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Removal of color from simulated textile wastewater by a modified dicyandiamide-formaldehyde polymeric flocculant

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ABSTRACT

Dicyandiamide-formaldehyde condensation product shows excellent decolorization performance for dyeing wastewater. The cross-linking agent plays an important role in the decolorization performance. In this work, a three-dimensional modified dicyandiamide-formaldehyde decolorizing decolorant (defined as DF_1) was synthesized using hexamethylenetetramine as the three-dimensional cross-linking agent. The influences of dosage of DF_1, settling time, settling temperature, pH value and inorganic salt on the flocculation ability of DF_1 were investigated. The existence of inorganic salt has a slight effect on the color removal of DF_1. The maximum color removal of 98.8% was achieved with the DF_1 dosage of 35 mg/L. The infrared spectra of samples demonstrate that chemical reactions occurred between DF_1 and Reactive Brilliant Red X-3B.

Keywords: Textile wastewater; Dicyandiamide; Formaldehyde; Cross-linking agent; Hexamethylenetetramine

1. Introduction

Textile wastewater is one of the most serious environmental problems in the world. Many kinds of artificial composite dyes are discharged into the water without proper treatment after dying operations. Some of the dyes are toxic to aquatic life and human, causing long-term environmental and ecological impacts [1–5]. Hence textile industries were forced to remove dyes from effluents before emission by the laws. At present, there are many ways for printing and dyeing wastewater decolorizing, including physical adsorption [6,7], chemical oxidation [8–10], flocculation settlement [11], membrane filtration [12], etc. The flocculation process is one of the most widely used techniques for water and wastewater treatment. Many attentions had been paid to flocculation, which has a great application prospect because of its simple operation, and excellent decolorizing. A wide range of flocculants has been developed or designed to improve the flocculation process in wastewater treatment [13–18]. Synthetic cationic polymers, such as PDMC [poly(2-methacryloyloxy)ethyl]trimethylammonium chloride and PDMDAAC [poly(dimethyldiallylammonium chloride)], showed good flocculating performance. However, their further application was restricted because of the expensive cost, hydrophilic and low molecular weights. Thus, the design and synthesis of a cationic biopolymer flocculant to overcome these disadvantages of the traditional synthetic cationic polymers are greatly desirable.

Dicyandiamide-formaldehyde decolorizing flocculant is one of the effective methods to treat printing and dyeing wastewater [19]. First, the polycondensate of dicyandiamide and formaldehyde was used as a fixing agent, and then it has shown a certain effect on the decoloring aspect. However, the problems existing in the unmodified decoloring agent are that the decoloring agent and dye molecules of flocs are small and scattered, the decoloring settlement is inefficient, etc. In order to address the above issues and improve the flocculation performance

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of the dicyandiamide-formaldehyde decoloring flocculant, different cross-linking agents were selected to modify the decoloring flocculant, such as urea, melamine, and so on [20]. Urea and melamine can react with formaldehyde because their molecular structure is similar to dicyandiamide. Hydroxymethyl polymer was generated in the reaction and condensed into a one-dimensional macromolecule. The condensation products have large molecular weight, sufficient active functional groups and large dye flocs. In order to improve the flocculation efficiency and reduce the dosage, it is a good choice to prepare a three-dimensional flocculant.

In this study, a kind of three-dimensional flocculant was synthesized using hexamethylenetetramine as the cross-linking agent due to its three-dimensional structure. The three-dimensional flocculant has the advantages of more netting and sweeping function to seek the excellent flocculation effect. Effect of cross-linking agents, settling time, DF_1 dosage, pH value, settling temperature and inorganic salt were studied through a beaker experiment. The infrared spectrum of DF_1, flocs and Reactive Brilliant Red X-3B were analyzed.

2. Experimental

2.1. Materials

Dicyandiamide ($C_2H_4N_4$), formaldehyde (HCHO), ammonium chloride (NH_4Cl), hexamethylenetetramine ($C_6H_{12}N_4$), ethylenediamine ($NH_2CH_2CH_2NH_2$), diethylenetriamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$), triethylenetetramine ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (Na_2SO_4), potassium chloride (KCl), sodium sulfate, sodium dodecylbenzene sulfonate ($C_{12}H_{25}$-C_6H_4-SO_3Na, SDBS) were analytical grade and obtained from the Sinopharm Chemical Reagent Co., Ltd., (P.R. China). Reactive Brilliant Red X-3B ($C_{19}H_{10}C_{12}N_6Na_2O_7S_2$) was industrial grade and obtained from Jinan Hao Hang Chemical Co., Ltd., (P.R. China). The structure of some reagents was shown in Fig. 1. All the reagents were used directly without further purification.

