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ARTICLE TYPE

Enhanced Decolorization of Dyes by a High Quality Copolymer Flocculant in Aqueous Solution

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A high quality copolymer (CATCS) was synthesized and applied for enhanced decolorization of dyes in aqueous solution based on starch and chitosan. The flocculant was characterized by scanning electron microscope and Fourier transform infrared spectrum. The effects of initial pH, dosage of CATCS, initial dye concentration, salt concentration and reaction time on decolorization ability of CATCS were studied.

10 Ultrahigh decolorization efficiency (97.1% ~ 99.7%) for the dye solutions was observed by CATCS. It was effective in a wide pH rang (2 to 10) and could stand a high salt concentration. The CATCS flocculant was ten times more efficient than commercial activated carbon in treatment of real dye wastewater. A decolorization efficiency of 98.3% for the real dye wastewater was reached by 0.34 g/L CATCS. Thermodynamics and kinetics of the decolorization process was investigated in details and the
15 decolorization mechanism of CATCS was determined. The enthalpy change was over 41 kJ/mol in the decolorization process of dye solutions by CATCS. The positive entropy change value for decolorization corresponded to a increase in the degree of freedom of the adsorbed species. The decolorization process was endothermic and interaction controlled with chemisorptions.

1 Introduction

20 Dye wastewater discharged from industries, such as dyestuff, textile, paper printing, cosmetic and leather industries would be harm to the environment and aquatic life if improperly disposed. Dyes in wastewater even though the amount of which is small, are highly visible and undesirable^{1,2}. If these highly colored and
25 undesirable components were discharged into the water bodies, the reoxygenation capacity of water would be damaged and sunlight would be cut off. Thus, the biological activity in aquatic environment would be destroyed^{3,4}. Moreover, some of these dyes are toxic and carcinogenic in nature and results in serious
30 health problems⁵. However, with increasing diversity of industrial products, the ingredients of dye wastewater have become more and more intricate in recent years, which make color removal one of the most difficult tasks^{6,7}.

Methods for processing dye wastewater involve physical, 35 chemical and biological approaches⁸⁻¹¹. Techniques such as adsorption, coagulation, chemical oxidation, electrolysis, and biological treatment, have been extensively applied in dye wastewater treatment. Among these techniques, the adsorption process is regarded as an attractive alternative treatment,
40 especially if the adsorbent is inexpensive and readily available^{12,13}. Many adsorbents such as activated carbon, peat, clay, silica, algae, fungi, etc, have been investigated to lower dye concentrations from aqueous solutions¹⁴⁻¹⁶. Nevertheless, most of them possess limitations such as hazardous by-products, high
45 cost or intensive energy requirements. Mover, It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by

conventional wastewater systems. Biological processes can overcome part of these disadvantages because it is low cost and
50 environmentally friendly, but it requires long hydraulic retention times and will form large amounts of solid residues^{17,18}. Therefore, color removal was extensively studied with physico-chemical methods as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation⁴. In terms of adsorption
55 processes, flocculant have been widely used to remove suspended particles and colored materials^{19,20}. However, some dyes such as reactive dyes cannot be easily removed by conventional flocculation and sedimentation process due to the poor biodegradability of the reactive dye. Moreover, application of
60 conventional flocculant may generate a significant amount of sludge or may easily cause secondary pollution due to excessive chemical usage^{7,21}. To improve the efficiency of the adsorption and sedimentation processes, it is essential to develop the more effective and cheaper flocculants with higher adsorption
65 capacities.

In the present study, we prepared a novel cationic co-polymer flocculant (CATCS) and applied it in decolorization for dyes in aqueous solutions. There are several reasons for carrying out this study. First, cationic polymeric flocculants can adsorb colored
70 matters through charge neutralization settle down subsequently. Second, the novel co-polymer flocculant (CATCS) was high positive charged and the unique strong bridging function of the flocculant CATCS could form a lots of dye-polymer-dye bridges, which is favourable to the adsorption and sedimentation
75 processes of dyes. Third, the co-polymer CATCS was first used for decolorization and presented ultrahigh capacities for dye

removal. Decolorization of four dye solutions and a real dye wastewater were investigated by CATCS. The effects of initial pH, dosage of CATCS, initial dye concentration, concentration of NaCl electrolyte and adsorption time on decolorization ability of CATCS were studied. The CATCS flocculant was ten times more efficient than commercial activated carbon in treatment of real dye wastewater. Thermodynamics and kinetics of the decolorization process was investigated in details and the decolorization mechanism of CATCS was determined.

2 Experimental section

2.1 Materials

Corn starch was obtained from Wenxing starch Co., Ltd., China; Chitosan with a molecular weight of 5.2×10^5 and deacetylation degree of 95% was purchased from Yuhuan Ocean Biochemical Ltd., China. Double distilled water was used throughout the experiments. Sodium hydroxide, potassium dichromate, ammonium ferrous sulfate and acetic acid were purchased from Shanghai Chemical Reagent Co., China. C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 were obtained from Taixing Dyestuff Co., Ltd., China and their chemical formula are shown in supporting information Figure S1.

