Preparation of Adsorbent Based on Cotton Fiber for Removal of Dyes

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Abstract: Synthetic dyes are used extensively in modern industries, which are toxic and harmful to environment and human. Cotton fiber is a kind of abundant, renewable and eco-friendly cellulose fiber in nature, however, the adsorption capacity of raw cellulose for pollutants was often low. Therefore, an efficient adsorbent for removal of dyes was successfully prepared by grafting beta-cyclodextrin (β-CD) and amino-terminated hyperbranched polymer (NH$_2$-HBP) onto cotton fibers in this study, which was effective to anionic dyes and cationic dyes. The adsorbent were characterized using FTIR, SEM and XPS analysis. The results of adsorption experiments showed that the adsorbent based on cotton fiber exhibited better adsorption performance for Congo red(CR) and methylene blue(MB). The experimental results revealed that the pH value had a great influence on the adsorption capacity.

Keywords: Cotton fibers, Adsorbent, Adsorption, Congo red, Methylene blue

Introduction

Synthetic dyes are used widely in textile, paper, plastic, coating and other industries, which are stable and difficult to degrade in the nature. A large of amount dyes were discharged into the water systems with dyeing wastewater due to improper processing and dying methods [1]. In the textile industry, it was reported that 10-15 % dyes has not been utilized during the dyeing process and released with the effluents [2-4]. Many kinds of synthetic dyes are toxic, which bring a risk to water system, aquatic organisms, soil and human [5-7]. Several methods were applied to remove dyes from wastewater, such as adsorption, membrane separation, flocculation, and oxidation, et al. Adsorption is a method commonly used to remove organic compounds from wastewater for its easy handling and efficiency. Activated carbon [8,9], graphene [10], bentonite [11], clay [12], composite fiber [13], nanofiber membranes [14], iron oxide nanomaterials [15], and magnetic multi-wall carbon nanotube nanocomposite [16], have been utilized as adsorbents. Among them, the activated carbon is a kind of adsorbent commonly applied. Although activated carbon shows often better adsorption capacity for dyes, but its adsorption capacity depends on the raw materials and methods of manufacturing [8,17]. Such as, adsorption capacity of polyvilnyldienefluoride activated carbon fibers for methylene blue could reach 486 mg/g, while adsorption capacity of corncob based activated carbon to methylene blue was 0.84 mg/g [8]. Many of these materials are high cost, or non-renewable, or non-biodegradable. In recent years, low cost biomaterials have been developed and used in the field of wastewater treatment, such as bagasse, rice husk, saw dust, pine cone, corncob,

straw, jute fiber [18-23]. But, most of them had a limitation in adsorption capacity and selectivity due to the surface charge diversity of pollutants.

Cellulose is a kind of regenerated, biodegradable and eco-friendly resource in nature. Cellulose molecules have many active hydroxyl groups, so it can easily be chemically modified according to the introduction of various functional groups on hydroxyl [23]. Cotton fiber is a kind of renewable, degradable natural cellulose fiber, which is low cost and don't cause secondary pollution. Hyperbranched polymers, such as hyperbranched poly(ethylene imine), hyperbranched polyamide-amine, and hyperbranched polyester, have shown efficiently to entrap heavy metal ions and organic molecules in their interior [24-28]. Beta-cyclodextrin (β-CD) is a torus-shaped cyclic oligosaccharide made up of seven a-1,4-linked-D-glucopyranose units. This structure gives rise to a remarkable capacity to form inclusion complexes with appropriate size organic molecules through host-guest interactions, apart from the interactions of physical adsorption, and hydrogen bonding [29-33]. Crini [32] prepared a serial of crosslinked polymers containing β-CD, which were applied to adsorb various dyes (C.I. Acid Blue 25, C.I. Basic Blue 3, C.I. Reactive Blue 19, C.I. Disperse Blue 3) from aqueous solutions. But, these crosslinked polymers were powder, which could cause inconvenient recycling of adsorbent. In this study, a versatile adsorbent based on cotton fibers was prepared. Specifically, cotton fibers were activated by NaOH to improve reactivity; then activated cotton was chemically modified with β-CD and NH$_2$-HBP, respectively. In this work, raw materials, such as cotton fiber, β-CD and NH$_2$-HBP, are biocompatible and bio-degradable, which were applied to prepared adsorbent. The modified cotton fibers were used to remove dyes from aqueous solutions. CR and MB were chosen as the

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representatives of anionic and cationic dyes in the experiments.

Experimental

Materials

Cotton fibers were purchased in the local market. hydrochloric acid (HCl), hydroxide (NaOH), sodium periodates (NaIO₄), triethylene tetramine, methyl acrylate, β-CD and glutaraldehyde ($C_5H_8O_2$), ethanol, phenolphthalein, CR and MB were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These reagents were used without purification further. An amino-terminated hyperbranched polymer ($HBP-NH_2$) was synthesized in laboratory according to our previous study [34].

