Sorption of Acid Green 25 on Chitosan: Influence of Experimental Parameters on Uptake Kinetics and Sorption Isotherms

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ABSTRACT: Acid Green 25, which is a diazoic dye bearing two sulfonic groups, is efficiently sorbed on chitosan. The protonation of chitosan may explain the electrostatic attraction of this anionic dye and that its optimum pH is close to 3. Preliminary protonation of amine groups (obtained by contact with a sulfuric acid solution) reduced the variation of solution pH following sorbent addition but significantly reduced sorption performance: the maximum sorption capacity of raw chitosan, 525 mg dye/g (0.84 mmol dye/g), was halved by acidic preconditioning. The acidic conditioning also reduced the kinetic rate—the time necessary to reach equilibrium increased up to threefold depending on the experimental conditions. The size of sorbent particles influenced sorption kinetics and equilibrium because of resistance to intraparticle diffusion, but the sorption appeared to occur not only at the surface of the sorbent but also in the intraparticle network of the polymer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1073–1080, 2003

Key words: Acid Green 25; chitosan; sorption isotherm; uptake kinetics; influence of pH; influence of particle size

INTRODUCTION

Though most dyes, widely used in the textile industry are nontoxic at the concentration found in wastewaters, the color they impart is very undesirable to the water user. On the other hand, some of these dyes are well known for their health effect. Discharge regulations are progressively becoming more stringent. For this reason many recent studies have focused on the development of efficient processes for the recovery of these organic contaminants and, as far as possible, their recycling. Conventional processes used in wastewater treatment such as precipitation, coagulation and flocculation have proved inefficient at removing several common dyes, especially from dilute solutions. Photooxidation has recently been proposed for the treatment of dye-containing effluents;[1] however, this process is relatively expensive and not appropriate for the treatment of large flows. Biological degradation has also been cited as an alternative process for the treatment of colored effluents.[2–3] However, adsorption processes remain the most commonly used for the decontamination of the effluents of textile industry. These processes are of most interest when the dyes can be selectively adsorbed, concentrated by desorption, and recycled. Many adsorbents have been tested in recent years, in particular mineral sorbents,[4] and activated carbon.[5–8] Though activated carbon has received a great deal of attention because of its high efficiency and high sorption capacity, its use is limited by nonselectivity and poor reusability. So, there is still a need for the development of alternative sorbents, especially low-cost sorbents. Biosorption processes have shown promise for the removal of organic and mineral contaminants using, for example, peat,[9] wood and derivatives, agriculture wastes, or fungal biomass.[10–16] However, several factors, including variability in composition, source, and low-sorption capacities, have limited their use despite their low cost. Chitosan is well known for its sorption properties. This biopolymer is extracted by a deacetylation procedure from chitin, the most abundant biopolymer in nature after cellulose (Fig. 1). It is characterized by a high content of amine functions, which make it very efficient at removing metal ions from dilute solutions through chelation or ion exchange reactions, depending on pH and metal ions.[17–19] Literature is less abundant on the sorption of organic materials. Chitosan has been studied not only for the sorption of phenols,[20–21] humic acid,[22] pesticides,[23] and polychlorobiphenyls,[24] but also for the removal of dyes.[25–35] Despite an increasing number of reports focusing on dye removal on chitin and chitosan, to date it remains difficult to establish clear trends in the sorption properties of these materials for the recovery of dyes. Indeed, the variability in published results may deter potential users. There are many reasons for this difficulty in comparing sorption performances: (1) differences in

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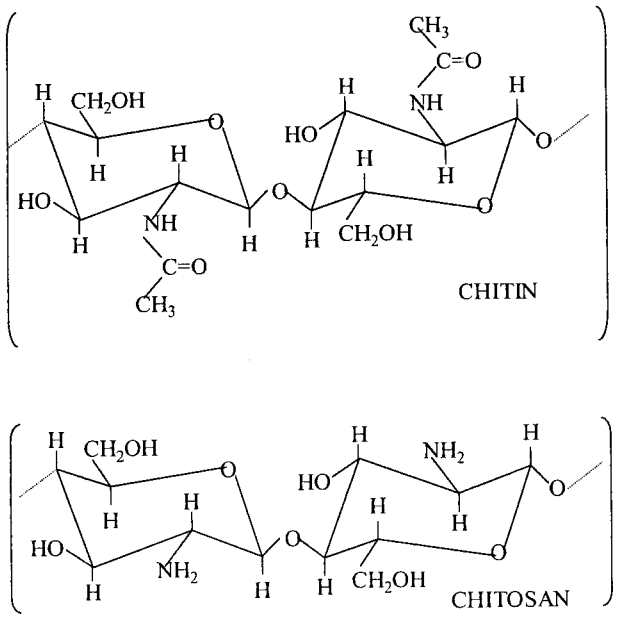

Figure 1 Structures of Chitin and Chitosan

the characteristics of chitosan (deacetylation percentage, crystallinity, particle size), as was pointed out for the sorption of metal ions,[36] (2) differences in the experimental conditions (sorbent dosage, equilibrium time, sorbent saturation), and (3) underestimation of the influence of physicochemical parameters (especially pH and pH variation effects during the sorption process).

