Effect of Deacetylation on Sorption of Dyes and Chromium on Chitin

CHA YOUNG KIM, HYUNG-MIN CHOI, HYEON TAE CHO

Department of Textile Engineering, Soong Sil University, Seoul, Republic of Korea

Received 3 March 1996; accepted 6 April 1996

ABSTRACT: Deacetylated chitins (10.7–67.2%) were prepared by alkaline hydrolysis to determine an optimal degree of deacetylation (DD) which can effectively remove four dyes and chromium ions from textile effluent. Sorption isotherms were carried by varying the treatment time, pH, and initial concentration of dyes or chromium ions. Experimental results were analyzed in three ways: (1) equilibrium sorption capacity and sorption rate constant, (2) Langmuir isotherms, and (3) separation factor. Results indicated that except for the chitin with a 67.2% DD, rate and capacity of the dye sorption on the chitin increased with the increase of the DD in chitin for each pH but decreased with the increase of pH for each deacetylated chitin. This was mainly due to the increase of $—NH_3^+$ groups in chitin with a high DD and the low pH of the system. On the contrary, dye desorption from the deacetylated chitin was highly effective at 80°C and pH $\geq$ 10, which could facilitate the reduction of $—NH_3^+$ ions and the increase of electrostatic repulsion. The number of chromium ions sorbed on the chitin also increased with the increase of the DD at a specific time. Therefore, by controlling the DD of the deacetylated chitin maximum efficiency can be achieved in the removal of dyes and metal ions from textile effluent. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 725–736, 1997

Key words: chitin; sorbent; sorption; dye; chromium

INTRODUCTION

Chitin and chitosan (deacetylated chitin) have been examined as sorbents to remove various dyestuffs or metal ions from textile effluent.[1–4] It has been shown that these polyaminosaccharides have a high sorption capacity for acid, mordant, and direct dyes.[1–3,5–8] They also show high chelating ability in removal of trace metal ions, such as mercury, copper, zinc, chromium, cadmium, nickel, and lead, from the effluent or sludge.[9–12] Their high capacity for sorbing dyes and metal ions has been attributed to a combination of many factors such as their ionic nature, affinity for water, and porous polymer structure.[4,11] Sorption of the dye mainly occurs into amorphous areas of the chitin polymer.[4]

Compared with other polysaccharides, chitin is unreactive. Its deacetylation process in production of chitosan, therefore, generally requires quite vigorous conditions; and a complete deacetylation reaction is not practically desirable.[5] Previous studies indicated that the sorption capacity of chitosan for certain acid dyes and metal ions was four to five times[4] or remarkably higher than that of chitin.[11,12] This was believed to be due to the higher number of free amine groups in the chitosan molecule.[4,11] This suggested that in chitin and chitosan sorbents, degree of deacetylation, a proportion between amine and acetylamino groups, could be a key parameter in controlling

Correspondence to: H.-M. Choi.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/060725-12

Table I Deacetylation Values of Chitin Prepared by Alkaline Hydrolysis

Concentration of NaOH [w/v (%)]	Temperature (°C)	Time (min)	Degree of Deacetylation (%)
8	90	180	10.7
20	105	60	21.4
40	100	70	36.3
50	100	60	46.8
35	120	140	67.2

sorption and desorption of sorbates such as dyes and metal ions.

A large fraction of textile effluent is discharged in strong acidic condition.[13] This acidic effluent could severely limit the use of chitosan as a sorbent in removing dyes and metal ions due to chitosan's dissolution tendency in the effluent. To reduce such a problem, chitosan has been stabilized by using various crosslinking agents.[12,13] This approach, however, could considerably increase the application cost. An alternative approach is to find a degree of deacetylation in chitin which could produce an optimal balance between its maximum sorption and stability in the acidic condition. However, little study has been carried out to systematically investigate the effect of deacetylation on sorption behavior and stability of chitin. Therefore, our objective was to study the effect of deacetylation on the sorption behavior of chitin, which also gives good stability in the system applied at various conditions.

EXPERIMENTAL

Deacetylation of Chitin

Crab shell chitin (Sigma Corp.) was sieved to obtain particles smaller than 1000 μm to eliminate any effects from particle discrepancy. It was hydrolyzed using various concentrations of NaOH under a nitrogen atmosphere. By varying alkaline concentration, temperature, and time, five different deacetylated chitins were obtained as shown in Table I. These deacetylated chitins were washed with distilled water to remove residual NaOH, rinsed by methanol followed by acetone rinse, and then vacuum dried at 60°C for 12 h. The degree of deacetylation (DD) on the hydrolyzed chitins was determined by a Fourier transform infrared (FTIR) spectroscope (Diamond-20, Analect, USA) using the following equation[14,15]:

$$\text{Degree of Deacetylation (\%)} = [1 - (A_{1655}/A_{3450}) \times 1/1.33] \times 100 \quad (1)$$

where A_{1655} and A_{3450} are absorbency values at 1655 cm^{-1} and 3450 cm^{-1} for carbonyl and hydroxyl peaks, respectively. Base lines were set up using a method described in a previous report.[14]

X-ray diffraction technique (D/MAX IIIB, Rigaku, Japan) was also used to analyze the deacetylated chitin. The instrument condition included Cu-Ka X-ray, which was filtered by a Ni filter at 40 kV and 30 mA, scan speed 10 degree/min, scan step 0.05, and diffraction angle between 5 and 30 range.

Sorption and Desorption

Four dyestuffs, which were obtained from commercial sources, were extracted with DMF to remove salts and other additives. Characteristics of these dyes are presented in Table II and their chemical structures are shown in Scheme 1. After purification these dyes were analyzed by paper chromatography using a propanol–aceton–water–acetic acid (5 : 5 : 3 : 1) eluent to confirm the purity of the dyes. Each dye showed a single R_f value after the purification, indicating an absence of additives.

