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H_2O_2-induced surface modification: A facile, effective and environmentally friendly pretreatment of chitosan for dyes removal

Chensi Shen[a], Yuezhong Wen[a,*], Xiaodong Kang[b], Weiping Liu[a]

[a] *Institute of Environmental Science, Zhejiang University, Hangzhou 310029, China*
[b] *Hangzhou Normal University, Hangzhou 310036, China*

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ABSTRACT

H_2O_2-induced modification of chitosan was developed to improve the adsorption of dyes onto chitosan. The modified chitosan showed a more ordered structure and a higher hydrophilic character without significantly change of functional group on surface, comparing with the untreated chitosan. By the analysis of the hydrophilic character, zeta potential and XPS of untreated and pretreated chitosan, it can be inferred that the enhancement of interaction between the dye and chitosan was attributed to the increase of free hydroxyl and amine groups on the chitosan surface due to the partial removal of amorphous components induced by H_2O_2. Thus, the H_2O_2-induced modification of chitosan should make it easily for amine groups on pretreated chitosan surface to get protonated in weak acidic solution and resulted in simultaneous enhancement of electrostatic interaction between the dye and chitosan molecule. The adsorption results indicated that the dye removal efficiency improved about 60% after the chitosan pretreated with 200 mM hydrogen peroxide for 2 h. In addition, the adsorption of other dyes and the regeneration studies demonstrated that the pretreated chitosan could be recovered and reused effectively for the adsorption of anionic dyes. These observations reveal that this pretreatment method of chitosan is much more facile, environmentally and interesting than previously reported and provide a paradigm for surface modification of adsorbents.

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1. Introduction

The waste effluents from the dyeing processes are characterized by high biochemical and chemical oxygen demand (BOD and COD), suspended solids, bad smells, toxicity, and, especially, color. These waste products are a major source of aquatic pollution [1]. Wastewaters containing dyes are very difficult to treat because dyes are persistent and resistant to aerobic digestion [2]. Dyes would be toxic to marine life when they are released into the aquatic environment. Therefore, dye industry wastes have to be treated prior to discharge. An effective and economical method to remove dyes is to pass the waste stream over effective adsorbents [3,4]. Among the common adsorbents, chitosan, a polysaccharide composed of polymers of glucosamine and N-acetyl glucosamine, has received a great deal of attention, according to its chemical stability and high capacity to retain dye. Chitosan is biodegradable, nontoxic, low in cost and abundant in nature. And the chemically reactive hydroxyl and amine groups in chitosan make it a versatile candidate for adsorption of dyes [5,6].

However, the ability of chitosan to adsorb anionic dyes is often attributed to its positive surface charge, which depends on the operating system. Chatterjee et al. indicated that chitosan would have a positively charged surface at the pH below 6.5 [7], and most of the previous studies on chitosan adsorption have been carried out at the solution condition of $pH < 5$. Nevertheless, the excess acidification of wastewater should be avoided, even though the adsorption ability of chitosan could be improved at the condition of low pH. It is because that the acidic solutions must be neutralized before discharge and the large scale use of acid is easy to cause the secondary pollution. Thus, several methods for chitosan modification have been developed to overcome this difficulty. The reactive functional groups of chitosan, such as the amino group at the C-2 position and the hydroxyl groups at C-3 and C-6, provide the molecular interactions that can adsorb dyes and allow for several specific modifications without too many difficulties [8]. Accordingly, the chemical grafting of chitosan with specific ligands to increase the density of adsorption sites is an area of great interest. Proposed chemical modifications to chitosan have included the use of succinic anhydride [9], enzymatic grafting of carboxyl groups and the synthesis of carboxymethylated chitosan [10–12]. Other studies have indicated that the cross-linking of chitosan can improve its physical properties and adsorption capacity [13–15]. Additionally, it has been reported that the preliminary protonation of amine

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* Corresponding author. Tel.: +86 571 8696 8415; fax: +86 571 8696 8415.
E-mail address: wenyuezhong@zju.edu.cn (Y. Wen).

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groups, obtained by acidic or oxidative depolymerization [16,17], could give a chitosan product with a higher adsorption capacity for dyes. However, such modifications require inconvenient procedures and large quantities of organic solvents.

From an environmentally friendly viewpoint, today there is an increasing demand to use hydrogen peroxide, which are environmentally friendly and do not give rise to any waste products. It has been widely reported that H_2O_2 of high concentration (above 1 M) and other similar radical reaction could destroy the crystalline structure of chitosan and depolymerize it [17,18,20]. And this depolymerized chitosan with low molecular weight has some special physical and chemical properties, differently from the ordinary chitosan, such as solubility and physiological functions. However, to the best of our knowledge, not much work about the effect of low concentration hydrogen peroxide treatment of chitosan on its adsorption for dyes has been published in the literature. Hence, the main goal of this work was to analyze the effect of H_2O_2 treatment on the adsorption capacity of chitosan for dyes at near-neutral conditions. Such studies are needed to develop a simple, effective and environmentally friendly pretreatment method to improve the adsorption of dyes by chitosan.

2. Materials and methods

2.1. Materials and reagents

C. I. Acid Red 73 is a commercial product and its structure is shown in Fig. 1a. Chitosan was purchased from Zhejiang Golden-shell Biochemical Co., Ltd, Zhejiang, China (deacetylation degree = 91.04%, Fig. 1b). A solution of 30% (w/w) hydrogen peroxide (H_2O_2) was obtained from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Doubly distilled water was used throughout this study. Other chemicals were of laboratory reagent grade and used without further purification.

2.2. Pretreatment of chitosan via hydrogen peroxide

Prior to adsorption of the dye, the chitosan samples were pretreated via surface reaction with different concentrations of H_2O_2 (10, 20, 50, 100, and 200 mM). Chitosan powder (0.5 g) was suspended in 50 mL of H_2O_2 solution with stirring for 2 h at room temperature. The reaction time for the chitosan pretreatment varied over several time intervals (15, 30, 45, 60 and 120 min). The pretreated chitosan powder was collected by centrifugation at 5000 rpm, washed with a large amount of water to remove the remaining H_2O_2 and then dried in oven at 80 °C.