2.2. Synthesis of polymeric flocculant

The polymerization reaction was performed in a three-necked flask, equipped with a reflux condenser and thermometer. Dicyandiamide (0.025 mol), formaldehyde (0.075 mol), ammonium chloride (0.01 mol) and cross-linking agent (0.001 mol) were added into the flask. After the flask was heated to 50°C for 10 min at an appropriate stirring speed, another 0.01 mol ammonium chloride was added and the temperature was adjusted to 80°C. The mixture was kept at 80°C for 4 h to make the monomers react completely. The modified dicyandiamide-formaldehyde decolorizing flocculant was colorless and viscous.

Dicyandiamide-formaldehyde decolorizing flocculant without a cross-linking agent was defined as DF. Dicyandiamide-formaldehyde decolorizing flocculants modified by hexamethylenetetramine, ethylenediamine, diethylenetriamine and triethylenetetramine were defined as DF_1, DF_2, DF_3 and DF_4 respectively.

2.3. Flocculation experiment

Flocculation decolorization tests were performed using simulated dyeing wastewater containing 100 mg/L Reactive Brilliant Red X-3B solution. For a typical procedure, a proper amount of decolorizing flocculant was added to 300 mL simulated dyeing wastewater in a beaker. The solution was stirred rapidly at 350 rpm for 2 min, followed by slow stirring at 50 rpm for 1 min, and sedimented for 20 h. After sedimentation, the supernatant sample was taken at a point of 3 cm below the water surface of the beaker for analysis.

2.4. Evaluation of color removal

The maximum absorption wavelength of the Reactive Brilliant Red X-3B was measured by 722S Visible Spectrophotometer, which was 536 nm. Then, the absorbance values of dyeing wastewater with different concentrations were measured at this wavelength, and the standard curve was obtained. The relationship between dyeing wastewater concentration and absorbance values was linear when other conditions remained unchanged.

The color removal efficiency was calculated according to the following sequence.

$$\text{Color removal}(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 and A_t are the initial and final absorbance of simulated textile wastewater, respectively.

2.5. Measurement

The decolorizing flocculants were purified by acetone and dried in a vacuum. Fourier-transform infrared spectra

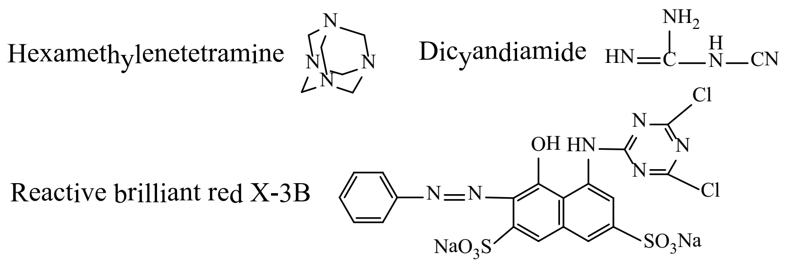

Fig. 1. Structure of some reagents.

of the samples were recorded by Tensor 27 (Bruker) within a wave number range of 400–4,000 cm^{-1} at the resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Effect of different cross-linking agents on the color removal

In order to improve the flocculating performance of dicyandiamide-formaldehyde decolorizing flocculant, hexamethylenetetramine, ethylenediamine, diethylenetriamine, triethylene and tetramine were selected and used as cross-linking agents. The flocculating performances of dicyandiamide-formaldehyde decolorizing flocculant modified by different cross-linking agents are shown in Table 1. Color removal of 78.6% was obtained by unmodified flocculants (DF). The modified flocculants (DF_1-DF_4) showed better performances than the unmodified flocculant. Color removal of 95.6% was obtained using DF_1. The structure of DF and the proposed structure of DF_1 and DF_2 are shown in Fig. 2. As we know that DF is a linear macromolecule. The hydroxymethyl of the macromolecule could react with the amidogen of the cross-linking agents. Because the amidogens of hexamethylenetetramine are three-dimensional structures in space, more DF flocculants were connected by them to form DF_1 that was a kind of three-dimensional net structure. The structures of DF_2, DF_3 and DF_4 were one dimensional because that the cross-linking agents were one-dimensional. Charge neutralization of these flocculants was close because no more positive charge was added after modification. However, the netting and sweeping function of DF_1 was stronger than that of other flocculants due to its three-dimensional net structure. It may explain the best performances of DF_1.