Pretreatment of Cotton Fibers

10 g Cotton fibers were boiled in 300 m*l* of NaOH aqueous solution (2 wt%) for 60 minutes. Then the fibers were filtered and transferred into 300 m*l* NaOH aqueous solution (18 wt%) for 120 minutes at room temperature. The fibers were then washed and dried to obtain activated cotton fibers (named as ACF).

Preparation of Adsorbent

ACF were cut into segments about 5 mm and added to sodium periodate aqueous solution (12 g/*l*) for 2 h under continuous stirring at 50 °C. Then the fibers were filtered, washed and dried. ACF were oxidized selectively to obtain dialdehyde-cotton fibers in this process (named as DA-cotton). 10 g β-CD and 5 g DA-cotton were suspended in 500 m*l* HCl aqueous solution (0.5 mol/*l*), and 10 m*l* glutaraldehyde solution (25 %) was added into the above mixture and stirred well. The resultant mixture was stirred at 70 °C for 2 h. After reaction, the fibers were filtered, washed and dried at 50 °C, and the fibers was named as CD-cotton. The CD-cotton were immersed into $HBP-NH_2$ solution (20 g/*l*) and stirred for 2 h at 60 °C, then the fibers were flitted, washed with plenty of deionized water and dried at

50 °C. The products were named as NC-cotton, and they were not further crushed, still retained the macro morphology of cotton fiber. The preparation of the adsorbent is summarized in Figure 1.

Characterization

The FT-IR spectroscopy measurements were used to identify NC-cotton fiber with a Nicolet 5700. XPS measurements were conducted with an Axis Ultra HAS system. The morphologies and surface structures of ACF, DA-cotton, CD-cotton and NC-cotton were characterized with Hitachi S-4800 scanning electron microscope (SEM). The grafting rate of β-CD on cotton fibers was determined according to spectrophotometric method [35]. The absorbance of CR and MB was estimated by UV/Visible spectroscopy (Hitachi, U3010) at 498 nm and 664 nm, respectively. The concentrations of CR and MB were calculated based on the corresponding standard curves [36].

Adsorption Experiments

In the static adsorption experiments, adsorbents were added to adsorbate solutions at a dosage of 1.0 g/*l* for CR and MB, respectively. Initial pH values of the CR and MB solution were adjusted using HNO_3 and NaOH solutions. The adsorption experiments were carried out at 30 °C, and adsorption equilibrium time for CR and MB was 12 h. The equilibrium adsorption capacities (q_e) was calculated according to the equation (1).

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where C_0, C_e are the initial concentration and equilibrium concentration of adsorbate (mg/*l*), respectively. V is the volume (L) of adsorbate solution, and m is the mass of adsorbent (g) used in the experiments. Three sets of level experiments were conducted and the average values were calculated for accurate investigation.

Results and Discussion

Characterization of NC-cotton Fibers

FTIR analysis, XPS characterization, and SEM study of NC-cotton were conducted to describe the characteristics of NC-cotton.

The infrared spectra of ACF, CD-cotton, and NC-cotton fibers prepared were shown in Figure 2. It showed infrared spectrum of ACF (a), CD-cotton (b) NC-cotton (c). In the spectrum of (b), a new peak appeared at 1729 cm⁻¹, which showed the carbonyl (C=O) stretching vibration of the aldehyde group. In the infrared spectrum of CD-cotton and NC-cotton, the characteristic peak of β-CD and cellulose roughly coincide due to β-CD and cellulose being composed of cyclic glucose [37]. While, a stronger peak at 896 cm⁻¹ corresponding to β-glucoside bond in the spectrum of (b)
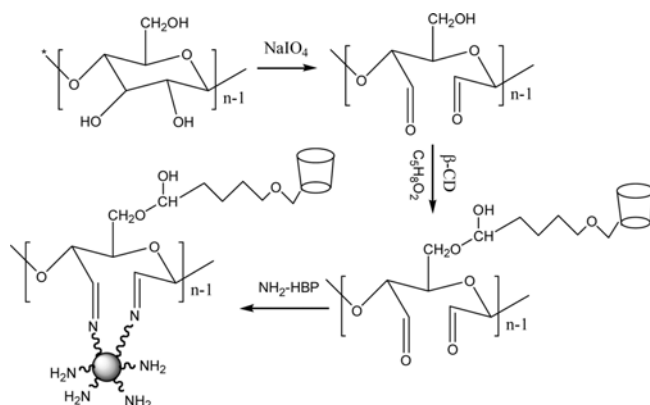

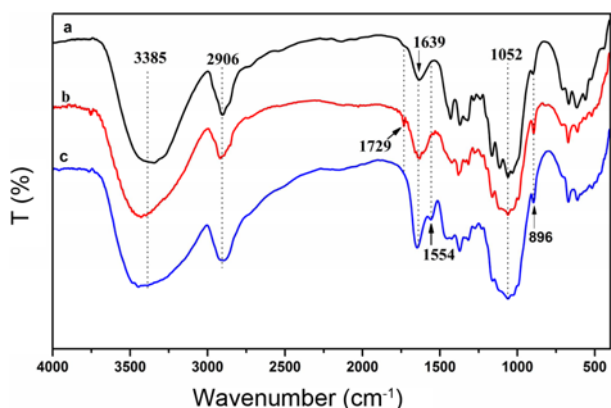**Figure 1.** Preparation route of NC-cotton fibers.