2.2 Preparation of CATCS flocculant

The adsorbent CSTCS was prepared by microwave-assisted heating method as described in our previous work²² using starch and chitosan as raw materials. First, Cat St (cationic starch) was prepared by reacting starch with 2,3-epoxypropyl trimethylammonium chloride in presence of sodium hydroxide under the condition of microwave irradiation. The Cat St obtained was washed with 80% ethanol aqueous solution and then dried in a vacuum oven at 50 °C for 4 h. Then, 2 g Cat St was dispersed in the distilled water and 0.4 g chitosan was dissolved in 1% acetic acid solution, mixed the both together in a reactor, then 1.5 mL epichlorohydrin was added as a crosslinker. This mixture was reacted at 70 °C for 1.5 h and the flocculant was dispersed. Schematic representation for the synthesis of the co-polymer is represented in supporting information Scheme 1.

2.3 Characterization

Scanning electron microscopy (SEM) was investigated using a scanning electron microscope (JSM-6390). The scanning electron microscope was operated at an accelerating voltage of 20 kV. Samples were dispersed in an appropriate concentration and cast onto glass sheets at the room temperature and sputter-coated with gold. Fourier transform infrared spectra (FT-IR) were obtained on a NEXUS-870 FT-IR spectrometer. The spectra widths are typically over the range of 400-4000 1/cm. All the dried samples were mixed with KBr and then compressed into thin pellets.

2.4 Decolorization experiments for dye solution

Dye solution was prepared by dissolving dye in deionized water to a concentration of 30 mg/L, 50 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, 140 mg/L, 160 mg/L and 180 mg/L, respectively. Each dye solution was scanned from 300 to 800 nm and its maximum absorbency wavelength was determined (the maximum absorbency wavelength of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 is 401 nm, 552 nm, 510 nm and 570 nm, respectively.). Dye solution was inoculated in erlenmeyer flask to 50 mL, then the flocculant CATCS was added. Decolorization experiments were carried out

in a constant temperature shaker. Concentration of dye in solution was measured by a spectrophotometer²³ at maximum absorbency wavelength. Dye solution without CATCS served as control. Decolorization efficiency or removal rate of dye was calculated using the following equation:

$$\text{Decolorization efficiency (\%)} = 1 - \frac{C_b}{C_o} \times 100$$

Where C_o refers to the initial dye concentration, C_b refers to the dye concentration after adsorption.

The effects of initial pH, dosage of CATCS, initial dye concentration, concentration of NaCl and adsorption time on decolorization ability of CATCS were studied. The pH in these experiments was original pH of the dye solutions unless mentioned specifically.

2.5 Decolorization experiments for real dye wastewater

Decolorization of real dye wastewater was carried out following section 2.4 and chemical oxygen demand (COD) was measured by a oxidation-reduction titration method using $K_2Cr_2O_7$ as standard solution (an international standard method, reference number ISO 6060)²⁴. Due to the real dye wastewater was a complex system and the amount of dyes was hard to be determined, the decolorization efficiency was calculated using the following equation²⁵:

$$\text{Decolorization efficiency (\%)} = 1 - \frac{A_b}{A_o} \times 100$$

Where A_o is the absorbance of original dye waste water, A_b is the absorbance of dye wastewater after decolorization.

3 Results and discussion

3.1 Characterization of CATCS

Morphologies of the flocculant CATCS is characterized by scanning electron microscopy (SEM) and shown in Figure 1. It was obvious that the specific surface of CATCS was very roughly. The macromolecule chains of components in CATCS assembled together and had a structure of network, which could promote the adsorption and bridging performance as a flocculant for dye decolorization.

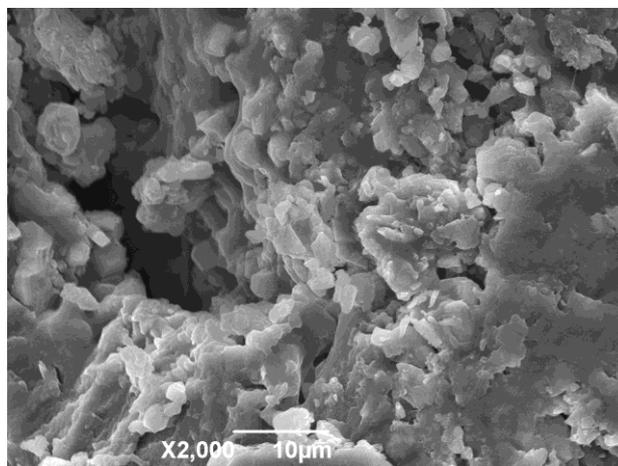


Figure 1. SEM photos of the CATCS flocculant.