Table 1
Effect of different cross-linking agents on the color removal

Sample name	Cross-linking agent	Color removal (%)
DF	None	78.6
DF_1	Hexamethylenetetramine	95.6
DF_2	Ethylenediamine	90.1
DF_3	Diethylenetriamine	88.9
DF_4	Triethylenetetramine	88.1

Dosage of decolorizing flocculant: 25 mg/L; pH = 4; Settling temperature 25°C, Settling time 20 h.

3.2. Effect of settling time on the color removal

The simulated dyeing wastewater was treated using DF and DF_1 respectively. Supernatant samples were taken every 2 h and measured to calculate the color removal. Fig. 3 summarizes the effect of settling time on the color removal of the modified dicyandiamide-formaldehyde flocculant by hexamethylenetetramine (DF_1) and unmodified dicyandiamide-formaldehyde flocculant (DF). In the first 4 h, color removal of DF_1 increased rapidly and 86.9% of color removal was obtained. While the color removal for DF was only 78.6% in 20 h. It is obvious that the decolorization performance of DF_1 is much better than that of DF. The DF_1 was characterized by a high sedimentation rate and a perfect decolorizing effect.

3.3. Effect of DF_1 dosage on the color removal

The effects of DF_1 dosage on color removal efficiency were studied by varying the amount of DF_1 from 5 to 40 mg/L and the results are shown in Fig. 4. As the DF_1 dosage increased, the dye removal efficiency increased rapidly when the DF_1 dosage was below 25 mg/L, then increased slightly when the DF_1 dosage was beyond this value. The maximum color removal of 98.8% was achieved with the dosage of 35 mg/L. In order to save cost and prevent the second pollution of water sample caused by too many

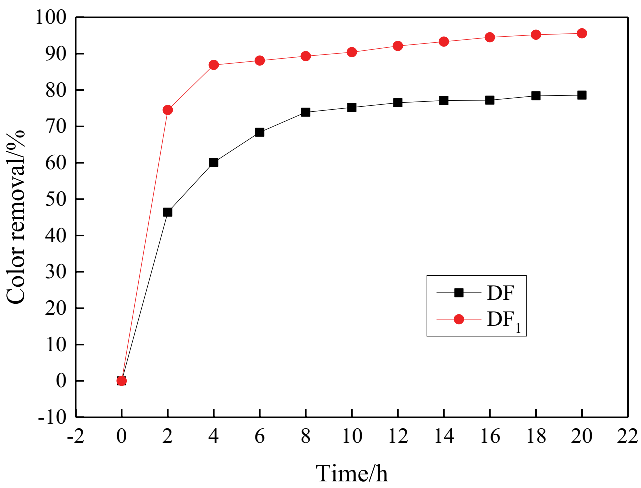

Fig. 3. Effect of settling time on the color removal. Dosage of DF_1 or DF: 25 mg/L; pH = 4, settling temperature 25°C.

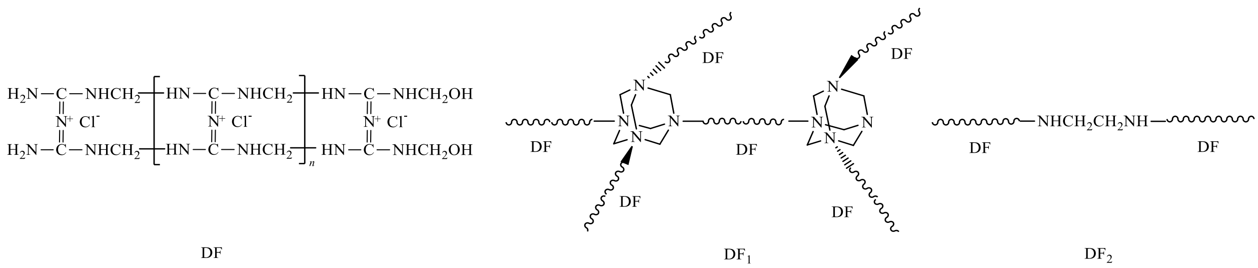

Fig. 2. Structure of DF and the proposed structure of DF_1 and DF_2. The ~~~~ of the proposed structure of DF_1 and DF_2 symbols for DF molecule.