Fifty milligrams of the chitin were suspended in 100 mL of aqueous dye solution, which was placed in 125 mL of a stainless dyeing container in an automatic dyeing machine (Polymat, Ahiba, Swizerland). The initial concentration of the dye solution was 145 mg/L, unless otherwise noted. The pH of the system was controlled by using 0.1 N NaOH and 0.1 N HCl to elucidate the effect of

Table II Characteristics of Dyes

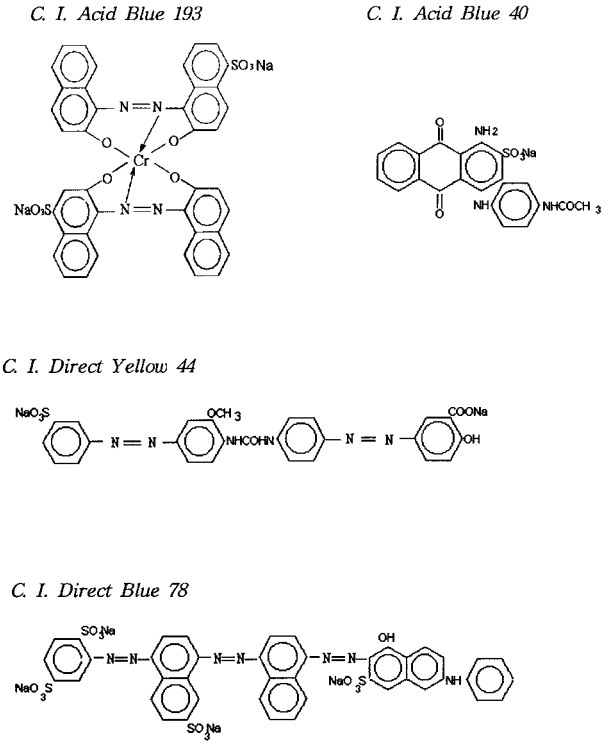
C.I. Number	Commercial Name	Chemical Class	Molecular Weight	λ_{max}	R_f Values: Before Purification	R_f Values: After Purification
Acid Blue 193	Lanasyn Navy S-DNL(S)	1 : 2 Chromium complex of monoazo	834	616	0.53, 0.38	0.53
Acid Blue 40	Nylosan Blue E-2GL(S)	Anthraquinone	378	578	0.73	0.73
Direct Yellow 44	Solophenyl Yellow 5GL(CGY)	Diazo	587	398	0.46, 0.59	0.46
Direct Blue 78	Solophenyl Blue 4GL(CGY)	Triazo	963	608	0.46, 0.12	0.12

S, Sandoz Ltd, Basle, Switerland; CGY, Ciba-Geigy Corporation, Dyestuffs and Chemicals, Clayton, England.

pH on the sorption behavior of chitin. Sorption treatment was carried out in this machine which was rotated for an appropriate time at room temperature (25°C).

Desorption is also important in terms of dye recycling after sorption treatment. Desorption of the dye-sorbed chitin (50 mg) was carried out with 100 mL of water at various pHs at 25°C and 80°C. A UV-visible spectrophotometer (HP 8452, Hewlett Packard, USA) was used to measure the residual dye concentration in the container at each λ_{max} (see Table II). Results were represented as mg of the sorbate per g of the sorbent for both sorption and desorption values. The system pH and treatment time were varied to study effects on equilibria and kinetics of the sorption and desorption.

Sorption of chromium ions on the deacetylated chitin was carried out in a water bath incubator (Yamato, Japan). A glass bottle with a capacity of 75 mL containing 50 mL of aqueous chromium solution in the form of potassium dichromate (chromium concentration 5 mg/L) and 25 mg of the deacetylated chitin was shaken in the water bath for an appropriate time at 25°C. Residual chromium ions in the solution after the sorption treatment were evaluated using Atomic Absorption Spectrometer (AA-646, Shimazu, Japan). Different pHs were also used to examine pH effects on the sorption equilibria and kinetics of the chromium ions.



Scheme 1

RESULTS AND DISCUSSION

Deacetylated Chitin

FTIR spectra of chitins, which were hydrolyzed by NaOH at different reaction temperatures and times, are shown in Figure 1. DDs were calculated using these spectra and listed in Table I. The DD of original chitin before the hydrolysis was 2.5%, which had been measured by a titration method[16] due to difficulty in making film. Peak intensities at 1655 cm^{-1} decreased and the DDs calculated

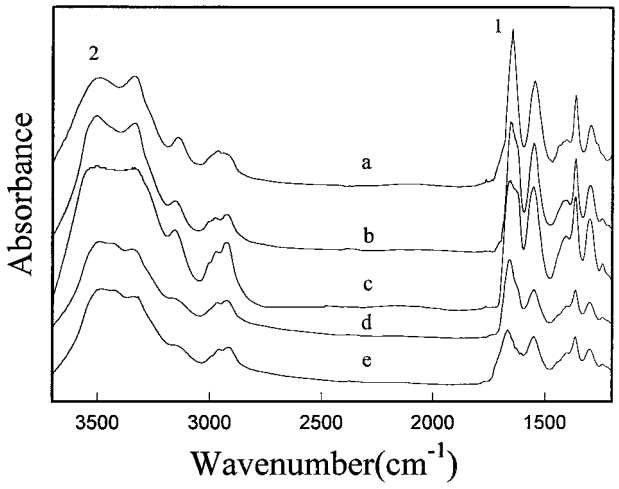


Figure 1 FTIR spectra of the deacetylated chitins hydrolized under various conditions: (a) 8% NaOH, 90°C; (b) 20% NaOH, 105°C; (c) 40% NaOH, 100°C; (d) 50% NaOH, 100°C; (e) 35% NaOH, 120°C (peak 1: 1655 cm^{-1}, peak 2: 3450 cm^{-1}).

increased with increases of NaOH concentration, and of reaction temperature and time as expected. In addition, it is also possible that the treatment could cause a discrepancy in the heterogeneity of the samples.

No observable difference was shown in X-ray diffraction diagrams on deacetylated chitins with DDs between 10.7 and 36.3% (Fig. 2). This suggested that up to 36.3% of DD, the deacetylation reaction mainly occurred in amorphous regions of chitin. On the other hand, a considerable reduction was shown in diffraction peak intensities

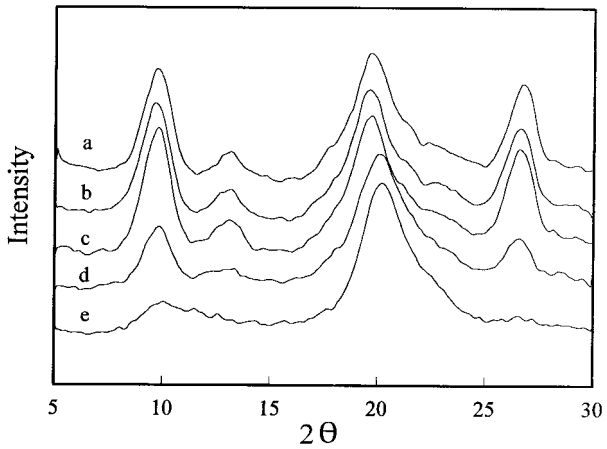


Figure 2 X-ray diffraction diagrams of the deacetylated chitins: (a) DD = 10.7%; (b) DD = 21.4%; (c) DD = 36.3%; (d) DD = 46.8%; (e) DD = 67.2%.