2.3. Dye adsorption and desorption on untreated and pretreated chitosan

Dye adsorption experiments were performed in 50 mL flasks, which were sealed and agitated at 100 rpm in a thermostatic shaker maintained at 25 °C. The typical reaction mixture was initiated with 10 mL of dye at 50 mg/L and 0.05 g of untreated or pretreated chitosan at the condition of pH 6.0. For chitosan desorption experiments, the used adsorbents were filtered and dried at 80 °C and then resuspended in 50 mL of 0.05 M eluent at 25 °C. Dye concentrations were analyzed using a Shimadzu UV-2401PC UV–vis spectrometer (Tokyo, Japan) at certain time intervals.

2.4. Adsorption isotherms measurements

The adsorption isotherms of C. I. Acid Red 73 on untreated chitosan or pretreated chitosan in water were carried out using the batch slurry method [19]. The slurry, containing 0.05 g of chitosan and 10 mL of dye solution at various concentrations, was agitated at 100 rpm in a thermostatic shaker until equilibrium was reached at temperatures of 30, 40, and 50 °C, respectively. The amount of adsorbed C. I. Acid Red 73, q_e, was calculated by Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e is the dye capacity in the sorbent at equilibrium (mg/g), C_0 is the initial dye concentration in the liquid phase (mg/L), C_e is the liquid-phase dye concentration at equilibrium (mg/L), V is the volume of solution (L), and M is the mass of sorbent used (g).

2.5. Characterization of untreated and pretreated chitosan

Fourier transform infrared spectroscopy (FTIR) of chitosan samples were recorded by a Shimadzu 8900-FTIR spectrometer (Tokyo, Japan) using KBr power containing ca. 1% (w/w) of sample.

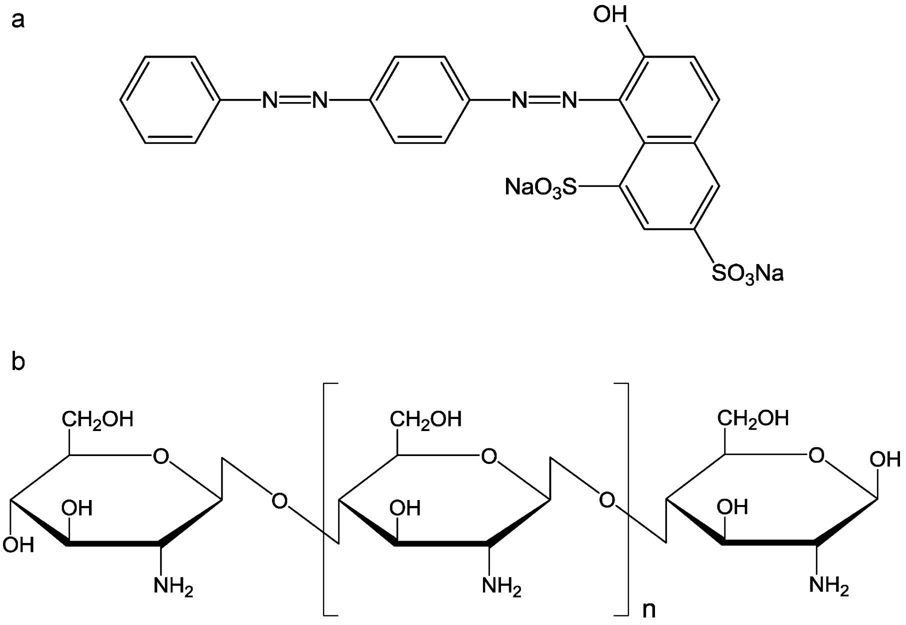

Fig. 1. The chemical structures of (a) C. I. Acid Red 73 and (b) chitosan.

X-ray diffraction (XRD) patterns of the chitosan sample were measured using a Panalytical XPert Pro MPD diffractometer (Almelo, Netherland) with a Cu Kα ray source ($\lambda = 1.54$ Å). The scanning diffraction angle range was set at 5–60° and the scan rate was 2° (2θ) per minute with the spectra being recorded at 40 kV and 36 mA. The crystallinity degree was calculated by the Material Data software Jade 5.0 on the basis of XRD data.

Scanning electron microscope (SEM) micrographs were taken on a field emission scanning electron microscope (FEI, SIRON) at a voltage of 25.0 kV to test the morphological characterization of the chitosan. The sample surfaces were gold-coated before analysis.

Static water contact angles (CA) of the chitosan samples were measured by the sessile drop method at room temperature with a Dataphysics OCA20 contact angle goniometer (Stuttgart, Germany). Each contact angle value reported represents the average of at least six readings from replicate chitosan surface samples.

X-ray photoelectron spectroscopy (XPS) study of chitosan samples was performed on the electron spectrometer Thermo ESCALAB 250 (Thermo Electron Corporation, US); the samples were excited with X-rays over a specific 400-μm area using monochromatic Al Kα radiation (1486.6 eV) at 150 W. All binding energies were referenced to the neutral carbon peak at 284.8 eV, and surface elemental stoichiometries were determined from sensitivity-factor corrected peak ratios.

Zeta potential measurements were determined at room temperature with the chitosan samples dispersed in deionized water obtained by supersonic. In these measurements, the pH of this dispersion was maintained at 6.0 ± 0.05 using 0.1 M HCl for adjustment. Zeta potential, ζ, of untreated and pretreated chitosan was carried out using a Zeta-Meter System 3.0 (Zeta-Meter Inc., USA).

3. Results and discussion

3.1. Surface compositions, structures, morphologies and properties of chitosan

3.1.1. Infrared spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical nature of chitosan after pretreatment with H_2O_2 (Fig. 2). The peaks at 3370 cm^{-1} (N–H), 1653 cm^{-1} (amide I band), 1597 cm^{-1} ($-NH_2$), 1259 cm^{-1} (twisting vibration of O–H), 1081 cm^{-1} (stretching vibration of the C–O–C in glucose circle), 1155 cm^{-1} and 897 cm^{-1} (the special absorb peaks of $\beta(1 \rightarrow 4)$ glucoside) representing the chemical bonds in chitosan were similar to previously reported spectra [20,21]. These data indicate that there was no significant difference between untreated and pretreated chitosan, and that the H_2O_2 pretreatment had no obvious impact on the principal chemical structures that compose chitosan.

