffractometer with Cu-$K\alpha$ radiation. Samples were dispersed in distilled water, sedimented on glass slides and air-dried.

Kinetic models for the adsorption mechanism of chitosan

Three different models were used for identification of the controlling mechanism of the adsorption process of chitosan on montmorillonite. The pseudo-first order equation is a simple kinetic model (Ho & McKay, 1999):

$$\ln (1 - \alpha) = -k_f * t \quad (5)$$

where k_f is the rate constant of pseudo-first order, $\alpha = q_t/q_e$ is the fractional attainment of equilibrium, and q_e and q_t denote the amounts adsorbed under equilibrium conditions and at any time *t*, respectively. Furthermore, a pseudo-second order equation, based on the adsorption equilibrium capacity (Ho & McKay, 2000), was used:

$$t/q_t = 1/(k_s * q_e^2) + (1/q_e) * t \quad (6)$$

where k_s is the rate constant of pseudo-second order. From equation 6, k_s and q_e can be determined by using the slope of the linear plot of t/q_t *vs.* *t* and the intersection with the vertical axis. As the two models do not identify the definite mechanism of adsorption, another simplified model, the intraparticle diffusion model which originates from Fick's second law (Wu *et al.*, 2001; Chang & Juang, 2004), was used:

$$q_e = k_i * t^{1/2} \quad (7)$$

where k_i is the rate constant of intraparticle diffusion, which can be calculated by using the slope of the linear plot of q_e *vs.* $t^{1/2}$.

For comparison of the validities of the models, the normalized standard deviations (NSD) (Vinod & Anirudhan, 2001; Wu *et al.*, 2001; Chang & Juang, 2004) were calculated using:

$$\text{NSD} = 100 * \{(\Sigma\, [(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}]^2)/(n - 1)\}^{1/2} \quad (8)$$

where q_{exp} and q_{cal} are the experimentally determined and calculated amounts adsorbed, respectively, and *n* is the number of measurements.

RESULTS AND DISCUSSION

Solubility of chitosan

With increasing pH, the transmittance of the chitosan solution is almost constant up to pH 6.7 (Fig. 1) A significant decrease in transmittance at higher pH indicates the chitosan solution to be stable up to pH 6.7. This result is in good agreement with the findings of Li *et al.* (2006), who observed stability for a chitosan solution in 1% HCl up to pH 6.5. The protonation of amine groups in the chitosan chain is an essential factor for stability, the electrical repulsion between chitosan chains being diminished and attractive forces becoming more important as protonation decreases.

Effect of T and pH on the amount of chitosan adsorbed

With increasing *T* and pH of the exchange solution, the amount of chitosan adsorbed on montmorillonite tends to increase significantly (Fig. 2). At pH 5.0, where the protonation degree, *P*, of chitosan is 0.95, the amount of chitosan adsorbed increases from 178% of the CEC at 50ºC (235 g kg^{-1}) to 218% of the CEC at 75ºC (288 g kg^{-1}), whereas at 25ºC the amount adsorbed is 124% of the CEC (164 g kg^{-1}). There is only a slight increase in the amount adsorbed with increasing *T* in the pH range 4.5–5.0. At pH >5.0, the effect of the pH value on the amount of chitosan adsorbed is enhanced. At 25ºC, the amount adsorbed is 1.33 times greater at pH 6.5 than at pH 5.0. At 50ºC, the amount adsorbed is 1.26 times greater at pH 6.0 than at pH 5.0. The observed temperature dependency of the amount of chitosan adsorbed on montmorillonite implies that the adsorption has endothermic properties.

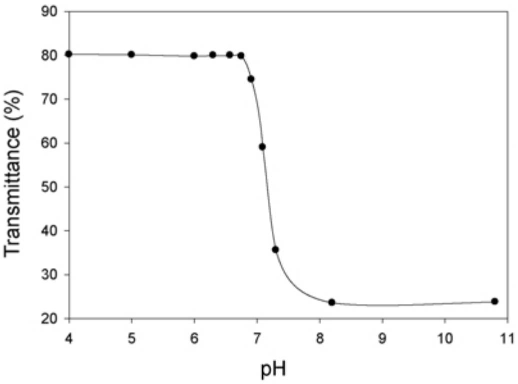

FIG. 1. Transmittance of a chitosan solution in relation to pH at room temperature.