Figure 2. FT-IR spectra of fibers; (a) AFC, (b) CD-cotton, and (c) NC-cotton.

and (c) could be observed, which suggested β-CD was crosslinked to the fibers. In the spectrum of (c), the peak at 1729 cm^{-1} disappeared and a new peak at 1554 cm^{-1} appeared, which was attributed to N-H bending vibration absorption peak of imine group in NC-cotton. The weakening band at 1427 cm^{-1} revealed the reduction in intermolecular or intramolecular hydrogen bonding between the hydroxyl groups of cellulose from cotton fibers to NC-cotton fibers. This indicated that the crystallinity of the cotton fibers reduced after chemical modification. The characteristic

absorption bands of cellulose at about 3409, 2906 and 1052 cm^{-1} have no significant change. It suggests that the main composition and structure of the cotton fibers didn't change after chemical modification [38].

The chemical state of the elements in NC-cotton was further investigated by XPS to (Figure 3). The wide scan XPS spectrum (Figure 3(a)) of ACF, CD-cotton and NC-cotton displayed photoelectron lines at binding energies of about 284, 399 and 530 eV, which can be attributed to C1s, N1s and O1s, respectively. The high resolution C1s peaks of ACF, CD-cotton and NC-cotton are showed in Figure 3(b)-(d). The C1s peak of ACF can be divided into two components (Figure 3(b)): the carbon in C-C (284.4 eV) and the carbon in C-O (286.3 eV). The C1s peak of CD-cotton can be divided into three components (Figure 3(c)): the C-C species (284.6 eV), C-O species (286.2 eV) and C=O species (288.3 eV). The C1s spectra of the NC-cotton contains three peaks at 284.6, 285.6, 286.4 eV, corresponding to the C-C, C-N, C-O bonds, respectively (Figure 3(d)). Obviously, the nitrogen element existed in the NC-cotton due to the chemical interaction.

The surface morphology of cotton fibers after chemical modification with β-CD and NH$_2$-HBP respectively were revealed by SEM. As shown in Figure 4, The surface of ACF (a) was smooth and no obvious feature. There are many grooves and cracks on the surface of DA-cotton (b),
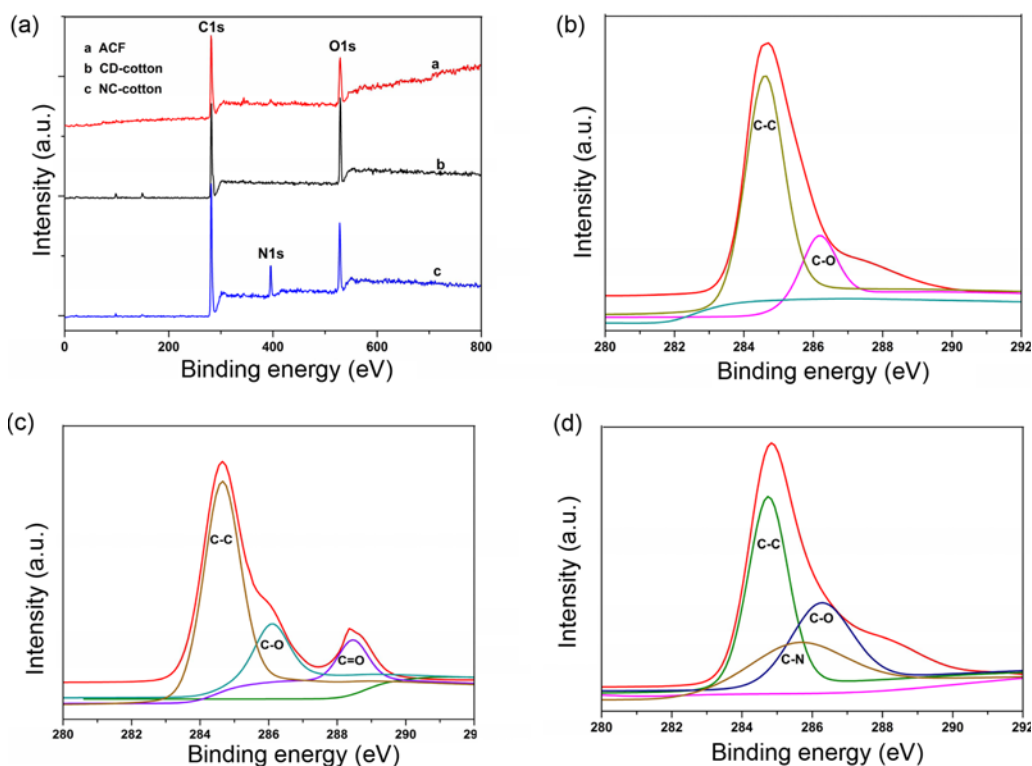