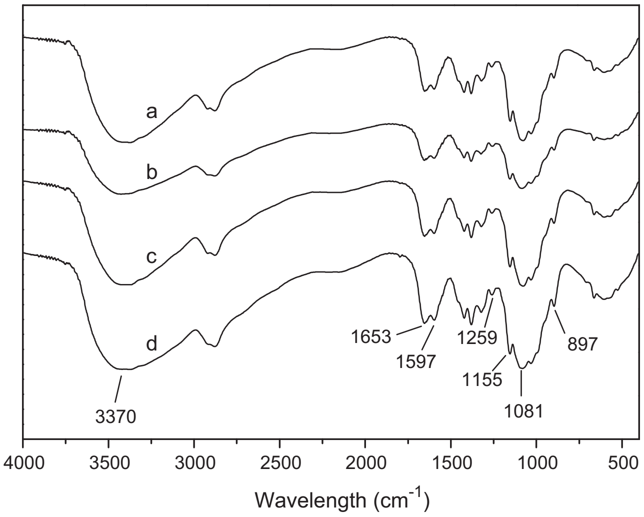

Fig. 2. FTIR spectra of (a) untreated chitosan, (b)–(d) pretreated chitosan (reacted with 50, 100, and 200 mM H_2O_2 respectively at room temperature for 2 h).

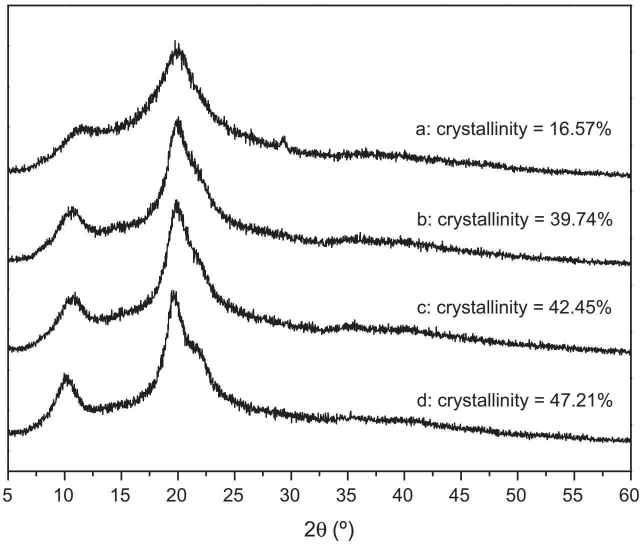

Fig. 3. X-ray diffraction patterns of (a) untreated chitosan, (b)–(d) pretreated chitosan (reacted with 50, 100, and 200 mM H_2O_2 respectively at room temperature for 2 h).

3.1.2. X-ray diffraction analysis

Previous studies have shown that high concentrations of H_2O_2 (above 1 M) or other similarly radical reaction conditions could destroy the crystalline structure of chitosan [17,18,20]. Therefore, we compared the X-ray diffraction patterns between untreated chitosan and chitosan that had been pretreated with different concentrations of H_2O_2 (Fig. 3). Rather than decreasing the crystallinity degree, pretreatment with properly low concentrations of H_2O_2 enabled the chitosan surface to have a more ordered structure. With the increasing concentration of H_2O_2 (i.e., Fig. 3 samples b, c, and d), an increase in the intensity and sharpness of the characteristic peak at $2\theta = 19.84°$ and $2\theta = 10.38°$ could be observed, which accompanied an increase in the degree of crystallinity of chitosan products. After the pretreatment (200 mM H_2O_2), the crystallinity degree of chitosan reached 47.21%, representing a 30% increase compared with untreated chitosan (crystallinity degree, 16.57%), which indicates that the chitosan surface had a more ordered structure.

Chitosan is composed of an amorphous part and a crystal part [20]. The peeling-off model developed by Schweiger [22] could be used to explain the change in crystallinity of the chitosan surface, and this model was also confirmed in chitosan degradation by Kang et al. [23]. During the degradation of chitosan, the amorphous part was preferentially degraded but the crystal part was temporally maintained. With further degradation, the amorphous part peeled off and was dissolved in reaction medium, and then the crystalline structure was destroyed and the crystallinity decreased accordingly. Hence, it could be concluded that the increase in the degree of crystallinity could be possibly resulted from the removal of the amorphous components on the surface of chitosan during the H_2O_2-induced oxidative degradation.

3.1.3. Scanning electron microscope micrographs

To further observe the morphological characteristics of the chitosan, the scanning electron microscope (SEM) micrographs of untreated and pretreated chitosan were carried out. Fig. 4A1–A2 and B1–B2 shows the images of untreated and H_2O_2 pretreated chi-