Protonation degree and the mode of chitosan adsorption

The adsorption of chitosan on montmorillonite occurs mainly by cation-exchange of the protonated amine groups in chitosan with inorganic cations such as Na^+ and Ca^{2+} (Darder *et al.*, 2003). At pH 5.0 (P = 0.95), most of the amine groups are protonated. At pH >5.0, the protonation degree is radically decreased, leading to a P = 0.38 at pH 6.5 (An & Dultz, 2007).

Due to the low protonation degree at pH >6.7, flocculation of chitosan was observed. On the other hand, the amount of aggregated polymer is ~20% of the concentration (Philippova *et al.*, 2001). Chitosan starts to aggregate at the critical aggregate concentration (CAC), which is about 1 g l^{-1} (Philippova *et al.*, 2001). Only free and protonated chitosan, which is not aggregated at a given concentration, can be adsorbed in the interlayer of montmorillonite (Darder *et al.*, 2003). At low protonation degree, the CAC of chitosan is also lower, but the aggregated amount in solution is limited (Petit-Agnely & Iliopoulos, 1999). For chitosan modified with pronounced hydrophobic compounds, the aggregation starts at very low concentrations (CAC: 0.1 g l^{-1}). Nevertheless, only small amounts of hydrophobic groups are aggregated at higher concentrations (Philippova *et al.*, 2001).

As shown in Fig. 2, the amount of chitosan adsorbed increases with the solution pH. This is due to the fact that, if chitosan with low P is adsorbed, more chitosan is needed to compensate for the negative charge of the silicate layer. This tendency can also be observed in the adsorption process of other polycations such as poly-trimethylaminoethylchloride acrylate (PCMA) on montmorillonite (Denoyel *et al.*, 1990; Breen, 1999). For cationicities of 0.01 and 0.05, the amounts of polycations adsorbed were found to be 8.4 and 5 times larger, respectively, than those obtained at a cationicity of 1.0.

According to the idealized adsorption model for polycations on the charged surface of the silicate layer of montmorillonite (Breen, 1999), the polycations can be adsorbed forming loops and trains on the surface of the interlayer. Whether this happens depends on the difference between the length of a positively charged segment of the polycation and the distance between negatively charged adsorption sites on the surface of the silicate layer. When the lengths are similar, polymers may form a stiff surface, but when the distance is smaller or larger, polycations may form loops and trains on the surface. In the case of chitosan with decreasing P, the length between two positive segments is increased, and consequently the difference between that length and the distance of adsorption sites on the surface may also increase.

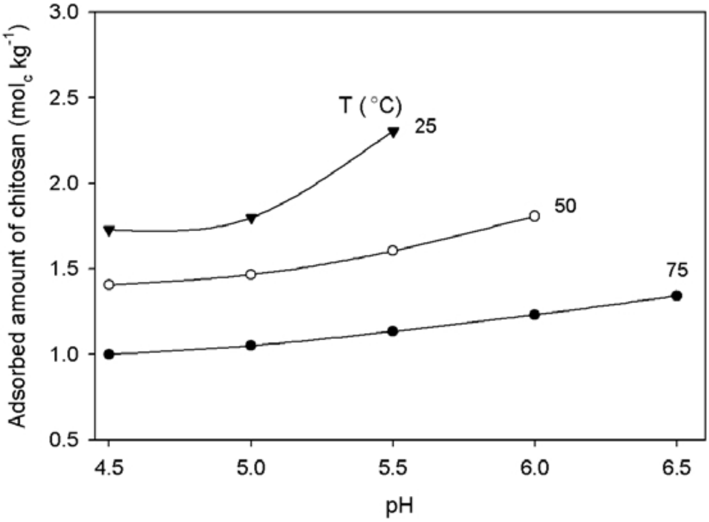

FIG. 2. Change in the amount of chitosan adsorbed as a function of the solution pH at 25, 50 and 75ºC. Chitosan applied: 500% of the CEC.

As a result, if chitosan with a low P is adsorbed, more loops and trains are formed than at $P = 1$.

Basal spacings of chitosan-montmorillonites

If fully protonated chitosan ($P > 0.95$) is adsorbed, the basal spacing of chitosan-montmorillonite adjusts to 2.21 nm (Fig. 3), suggesting that chitosan forms a bilayer structure (Darder *et al.*, 2003). The interferences are weakened, and the basal spacings are shifted to larger d values (2.58 nm), when chitosan with $P = 0.85$ is applied. A further increase of the basal spacing to 2.80 nm is observed if chitosan with $P = 0.67$ is adsorbed. Due to the increase of the adsorption of chitosan with lower P, a third layer of chitosan could be formed.