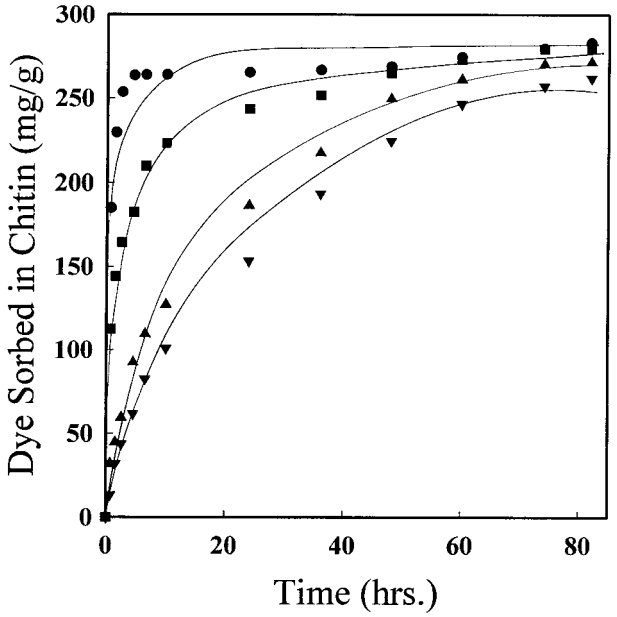


Figure 3 Sorption of C.I. Acid Blue 193 on the deacetylated chitin (DD = 36.3%) over time: (●) pH 3; (■) pH 4; (▲) pH 5.5; (▼) pH 7.

around $2\theta = 27$ for chitins with 46.8 and 67.2% DDs [Fig. 2(d,e)], indicating the occurrence of deacetylation at crystalline regions. However, the positions of the diffraction peaks were the same for all the chitins with different DDs. This revealed that deacetylation had a minimal effect on the size of the crystalline structure at these DDs. These analyses confirmed previous results obtained by Kurita and Iwakura[17]: (1) the initial reduction of crystallinity with 45% DD, (2) the disappearance of the crystalline peak with 89% DD, and (3) the reappearance of the new crystalline structure with a 95% DD at a different diffraction peak position.

Dye Sorption on Deacetylated Chitin

Figure 3 shows sorption isotherms of the deacetylated chitin with a 36.3% DD over time at different pHs, measured with C.I. Acid Blue 193. Other deacetylated chitins with different DDs generally showed similar results to those of the deacetylated chitin with a 36.3% DD. An exception, however, was shown in the chitins with 46.8 and 67.2% DDs, which caused a partial dissolution in acidic condition, resulting in no data. At pH 4 the sorption equilibria of the deacetylated chitins with 67.2, 46.8, 36.3, 21.4, and 10.7% DDs were

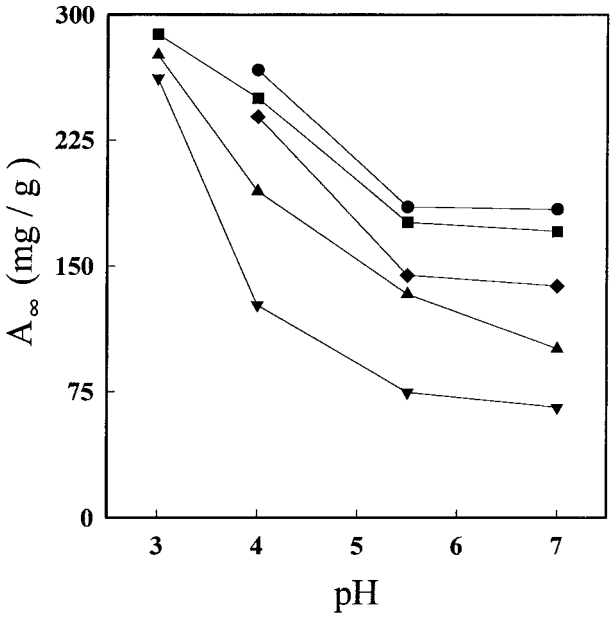


Figure 4 Equilibrium sorption capacity (A_∞) of various deacetylated chitins over different pHs: (♦) DD = 67.2%; (●) DD = 46.8%; (■) DD = 36.3%; (▲) DD = 21.4%; (▼) DD = 10.7%.

reached by about 92, 60, 82, 92, and 120 hours, respectively. At pH 3 the sorption reached the equilibrium within a much shorter time, e.g., 12 hours for chitin with 36.3%. Effects of the DD on the sorption equilibria of the deacetylated chitins can also be expressed by the time of half-sorption ($t^{1/2}$), which is the time required for the sorbent to sorb half as much dye as it will sorb in the equilibrium state.[18] At pH 4 the values of $t^{1/2}$ of chitins with 67.2, 46.8, 36.3, 21.4, and 10.7% DDs were 2.8, 1.1, 1.3, 11.3, and 21 h, respectively. These values could be more useful than sorption equilibria data since equilibria are rarely reached in practice. In both cases, the chitin with a 46.8% DD showed the least amount of time in sorbing dyes.

The rate of sorption of dyes on the deacetylated chitin can be alternatively expressed using sorption rate constant and equilibrium sorption capacity as follows[18]:

$$kt = 1/(A_\infty - A_t) - 1/A_\infty \quad (2)$$

$$1/A_t = 1/(A_\infty^2 kt) + 1/A_\infty \quad (3)$$

where k is the sorption rate constant, A_∞ is the equilibrium sorption capacity, and A_t is the sorption capacity at time t. Therefore, A_∞ and k can be calculated from the plots between $1/A_t$ and $1/t$ by using data previously represented in Figure 3 for chitin with a 36.3% DD and other chitins' data (not shown). The results calculated are illustrated in Figures 4 and 5 with C. I. Acid Blue 193 to examine the effects of deacetylation on sorption of chitin at various pHs.

Results showed that except for the chitin with a 67.2% DD, both A_∞ and k were proportional to the DD in chitin for each pH. Within each deacetylated chitin, however, both A_∞ and k increased with a decrease in pH of the systems. The difference in the rate constant, k, was much greater at low pH ranges than at high pH ranges (Fig. 5). Sorption of dye anions on chitin could be attributed to many different interactions between the sorbate and sorbent molecules, such as ionic bonding ability, hydrophobic interaction due to planarity and other geometric configurations of the dye molecules, chelating ability of the chitin-dye system through coordinating bonding in premetallized dyes, and hydrogen bonding.[1,2] In this study, the increase in both A_∞ and k values was mainly due to an increase in $—NH_3^+$ groups within the sorbent, caused by the high DD and low pH of the system, which could facilitate ionic bondings between chitin and dye. A similar result was obtained in a previous study.[1,2] However, in