The present study focused on the evaluation of the sorption properties of chitosan for the recovery of Acid Green 25. This dye is an anthraquinonic anionic dye characterized by the presence of two sulfonic groups and two azoic groups (Fig. 2). The influence of the pH on sorption properties was considered under different experimental conditions: a series of experiments was performed with pH controlled, and a second series performed without pH controlled. Because of the large variation in the pH during dye sorption, it was decided to determine the ability of preconditioned chitosan to sorb Acid Green 25. Chitosan was protonated with a pH 3 solution (prepared with a sulfuric acid solution), and the sorption properties of protonated chitosan were compared to those of raw chitosan in the experiments in which pH was not controlled. The influences of dye concentration and sorbent particle size on uptake kinetics and sorption isotherms were evaluated using both raw and protonated chitosan.

EXPERIMENTAL

Materials

Chitosan was supplied by Aber Technologies (Plovien, France). The sample characteristics of deacetylation degree and molecular weight were determined by Fourier transform infrared (FTIR) spectroscopy and size-exclusion chromatography coupled with light scattering and refractometry, respectively. The degree of deacetylation was 87%, whereas the molecular weight was 125,000 g/mol. Chitosan was ground and sieved in four fractions: G1 $<$ 125 μm $<$ G2 $<$ 250 μm $<$ G3 $<$ 500 μm $<$ G4 $<$ 710 μm.

Protonation was achieved by contact of chitosan with a sulfuric acid solution maintained at the optimum pH of sorption (ca. pH 3) overnight. Chitosan particles were recovered by filtration and rinsed to remove interstitial acidic water, and then the powder was oven-dried overnight at 60°C. Acid Green 25 (Alizarine Cyanine Green G, $C_{28}H_{20}N_2Na_2O_8S_2$, Fig. 2) was supplied by Aldrich (France) (C.I. number: 61570). Its molecular weight is 622.59 g/mol. It was supplied as a mixture of dye with an inert material. The actual fraction of dye in the powder was 75%. The dye was used as supplied without purification, and the fraction of inert material was not taken into account in the calculation of dye concentrations. As a consequence, it should be necessary to correct the sorption capacities and concentration by the fraction of pure dye to get the actual absolute sorption performances (multiplying the concentrations by 0.75). Acid Green 25 was directly diluted in water and the solubility of the dye was checked over the experimental pH range (ca. pH 1–10).

Procedures

The study of the influence of pH on dye sorption was performed by mixing 10 mg of sorbent (raw chitosan, G1 particle size) with 100 mL of dye solution (at the concentration of 100 mg/L). One series of experiments was performed keeping the pH constant with microadditions of 1*M* sulfuric acid or 1*M* sodium hydroxide solutions. The other series was performed allowing the pH to vary during the sorption and mea-

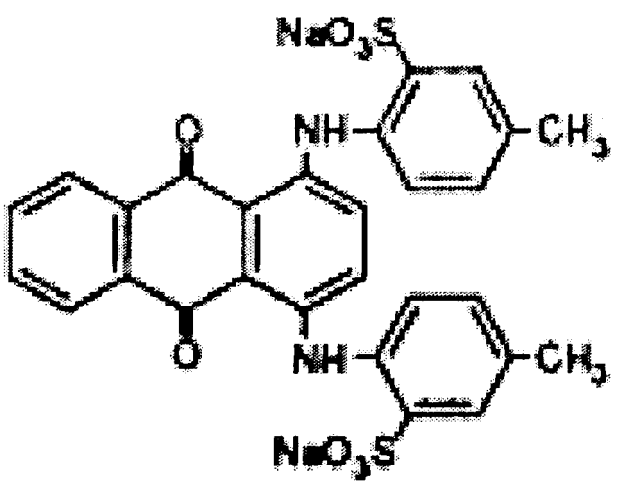

Figure 2 Structure of Acid Green 25

suring the pH only at the end of the sorption, after 3 days of contact. Dye concentration was measured by visible spectrophotometry using the peak of Acid Green 25 at 643 nm. This peak was less sensitive to pH variations of the solution and exhibited greater absorbance (molecular extinction coefficient, ε). The samples were diluted three times with demineralized water and by adding two drops of 1*M* NaOH. The calibration curve was linear over the 0–100 mg/L concentration range.