Surface charge of chitosan-montmorillonite

The increase in the amount of chitosan adsorbed on montmorillonite from 0.98 to 2.34 $\text{mol}_c\ \text{kg}^{-1}$ results in an increase of surface charge from 0.6 to 30.0 $\text{mmol}_c\ \text{kg}^{-1}$ (Fig. 4). In comparison with the amount of chitosan adsorbed, the increase in surface charge is relatively low. Chitosan is obviously preferentially adsorbed in the interlayer, where charged sites could not be detected by polyelectrolyte titration.

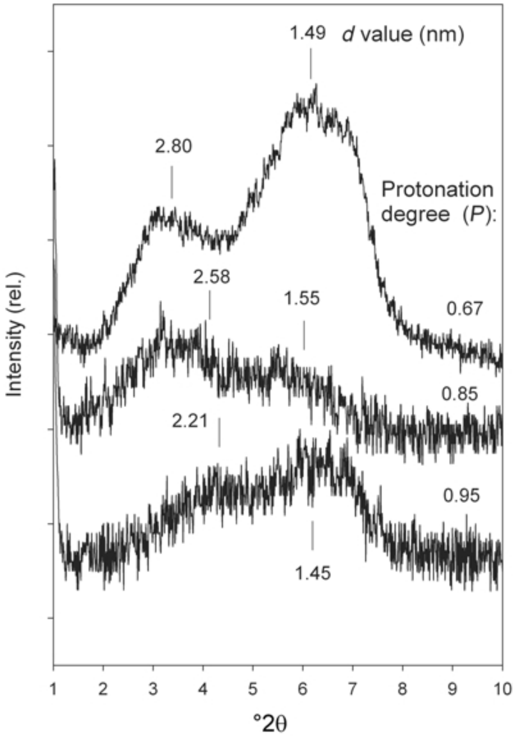

FIG. 3. XRD patterns of chitosan-montmorillonite prepared at chitosan protonation degrees (P) of 0.67, 0.85 and 0.95. Cu-$K\alpha$ radiation.

The surface charges of chitosan-montmorillonites prepared at 25ºC and pH <5.0, where chitosan is completely protonated ($P = 1$), are close to the point of zero charge, whereas some increase in surface charge is observed for chitosan-montmorillonites which were prepared at $P < 1$. The surface charge of chitosan-montmorillonite prepared with chitosan of $P = 1$ at 25ºC is 0.6 $\text{mmol}_c\ \text{kg}^{-1}$ (smallest value in Fig. 4), whereas that prepared with chitosan of $P = 0.38$ is 6.8 $\text{mmol}_c\ \text{kg}^{-1}$. For preparations at 50 and 75ºC, the same tendency is observed.

Free positively charged amine groups in loops or trains on the external surface of the silicate layer are the reason that the surface charge of chitosan-montmorillonite becomes positive. Increasing positive values with decreasing P clearly indicate that more loops and trains are formed at low P.

Adsorption kinetics of chitosan on montmorillonite

The amount of chitosan adsorbed increases significantly with increasing temperature (Fig. 5a).

There is also a difference in the time profiles of the adsorption. After 0.5 h, the adsorbed amounts were 65, 61 and 49% of the maximum values at 25, 50 and 75ºC, respectively, indicating that the adsorption ratio decreases with increasing temperature. After 12 h, the amounts adsorbed at 25 and 50ºC were 83% (153 g kg^{-1}) and 84% (210 g kg^{-1}) of the maximum amount adsorbed, respectively. At 75ºC and 12 h, the amount adsorbed increased significantly to 81% (256 g kg^{-1}) of the final amount. The time to reach equilibrium conditions is ~100 h at all T and pH (Fig. 6a,b).

