Synthesis of cross-linking cationic starch and its adsorption properties for reactive dyes

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Abstract. In the presence of alkaline catalyst NaOH, natural polymer polysaccharide based cross-linking cationic starch (CCSt), the adsorbent for reactive dye, was synthesized by corn starch as raw material, 30% trimethylamine solution as cross-linking agent and 3-chloro-2-hydroxypropyltrimethyl ammonium chloride as cationic agent. Structure of the product confirmed by Fourier transform infrared spectrum (FTIR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) indicated that the cationic groups were successfully introduced into corn starch. The adsorption properties for reactive dyes by CCSt were investigated in terms of adsorption kinetics, adsorption isotherms and adsorption thermodynamics. Adsorption behavior of CCSt on reactive dyes fitted pseudo-second-order model and Langmuir isotherm, and the adsorption process was endothermic. CCSt with favorable adsorption capacity for reactive dyes was expected to be an ideal substitute for inorganic adsorbent and synthetic resin adsorbent applied in the treatment of industrial dye wastewater.

1. Introduction
Printing and dyeing wastewater with large discharge, complex composition, high chroma and poverty biodegradability has been regarded as the key and difficult point of industrial wastewater treatment[1,2]. The printing and dyeing wastewater is mainly containing dyes, dyeing auxiliaries, size, fiber impurities and inorganic salt, among which the most serious pollution is the highly visible dye pollution due to its effects on both the environment, and living creatures[3-5]. Therefore, when it comes to printing and dyeing wastewater treatment, the first assignment is to cope with the issue of decolorization.

Adsorption is a commonly used method for decolorization. It has quite a few advantages, such as wide application range, good treatment effect and reusable property. The adsorbent for decolorization of printing and dyeing wastewater contains inorganic and organic adsorption materials. Active carbon[6,7], zeolite[8-10] and bentonite[11,12] as adsorbent materials are commonly used to deal with printing and dyeing wastewater in depth. Nevertheless, the adsorption property of inorganic adsorbent, determined by its own specific surface area and porous structure, is restricted especially for the treatment of high concentration wastewater, leading to the large amount, low efficiency and limited application[13-15]. Organic adsorption materials mainly comprise chitosan and starch based adsorption materials.

Starch as a kind of natural high molecular material has gained more and more attention for industrial use in recent years because of its wide origin, low cost, biodegradability, renewability and...
non-toxicity[16,17], making starch based products have been proposed as adsorption agents to remove dyes from printing and dyeing wastewater. Xu et al. investigated crosslinked amphoteric starch with carboxymethyl and quaternary ammonium groups as an adsorbent for removal of both acid and basic dyes in solution[18]. Frédéric et al. prepared cationized starch-based adsorbent to adsorb an anionic dye, namely C.I Acid Blue 25[19]. Haradhan and Tridib reported the removal of Malachite green, a cationic dye from aqueous solution, by hydroxyethyl starch-g-poly-(N, N-dimethylacrylamide-co-acrylic acid) [20]. Xing et al. synthesized novel and cost-effective cationic starch intercalated clay composite matrix and studied its adsorption behavior for brilliant blue X-BR[21]. Bidyadhar and Samit incorporated starch and acrylic gels and used it for adsorption of Brilliant Cresyl Blue dyes from water[22].

Cross-linking cationic starch (CCSt), one of the chemically modified starches, with quaternary ammonium groups carrying positively charged groups can closely combine with the direct dyes, acid dyes and reactive dyes containing anionic groups through electrostatic attraction [23-25], so as to achieve the purpose of decolorization. At present, reactive dyes are widely used in printing and dyeing industry. They have gradually replaced azoic dyes, direct dyes, sulfur dyes and vat dyes, becoming the main dyes in printing and dyeing of cellulose fibers. Therefore, the treatment of dyeing wastewater with reactive dyes is facing great challenges. So in this paper, reactive dyes as adsorbate were studied.

In the present investigation, the obtained products were characterized by Fourier transform infrared spectrum (FTIR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The adsorption properties of CCSt for reactive red 195 dye and reactive golden yellow SNE dye were also investigated including adsorption kinetics, adsorption isotherm and adsorption thermodynamics.