flocculants, 35 mg/L of DF_1 dosage should be suitable. The positive electricity and active sites increased with the DF_1 dosage increase. Then, adsorption of dye molecules by flocculants increased, leading to more dye molecules were flocculated and settled. As a result, the color removal increased.

3.4. Effect of settling temperature on the color removal

The influence of settling temperature from 20°C to 60°C on the color removal was studied and is indicated in Fig. 5. The beaker containing simulated dyeing wastewater was put into the thermostat water bath. The settling temperature was adjusted and controlled by the thermostat water bath. It was found that the color removal changes a little when the settling temperature was 20°C–30°C. The Color removal dropped sharply when the settling temperature was higher than 30°C. The thermal motion of molecules intensified as temperature increased. Some incompact flocs were dispersed and returned to the solution, which caused the decrease of the DF_1 decolorization performance. The suitable settling temperature of DF_1 was between 20°C and 30°C. The best operating temperature was 25°C.

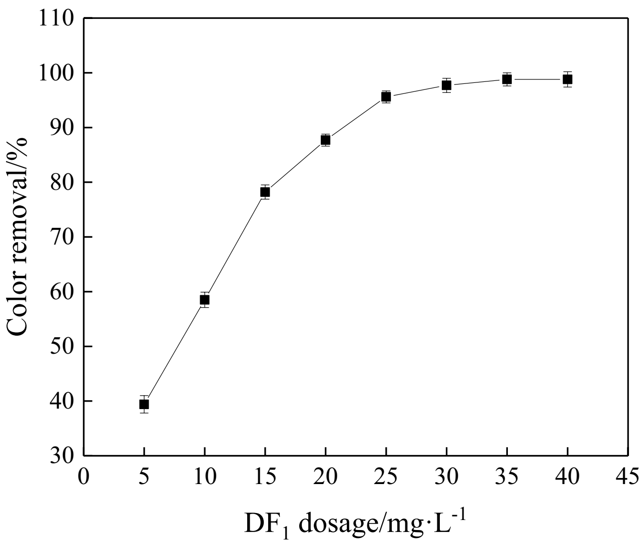

Fig. 4. Effect of DF_1 dosage on the color removal. Settling temperature 25°C; pH = 4; settling time 20 h.

3.5. Effect of pH value on the color removal

The pH value of dyeing wastewater had a prominent influence on the surface charge of the decolorizer and the existing form of dye molecules. So the color removal was closely related to the pH of dyeing wastewater. To study the effect of pH on color removal, the pH value was adjusted by 0.1 M HCl or 0.1 M NaOH. The pH value was measured by a pH meter. The DF_1 dosage was kept at 35 mg/L. Fig. 6 demonstrates the results of DF_1 performance at different pH values. The results revealed that the color removal changed slightly at pH ≤ 6 and decreased quickly at pH > 6. The DF_1 displayed the highest performance at pH = 4 with a color removal of 98.8%. In the acidic and neutral conditions, the decolorizing effect was remarkable, but the decolorizing ability was low in alkaline conditions. The reason is that the structure of dye molecules changes with the change of pH value. The sulfonic groups in the dye molecules existed in the form of $-SO_3H$ at acidic and neutral conditions. The chemical effect of dye molecules and amino groups in DF_1 was strengthened, the bridging adsorption was obvious, and more dye molecules were flocculated and precipitated. When it was alkaline, the sulfonic groups existed in the form of $-SO_3Na$. The chemical effect of dye molecules and the DF_1 amino group was weakened, the bridging adsorption was abated, and the color removal was reduced. Therefore, DF_1 was suitable for the treatment of simulated dyeing wastewater under acid and neutral conditions, and the optimal pH range was 3~5.