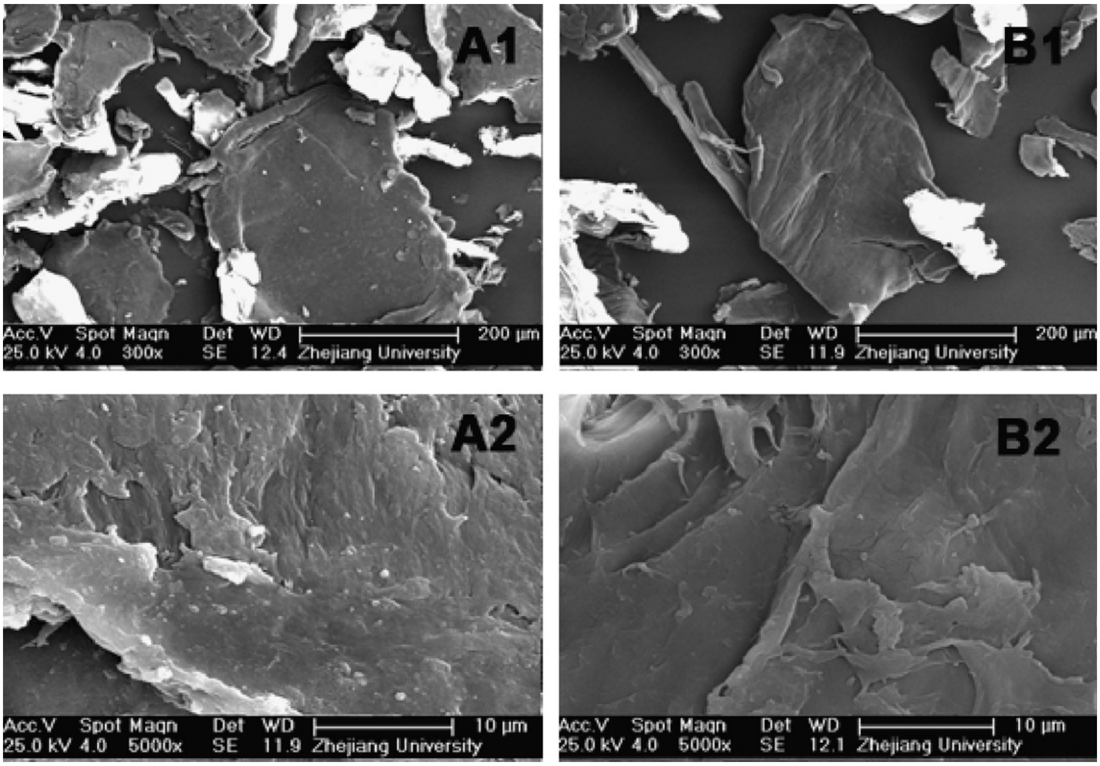

Fig. 4. Scanning electron micrographs (SEMs) of the untreated chitosan and chitosan pretreated with H_2O_2 at low and high magnification: A1–A2, untreated chitosan; B1–B2, pretreated chitosan.

tosan, respectively. Based on images A1 and B1, it is clear that both the untreated and pretreated chitosan were irregularly shaped and had a diameter around 200 μm. Changes in the external morphology after H_2O_2 pretreatment could be evaluated by comparing with A2 and B2. It can be seen that the surface of pretreated chitosan was much smoother than untreated chitosan and the crude aspects of untreated chitosan were removed. Considering the results of FTIR and XRD that were mentioned earlier, the change of chitosan in surface morphology could be attributed to the surface modification via the reaction of chitosan with H_2O_2. During the pretreatment, the amorphous aspects of the chitosan were preferentially degraded by H_2O_2 and dissolved in reaction medium. Therefore, by controlling the concentration of H_2O_2, the amorphous parts of chitosan were removed while the crystal parts were retained, and thus the surface of chitosan became fine and smooth.

3.1.4. Static water contact angles

A hydrophobic surface can decrease the adsorption affinity of materials for polar molecules [24]. Thus the surface hydrophilic/hydrophobic performance of chitosan was characterized by static contact angle analysis. The contact angles of water for pretreated and untreated chitosan samples represent the average value of seven water contact angle measurements. Because the hydroxy groups of untreated chitosan are believed to be strongly hydrogen bonded internally and hence unavailable for binding, the contact angle of untreated chitosan was 101.5°. However, after the pretreatment of 50 mM, 100 mM and 200 mM H_2O_2, the contact angles were lowered to 99.7°, 97.1°, and 91.3°, respectively. The gradual decrease in the water contact angle corresponding to increasing H_2O_2 concentrations indicates that H_2O_2-induced surface modification of chitosan can increase its surface hydrophilicity.

Table 1
Binding energies and relative amounts of components on the chitosan surface.

	Proposed components	Binding energy (eV)	Relative amounts (at%)
C 1s valence state			
(a) Untreated chitosan	C–C or C–H	284.8	21.8
	C–N or C–O or C–O–C	286.3	30.6
	C=O or O–C–O	287.8	8.63
(b) Pretreated chitosan (200 mM H_2O_2)	C–C or C–H	284.8	20.4
	C–N or C–O or C–O–C	286.2	30.8
	C=O or O–C–O	287.8	9.09
N 1s valence state			
(a) Untreated chitosan	$-NH_2$	399.3	5.87
	$-NH_3^+$	401.9	0.47
(b) Pretreated chitosan (200 mM H_2O_2)	$-NH_2$	399.3	5.88
	$-NH_3^+$	401.4	0.65
O 1s valence state			
(a) Untreated chitosan	C–O–H or C–O–C	532.7	32.8
(b) Pretreated chitosan (200 mM H_2O_2)	C–O–H or C–O–C	532.6	33.2

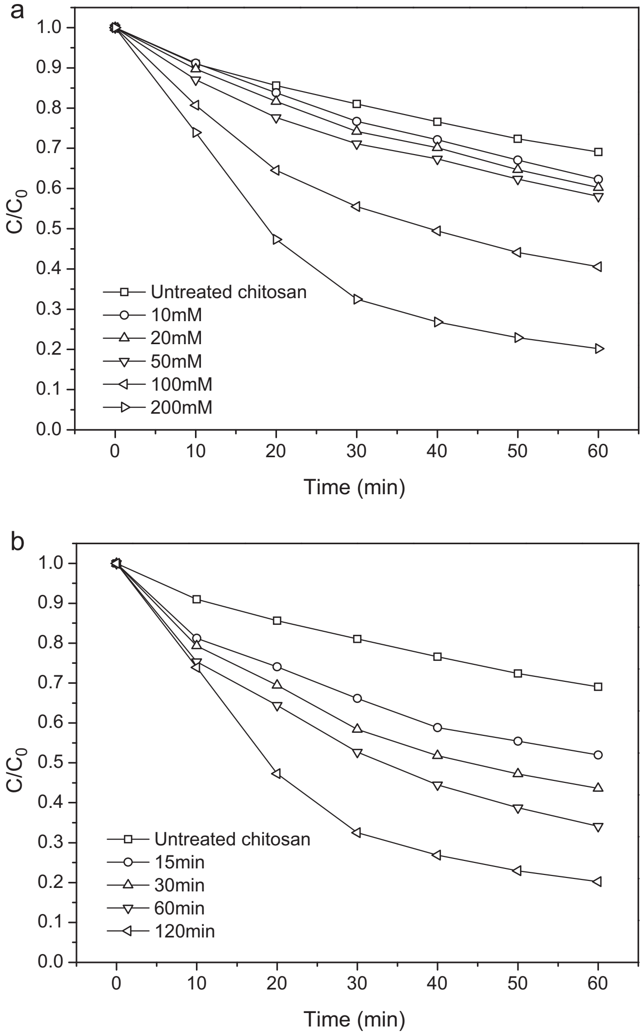

Fig. 5. Removal of C. I. Acid Red 73 (initial concentration 50 mg/L, 10 mL, pH 6, $T = 25\,^\circ C$) using untreated or pretreated chitosan (0.05 g). (a) Effect of the concentration of H_2O_2 in the pretreatment; (b) effect of the reaction time of the pretreatment (H_2O_2: 100 mM).