Sorption kinetics studies were performed by mixing a known amount of sorbent (400 or 150 mg) with 1 L of dye solution (concentration: 50, 100, or 200 mg/L) for 72 h. Samples were collected at fixed contact times; they were filtered using 1.2 μm pore size membranes and finally analyzed, as described above. A small fraction of the dye (less than 3% was retained on the filter membrane), this small variation in the concentration from filtration was neglected. Sorption isotherms were determined by mixing known amounts, m, mg in milligrams (in the range 10–40 mg) of sorbent with a fixed volume of solution (V; 100 or 150 mL in for the lowest dye concentration, i.e., 50 mg/L) of the dye solution at the initial concentration, C_0 (mg/L), of 50, 100, and 200 mg/L. After 4 days of contact, the pH of the solution was measured, and samples were collected, filtered, and analyzed for dye content (C_{eq}, mg/L). The mass balance equation was used to calculate the amount of dye sorbed on the polymer (q, mg/g): $q = V(C_o - C_{eq})/m$.

The octanol/water partition coefficient (K_{ow}) was determined by contact of the dye solution for 20 min with an equal volume of *n*-octanol. After phase separation the dye concentration was determined in the aqueous phase, and by mass balance, the concentration of the dye in the organic phase was calculated. The distribution coefficient, K_d (L/kg, sorption studies), and the octanol/water partition coefficient, K_{ow} (L/L) were obtained by the ratio of dye concentration in the organic phase (or, the sorption studies, on the sorbent) to the residual concentration in the aqueous phase.

RESULTS AND DISCUSSION

Influence of pH

The pH strongly influenced Acid Green 25 uptake (Fig. 3). The experimental conditions were selected so as to avoid reaching complete removal of the dye in order to observe the saturation of the sorbent, independently of the pH. It appeared that the sorption efficiency was systematically greater for solutions whose pH was controlled during the sorption than for solutions for which pH varied along the uptake process. The figure shows that the shape of the curve significantly changed when the sorption efficiency was plotted versus either initial pH or final pH. It

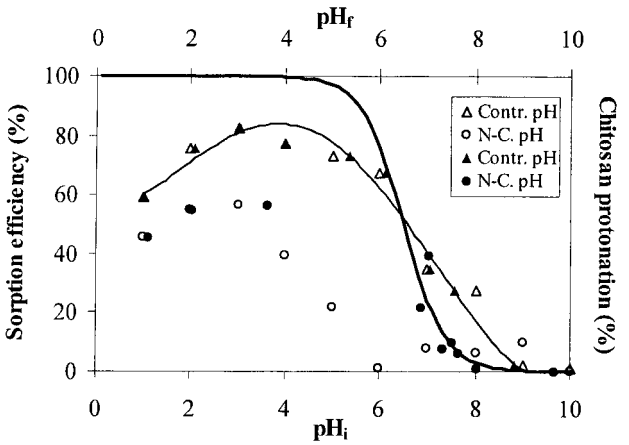

Figure 3 Influence of pH on Acid Green 25 uptake by chitosan - Effect of pH control on sorption efficiency (controlled pH and non-controlled pH (N-C.); open symbols: sorption efficiency as a function of initial pH, closed symbols: sorption efficiency as a function of final pH; bold line: percentage of protonation of chitosan) (dye concentration: 100 mg L^{-1}; sorbent dosage: 100 mg L^{-1}).

confirms that a source of discrepancies in published studies may be related to misunderstanding the impact of pH variation on the sorption performance. It is especially important in some cases (for example, for metal ions) that deal with precipitation mechanisms: a small pH variation (due to chitosan addition) may cause artificial precipitation and an overestimation of sorption performance.

Another important observation is related to the correlation between the sorption efficiency and the decrease in the protonation of the amine groups of chitosan for the solutions whose pH was not kept constant. It confirmed that for Acid Green 25 the key mechanism is ion exchange, or at least electrostatic attraction. The dye is characterized by the presence of sulfonic groups: these anionic functions are attracted by protonated amine groups of chitosan. The pK_a of chitosan depends on the degree of deacetylation and the degree of neutralization of the amine groups.[37] It tended toward 6.5 in the chitosan used in this study. So, below pH 6.5, most of the amine groups were protonated. The protonation of amine groups was necessary for the attraction of anionic sulfonic groups; however, an excess of acidity, corresponding to a pH lower than 2, resulted in strong competition of the anions, brought about by the dissociation of the acid used for pH control, and the sorption capacity significantly decreased. When the pH was controlled during sorption, the optimum pH range was between pH 2 and pH 5: the sorption efficiency varied by less than 10% to around 75%. In the noncontrolled pH solutions a similar optimum pH range was observed, although the sorption efficiency was significantly lower, decreasing from 80% to 60% for maximum sorption efficiency. When the pH was controlled during sorption, the optimum conditions for dye sorption were main-