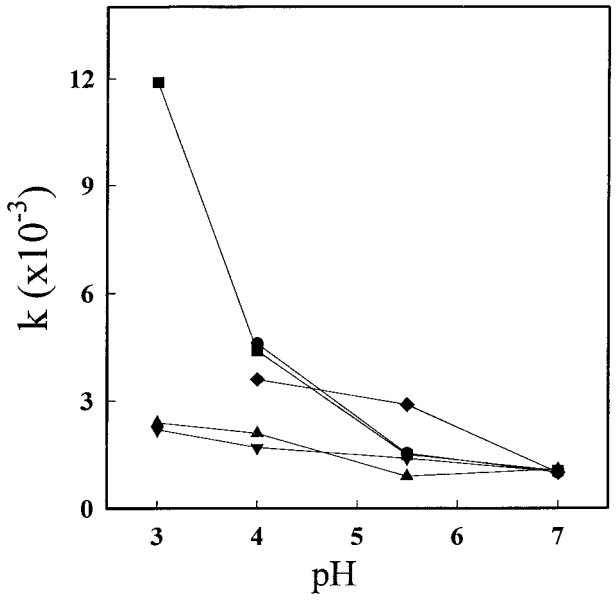


Figure 5 Sorption rate constant (k) of various deacetylated chitins over different pHs: (♦) DD = 67.2%; (●) DD = 46.8%; (■) DD = 36.3%; (▲) DD = 21.4%; (▼) DD = 10.7%.

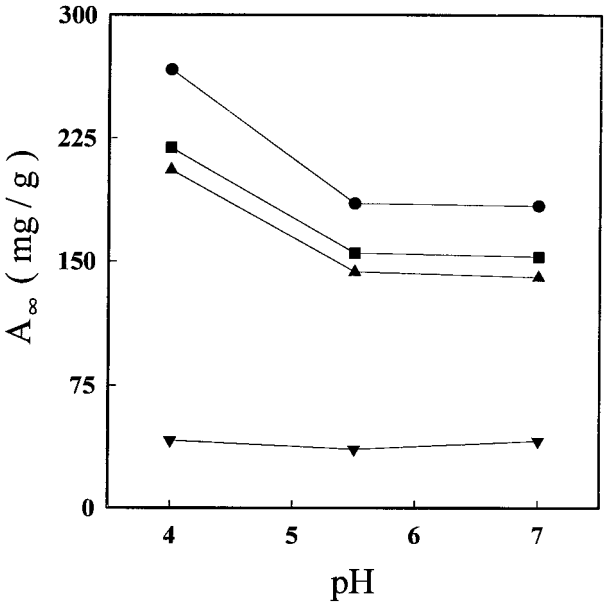


Figure 6 Equilibrium sorption capacity (A_∞) of the deacetylated chitin (DD = 46.8%) measured with various dyes over different pHs: (●) C.I. Acid Blue 193; (■) C.I. Acid Blue 40; (▲) C.I. Direct Yellow 44; (▼) C.I. Direct Blue 78.

chitin with a 67.2% DD, reduction in the hydrophobicity of the deacetylated chitin became substantial, resulting in low A_∞ and k.

Sorption of Various Dyes

Figures 6 and 7 show the equilibrium sorption capacity and sorption rate constant of the deacetylated chitin (DD = 46.8%) measured with four dyes at different pHs. In general, both A_∞ and k values were increased with decrease in pH for all dyes. At slight acidic and neutral conditions, such as pH 5.5 and 7, differences in k values were small among four dyes, whereas at pH 4 a considerable difference was shown in k values (Fig. 7).

Acid dyes such as C.I. Acid Blue 193 and C. I. Acid Blue 40 generally showed higher A_∞ and k values than those of direct dyes, but the difference was not considerable with C.I. Direct Yellow 44. In the case of C.I. Direct Blue 78, the sorption of the dye represented by A_∞ and k values was minimal due to the molecular size effect, which could hinder penetration of the dye molecule into internal pores. The similar molecular size effect was also shown in previous studies.[1,4,7] On the other hand, sorption of the deacetylated chitin with C. I. Acid Blue 193 resulted in the highest A_∞ and k values, even with its large molecule, indicating the importance of the chelating effect in the sorption. Further study is needed to elucidate effects of chelation on dye sorption of the chitin in more detail.

Langmuir Isotherms

We also carried out an additional experiment for the sorption isotherms of the deacetylated chitin against various dye concentrations at pH 4 and 25°C for an appropriate time. Figure 8 illustrates the results for C.I. Acid Blue 193. The deacetylated chitin with a 46.8% DD resulted in the highest sorption capacities with all dyes. The shapes of the curves were similar to the Langmuir isotherm which was represented as follows[1]:

$$C_e/Y_e = 1/Qb + C_e/Q \qquad (4)$$

where Q is an ultimate saturation sorption capacity (mg/g), b is a Langmuir constant (dm^{-3}/g), C_e is a dye concentration in solution at equilibrium (mg/g), and Y_e is a dye concentration on deacetylated chitin at equilibrium (mg/g). As shown in Table III, values of Q and b can be ob-

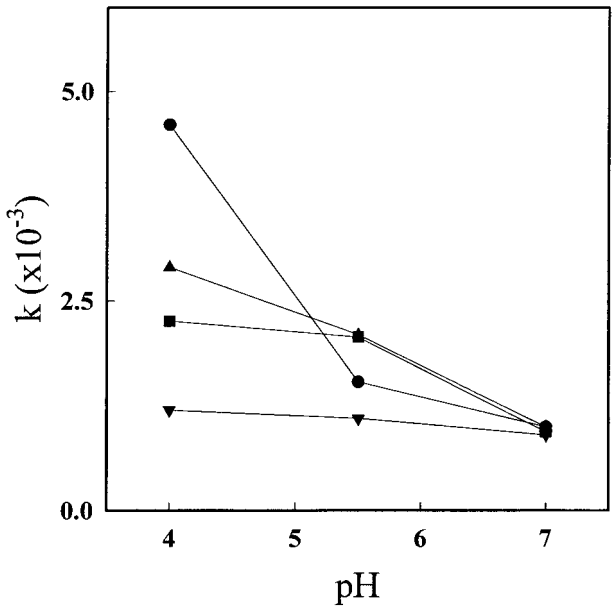


Figure 7 Sorption rate constant (k) of the deacetylated chitin (DD = 46.8%) measured with various dyes over different pHs: (●) C.I. Acid Blue 193; (■) C.I. Acid Blue 40; (▲) C.I. Direct Yellow 44; (▼) C.I. Direct Blue 78.