3.1.5. X-ray photoelectron spectroscopy

To further investigate the changes in the surface functional groups of chitosan after pretreatment, XPS studies of chitosan were conducted. The elemental surface composition and the relative amounts of the different functional groups in untreated and pretreated chitosan were calculated and are summarized in Table 1. As revealed by Table 1, chitosan samples with or without pretreatment have no prominent differences in the calculated relative amounts of functional groups, indicating that the main functional group of chitosan was not significantly altered by pretreatment with H_2O_2. These data further confirmed the results of FTIR analysis.

3.2. Removal of C. I. Acid Red 73

The rapid interaction between adsorbents and the dye molecule to be removed is desirable and beneficial for practical pollutant adsorption applications. From the kinetic experiment of C. I. Acid Red 73 adsorption on untreated and pretreated chitosan, we observed that dye uptake on pretreated chitosan was a faster process than adsorption on untreated chitosan. The amount of adsorption increased rapidly in the first hour, contributing to about 80% of the total adsorption amount. Adsorption then augmented slowly and approached equilibrium in about 3 h at 9.47 mg/g. In contrast, dye adsorption on untreated chitosan was a much slower process that took about 6 h to reach equilibrium and only adsorbed 7.23 mg/g at equilibrium.

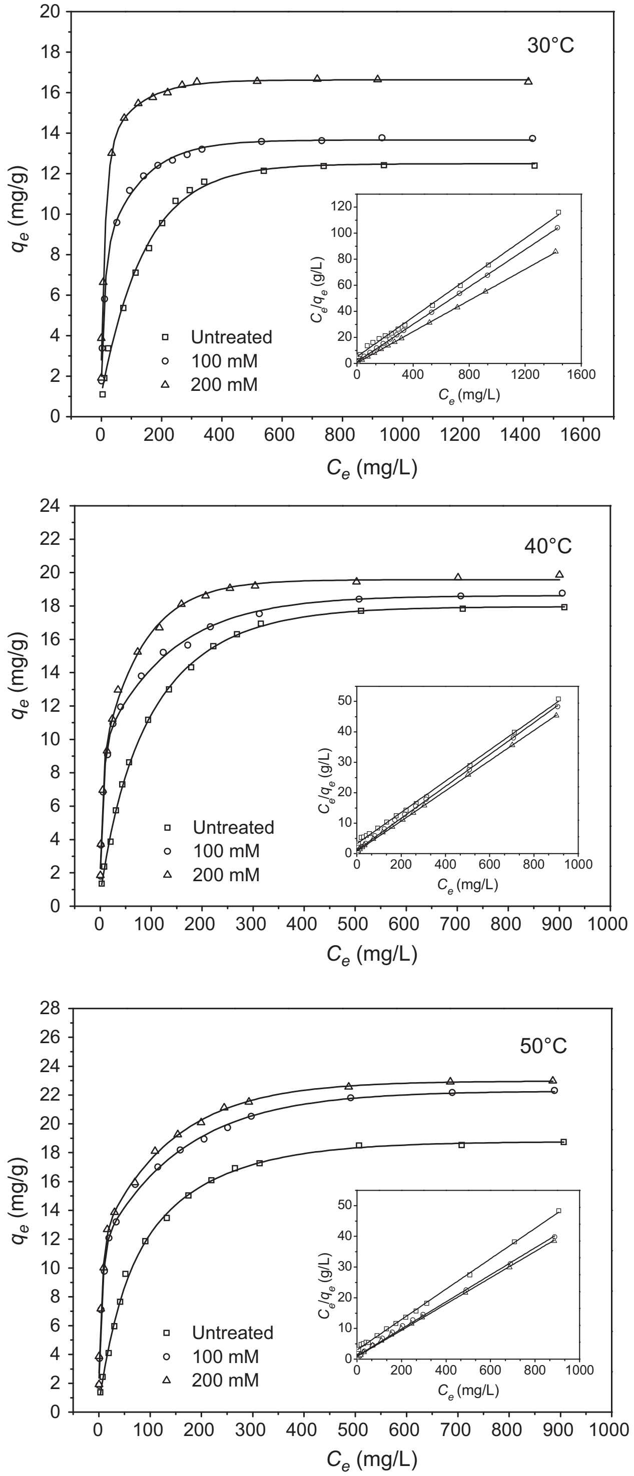

Fig. 6. Adsorption isotherm of C. I. Acid Red 73 on initial and pretreated chitosan (reacted with 100 and 200 mM H_2O_2 at $25\,^\circ C$ for 2 h) at different temperatures.

Fig. 5a and b shows the time profiles of C. I. Acid Red 73 removal by chitosan that had been pretreated under different conditions. As shown in Fig. 5a, the adsorption efficiency obviously increased with the increase of H_2O_2 concentrations in pretreatment. When the concentration of H_2O_2 reached 200 mM, 80% of C. I. Acid Red

Table 2
Parameters of the Langmuir equation for the adsorption of C. I. Acid Red 73 by chitosan at 30 °C, 40 °C and 50 °C.

Adsorbent	Temperature (°C)	R^2	q_m (mg/g)	$b \times 10^{-3}$ (L/g)	R_L
Untreated chitosan	30	0.9973	13.21	14.48	0.065
	40	0.9980	19.46	15.79	0.060
	50	0.9987	20.18	16.61	0.057
Pretreated chitosan (100 mM H_2O_2)	30	0.9998	13.94	54.38	0.018
	40	0.9987	19.07	45.96	0.021
	50	0.9979	22.69	42.73	0.023
Pretreated chitosan (200 mM H_2O_2)	30	0.9999	16.68	151.69	0.007
	40	0.9996	20.14	63.76	0.015
	50	0.9985	23.35	51.75	0.019

73 was removed within 60 min and the adsorption efficiency was increased by ca. 60% compared with the untreated chitosan. The reaction time of pretreatment also strongly influenced the adsorption behavior of chitosan (Fig. 5b). When the pretreatment time increased from 0 to 120 min, it resulted in a 30–80% increase in adsorption efficiency.