Figure 3. XPS spectra of ACF, CD-cotton and NC-cotton; (a) wide scan, (b) C1s spectra of ACF, (c) C1s spectra of CD-cotton, and (d) C1s spectra of NC-cotton.
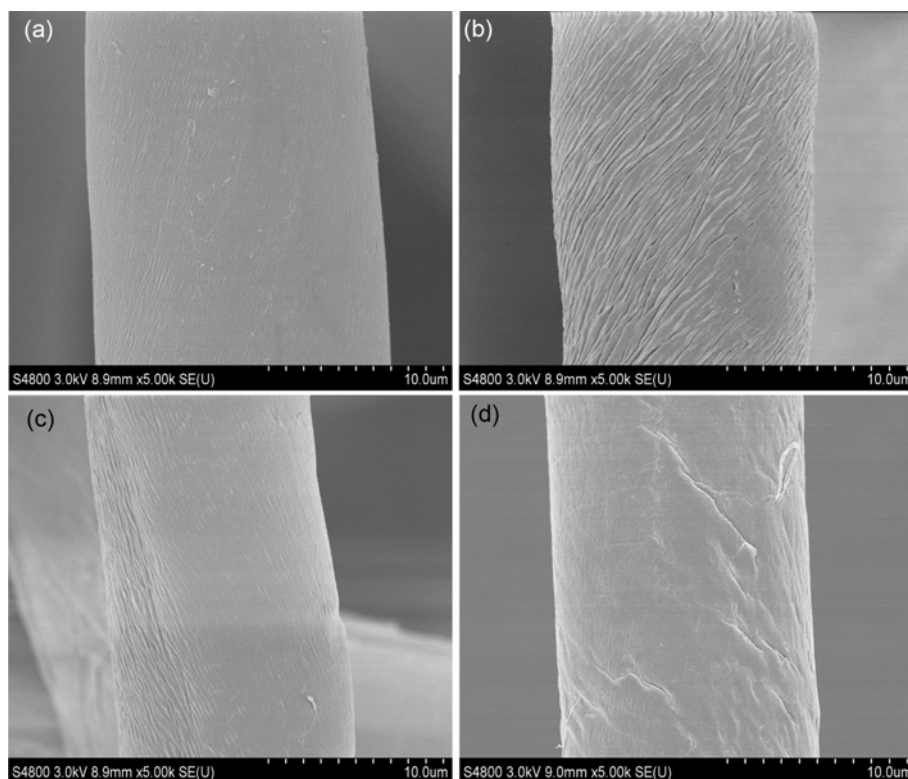
Figure 4. SEM images; (a) ACF, (b) DA-cotton, (c) CD-cotton, and (d) NC-cotton.

which could be attributed to the oxidation and hydrolysis of the cellulose macromolecule chains, leading to part of the cellulose chain breaking, and the further decomposition of the cotton fiber crystal zone. While some grooves on the surface of CD-cotton (c) were filled up after β-CD grafted, and the grooves on the surface of NC-cotton are obviously covered by a layer of film after grafting NH2-HBP (d). These changes indicated β-CD and HBP-NH2 being crosslinked or grafted to the surface of cotton fibers.

The grafting rate of β-CD on cotton fibers was determined according to spectrophotometric method [34]. 250 mg/l phenolphthalein standard solution (volume ratio of ethanol

to water was 1:1), 30 mg/l anhydrous sodium carbonate standard solution, and a series of β-CD standard solutions of different concentration (10, 15, 20, 25, 30, 35, 40, 45, 50 mg/l) were prepared were prepared. 2 ml phenolphthalein standard solution and 2 ml anhydrous sodium carbonate standard solution were added into the above β-CD standard solutions and mixed evenly, respectively, and the absorbance were measured at 553 nm. The absorbance drop value was obtained using the absorbance value of the blank solution without β-CD subtracting the absorbance value of mixture solutions with β-CD and phenolphthalein. Then the corresponding standard curve and regression equation could be
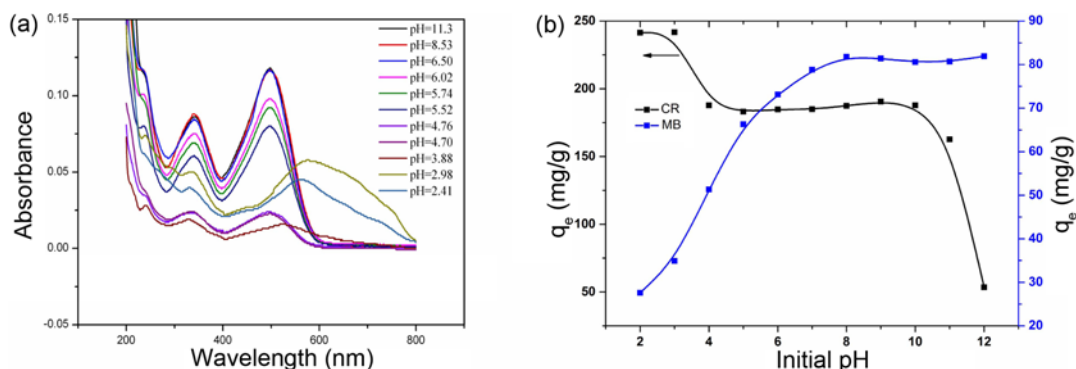