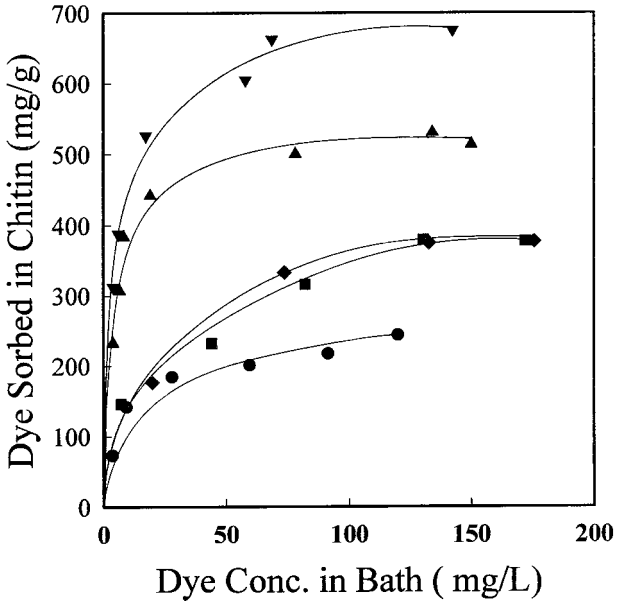


Figure 8 Sorption isotherms of various deacetylated chitins for C.I. Acid Blue 193 at pH 4: (♦) DD = 67.2%; (▼) DD = 46.8%; (▲) DD = 36.3%; (■) DD = 21.4%; (●) DD = 10.7%.

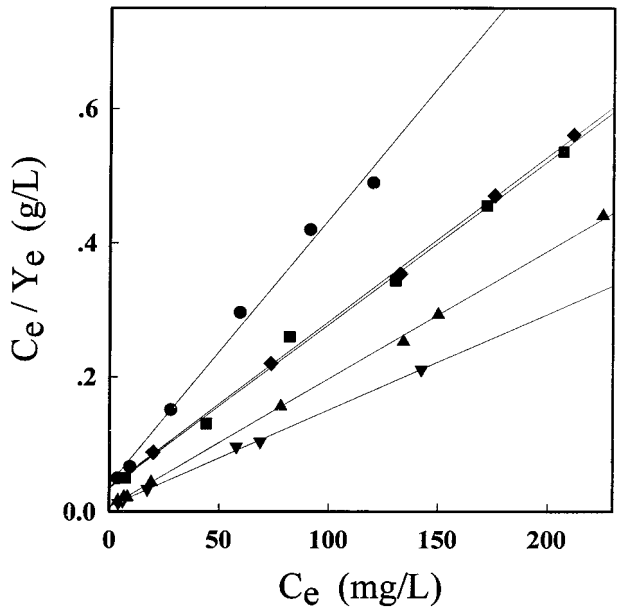


Figure 9 Langmuir plots of various deacetylated chitins for C.I. Acid Blue 193 at pH 4: (♦) DD = 67.2%; (▼) DD = 46.8%; (▲) DD = 36.3%; (■) DD = 21.4%; (●) DD = 10.7%.

tained by using plots of C_e/Y_e versus C_e, which are illustrated in Figure 9 for C.I. Acid Blue 193 as an example. The Q and b values for other dyes were obtained by the same method. These plots were all linear, confirming the use of the Langmuir isotherm was suitable in analysis of dye sorption on the deacetylated chitin.

Results in Table III indicated that Q values for acid dyes were generally higher than those of direct dyes. Especially, for each deacetylated chitin, C.I. Acid Blue 193 resulted in the highest Q values, again revealing the importance of the chelating effect on premetallized dyes during the sorption. Like the A_∞ and k values, C.I. Direct Blue 78 also showed the lowest Q values. This further substantiated that substantivity, which was often important in the sorption of direct dyes on cellulosic fiber, was not crucially important in the sorption of dyes on the deacetylated chitin. For each dye, the highest Q value was shown with the deacetylated chitin with a 46.8% DD. Q values of the hydrophilic deacetylated chitin with a 67.2% DD were again lower than those of the chitin with a 46.8% DD. The effect of deacetylation on sorption of dyes by chitin as analyzed by the Langmuir isotherm was, therefore, exactly the same as the effect analyzed by the A_∞ and k values.

We also investigated the effect of pH on Q value as shown in Table III for the deacetylated chitin with a 36.3% DD. Sorption time was 12 h at pH

Table III ***Q*** **and** ***b*** **Values of Dyes on Chitins with Different Degrees of Deacetylation**

DD		C.I. Acid Blue 193		C.I. Acid Blue 40		C.I. Direct Yellow 44		C.I. Direct Blue 78	
(%)	pH	Q (mg/g)	b (L/mg)	Q (mg/g)	b (L/mg)	Q (mg/g)	b (L/mg)	Q (mg/g)	b (L/mg)
67.2	4	440.5	0.03	294.1	0.03	169.2	0.25	32.4	0.1
46.8	4	699.3	0.18	311.5	0.14	256.1	0.46	70.9	0.09
36.3	4	523.6	0.29	284.7	0.28	212.2	0.67	58.6	0.13
36.3	3	1123.8	0.11	666.7	0.05	680.1	0.03	113.8	0.05
21.4	4	432.9	0.04	225.7	0.04	160.8	0.11	56.8	0.15
10.7	4	267.4	0.09	145.4	0.11	111.1	0.54	52.2	0.09

3 and 82 h at pH 4. As the pH of the system changed from 4 to 3, Q values increased two- to threefold for all dyes. This favorable sorption at lower pH was due to an increase in ionic bonding sites at both dyes and the deacetylated chitin. However, at pH 3 the deacetylated chitin with a 46.8% DD showed slight dissolution in preventing its use at low pH. Therefore, an optimal condition to remove dyes from textile effluent could be obtained by employing the deacetylated chitin with a 36.3% DD at pH 3 or with a 46.8% DD at pH 4.

Separation Factor

McKay et al.[1] further utilized the Langmuir constant, b, in calculation of the separation factor (or equilibrium parameter), r, which was originally defined by Hall et al.[19] as follows:

$$r = 1/(1 + bC_0) \tag{5}$$

where C_0 is an initial dye concentration in solution (mg/dm^3). This parameter could predict whether sorption of the dyes on chitin was "favorable" or "unfavorable," such as unfavorable isotherm if $r > 1$, linear isotherm if $r = 1$, favorable isotherm if $0 < r < 1$, and irreversible isotherm if $r = 0$. In a real sorption process, however, r values always lie between 0 and 1, and as the r value approaches zero, the sorption becomes more favorable. The r values can also be illustrated by using the relationship between the Langmuir isotherm and the parameter defined as follows:

$$q = x/r(1 - x) + x \tag{6}$$

where x equals a ratio between C_e and C_{ref} (maximum fluid-phase dye concentration, mg/L), and q equals a ratio between Y_e and Y_{ref} (maximum solid-phase dye concentration on chitin, mg/g). The r values calculated are listed in Table IV, and the sorption behavior of the chitin with 36.3% DD is represented by r values for various dyes in Figure 10. For each deacetylated chitin, r values showed the least favorable isotherm for C.I. Direct Blue 78, and the r values of the sorption with other dyes approached zero indicating favorable sorption. For each dye, r values were the lowest with the deacetylated chitins with 36.3 and 46.8% DDs as shown in Table IV and Figure 11, revealing their favorable sorption.