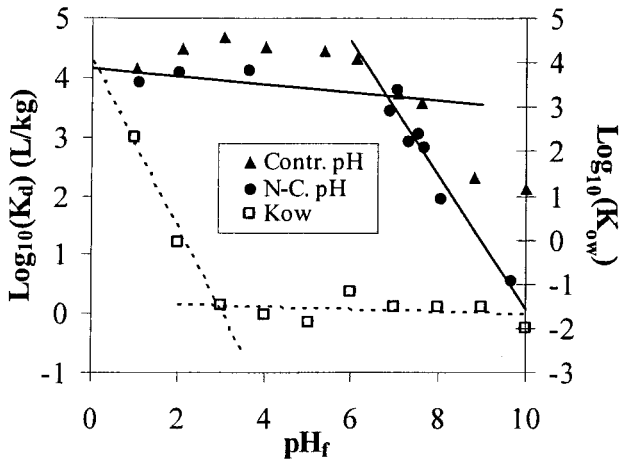

Figure 4 Influence of pH (equilibrium pH) on the distribution coefficient (K_d) for Acid Green 25 uptake by chitosan and on the octanol/water separation coefficient (K_{ow}) (dye concentration: 100 mg L^{-1}; sorbent dosage: 100 mg L^{-1}; Vol. octanol = Vol. solution).

tained throughout the sorption process, whereas when the solution pH was uncontrolled, the sorbent addition markedly increased the pH above optimum, in some cases by as much as 2 pH units. The distribution coefficients were plotted versus final pH (Fig. 4). Although the distribution coefficient remained almost constant (at approximately 10^4 L/kg) over a wide range of pH values (between pH 1 and pH 6), it strongly decreased above pH 6, with a slope tending to -1 (actually -1.14). In ion exchange processes, or in solvent extraction systems, when the plot of $\log_{10} K_d$ varies versus pH with a given slope, n, it is usually interpreted as the stoichiometric ratio of the exchange of the solute with n protons or counterions. In this case it should indicate that the dye is sorbed via the exchange of 1 proton per mole of dye sorbed on the polymer. Figure 4 also shows the octanol/water separation coefficient as a function of the pH. Although at a pH above 3, Acid Green 25 was not extracted, when the pH decreased, the extraction efficiency strongly increased and the plot of $\log_{10} K_{ow}$ varied with a slope close to -2 (actually -1.9). This can be explained by the extraction of the dye by a nonpolar solvent such as octanol requiring the complete neutralization of anionic sulfonic functions. It means the neutralization of two functional groups per mole of solute. The neutral compound can then be removed from the solution by hydrophobic extraction in the solvent. For sorption on chitosan, the stoichiometry of counterion exchange or electrostatic attraction seems to be different. The dye could be sorbed in a partially neutralized form (one sulfonic group being neutralized by a cation in the solution) by electrostatic attraction or counterion exchange. This hypothesis could help explain the observed effect of pH, which is quite different to that observed with solvent extraction (change in the slope of the curve).

For optimum sorption of the dye it appeared necessary to maintain the pH of the solution at a fixed optimum pH (close to pH 3). Several possibilities exist for how to keep the pH at a constant value, using, for example, (1) continuous control of the pH with either acidic or alkaline solutions or (2) a preconditioning of the sorbent at the optimum value in order to reduce its impact on the pH of the solution. So protonated chitosan was prepared by contact with sulfuric acid solution at pH 3, and the sorption performance of the treated chitosan was compared to that of raw chitosan.

Influence of dye concentration on sorption kinetics

With increasing Acid Green 25 concentration relative to a fixed sorbent dosage, as expected, the time required to reach equilibrium strongly increased. For example, although 1–2 h was sufficient to achieve complete recovery of the dye at initial concentrations below 100 mg/L, for the highest concentration (200 mg/L) with raw chitosan 8 h was necessary to reach equilibrium and the complete elimination of the dye (Fig. 5).

At a high sorbent dosage such as 400 mg/L and using a small particle size (G1, 0–125 μm), there was a large excess of sorption sites at the surface of the sorbent, and consequently sorption was very fast, and the concentration of the solution drastically decreased within the first minutes of contact. When initial dye concentrations were increased, the excess of sorption sites at the surface of the particles decreased, and it is the gradient between the dye concentration at the surface and the concentration inside the particle that was the driving force for transfer of the dye. Clearly, the resistance to intraparticle diffusion also plays an important role in the control of mass transfer.

For protonated chitosan the sorption kinetics were significantly slower: with increasing dye concentration from 50 to 100 mg/L, the time required to achieve complete removal of the dye increased from 6 to 48 h. For the 200 mg/L solution, even after 72 h of contact, equilibrium was not reached, and sorption efficiency did not exceed 60%. Protonation significantly decreased the sorption performance of the polymer. Protonated amine groups attracted counteranions from the acidic solutions used for polymer preconditioning, and these counteranions may have hindered sorption of anionic dyes in both equilibrium uptake (limited exchange of bound counterions) and kinetic (rate of exchange) performance.