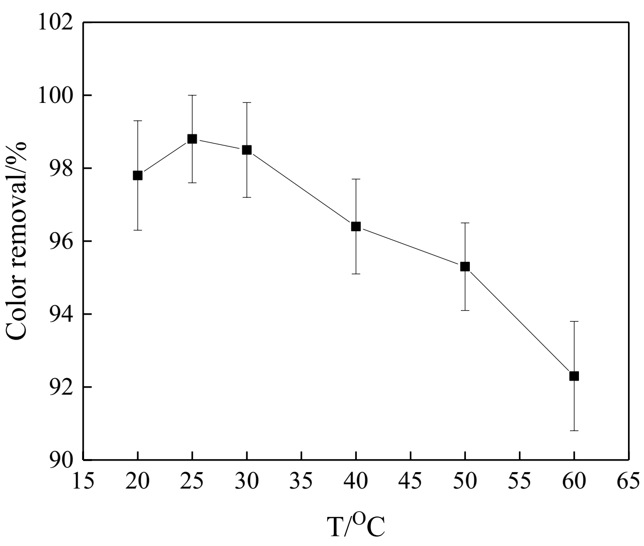

Fig. 5. Effect of settling temperature on the color removal. Dosage of DF_1: 35 mg/L; pH = 4; settling time 20 h.

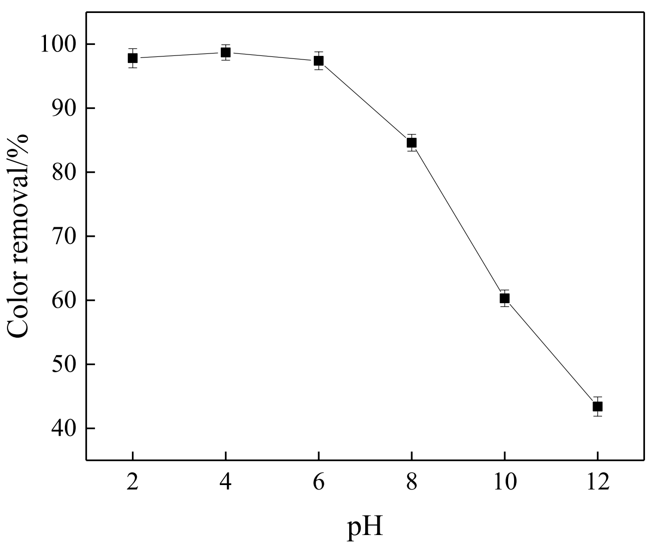

Fig. 6. Effect of pH value on the color removal. Dosage of DF_1: 35 mg/L; settling temperature 25°C; settling time 20 h.

3.6. Effect of amount and kinds of salt on the color removal

Usually, inorganic salts are used in the process of dying. So the dyeing wastewater generally contains inorganic salts. The presence of inorganic salts has a greater impact on the decolorization performance of the decolorizer. Here, frequently-used inorganic salt (NaCl) was added to the simulated textile wastewater to study the effect of inorganic salt on the decolorization performance of the decolorizer. The effect of the different additive amount of NaCl on the color removal is presented in Fig. 7. As shown in this figure, color removal decreased from 98.7% to 93.7% with the NaCl amount increased from 0 mol/L to 0.1 mol/L, which indicated that inorganic salt had a slight effect on the color removal of DF_1. It illustrated that DF_1 can be used to treat wastewater containing inorganic salts. Salt causes an increase in ionic strength and anion concentration that neutralizes the positive charge of DF_1. The charge neutralization of the decolorizer during flocculation was weakened and color removal decreased.

Fig. 8 illustrates the effect of different kinds and amount of salt on color removal. When the content of all salts is 0.1 mol/L, the color removal of NaCl is slightly higher than that of KCl but much higher than that of Na_2SO_4. It could be attributed to the low ionic strength of NaCl. When the amount of Na_2SO_4 decreased to 0.05 mol/L, the color removal increased to 89.5%.