Figure 5. Effect of pH; (a) UV-vis spectra of CR with different pH and (b) effect of pH values on the adsorption capacity of NC-cotton.

acquired. A certain amount of grafted β-CD cotton fibers was added to the solution containing phenolphthalein and sodium carbonate, and the absorbance were determined at 553nm. The grafting rate of β-CD on cotton fibers was calculated according to the formula (2).

$$R \ (mg/g) = C \times V/m \qquad (2)$$

where R (mg/g) is the grafting rate of β-CD on cotton fibers, C is the concentration of β-CD (g/l), V is the volume of solution (ml), and m is the mass of fibers (g).

The experimental results showed that the grafting rate of β-CD on cotton fibers was about 96 mg/g in CD-cotton .

Effect of the pH Value on Adsorption

The effect of solution pH on adsorption capacity was investigated at initial concentration being 250 mg/l, 12 h and 1.0 g/l adsorbent at 30 °C. The pH value of the solution plays a significant role in the adsorption process, which can influence the surface charge of the adsorbent, the degree of ionization, even the molecule structure of the adsorbate in the solution [39,40]. Figure 5(a) showed the variation of maximum absorption wavelength and absorbance at the same concentration (10 mg/l) and different pH values. It could be seen the maximum absorption wavelength and absorbance changed constantly when pH smaller than 6.5, while the maximum absorption wavelength and absorbance did not change with increasing the pH value . This suggested that the pH value can changed the molecule structure of CR in aqueous solution. As shown in Figure 5(b), The adsorption capacity for CR was relatively large when the pH value was small, which could be attributed to protonated adsorbent promoting adsorption at lower pH value. The adsorption capacity declined and remained stable with the pH value increasing from 4 to 10; and decreased dramatically with increasing the pH value, which could be due to the electrostatic repulsion increasing between the adsorbent and CR. It can be seen from Figure 5(b) that the adsorption capacity for MB by NC-cotton remarkably increased as the initial solution pH increased from 2 to 6, which can be attributed to excess H$^+$ competed with MB for adsorption sites of NC-cotton when pH was lower. In addition, NC-cotton became protonated at lower pH, and the electrostatic repulsion of the high concentration of H$^+$ prevents MB approaching to the surface of the adsorbent. With an increase in the solution pH, the electrostatic attraction between MB and the adsorbent was improved, which resulted in an increase adsorption capacity. In addition, hydrophobicity of MB was enhanced and the effect on electron-rich cavity of β-CD was weakened with the increase of pH value, and promoting MB molecule more easily enter the cavity of β-CD forming stable inclusion. CR is a typical anionic dye, and NC-cotton showed larger adsorption capacity for it, which could be due to comprehensive effects of electrostatic attraction, chemisorption and host-guest interactions. The

results showed the pH value played a significant role in the adsorption process. According to effect of the pH value on adsorption, the pH value of CR and MB solutions were adjusted to 7.3 and 8.0 in the adsorption experiments, respectively.

Adsorption Capacity of NC-Cotton for Dyes

Figure 6 showed the adsorption capacity of raw cotton, CD-cotton, and NC-cotton. As shown in the image, CD-cotton and NC-cotton exhibited a more large adsorption capacity for CR and MB than that of raw cotton, indicating both CD-cotton and NC-cotton could enhance the adsorption performance of cotton fibers for dyes. The adsorption capacity of raw cotton was 15.3 mg/g for CR and 9.6 mg/g for MB, and the adsorption capacity of CD-cotton was 35.2 mg/g for CR and 40.6 mg/g for MB. Compared with CD-cotton, NC-cotton showed better adsorption performance for CR and MB with corresponding equilibrium adsorption capacities reaching up to 188.6 mg/g and 81.7 mg/g respectively. The adsorption of cotton fiber for CR and MB can be attributed to surface adsorption, hydrogen-bonding and inclusion. NC-cotton had a larger adsorption capacity for CR, which can be attributed to strong electrostatic attraction between adsorbent and CR due to NC-cotton containing many amino groups. In addition, hydrogen-bonding force between adsorbent and dyes cannot be ignored. After chemical modification of cotton fibers, the crystallinity decreases, the micropores increase and the surface coarsens, which could improve the adsorption performance of cotton fibers for dyes. So, the adsorption mechanism for CR and MB can involve several kinds of interactions: physical adsorption, hydrogen-bonding, electrostatic attraction, and formation of an inclusion complex between β-CD molecules and dyes.