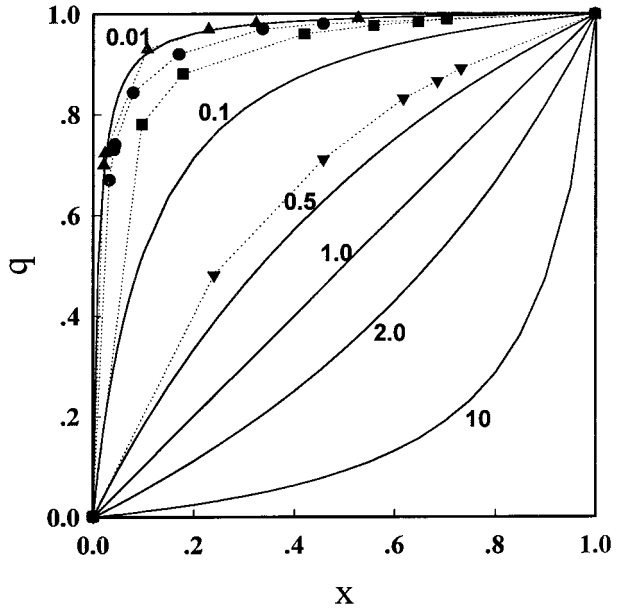


Figure 10 Separation factors of the deacetylated chitin (DD = 36.3%) expressed as a function of q and x: (●) C.I. Acid Blue 193; (■) C.I. Acid Blue 40; (▲) C.I. Direct Yellow 44; (▼) C.I. Direct Blue 78.

Desorption of Dye

The deacetylated chitin with a 46.8% DD was used in a desorption experiment. As shown in Figures 12 and 13, dye desorption from the deacetylated chitin was almost negligible up to pH 9 at 25°C, but it increased considerably at pHs higher than 10. This was because increasing the pH could result in reduction of —NH_3^+ ions from the deacetylated chitin, facilitating desorption of the dyes from the sorbent. In addition, OH groups in the deacetylated chitin would be negatively charged at an alkaline condition, causing electrostatic repulsion between the chitin and dye anions.

It was interesting to note that C.I. Acid Blue 193, which showed the highest sorption in every case, also resulted in the highest desorption, indicating a complete reversible nature in the sorption of premetallized dye. On the other hand, C.I. Direct Blue 78 also showed the lowest desorption, revealing a relative stability of nonionic bondings at different pHs. In addition, increase of temperature to 80°C substantially enhanced efficiency of the desorption, even at neutral condition (Fig. 13); and, for C.I. Acid Blue 193, the desorption reached almost 90%. This suggested synergistic swelling effects of the deacetylated chitin caused by high temperature and pH, resulting in easy desorption.

Table IV ***r*** **Values of Dyes on Chitin with Different Degrees of Deacetylation**

DD (%)	pH	C.I. Acid Blue 193	C.I. Acid Blue 40	C.I. Direct Yellow 44	C.I. Direct Blue 78
67.2	4	0.16	0.03	0.09	0.60
46.8	4	0.02	0.04	0.02	0.42
36.3	4	0.016	0.03	0.009	0.34
36.3	3	0.03	0.17	0.11	0.65
21.4	4	0.17	0.37	0.14	0.40
10.7	4	0.15	0.15	0.07	0.55

Sorption of Chromium Ions

Figure 14 presents sorption of chromium ions on three different deacetylated chitins with 46.8, 36.3, and 10.7% DDs as a function of time at pH 3 and 25°C. Results indicated that as the DD increased, the amount of chromium sorbed on the chitin increased in each time. The sorption of chromium ions was initially very rapid, with about 70 to 80% of total sorption capacity obtained within 2 and 3 hours of the treatment time. Equilibrium sorption capacities of the chitins with 46.8, 36.3, and 10% DDs were 9.1, 8.9, and 7.5 mg/g at pH 3 within 24, 40, and 52 h, respectively. In a previous study by Udaybhaskar et al.[20] at the same initial chromium concentration ($0.96 \times 10^{-1} M$), chromium sorption on the deacetylated chitin, which had been hydrolyzed with 50% NaOH at 80°C for 5 h in the nitrogen atmosphere, showed about 8 mg/g at pH 4. Considering this reaction condition, the DD of the chitin was believed to be more than 50%. Therefore, our results were in good agreement with the previous result.

On the other hand, by varying pH there was a considerable decrease in chromium sorption between pH 3 and pH 5, depending on the DD of the deacetylated chitin (Fig. 15). After pH 5, chromium sorption was consistent at low levels with pH variation. The decrease in chromium sorption at a low pH range was due to the effect of pH on

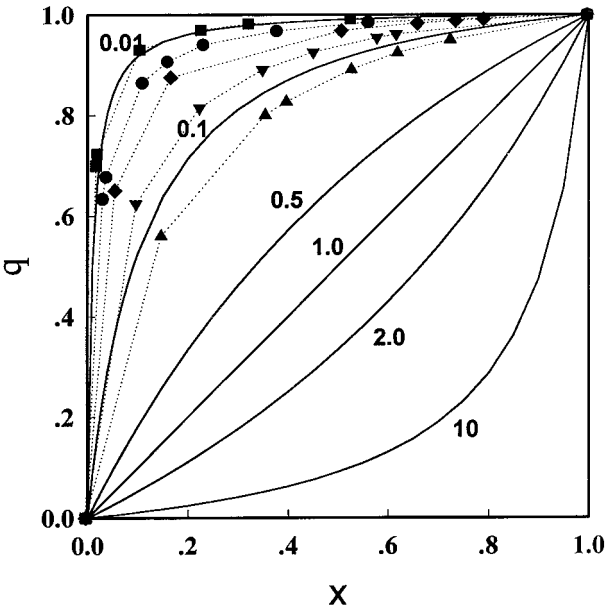


Figure 11 Separation factors of various deacetylated chitins expressed as a function of q and x: (♦) DD = 67.2%; (●) DD = 46.8%; (■) DD = 36.3%; (▲) DD = 21.4%; (▼) DD = 10.7%.