The faster sorption of the anionic dye on free chitosan (compared with protonated sorbent) can be explained by an easier attraction by protonated amine groups in contact with the solution. On the other hand, for protonated amine groups, counteranion exchange was slowed down because of possible saturation of sorption sites.

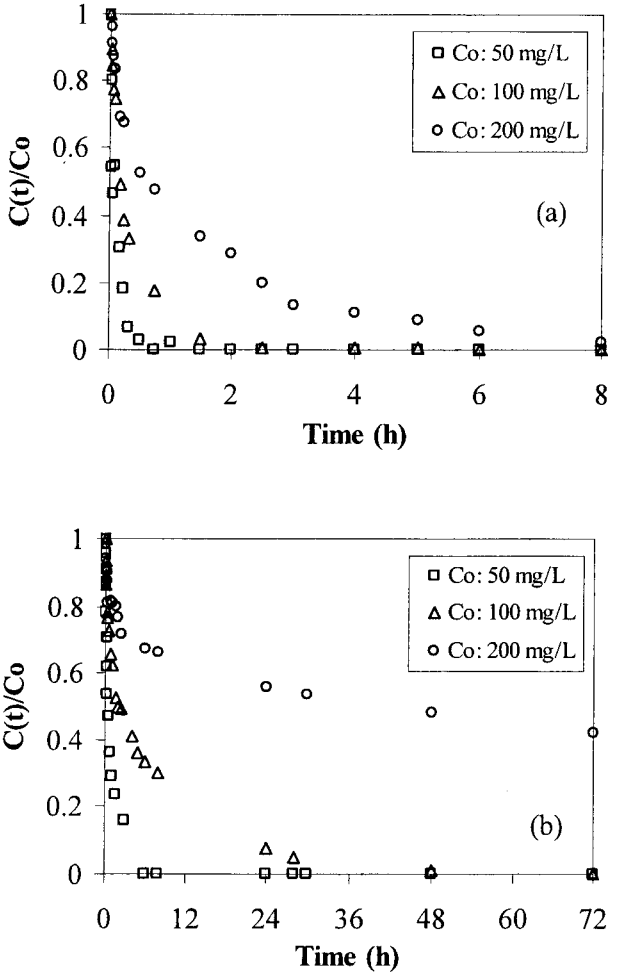

Figure 5 Influence of dye concentration on Acid Green 25 uptake kinetics at pH 3 (pH non-controlled) using raw chitosan (a) and protonated chitosan (b) (Sorbent dosage: 400 mg L^{-1}).

Influence of particle size on sorption kinetics

The influence of intraparticle mass resistance on kinetic control was evaluated by comparing sorption kinetics obtained with sorbent particles of different sizes. Figure 6 shows the results obtained with different particle sizes ranging between 0 and 500 μm for both raw and protonated chitosan. In this case, to measure the influence of intraparticle diffusion resistance, it was necessary to limit the sorbent dosage to avoid complete removal of the dye by the external sorption sites.

When the size of sorbent particles [raw chitosan, Fig. 6(a)] increased, the shape of the kinetic curves significantly changed, especially in the second section of the curve. Indeed, the initial part of the curve, which is usually controlled predominantly by the external film diffusion, appeared to be less influenced by the size of the particles: the curves overlapped. It is important to note that, after 24–30 h of contact equilibrium did not appear to have been reached for the largest particles: a slight decreasing trend was observed, whereas for the smallest particle size, the difference in dye concentrations was not significant between 24 and 30 h. The residual concentrations after 30 h of contact were significantly different for the different-sized fractions of sorbent. These trends also were observed with protonated chitosan [Fig. 6(b)] on increasing the size of sorbent particles, the residual concentration increased, and a 30-h contact time was not sufficient to reach equilibrium.

The resistance to intraparticle mass transfer appeared to be a limiting step in the sorption process that could influence sorption kinetics; and the sorption capacity may be affected if the contact time is not sufficient. To verify whether the sorption occurred in the whole mass of the sorbent or only at the external surface sorption isotherms were performed with two particle sizes (G1, 0–125 μm, and G4, 500–710 μm).

Influence of particle size on sorption isotherms

Figure 7 shows the sorption isotherms obtained for Acid Green 25 sorption at pH 3 (initial pH, noncon-