2. Materials and methods

2.1. Materials

Corn starch (CR, Zhucheng XingMao Products Development Co. Ltd, Shandong, China) was used as the raw material of CCSt. Epichlorohydrin (ECH) and 30% trimethylamine solution (AR, Tianjin Guangfu Technology Development Co. Ltd, Tianjin, China) were used as cross-linking agent and the raw material of etherifying agent CHPTMAC, respectively. Reactive red 195 dye (AR, Shanghai Linen Technology Development Co. Ltd, Shanghai, China) and reactive golden yellow SNE dye (AR, Jiangsu Shenxin Dyestuff Chemical Limited by Share Ltd, Jiangsu, China) were used for the preparation of the dye solutions. All standards and aqueous solutions used in this study were prepared with distilled water.

2.2. Synthesis of CCSt adsorbent

Cross-linking starch (CSt) synthesized by corn starch as raw material and 30% trimethylamine solution as cross-linking agent was dissolved in a mixture of distilled water and ethanol, and the starch solution was transferred to a three-neck flask equipped with a magnetic stirrer and a condensing unit. 5% (w/w) sodium chloride solution containing a certain amount of sodium hydroxide was added to the starch solution with a constant pressure funnel, and the mixed solution was alkalized at 50°C for 30 min. To this mixture, the etherifying agent CHPTMAC was added. After stirring at 50°C for 6h, the reaction mixture was isolated by precipitation in absolute ethanol. The obtained precipitate was washed thoroughly with 70% (w/w) ethanol solution to no chloride ion and dried at 50°C for 24h.

2.3. Characterizations of CCSt adsorbent

FTIR spectra of St and CCSt adsorbent were recorded on a TENSOR 37 spectrometer (Bruker Corporation, Germany) with KBr dispersion method. The FTIR spectra were in the range of 4000cm⁻¹-400cm⁻¹. XRD patterns of corn starch and CCSt adsorbent were determined using a D8 ADVANCE diffractometer (Bruker Corporation, Germany). The samples were scanned from 2θ of 4° to 50° (θ being the scattering angle) with a step width of 0.02°.SEM images were obtained using a Hitachi
S4800 cold field scanning electron microscopy (Hitachi Corporation, Japan) with 10.0kV voltage and 2.0k and 5.0k magnification.

2.4. Adsorption properties of CCS\textsubscript{t} adsorbent

Reactive red 195 dye and reactive golden yellow SNE dye was dissolved in deionized water to the required concentrations (100 mg/L for adsorption kinetics study and 150mg/L for adsorption isotherms study), respectively, and the initial pH of the dye solution is 6. The adsorption experiments were carried out in a series of 50 mL conical flasks with cover containing 10 mg CCS\textsubscript{t} adsorbent and 20 mL reactive dye solution in a thermostated shaking bath. After shaken at 150 r/min for a definite time, the adsorbents were removed by suction filtration and the concentrations of reactive dye in aqueous solution after adsorption were analysis by ultraviolet spectrophotometer. The reactive red 195 dye and reactive golden yellow SNE dye solution was calculated at 515nm and 417nm, respectively. The adsorption amounts of the adsorbents were calculated by the following equation\cite{26}:

\[
Q = \frac{(C_0 - C_t)V}{w}
\]  

(1)

where Q is the adsorption capacity of the adsorbent on the reactive dye (mg/g), C\textsubscript{0} and C\textsubscript{t} are the concentration of reactive dye at initial time and time t, respectively, V is the volume of the reactive dye solution (mL), and w is the dose weight of the adsorbent (mg).