The results above show that the H_2O_2-induced surface modification resulted in an improved adsorption ability of chitosan to remove dye with a shorter process time. The concentration of H_2O_2 and the reaction time of chitosan pretreatment are two crucial factors that could significantly improve the removal efficiency of C. I. Acid Red 73 in water. These improvements of dye adsorption could be due to the removal of the amorphous surface components and an increase in the hydrophilic character. And the specific mechanisms will be discussed in detail below.

3.3. Adsorption isotherms and thermodynamics parameters

The adsorption isotherm of C. I. Acid Red 73 by chitosan was investigated at temperatures of 30 °C, 40 °C and 50 °C. Langmuir isotherm can be represented as [25]:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of dye in the bulk solution (mg/L), b is the Langmuir constant related to energy (L/mg), and q_m is the adsorption capacity, defined as the maximum amount of dye forming a complete monolayer on the adsorbent surface (mg/g).

And the experimental results were fitted to the linearized form of the Langmuir model below:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{3}$$

According to the literature, the essential features of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter R_L that can be calculated from the relationship [30]:

$$R_L = \frac{1}{(1 + bC_0)} \tag{4}$$

where C_0 is the highest initial concentration (mg/L). The value of R_L indicates whether the type of isotherm is irreversible adsorption ($R_L = 0$), favorable adsorption ($0 < R_L < 1$), unfavorable adsorption ($R_L > 1$), or linear adsorption ($R_L = 1$).

The adsorption isotherm experimental results for C. I. Acid Red 73 on untreated and pretreated chitosan are shown in Fig. 6, and the fitted results from Langmuir are also exhibited in the inset of Fig. 6. All constant values obtained by this model are listed in Table 2. The values of the correlation coefficients (R^2) indicate that the sorption systems above closely follow the Langmuir model. From the model fitting, the value of maximum adsorption amount (q_m) and Langmuir constant (b) at different temperatures were determined from the slope and intercept of the Langmuir plots. The q_m values of C. I. Acid Red 73 adsorption by chitosan followed the order: untreated chitosan < pretreated chitosan (100 mM H_2O_2) < pretreated chitosan (200 mM H_2O_2), implying that the chitosan treated by H_2O_2 had a higher maximum adsorption amount in comparison with the untreated chitosan, and the higher the concentration of H_2O_2 in the pretreatment, the higher the q_m values. These trends were consistent at all reaction temperatures. And the all the R_L for untreated and pretreated chitosan had values less than 1, indicating the favorable adsorption.

The thermodynamic quantities such as change in Gibbs free energy (ΔG°), change in enthalpy of adsorption (ΔH°), and change in entropy (ΔS°) were calculated at different temperatures to evaluate the feasibility of the adsorption process [31].

The ΔG° of the sorption reaction was calculated by the Van't Hoff equation:

$$\Delta G^\circ = -RT \ln K_d \tag{5}$$

where R is the universal gas constant (8.314 J/mol K), K_d is the sorption equilibrium thermodynamic constant and T the absolute temperature (K). K_d can be obtained according to the method of Khan and Singh by plotting a straight line of $\ln(q_e/C_e)$ versus q_e and extrapolating q_e to zero. Its intercept gives the values of K_d.

The ΔH° and ΔS° of dye adsorption can be determined by the following equation:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

A plot of $\ln K_d$ versus $1/T$ was found to be linear, ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively.

The thermodynamic parameters for the adsorption of C. I. Acid Red 73 by chitosan are also summarized in Table 3. The negative free energy change (ΔG) indicates the process to be feasible and adsorption to be spontaneous. The parameters ΔG summarized in Table 3 are ranked as follows: pretreated chitosan (200 mM H_2O_2) < pretreated chitosan (100 mM H_2O_2) < untreated chitosan, demonstrating that the system became more favorable for dye adsorption when chitosan was pretreated with H_2O_2. The positive values of ΔH and ΔS indicate that the adsorption interaction of dye and chitosan is endothermic and there is increased randomness at the chitosan interface during the adsorption of dyes. All these results above suggested that chitosan can be successfully pretreated with H_2O_2 to induce surface modification that enhance the adsorption of C. I. Acid Red 73 in weak acid solution.

3.4. Mechanism of enhanced adsorption

According to the variations in the chitosan preparation and the actual methodology, the mechanisms for adsorption of dye

Table 3
Parameters of the thermodynamics for the adsorption of C. I. Acid Red 73 by chitosan at 30 °C, 40 °C and 50 °C.

Adsorbent	Temperature (°C)	K_d (L/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K mol)
Untreated chitosan	30	1.168	−0.39	7.60	28.03
	40	1.561	−1.16		
	50	1.723	−1.46		
Pretreated chitosan (100 mM H_2O_2)	30	1.693	−1.33	12.01	44.26
	40	2.173	−2.02		
	50	2.268	−2.20		
Pretreated chitosan (200 mM H_2O_2)	30	1.853	−1.55	9.04	34.71
	40	1.905	−1.68		
	50	2.316	−2.26		

molecules onto chitosan can be interpreted in a variety of ways [26]. The mostly cited mechanism for the adsorption of anionic dyes by chitosan in acidic solution is likely to be electrostatic interaction of the dye ions with the amino groups on the chitosan as the following proceeds [27]

$$\text{D-SO}_3\text{Na} \rightarrow \text{D-SO}_3{}^- + \text{Na}^+ \tag{7}$$

$$\text{R-NH}_2 + \text{H}^+ \rightarrow \text{R-NH}_3{}^+ \tag{8}$$

$$\text{R-NH}_3{}^+ + \text{D-SO}_3{}^- \rightarrow \text{R-NH}_3\cdots\text{O}_3\text{S-D} \tag{9}$$

First, due to the pK_a value of the sulfonate group in dye is quite low [32–34], the sulfonate groups dissociate and are converted to anionic ions at the condition of pH 6 (7). In the presence of H^+, the amino groups of chitosan become protonated (8). Then the adsorption proceeds due to the electrostatic attraction between these two counterions (9).