Depending on pH, great differences in the time profiles are observed (Fig. 5b). Time profiles are similar at pH = 6.0 but not at pH 6.5. Here, the adsorbed amount after 0.5 h is 41% (306 g kg^{-1}) of the maximum value and increases progressively with time. In the time profile at pH 6.5, a change in the adsorption curve is observed after 6 h (Fig. 5b, arrow). The condensation of aggregated chitosan is probably most intense here. In SEM images (not shown), besides chitosan-montmorillonite, another

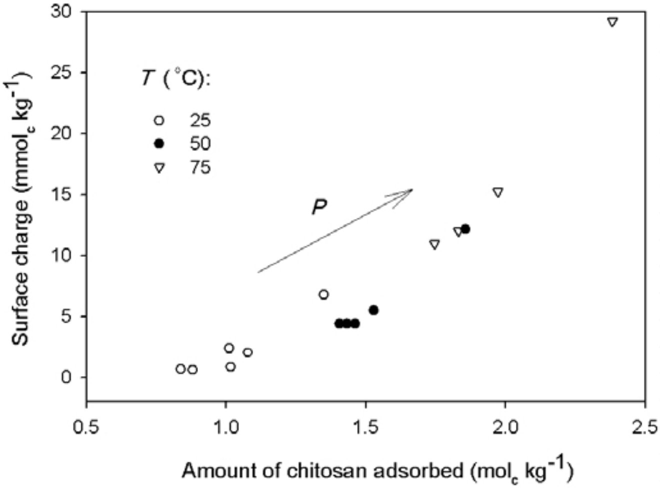

FIG. 4. Surface charge of chitosan-montmorillonite and its relationship with the amount of chitosan adsorbed. The symbols refer to the temperature during preparation. The decrease of the protonation degree, *P*, of chitosan is indicated by the arrow.

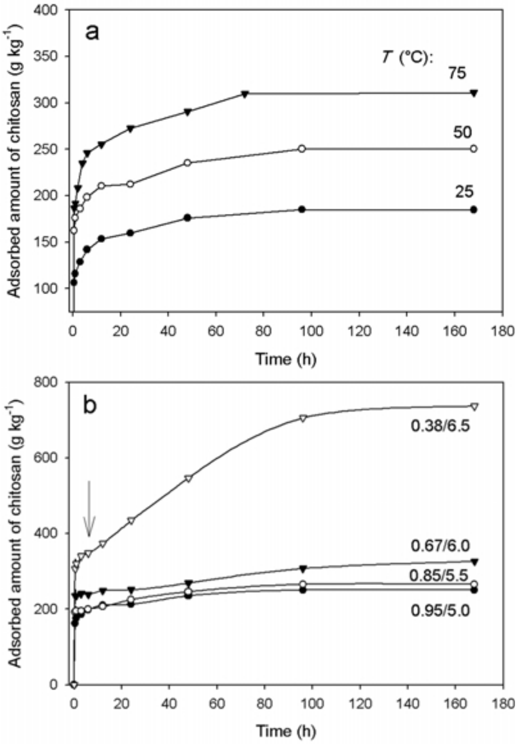

FIG. 5. Time dependence of the amount of chitosan adsorbed: (a) at three different temperatures and pH 5.0 and (b) at four different protonation degrees of chitosan at T = 50ºC. Chitosan applied: 500% of the CEC. The arrow in Fig. 5b marks a change in the adsorption curve.

phase consisting of a 'lump' of chitosan was also observed.

Model calculations for the adsorption of chitosan on montmorillonite

From the three applied models, the uptake process of chitosan on montmorillonite is fitted best by the intraparticle diffusion model. This is shown in Fig. 6 for different T (Fig. 6a) and P (Fig. 6b). As can be deduced from quantitative comparison by the NSD (Table 1), the kinetic curves applying to pseudo-first order and pseudo-second order models do not provide a fit which is as good as that from the intraparticle diffusion model for the mechanism of adsorption (Fig. 7).

Values for NSD from the intraparticle diffusion model are smaller than those from the pseudo-first and pseudo-second order models at all conditions tested, except for the adsorption at 25ºC, showing that the adsorption process is well described by the intraparticle diffusion model at 50 and 75ºC. This can also be seen in Fig. 7b, where at 50ºC the adsorption of chitosan of each P is well fitted by the intraparticle diffusion model, indicating that the diffusion process is facilitated at higher temperatures. The diffusion rate in the interlayer is probably the controlling mechanism of adsorption.