3. Results and discussion

3.1. CCS\textsubscript{t} adsorbent characterizations

Figure 1 shows the FTIR spectra of (a) St and (b) CCS\textsubscript{t}. In the FTIR spectrum of St, the extremely broad adsorption peak at 3380cm\textsuperscript{-1} and the peak at 2930cm\textsuperscript{-1} were assigned to the O-H stretching vibration and C-H stretching vibration of methylene groups, respectively, which was stronger in the FTIR spectrum of CCS\textsubscript{t}, indicating that after cross-linking process there were more hydroxyl groups and methylene groups in the starch molecules. Compared with the St, the intensity of the adsorption peak of CCS\textsubscript{t} at 1160 cm\textsuperscript{-1} and 1080 cm\textsuperscript{-1} characteristic of the C-N stretching vibration and C-O-C stretching vibration\cite{14,16,27}, respectively, increased, which illustrated that the etherification was successfully carried out and the quaternary ammonium radical groups were introduced into starch molecules.

![Figure 1](image1.png)

**Figure 1.** The FTIR spectras of (a) St and (b) CCS\textsubscript{t}.

The XRD patterns of St and CCS\textsubscript{t} are shown in Figure 2. From the Figure, the XRD curves of St expressed a typical A-type crystalline pattern illustrated by strong reflection at 2θ of about 15°, 17°, 18° and 23° and the strength for the diffraction peaks of CCS\textsubscript{t} obviously reduce\cite{28}, which means that the cationization process after cross-linking reaction resulted in relatively low damage to the crystallinity. That is, after modification, the crystallinity of starch decreased only, but not disappeared. This is due to the introduction of covalent bonds between the starch molecules in the presence of cross-linking, whose interaction force is significantly higher than the hydrogen bond force, enhancing the

![Figure 2](image2.png)

**Figure 2.** The XRD patterns of (a) St and (b) CCS\textsubscript{t}.
intermolecular binding of starch. Therefore, the cationization reaction has little effect on the crystallinity. However, because of the mutual exclusion effect of ionic groups carrying the same charge, the distance between the chains in crystalline region increased, which made the starch particles expand and the crystalline structure was destroyed. That is, the internal tight structure of starch was destroyed.

SEM images of St and CCSt are exhibited in Figure 3. Both St and CCSt were composed of granules with round and polygonal shapes. Whereas there were tiny holes in the surface of CCSt, but the surface of St was smooth. The above phenomenon is due to the fact that the integrity of starch granules is mainly determined by their crystalline structure, and the more serious destruction of the crystalline zone is, the more obvious changes into the macro structure of starch particles are. This result is consistent with the analysis of XRD.

3.2. Adsorption kinetics study

In order to investigate the adsorption mechanism and possible velocity control step, kinetic model is often used to simulate the experimental datas. The commonly used kinetic models include pseudo first and second order kinetic models[29].

The pseudo-first-order equation is expressed as:

$$\ln(q_t - q_i) = \ln q_e - k_1 t$$  \hspace{1cm} (2)

where $q_t$ (mg/g) is the adsorption capacity at any time $t$ (min); $q_e$ is the equilibrium adsorption capacity (mg/g); $k_1$ is the pseudo-first-order rate constant of the equation $(\text{min}^{-1})$. The correlation coefficient $(R^2)$ obtained by fitting are displayed in Table 1.

The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}$$ \hspace{1cm} (3)

Figure 3. SEM photos of (a) St and (b) CCSt.
where \( q_t \) (mg/g) is the adsorption capacity at any time \( t \) (min); \( q_e \) is the equilibrium adsorption capacity (mg/g); \( k_2 \) is the pseudo-second-order rate constant of the equation (g/(mg\cdot min)). The rate constants (\( k_2 \)), equilibrium adsorption capacities (\( q_e \)) and the correlation coefficient (R\(^2\)) were calculated and are shown in Table 1. The values of the correlation coefficient of pseudo-second-order model are more close to 1.0 compared with those of pseudo-first-order model and the calculative \( q_e \) of pseudo-second-order model is closer to the \( q_e \) obtained from experiment, which indicated that the adsorption for reactive dyes by CCSt fitted better with pseudo-second-order model. That is to say, chemical reaction is the main rate-determining step of reactive dyes adsorption process by CCSt rather than mass transfer[21].