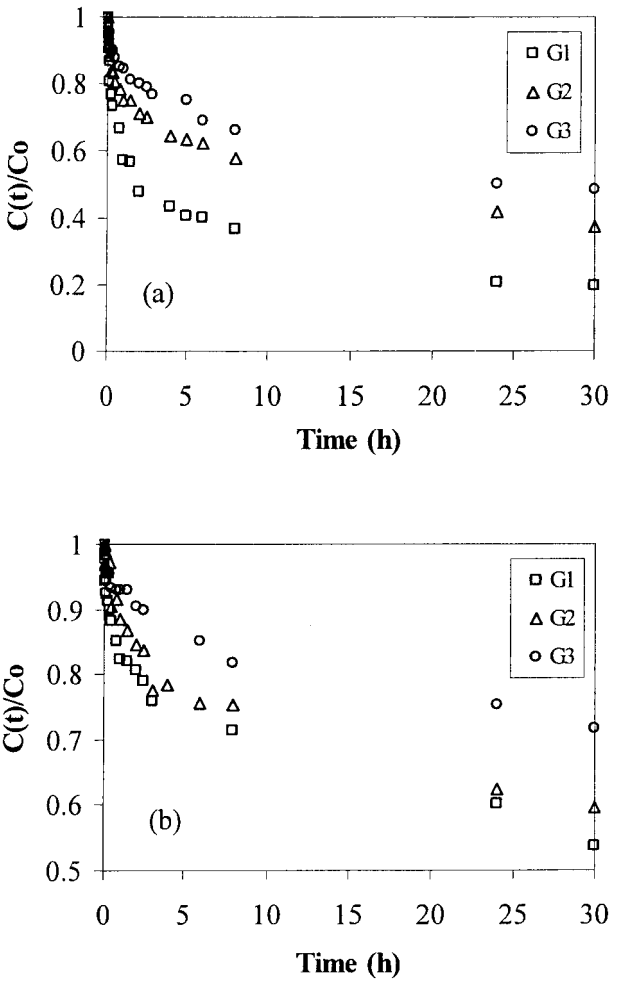

Figure 6 Influence of chitosan particle size on Acid Green 25 uptake kinetics at pH 3 (pH non-controlled) using raw chitosan (a) and protonated chitosan (b) (Dye concentration: 100 mg L^{-1}; Sorbent dosage: 150 mg L^{-1}).

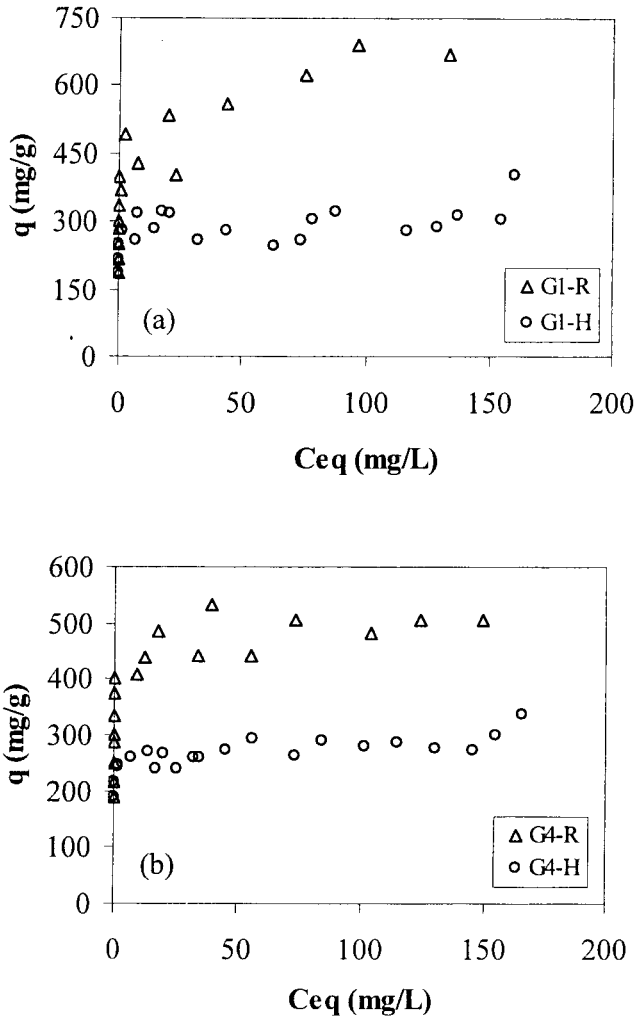

Figure 7 Influence of protonation of chitosan on Acid Green 25 sorption isotherms at pH 3 (pH non-controlled; including only data which equilibrium pH was less than pH 5) ((a) G1 particle size: 0–125 μm, (b) G4 particle size: 500–710 nm).

trolled) using raw and protonated chitosan (G1 and G4 fractions). Because the pH was not controlled during the sorption the final pHs strongly increased, especially with raw chitosan: pH variation may exceed 2 units. So it was difficult to properly compare experimental data for the different experimental series. Actually, the sorption isotherms were plotted using only the experimental points whose final pH was less than 5 (Fig. 7) because the optimum pH range was determined to be between pH 3 and pH 5.

The sorption capacities were systematically higher for raw chitosan than for protonated chitosan: the maximum sorption capacity was halved for protonated chitosan compared to raw material. The sorption sites occupied by the counterions definitively could not be exchanged with dye anions. The number of available sorption sites decreased, and the sorption capacity drastically decreased.