3.7. Effect of SDBS on the color removal

SDBS is an anionic surfactant that is widely used as dyeing auxiliaries in the textile industry. In order to study its influence on the decolorization performance of DF_1, simulated dyeing wastewater containing SDBS (mass concentration of 100 mg/L) was prepared and treated by DF_1. The experimental results are shown in Fig. 9. It was obvious that color removal of wastewater was decreased when SDBS was added. It might be due to the fact that SDBS could interfere with the colloids and stabilize dye molecules in suspension, leading to the aggregation being more difficult. It can also be seen from Fig. 9 that under the lower dosage of decolorizer, the color removal of the SDBS wastewater decreased greatly. When the DF_1 dosage is 20 mg/L, the color removal of the SDBS wastewater decreased from 87.7% to 79.6%. With the increase in the DF_1 dosage, the color removal decrease range was less and less. When the DF_1 dosage is 40 mg/L, the color removal of the SDBS wastewater decreased slightly (98.8% to 97.7%). Under the condition of higher DF_1 dosage, the bridge adsorption, roll sweep net catching and other functions of DF_1 were enhanced, which make up for the negative factor of the SDBS.

3.8. IR spectra DF_1, X-3B and floc

To explore the interaction between dye molecules and DF_1, infrared spectra of DF_1, X-3B and floc were analyzed

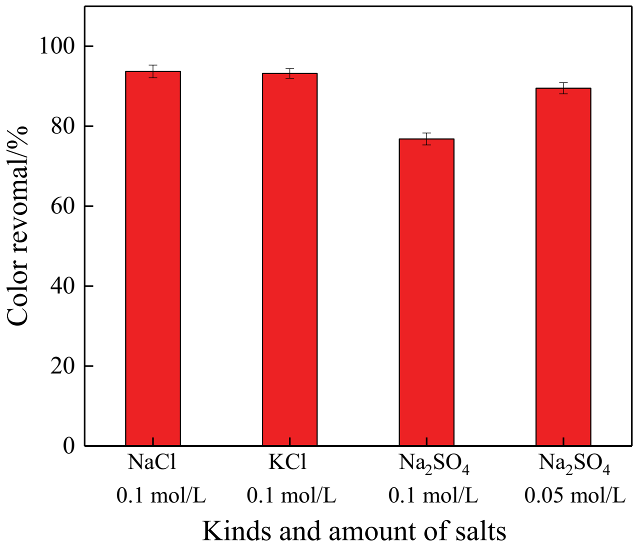

Fig. 8. Effect of amount and kinds of salt on the color removal. Dosage of DF_1: 35 mg/L; pH = 4; settling temperature 25°C; settling time 20 h.

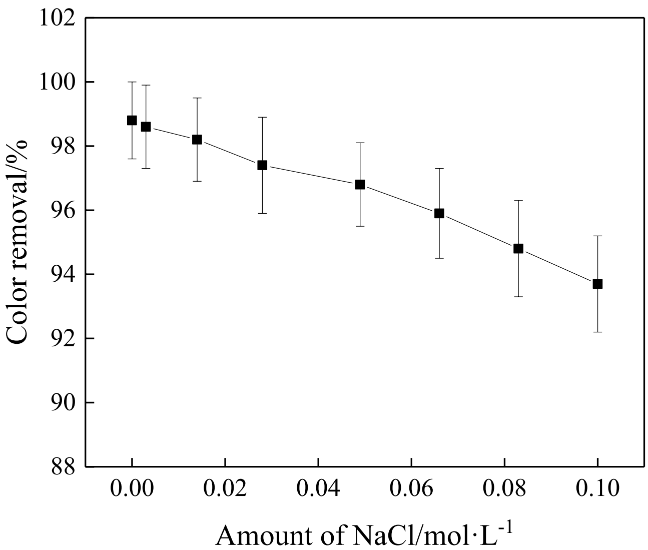

Fig. 7. Effect of amount of NaCl on the color removal. Dosage of DF_1: 35 mg/L; pH = 4; settling temperature 25°C; settling time 20 h.