Adsorption Kinetics

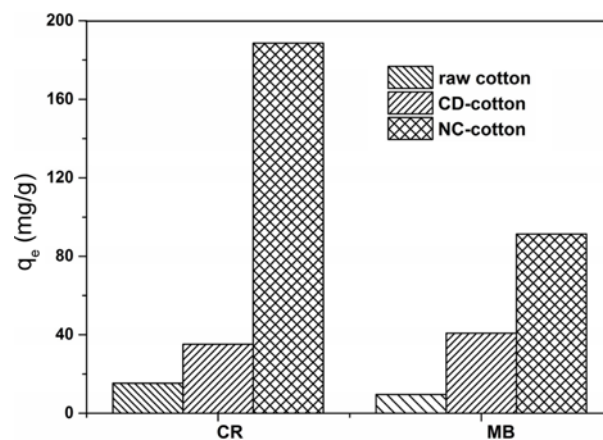The study of adsorption kinetics describes the solute

Figure 6. Adsorption capacity for both CR and MB of raw cotton, CD-cotton, and NC-cotton.

Table 1. Kinetic parameters and experimental adsorption capacities

Adsorbate	q_e (exp) (mg/g)	Pseudo-first order			Pseudo-second order		
		q_{e1} (mg/g)	k_1 (g/mg·min)	R_1^2	q_{e2} (mg/g)	k_2 (g/mg·min)	R_2^2
CR	188.6	146.9	0.0048	0.8348	179.8	0.0003	0.9954
MB	81.7	43.2	0.0059	0.7680	84.5	0.0007	0.9895

adsorption rate, which commands the residence time of adsorbate adsorption at the solid-solution interface, and it's beneficial to design a fast and effective model [41]. The adsorption kinetics for CR and MB by NC-cotton were evaluated using the pseudo-first order (3) and the pseudo-second order equations (4) [41], which express the mechanism of solute adsorption onto an adsorbent.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), k_1 (min^{-1}) and k_2 (g/mg·min) represent the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations, respectively.

The adsorption kenitics was investigated at dye initial concentration being 250 mg/*l*, and the adsorption process for CR and MB was completed within 12 h. Figure 7 illustrates adsorption capacity (q_t), the pseudo-first order, and pseudo-second order adsorption kinetics for CR and MB. It can be seen that adsorption equilibrium was reached within 2 h for MB, and within 4 h for CR. The adsorbent capacity for CR and MB increased rapidly within first hour, which due to the electrostatic attraction and host-guest inclusion between the adsorbate and adsorbent. A considerable amount of adsorption before equilibrium may be attributed to other chemical interactions or physical forces, such as the hydrogen bond, complexation between the adsorbate and the active groups of NC-cotton, and the needed interaction time may be the result of the slower adsorption process [36]. The corresponding parameters calculated and experimental adsorption capacities were shown in Table 1. It can be seen that the correlation coefficients (R^2) and the theoretical adsorption capacities (Q_{2e}) calculated from pseudo-second order kinetic equation shows a higher correlation and consistence to the experimental data than those from pseudo-first-order kinetics, which demonstrates pseudo-second-order kinetic could describe reasonably the adsorption process.