A comparison of maximum sorption capacities for G1 and G4 particle sizes showed that the smallest particles exhibited 15% higher sorption capacities for raw chitosan, the differences were less marked for protonated sorbent. So there was an effect of sorbent particle size, but the difference was not high enough to attribute the sorption to pure surface sorption. Sorption occurred in the whole mass of the particle, with a small surface effect that may be due to a contact time insufficient to achieve the saturation of internal sites.

For the G1 particle size, the maximum sorption capacity was close to 700 mg/g. Taking into account that the dye was not pure (addition of inert material), the actual maximum sorption capacity was close to 525 mg/g, that is, 0.84 mmol/g. Taking into account both the equivalent molecular weight of the chitosan used in this study ($\approx$ 166 g/mol) and the degree of deacetylation (87%), 1 g of chitosan has 5.24 mmol $-NH_2$. This means that at saturation of the sorbent under optimum sorption conditions, the maximum molar ratio between the dye and amine groups of chitosan was 0.16:1. For protonated chitosan the max-

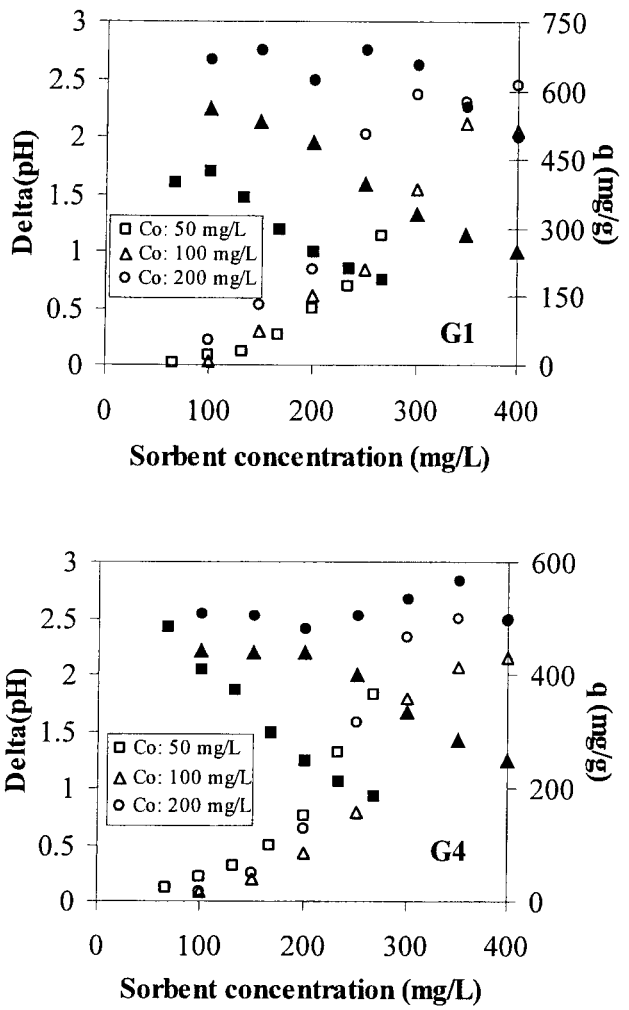

Figure 8 Variation of the equilibrium pH (open symbols) and sorption capacity (closed symbols) as a function of initial dye concentration and sorbent dosage for G1 and G4 particle sizes using raw chitosan.

imum sorption capacity was close to 300 mg/g. With the corrections from the presence of inert material, the sorption capacity decreased to 225 mg/g, or 0.36 mmol/g. Compared to total amine groups, the maximum molar ratio between the dye and amine groups of chitosan did not exceed 0.07:1. Maghami and Roberts postulated a 1:1 stoichiometry for the interaction of sulfonic acid groups on the dyes with protonated amine groups of chitosan for mono-, di- and trisulfonated dyes, working with concentrations of dyes as high as 5 mmol dye/L, with a chitosan dosage of 0.5 or 1 g/L in 0.083*M* aqueous acetic acid solutions.[27] Although the experimental conditions were significantly different, including the dye and chitosan concentrations, the presence of other co-ions, and the state of chitosan (dissolved in the case of Maghami and Roberts study), which may affect the accessibility to sorption sites (the polymer being expanded in the solution), in this study we observed a significant discrepancy with their findings.

pH variation during dye sorption and sorption isotherm modeling

Because the pH variation during dye sorption was large, which made modeling of sorption isotherms for the experimental data impossible, it was of interest to investigate the influence of experimental conditions (sorbent dosage and initial dye concentration) on the pH variation and to correlate these pH variations to sorption capacities. Figure 8 shows the results for G1 and G4 particle sizes of raw chitosan (pH variations were significantly lower, below 0.4 pH units, for protonated chitosan).