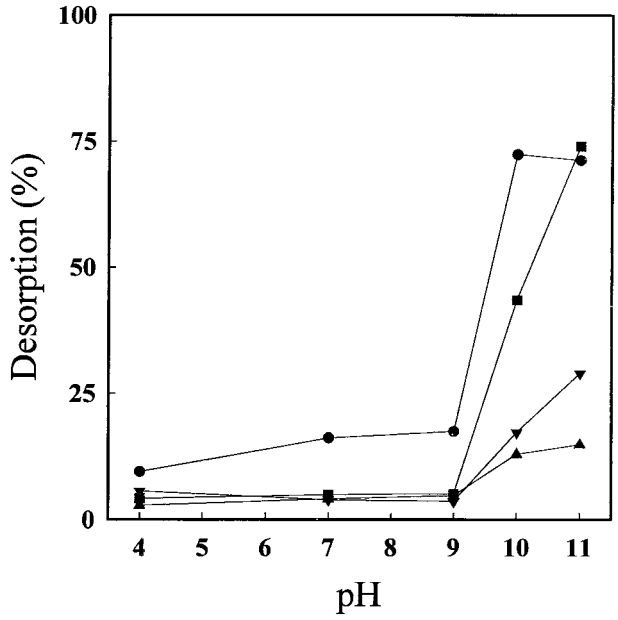


Figure 12 Effect of pH on the desorption of various dyes at 25°C: (●) C.I. Acid Blue 193; (■) C.I. Acid Blue 40; (▲) C.I. Direct Yellow 44; (▼) C.I. Direct Blue 78.

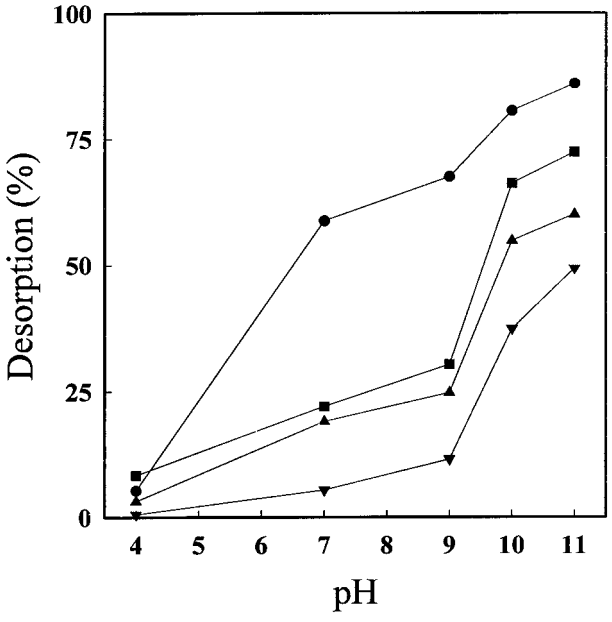


Figure 13 Effect of pH on the desorption of various dyes at 80°C: (●) C.I. Acid Blue 193; (■) C.I. Acid Blue 40; (▲) C.I. Direct Yellow 44; (▼) C.I. Direct Blue 78.

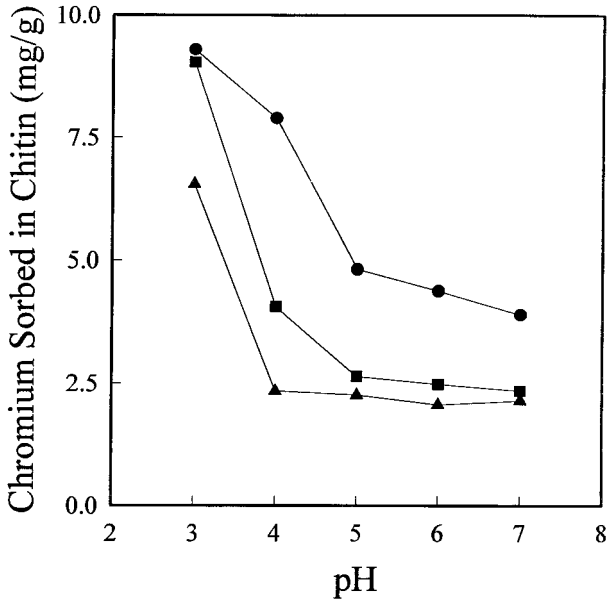


Figure 15 Sorption of chromium ions on various deacetylated chitins over different pHs: (●) DD = 46.8% (treatment time 24 h); (■) DD = 36.3% (40 h); (▲) DD = 10.7% (52 h).

electrostatic interaction between the sorbent and the sorbate.[20] It was postulated that potassium dichromate formed stable complexes such as $Cr_2O_7^{-2}$, $HCrO_4^-$, CrO_4^{-2}, and $HCr_2O_7^-$, depending on chromium concentration and pH. For each deacetylated chitin there would be a substantial decrease of protonated amine groups at higher pH which would consequently reduce the sorption of chromium ions. As described previously,[11] the sorption of other metal ions such as mercury(II) and copper(II) was increased, up to 50% of amino group content in the chitin, and then started to decrease. In addition, at high pH conditions the percentage of bichromate also decreased; and, consequently, the chromium sorption was reduced.[21]

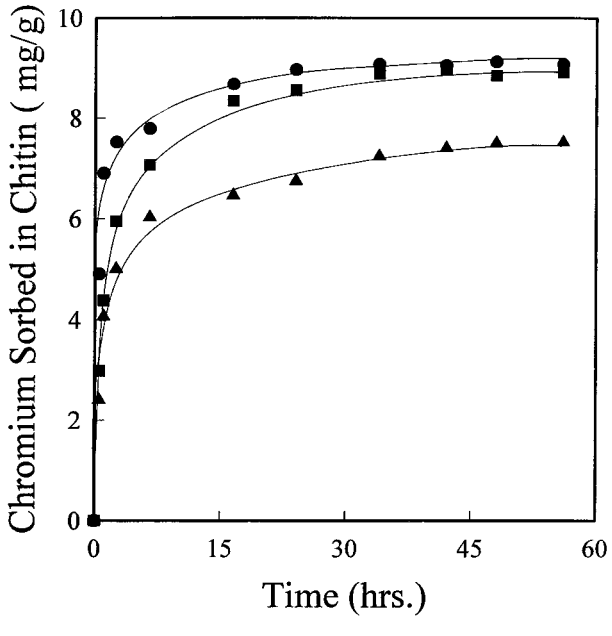


Figure 14 Sorption of chromium ions on various deacetylated chitins over time at pH 3: (●) DD = 46.8%; (■) DD = 36.3%; (▲) DD = 10.7%.