Adsorption Isotherms

Adsorption isotherms describe how the adsorbent interacts with the adsorbate, which are important for optimizing the use of the adsorbent. Adsorption equilibrium is established when an adsorbate has been contacted with the adsorbent for sufficient time, and the adsorbate concentration in the bulk
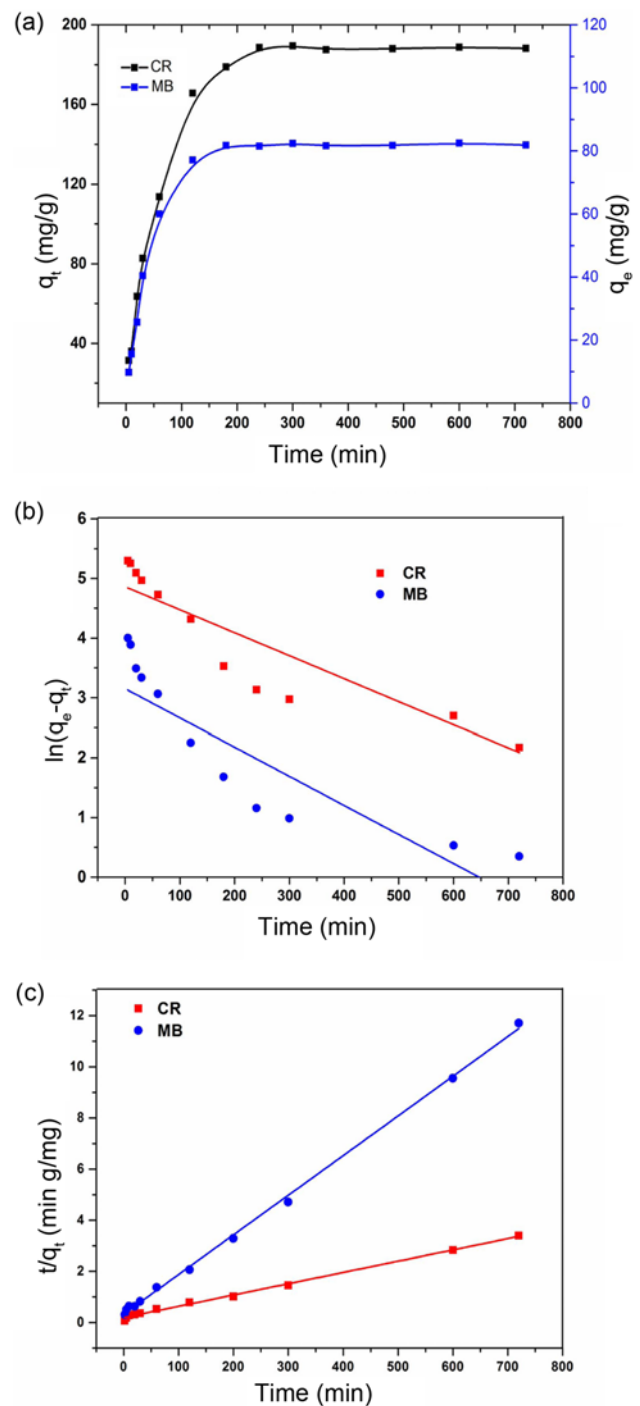

Figure 7. (a) Adsorption behavior for CR and MB, (b) pseudo-first-order kinetic plots, and (c) pseudo-second-order kinetic plots.
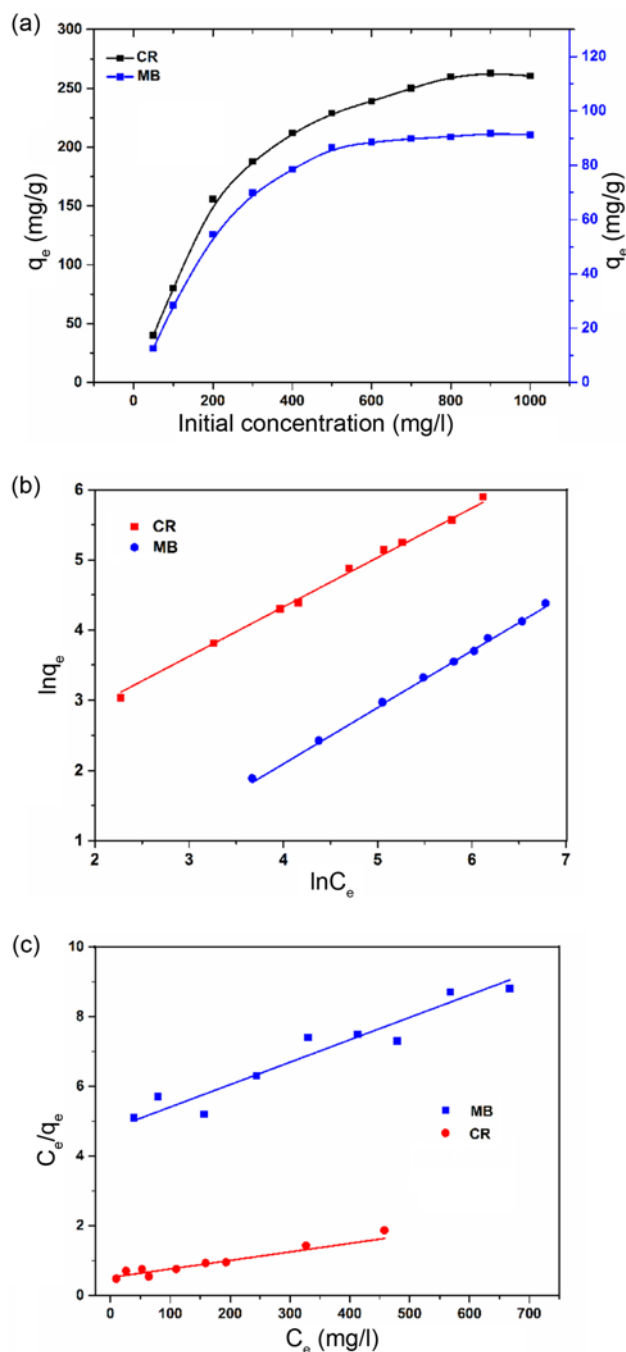
solution reaches a dynamic balance with the interface concentration [42]. Langmuir and Freundlich adsorption isotherms are investigated in this study. The Langmuir isotherm model presumes that the surface of adsorbent is homogeneous, and adsorbate can cover on the surface of adsorbent with monolayer, and adsorption can only occur at a fixed number of definite localized sites, with no lateral interaction and steric hindrance between the adsorbed molecules [43]. The Freundlich isotherm mode can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [43]. The linearized Langmuir equation (5) and Freundlich equation (6) [44] are expressed as below, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \tag{5}$$

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_F \tag{6}$$

where, q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/l) in solution, q_{max} is the maximum monolayer amount of adsorbent (mg/g). Langmuir constants (K_L) is the adsorption equilibrium constant related to the energy of adsorption.