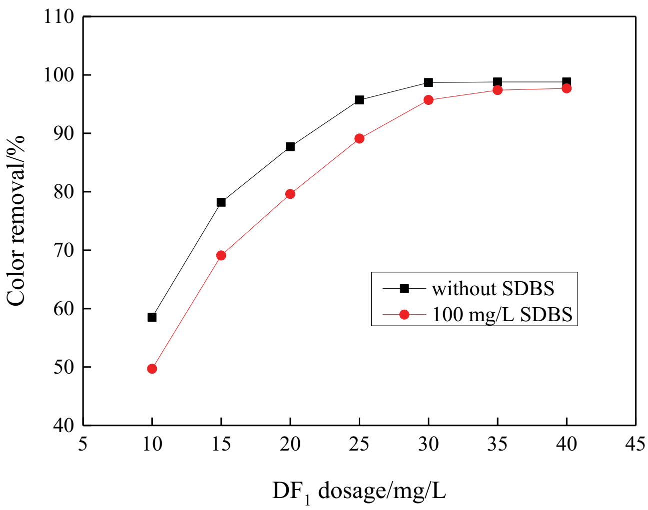

Fig. 9. Effect of SDBS on color removal. Dosage of DF_1: 35 mg/L; pH = 4; temperature 25°C; settling time 20 h.

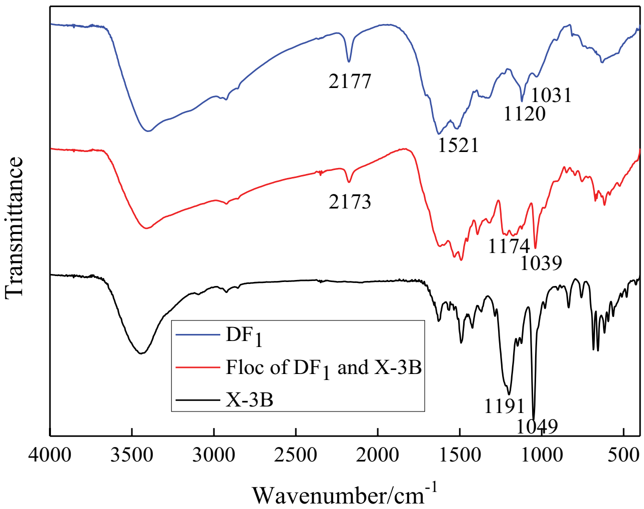

Fig. 10. IR spectra of DF_1, X-3B and floc.

and are shown in Fig. 10. The absorption peak at 2,177 cm^{-1} in the spectrum of DF_1 was attributed to the $C=N^+=C$ or C≡N band [21]. As the C≡N band usually had wide and strong peak shapes, the peak at 2,177 cm^{-1} was assigned to the $C=N^+=C$ band. The positive charge of $C=N^+=C$ is neutralized with dye molecules. The peak of $C=N^+=C$ shifted to 2,173 cm^{-1} in the spectrum of floc. The peaks at 1,521; 1,120 and 1,031 cm^{-1} in the spectrum of DF_1 were attributed to C=N, –C–NH–, and $–CH_2–O–CH_2–$ band, respectively. The above peaks were weakened in intensity or shifted in the spectrum of floc. This indicated the sharing of the groups in the reaction with X-3B. The bands at 1,193 and 1,049 cm^{-1} were assigned to a sulfonic acid group of the dye molecules in the spectrum of X-3B. The peaks were shifted to 1,173 and 1,039 cm^{-1} in the spectrum of floc, indicating the formation of $–NH_2^+SO^{3-}$, $=NH^+SO^{3-}$ [22,23].

Changes of the above peaks indicated that the amino of the flocculant reacts with the sulfonic acid group in the dye molecules. Then the dye molecules left easily from the water phase with DF_1 to form the thick and dense flocs. The settling speed was fast and the decolorization effect was obvious.

4. Conclusions

The removal efficiency of X-3B from simulated dyeing wastewater by DF_1 was studied. The DF_1 was effective in reducing the color of simulated dyeing wastewater. The pH value played a major role in all the parameters examined, as a result, the selection of appropriate pH was necessary. The optimum conditions, pH of 4, DF_1 dosage of 35 mg/L, settling temperature of 25°C, settling time of 20 h were determined to obtain a color removal of 98.8%. The addition of inorganic salt and SDBS reduced the decoloring performance of DF_1. Tests indicated that the existence of inorganic salt has little effect on the color removal of DF_1. DF_1 reacts with Reactive Brilliant Red X-3B was confirmed by the infrared spectra of samples. There are two flocculating actions for the excellent performance of DF_1. One is the charge neutralization from the $C=N^+=C$, which is the major factor. The other is the netting and sweeping function from its three-dimensional net structure, which improves the flocculating action.

Acknowledgments

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