Table 1. Pseudo first and pseudo second order kinetic parameters for reactive dyes adsorption by CCSt.

| Dyes        | \( q_e(\text{exp}) \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( q_e(\text{cal}) \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( q_e(\text{cal}) \) (mg/g) |
|-------------|-------------------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|
| red 195     | 101.73                        | 0.2677                   | 35.69                       | 101.73                   | 0.2677                      |
| golden yellow SNE | 120.14               | 0.4037                   | 29.12                       | 120.14                   | 0.4037                      |

3.3. Adsorption isotherms study

To study the equilibrium of an adsorption process between the liquid and solid phases, the experimental data were fitted using the Langmuir and Freundlich equations[30,31]. The Langmuir isotherm is applied to monolayer adsorption. The linear Langmuir equation is:

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_mK_L}C_e
\]

where \( q_e \) is the equilibrium adsorption capacity (mg/g), \( q_m \) is the maximum adsorption capacity (mg/g), \( C_e \) is the equilibrium concentration of reactive dyes (mg/L), and \( K_L \) is the Langmuir constant representing the adsorption energy (L/mg). The values of Langmuir isotherm parameters calculated by fitting are shown in Table 2. The maximum adsorption capacity and Langmuir constant enhanced with the increase of temperature, which indicated that the adsorption process of CCSt on reactive dyes was endothermic. The linear Freundlich equation is as follows:

\[
lnq_e = lnK_f + \frac{1}{n}lnC_e
\]

where \( K_f \) is the Freundlich adsorption coefficient (mg/g) and \( n \) is the Freundlich characteristic constant related to adsorption intensity. The relevant parameters are given in Table 2. It is generally believed that \( n > 1 \) represents favorable nature of adsorption [32]. Compared with the correlation coefficient of Langmuir isotherm, the correlation coefficient of Freundlich isotherm was lower, therefore, the adsorption for reactive dyes by CCSt fitted better with Langmuir isotherm. It showed that the process of adsorption occurred on a homogeneous surface and the adsorption was monolayer adsorption.

Table 2. Langmuir and Freundlich adsorption isotherms parameters for reactive dyes adsorption by CCSt.

| Reactive dyes | \( T \) (K) | \( q_m \) (mg/g) | \( K_f \) (L/mg) | \( R^2 \) | \( q_f \) (mg/g) | \( n \) | \( R^2 \) |
|---------------|-------------|-----------------|-----------------|----------|-----------------|------|----------|
| red 195       | 298.15K     | 153.61          | 0.0410          | 0.9960   | 35.53           | 3.66 | 0.9797   |
| golden yellow | 303.15K     | 169.78          | 0.0526          | 0.9980   | 45.98           | 3.99 | 0.9846   |
| yellow SNE    | 308.15K     | 173.31          | 0.0600          | 0.9989   | 51.69           | 4.27 | 0.9798   |
| red 195       | 298.15K     | 194.93          | 0.0533          | 0.9970   | 49.76           | 3.74 | 0.9590   |
| golden yellow | 303.15K     | 197.63          | 0.0778          | 0.9971   | 67.56           | 4.65 | 0.9792   |
| yellow SNE    | 308.15K     | 208.77          | 0.1137          | 0.9995   | 79.29           | 4.85 | 0.9859   |
4. Conclusions
In the presence of alkaline catalyst NaOH, natural polymer polysaccharide based CCSt, the adsorbent for reactive dye, was synthesized by corn starch as raw material, 30% trimethylamine solution as cross-linking agent and 3-chloro-2-hydroxypropyltrimethyl ammonium chloride as cationic agent. The product was characterized by FTIR, XRD and SEM, which exhibited that the quaternary ammonium radical groups were introduced into starch molecules, after modification the crystallinity of starch decreased and that there were tiny holes in the surface of CCSt, respectively, indicating CCSt successfully synthesized.

The adsorption properties of CCSt for reactive dyes such as reactive golden yellow SNE and reactive red 195 were studied in terms of adsorption kinetics and adsorption isotherms. Adsorption behavior of CCSt on reactive dyes fitted pseudo-second-order model and Langmuir isotherm. It was found that the CCSt with favorable adsorption capacity for reactive dyes was expected to be an ideal substitute for inorganic adsorbent and synthetic resin adsorbent applied in the treatment of industrial dye wastewater.

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