Figure 8 shows Influence of initial concentrations on the adsorption capacity and the linear fitting of Langmuir isotherm and Freundlich isotherm for CR and MB. As shown in Figure 8(a), the adsorption capacity at equilibrium for CR and MB increase rapidly at beginning, and then tends to level off with increasing initial concentration. The adsorption constants for Freundlich and Langmuir isotherm models, and the correlation coefficients (R^2) were listed in Table 2. As show in Table 2, the q_{max} of NC-cotton was 236.6 mg/g for CR, 95.8 mg/g for MB, and the adsorption conformed better to the Freundlich isotherm model ($R^2=$ 0.9935, 0.9962) than Langmuir isotherm model (R^2=0.9434, 0.8368). It can be seen from Figure 8(a) that the adsorption capacity for CR was higher than MB by NC-cotton, which can be attributed to NC-cotton containing multiple amino groups, and CR is an anionic dye at pH>5.5, so it could aggregate more CR molecules by electrostatic attraction.

Regeneration of NC-cotton

After five recycles of desorption and re-adsorption experiment, the adsorption capacity of NC-cotton for CR

Figure 8. (a) Influence of initial concentrations on the adsorption capacity, (b) Freundlich adsorption isotherm, and (c) Langmuir adsorption isotherm.

Table 2. Langmuir and Freundlich parameters for adsorption isotherms of NC-cotton

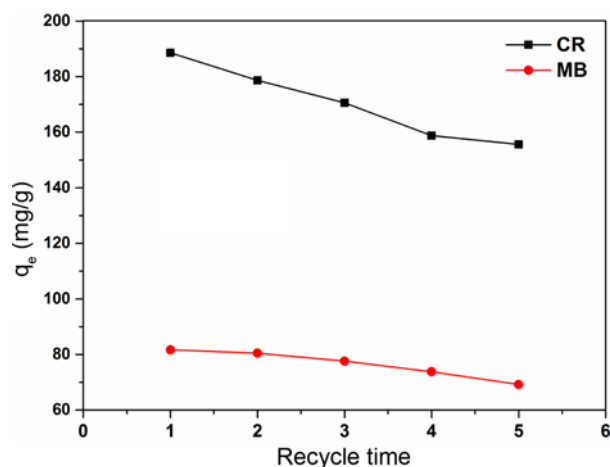| Adsorbate	Langrnuir			Freundlich		
	q_{max}	K_L	R^2	n	K_f	R^2
CR	236.6	0.0051	0.9434	2.9585	4.6342	0.9935
MB	95.8	0.0024	0.8368	1.4396	3.1574	0.9962

Figure 9. Adsorption capacity of the regenerated NC-cotton.

and MB showed a decrease (Figure 9). Nevertheless, the adsorption capacity maintained still for CR and MB was above 80 % after five regenerations. The desorption experiments in this work were done using 0.1 M HCl aqueous solution or 0.1 M NaOH solution. The regeneration property of the adsorbent has an important effect on its cost, and desorption studies of adsorbent can provide important insight for the adsorption mechanism [36]. Desorption of the adsorbate using water suggests the attachment of weak physisorption between adsorbate and adsorbent, and desorption with strong mineral acid or base shows the involvement of electrostatic interaction [45]. The amino groups in the NC-cotton are deprotonated under alkaline conditions, reducing the electrostatic attraction between CR and the CR, whereas the interaction between NC-cotton and methylene blue is weakened in acidic solution, which are favorable for dyes desorption. This is consistent with the result of the effect of pH values on adsorption. When desorbing, some dye molecules are not released from NC-cotton, resulting in adsorption sites decreased, so adsorption capacity for CR and MB decreased as the increase of cycles.

Conclusion

Cotton fibers was chemically modified with NH_2-HBP and β-CD, and its characteristics and application for the removal of CR and MB from aqueous solution were investigated in this work. It could reach adsorption equilibrium within 4 h for MB and CR. NC-cotton showed better adsorption performance for CR and MB than raw cotton and CD-cotton. The adsorption behaviors for dyes were more agreed with pseudo-second-order kinetic equation and Freundlich isothermal model. The proposed adsorption mechanism could be attributed to several kinds of interactions: physical adsorption, hydrogen-bonding force, electrostatic attraction, and formation of an inclusion complex through host-guest interactions. Adsorption isotherms investigation showed After five repetition of desorption and re-adsorption, the adsorption capacity of NC-cotton maintained still for CR and MB was above 80 %.

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