Hence, to estimate the enhancement of electrostatic interaction, the zeta potential value of chitosan samples, which could indicate the charge density of the chitosan surface, was determined. All chitosan dispersions possessed positive zeta potential, and their values increased sharply from 2.8 mV (unpretreated chitosan) to 34.7 mV (pretreated chitosan with 200 mM H_2O_2) with increasing concentrations of H_2O_2. This result suggests that the increasing dye adsorption after surface modification could possibly be due to increased electrostatic interaction between C. I. Acid Red 73 and chitosan. Nevertheless, it is worth noting that N 1s valence state of chitosan before and after pretreatment, the peak that occurred at a binding energy of 401.9 eV, which could be assigned to the nitrogen atoms in protonated amines ($-NH_3{}^+$), increased slightly (Table 1, Fig. 7). This indicates that almost no preliminary protonation of amine groups occurred on the chitosan surface during the pretreatment. Therefore, one reason that may explain the different results of XPS and zeta potential is that the H_2O_2-induced modification of chitosan could make it easy for amine groups on the pretreated chitosan surface to become protonated in a weak acidic solution.

The hydrogen bonds linked between monomer units of different chains (intermolecular bonds) would affect the availability of amine groups in chitosan [28,29]. As reported above, the chitosan surface is composed of an amorphous part and a crystal part. By controlling the concentration of H_2O_2 during pretreatment, the chemical structure and crystal part of chitosan were retained. However, the amorphous part of chitosan was preferentially degraded by H_2O_2 and removed. Thus, the hydrogen bonds between the amorphous and crystal parts were destroyed, which resulted in an increase of free amine groups and OH groups on the chitosan surface as shown in Fig. 8. We suggested that it was the reason for the increase of hydrophilicity and zeta potential of chitosan after pretreatment by H_2O_2.

Additionally, the enhanced hydrophilic character of pretreated chitosan suggests that the number of hydroxyl groups on the chitosan surface was increased by H_2O_2 pretreatment. Nevertheless, we did not find that the increased oxygen atoms in hydroxyl groups corresponded to the same phenomenon of amine groups on pretreated chitosan surface. Thus, we inferred with certainty that the enhancement of hydrophilic character could be attributed to the increase of free hydroxyl on the chitosan surface.

As stated above, the partial removal of amorphous components on the chitosan surface resulted in the increase of free amine and hydroxyl groups on its surface, and thus it successfully improved the adsorption of dyes due to the enhancement of electrostatic interactions between dye and chitosan molecules.

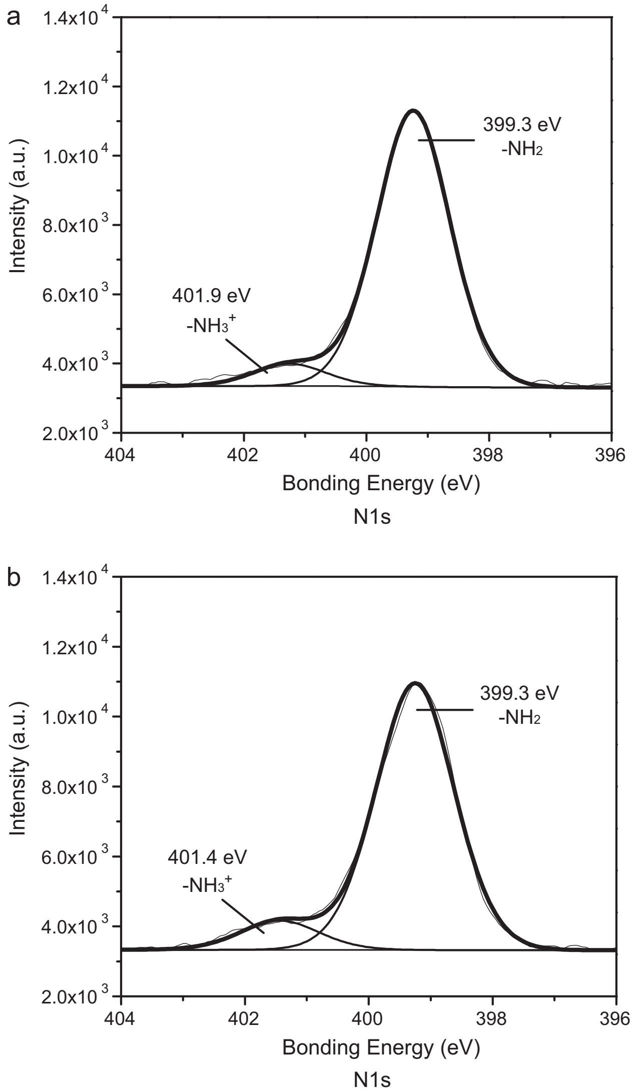

Fig. 7. XPS spectra of N 1s. (a) Untreated chitosan; (b) pretreated chitosan with 200 mM H_2O_2.

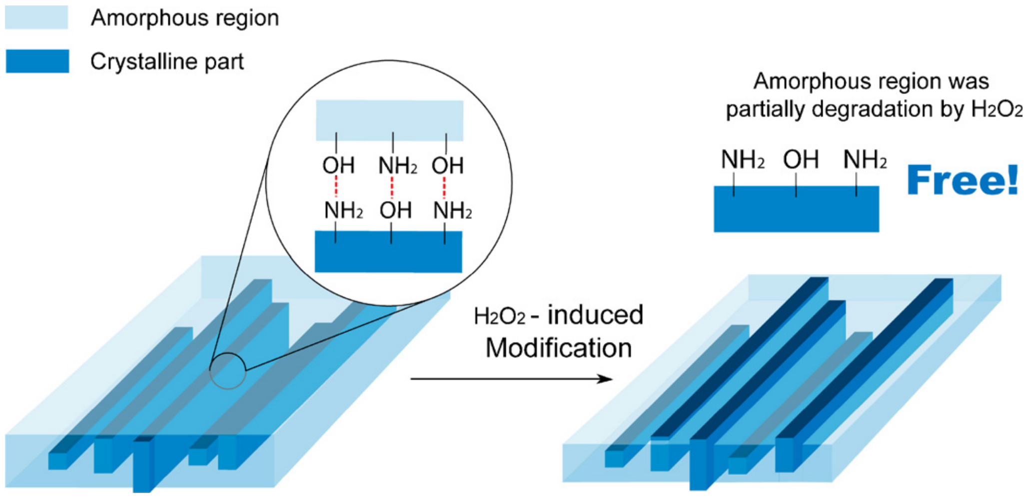

Fig. 8. Scheme of the production of the free amine groups and OH groups on chitosan surfaces via H_2O_2-induced surface modification.