Comparison of the NSD values of the pseudo-first and pseudo-second order model show the latter model to represent a much better fit despite the fact

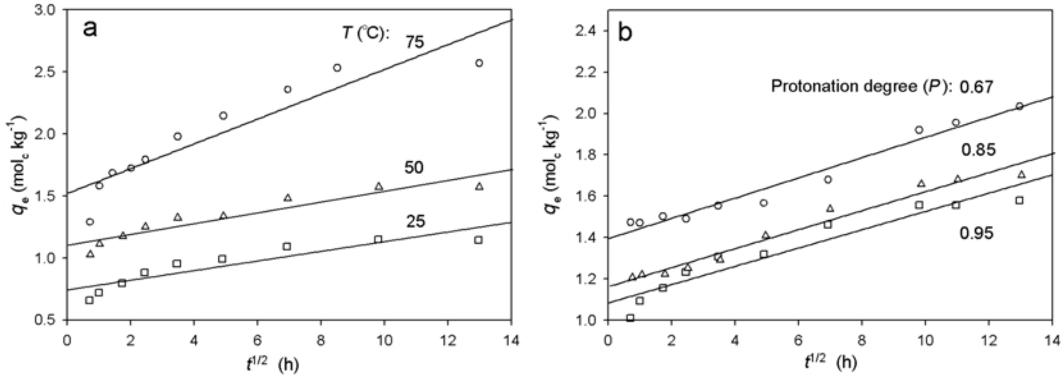

FIG. 6. Plots of the intraparticle diffusion model for the adsorption of chitosan on montmorillonite for temperatures of 25, 50 and 75ºC (a) and for protonation degrees of 0.38, 0.67, 0.85 and 0.95 (b)

that the NSD values for the intraparticle diffusion model are the lowest. The results from the NSD values in Table 2 are in good agreement with the comparison between the experimental results and modelled time profiles from the three kinetic models (Fig. 7).

The time profiles indicate that the intraparticle diffusion model represents the best fit to the adsorption processes. The pseudo-first order model underestimates the experimental values, whereas the pseudo-second order model tends to a slight overestimation. One exception is that at 25ºC the adsorption profile is fitted well to the pseudo-second order model, and NSD is 1.8% in comparison with NSD = 3.0% for the intraparticle diffusion model. Thus at 25ºC the main mode for the adsorption of chitosan is the pseudo-second order model, whereas with increasing temperature at 50 and 75ºC it is shifted to the intraparticle diffusion model.

As shown in Table 1, the diffusion rate constant k_j increases from 0.046 (50ºC) to 0.101 (75ºC), indicating that temperature is a decisive factor for the diffusion rate into the interlayer. On the other hand, k_j increases slightly with increasing pH from 5.0 to 6.0, indicating that the pH has only a slight effect on the diffusion rate of chitosan.

Our experimental results show that much larger amounts of chitosan can be adsorbed on montmorillonite than the CEC would suggest (up to 212% of the CEC). In the first step of adsorption, chitosan is adsorbed rapidly on exchange sites on the external surface and in the interlayer by electronic attraction forces until charge neutrality is achieved (100% of CEC). At 25ºC, further adsorption might be limited, because the interlayer space is already filled with poly-cations, and the movement of free polymer into the interlayer is limited due to the sterical obstacle. Further adsorption of chitosan, promoted by temperatures

TABLE 1. Rate constants and normalized standard deviations (NSD) for the adsorption of chitosan on montmorillonite. Comparison of three different models. Chitosan applied: 500% of CEC.

	Pseudo-first order		—— Pseudo-second order ——			Interparticle diffusion	
	k_f (h^{-1})	NSD (%)	k_s (kg mol^{-1} h^{-1})	q_e (mol kg^{-1})	NSD (%)	k_i (mol kg^{-1} h$^{-1/2}$)	NSD (%)
T 25 (ºC)	0.030	6.32	0.47	1.16	1.8	0.039	3.0
50	0.049	6.21	0.36	1.56	2.6	0.46	2.0
75	0.034	5.21	0.16	2.56	5.6	0.101	3.2
pH 5.0	0.029	4.61	0.31	1.59	1.5	0.043	1.3
5.5	0.030	5.26	0.24	1.69	1.8	0.046	0.9
6.0	0.025	8.37	0.15	2.01	2.7	0.049	0.9