It is worthwhile to note that unlike dye sorption of the deacetylated chitin, there was no partial dissolution of the chitin with a 46.8% DD when it was exposed to the solution with pH 3. This implied that the deacetylated chitin had been crosslinked through chelation of chromium ions, consequently increasing the stability of the chitin molecule in acidic solution. It has been reported that the deacetylated chitin with high hydrophilicity and water insolubility through glutaldehyde crosslinking showed remarkable sorption capacity of copper.[12]

Langmuir Isotherm of Chromium Ions

The same approach was used to analyze the sorption of chromium ions using the Langmuir iso-

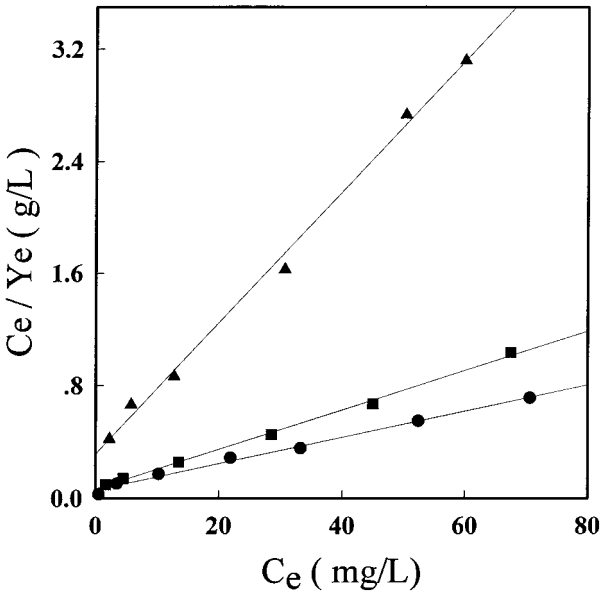


Figure 16 Langmuir plots of various deacetylated chitins for chromium ions at pH 3: (●) DD = 46.8%; (■) DD = 36.3%; (▲) DD = 10.7%.

therm as described previously for dye sorption. Figure 16 shows the Langmuir isotherms, which were obtained at pH 3 and 25°C at various initial concentrations of chromium ion. In plots of C_e versus C_e/Y_e to obtain Q and b values, linear lines also indicated suitability of Langmuir isotherms in analyses of chromium sorption on the deacetylated chitin. The Q values for the deacetylated chitins with 46.8, 36.3, and 10.7% DDs were 106.8, 70.18, and 18.17 mg/g, respectively, which were again proportional to the increase of the DD of the chitin.

CONCLUSIONS

Crab shell chitin was hydrolyzed into deacetylated chitin with various DDs (10.7–67.2%) at different alkali concentrations and reaction times and temperatures. The DD in the deacetylated chitin was measured by FTIR, using a ratio of peak intensities at 1655 and 3450 cm^{-1}. X-ray diffraction study revealed that in the deacetylated chitin with up to 36.3% of DD, deacetylation mainly took place at an amorphous region of chitin.

Sorption isotherms were carried by varying treatment time, pH, and initial concentration of dyes or chromium ions. Experimental results were analyzed in three ways by using equilibrium sorption capacity (A_∞) and sorption rate constant (k), ultimate saturation sorption capacity (Q) and Langmuir constant (b), and separation factor (r) to determine if the sorption was favorable.

Results indicated that except for the chitin with a 67.2% DD, the rate and capacity of the dye sorption on the chitin were proportional to the DD in chitin in each pH. However, the opposite effect was shown with pH change for each deacetylated chitin. This was mainly due to the increase of $-NH_3^+$ groups in chitin with high DD and the low pH of the system.

The highest A_∞ and k values in sorption of C.I. Acid Blue 193, which was a premetallized dye, indicated the importance of the chelating effect. Linear shapes of Langmuir plots obtained by relationships between C_e/Y_e and C_e substantiated the suitability of using Langmuir isotherms in analysis of dye sorption on the deacetylated chitin.

Dye desorption from the deacetylated chitin was more efficient at higher temperatures. At pH 10 or higher, reduction in the number of $—NH_3^+$ ions in the deacetylated chitins also facilitated desorption of dyes. A maximum desorption of C.I. Acid Blue 193 from the dye-sorbed chitin was about 90% at 80°C and pH 11.

The amount of chromium sorbed on the chitin increased with the increase of the DD at a specific time. The deacetylated chitin with different DDs also responded differentially to pH changes in chromium sorption. During the chromium sorption, stability of highly deacetylated chitins, i.e., 46.8% of DD, was increased at low pH conditions due to a crosslinking effect.

As a conclusion, the deacetylated chitins with 36.3 and 46.8% DDs were generally the most effective in removal of four dyes and chromium ions at pH 3 and 4, respectively. Therefore, by controlling the DD of the deacetylated chitin, it is possible to maximize the removal of dyes and metallic ions presented in textile effluent at a specific pH.

REFERENCES

1. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.,* **27,** 3043 (1982).
2. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.,* **27,** 4251 (1982).
3. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.,* **28,** 1767 (1983).

4. B. Smith, T. Koonce, S. Hudson, *Am. Dyestuff Rep.,* **82,** 18 (1993).
5. H. S. Blair and T. Ho, *J. Chem. Tech. Biotechnol.,* **31,** 6 (1980).
6. G. McKay, *Chem. Eng. Process.,* **21,** 41 (1987).
7. H. Yosida, S. Fukuda, A. Okamoto, and T. Takaoka, *Wat. Sci. Tech.,* **23,** 1667 (1991).
8. C. H. Giles and A. S. A. Hassan, *J. Soc. Dyers and Colourists,* **74,** 846 (1958).
9. R. A. A. Muzzarelli, *Chitin,* Pergamon Press, New York, 1977.
10. T. Yan and R. R. Zall, *Industrial Water Eng.,* **21**(4), 16 (1983).
11. K. Kurita and Y. Iwakura, *J. Appl. Polym. Sci.,* **23,** 511 (1979).
12. K. Kurita, Y. Koyama, and A. Taniguchi, *J. Appl. Polym. Sci.,* **31,** 1169 (1986).
13. J. S. Lee, S. I. Hong, and D. W. Jeon, *J. Korean Fiber Society,* **31,** 966 (1994).
14. T. Sannan and K. Kurita, *Polymer,* **19,** 458 (1978).
15. G. H. Moore and G. A. F. Roberts, MIT Sea Grant Report 78-7, 406, 1978, quoted by H. S. Blair and J. Guthrie, in *J. Appl. Polym. Sci.,* **33,** 641 (1987).
16. A. Kawata, Jpn. Pat. 2-307915 (1990).
17. K. Kurita and Y. Iwakura, *Makromol. Chem.,* **178,** 3197 (1977).
18. V. Vickerstaff, *The Physical Chemistry of Dyeing,* 2nd ed., Interscience, New York, 1965, pp. 147–150.
19. K. R. Hall and L. C. Eagleton, *Ind. Eng. Chem. Fundam.,* **5,** 212 (1966).
20. P. Udaybhaskar, L. Iyengar, and A. V. S. Prabhakara Rao, *J. Appl. Polm. Sci.,* **39,** 739 (1990).
21. C. P. Huang and M. H. Wu, *J. Water Pollution Control Fed.,* **47,** 2437 (1975).