3.5. The regeneration and reuse of pretreated chitosan

The regeneration of the adsorbent is important for lowering the cost of the adsorption process and for possibly recovering the pollutant extracted from wastewater. The adsorption of dyes is mainly dependent on the protonated amino groups of chitosan in the presence of H^+. Hence desorption of C. I. Acid Red 73 is possible by controlling the H^+ concentration. To find the optimal eluent for desorption, 10 mL of 0.05 M basic solutions (NaAc, NaOH, $NaHCO_3$, Na_2CO_3, and Na_2HPO_3) were mixed with 0.05 g dye-adsorbed chitosan for 5 min. The desorption efficiencies of NaAc, NaOH, $NaHCO_3$, Na_2CO_3, and Na_2HPO_3 were found to be 0.72%, 85.18%, 81.18%, 68.35%, and 56.35%, respectively. To avoid a negative impact on chitosan surface caused by the strong basicity of NaOH, we chose 0.05 M $NaHCO_3$ as the eluent for the desorption process.

The adsorption and desorption efficiency of pretreated chitosan undergoing six cycles are illustrated in Table 4. Reuse experiments showed that the adsorption efficiency of the chitosan pretreated with 200 mM H_2O_2 remained almost constant for six cycles of adsorption and desorption, which indicated that there were no irreversible sites on the surface of the adsorbent. However, it should be mentioned that after each cycle of adsorption/desorption, some ultrapure water was applied to rinse the surface of the adsorbent to remove basic ions that could affect the pH conditions of the adsorption system. This result further supports the implementation of H_2O_2 pretreatment as a simple, efficient and environmen-

Table 4
Adsorption and desorption behaviors of C. I. Acid Red 73 on pretreated chitosan.

Cycle	Adsorption (mg/g)	Desorption (%)
Cycle I	8.00	80.68
Cycle II	7.88	80.48
Cycle III	7.82	81.16
Cycle IV	7.65	83.47
Cycle V	7.57	82.67

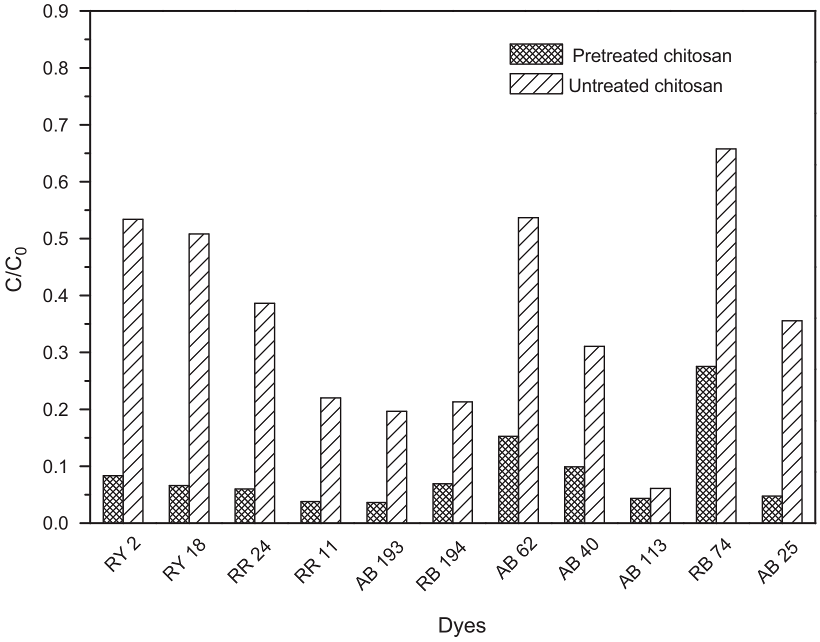

Fig. 9. Adsorption curves of other organic dyes (initial concentration: 50 mg/L, 10 mL, pH 7, $T = 25\,^{\circ}C$) on untreated (0.05 g) and pretreated chitosan (0.05 g, reacted with 200 mM H_2O_2 at 25 °C for 2 h).

tal friendly method to improve the adsorption capacity of chitosan.

3.6. Adsorption of other organic dyes

It is well known that the complicated structures of dye molecules, which vary with respect to the organic chains and the numbers and positions of functional groups, are directly related to their adsorption behaviors. Thus, the same adsorption condition used for C. I. Acid Red 73 was next applied to the removal of a variety of anionic dyes. The acid dyes, such as C. I. Acid Blue 25 (AB 25), C. I. Acid Blue 40 (AB 40), C. I. Acid Blue 62 (AB 62), C. I. Acid Blue 113 (AB 113) and C. I. Acid Blue 193 (AB 193), the reactive dyes, such as C. I. Reactive Yellow 2 (RY 2), C. I. Reactive Yellow 18 (RY18), C. I. Reactive Red 11 (RR11), C. I. Reactive Red 24 (RR 24), C. I. Reactive Blue 194 (RB 194) and C. I. Reactive Blue 74 (RB 74), were chosen as prototypical dye pollutants. The results are shown in Fig. 9. Our data suggest that pretreatment of chitosan with H_2O_2 could improve the adsorption of both acid and reactive dyes to varying degrees. Furthermore, we found a high probability that pretreatment of chitosan with H_2O_2 may allow for the removal of less adsorbable dyes as a result of the enhanced interactions between dyes and chitosan.

4. Conclusion

Chitosan can be efficiently pretreated with H_2O_2 to induce modifications that allow improved removal of C. I. Acid Red 73 from weak acid solution. The pretreated chitosan appeared to have a more ordered structure and a higher hydrophilic character than untreated chitosan, but no significant changes in functional groups on the chitosan surface were detected. The adsorption results show that the pretreated chitosan able to rapidly adsorb dyes and had a larger adsorption capacity. The improvement was dependent on the H_2O_2 concentration and the reaction time of the pretreatment. Our mechanistic study suggested that the improved dye adsorption was due to the enhancement of electrostatic interactions between the dye and chitosan molecules. Furthermore, it could be attributed to the partial removal of amorphous components on chitosan surface, which resulted in an increase of free amine and hydroxyl groups. The adsorption of other dyes and the regeneration studies demonstrated that the pretreated chitosan could be recovered and reused effectively for the adsorption of mostly anionic dyes.

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