At increasing sorbent dosage, the pH variation exponentially increased: the number of amine groups available for protonation increased and consequently the pH markedly increased. This effect was reinforced by the dye molecules also occupying a decreased relative number of amine groups at high sorbent dosage (increasing sorbent dosage reduced polymer saturation), with the influence of chitosan protonation then increasing. However, when the initial dye concentration increased, pH variation also increased; indicating that this variation was not only a result of the protonation of chitosan—the protonation of the dye also influenced the pH variation. Combining this observation with the slope of the distribution curve with changing pH (see the section on the influence of pH on dye sorption), it is proposed that Acid Green 25 is adsorbed in a partially neutralized form.

As pointed out above, for raw chitosan the strong variation of pH during sorption made it impossible to model sorption isotherms using the Langmuir equation. The use of protonated chitosan strongly decreased the pH variation of less than 0.3 pH units. In this case, the pH may be considered almost constant during the sorption procedure. Therefore, sorption isotherms may be modeled using the Langmuir and the Freundlich equations. However, Figure 7 clearly shows that the sorption isotherms were very favorable: they were characterized by saturation plateaus that were reached at very low residual concentrations. The sorption isotherms may be considered almost irreversible. Yoshida et al. also observed a pseudo-irreversible sorption isotherm for the uptake of Acid Orange II (acid dye) on crosslinked chitosan fibers.[38] The shape of the sorption curves was characterized by a plateau at a high residual dye concentration. This shape forced the modeling of the isotherm by the Langmuir equation, $q = q_m b C_{eq}/(1 + bC_{eq})$ (in preference to the Freundlich equation). The steep increase in the sorption capacity at a low residual concentration (below 5 mg/L) and the relative inaccuracy in the analysis of the solution in the low-concentration range made mathematical determination of the parameters of the model only indicative of their orders of magnitude. The superimposition of the modeled curves over the experimental data (not shown) confirmed that the modeling underestimated sorption capacities at low dye concentrations, showing that the sorption isotherms would be better modeled using the hypothesis of an irreversible isotherm. The maximum sorption capacities (at monolayer coverage) calculated from the linearization of sorption isotherms [$C_{eq}/q = f(C_{eq})$] for protonated chitosan were q_m = 320.5 and 300.5 mg dye/g for G1- and G4-sized fractions, respectively. The affinity coefficients were b = 0.302 and 0.307 L/g for G1 and G4, respectively. With protonated chitosan, the differences due to particle size were not significant.

CONCLUSIONS

Chitosan is very efficient at removing dyes from dilute solutions. For Acid Green 25 (di-sulfonic diazoic dye), sorption was optimum in the pH range of 2–4. Sorption occurs by electrostatic attraction to protonated amine groups at these pH values. A direct correlation can be observed between the theoretical neutralization curve of chitosan (calculated from the pK_a) and sorption performance at different pHs. The addition of chitosan to the solution strongly increases the pH of the solution. To diminish the influence of pH change on the modeling and interpretation of sorption performance, chitosan was conditioned (protonated) by contact with a solution of sulfuric acid at a pH of 3. In this case, pH variation during the sorption process was significantly lower; however, this pretreatment strongly reduced sorption performance at both equilibrium and kinetic levels. The maximum sorption capacity for protonated chitosan was halved, compared to raw material, and the time required for reaching sorption equilibrium strongly increased (up to 3 times), indicating that the sorption did not occur solely through a direct anion exchange process. The

maximum sorption capacity for the smallest-size particles (below 120 μm) was around 700 mg dye/g or, taking into account the inert fraction in the commercial dye (25%), 525 mg dye/g, corresponding to 0.84 mmol dye/g. For the given chitosan sample (deacetylation fraction: 87%), it corresponds to a dye/amine molar ratio of 0.16:1, which is far from the 1:1 stoichiometry proposed by Maghami and Roberts. The discrepancy increases when considering protonated chitosan. In this case, the dye/amine molar ratio decreases to 0.07:1.

At a low dye concentration/sorbent dosage ratio, the relative excess of sorbent made the sorption efficient and fast—sorption occured at the surface of the sorbent particles. However, on increasing the ratio, the experimental conditions became less favorable for sorption, and the contribution of intraparticle diffusion in the control of sorption kinetics could be observed. Increasing particle size influenced sorption kinetics, especially in the second stage of the process, which is usually controlled by intraparticle diffusion more significantly in the case of raw chitosan (less in the case of protonated material). The residual concentration (after 30 h of contact) increases with increasing particle size, which tended to confirm the role of intraparticle diffusion resistance, but the change in sorption capacity at equilibrium (after 3 days of contact on sorption isotherms) was not so large and not sufficient to conclude that sorption only occured at the surface of the particle. Increasing the concentration of the dye also increased the time required to achieve complete recovery of the dye. The sorption process consists of two steps—surface sorption during the first minutes (complete sorption at a low dye concentration within the first 30 min of contact), followed by diffusion and sorption of dye molecules in the intraparticle polymer network.

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