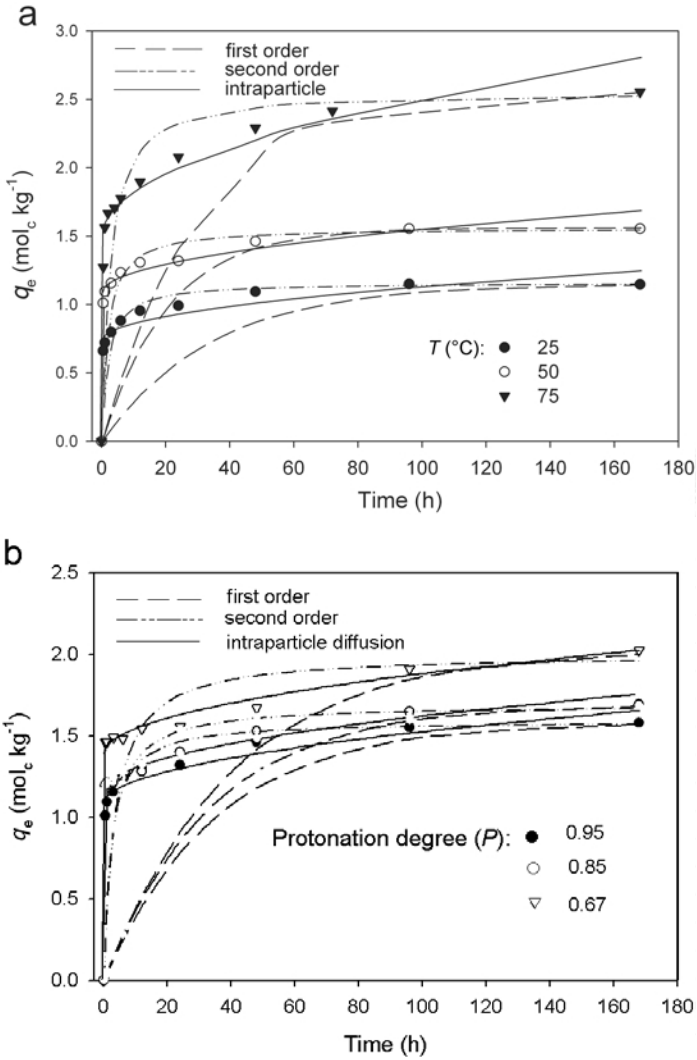

FIG. 7. Comparison between measured and modelled time dependencies of the adsorption of chitosan on montmorillonite. Plots of the adsorbed amounts against time (a) for different temperatures and (b) for different protonation degrees.

at ⩾50ºC, depends on the diffusion rate in the interlayer. Expansion of the interlayer at higher temperatures probably facilitates the diffusion of chitosan. At loadings >100% of the CEC, the adsorption is believed to occur by van der Waals interactions between free chitosan chains and previously adsorbed chains (Darder *et al*., 2003). Denoyel *et al*. (1990) suggested that the adsorption of much larger amounts of polycations than the CEC might also originate from electrostatic attractive forces of the adsorption sites on the silicate layer that are covered by uncharged units of chitosan. With the help of the attractive forces of such free charged sites as well as of weak van der Waals interactions, additional chitosan could diffuse into the interlayer.

Anion exchange capacity

The experimentally determined AEC for chitosan-montmorillonite prepared at pH 5.0 and 75ºC was found to be 0.36 mol$_c$ kg^{-1}. The value corresponds to 83% of the calculated AEC (0.43 $\mathrm{mol_c\ kg^{-1}}$) and shows that >80% of the free amine groups in chitosan-montmorillonite can act as anion adsorption sites.

CONCLUSIONS

Temperature and pH of the solution are the main factors governing chitosan adsorption on montmorillonite. To describe the adsorption kinetics of polycations with a complex structure and several functional groups such as chitosan on montmorillonite, the intraparticle diffusion model was found to be most suitable. Temperature affects the kinetics and mode of adsorption of chitosan by controlling the diffusion of chitosan into the interlayer. The solution pH controls the protonation degree of chitosan, which is crucial for the mode of chitosan adsorption on montmorillonite. The maximum amount of chitosan adsorbed on montmorillonite was found to be 2.34 $\mathrm{mol_c\ kg^{-1}}$, which corresponds to 212% of the CEC of the montmorillonite utilized. More than 80% of the free amine groups act as adsorption sites for anions in chitosan-montmorillonite. Because of the relatively large effective AEC, chitosan-montmorillonite has excellent potential as an adsorbent for anions.

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