The FT-IR spectra of CATCS in range of 4000 - 400 1/cm were taken to confirm the presence of functional groups. The broad

band (Figure 2) at 3411 $1/\text{cm}$ was due to the stretching mode of the O–H groups; 2927 $1/\text{cm}$ was due to the C–H stretching; An intense band at 1646 $1/\text{cm}$ was assigned to the first overtone of the O–H bending vibration. the peaks at 1489 $1/\text{cm}$ were due to the scanty amount of O=C–NH–. The bands at 1157 $1/\text{cm}$ were assigned to C–O stretching vibration. Two bands at 1082 $1/\text{cm}$ and 1018 $1/\text{cm}$ were attributed to $\text{CH}_2\text{--O--CH}_2$ stretching vibrations. The presence of an additional band at 1417 $1/\text{cm}$

assignable to the C–N stretching vibration, which was clear proof of the successful crosslinking reaction of macromolecular chain between chitosan and cationic starch. The adsorption of C–N–O (706 $1/\text{cm}$) and C–N–N (572 $1/\text{cm}$ and 562 $1/\text{cm}$) bands resulted from the crosslinking reaction were in the fingerprint area, which were difficult to distinguish one by one, because of combination between functional groups, some peaks were overlapped or enhanced.

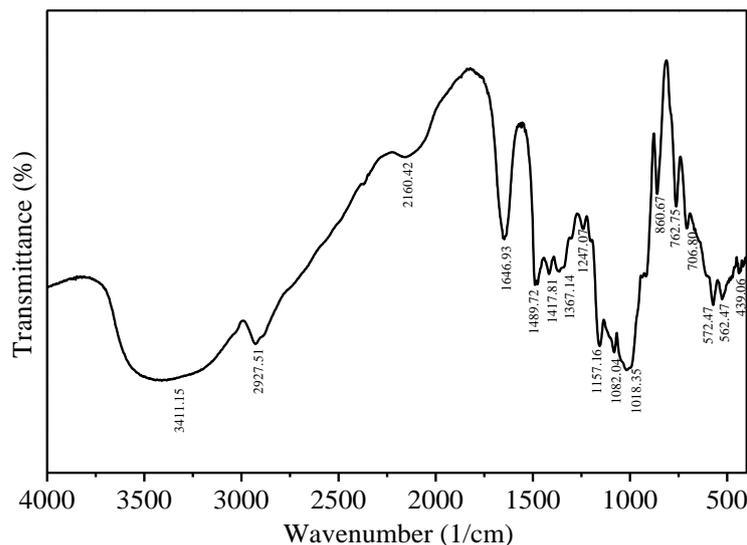


Figure 2. FT-IR spectrum of the CATCS flocculant.

3.2 Effect of CATCS dosage on decolorization efficiency

Solutions of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 were investigated in this section. The decolorization of the four dye solutions by different dosage of CATCS were carried out. The results (Figure 3) shown that dosage of CATCS had a significant effect on color removal. The decolorization efficiency of dye solutions increased sharply with the dosage of CATCS increased, then kept at a level after reaching peak value. The peak value of decolorization efficiency for the four dye solutions was 99.7%, 97.1%, 97.3% and 99.2%, respectively, and corresponding dosage of CATCS was 0.36, 0.32, 0.35 and 0.10 g/L, respectively.

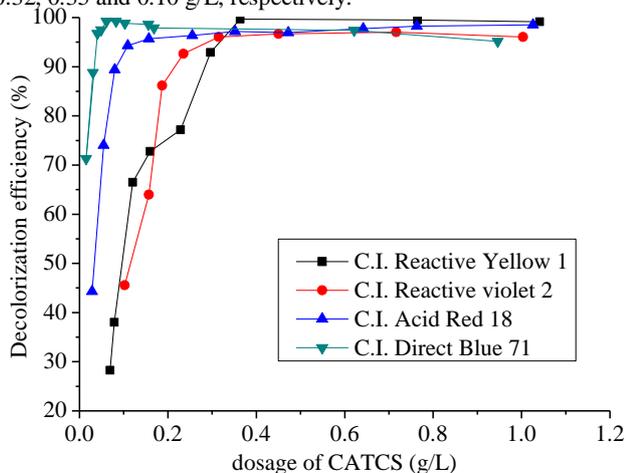


Figure 3. Effect of the dosage of CATCS on decolorization efficiency (dye concentration 100 mg/L, temperature 25 °C, reaction time 90 min).

3.3 Effect of reaction time on decolorization efficiency

The results described in Figure 4. It illustrated the effect of reaction time on the decolorization of the dye solutions by CATCS. More than 90% of the colour was removed within 60 min for all dye solutions and the decolorization reaction reached equilibrium in 70 min. The difference time to reach equilibrium may be explained by difference in monocular weight and chemical structure. The monocular weight order of the four dyes is C.I. Acid Red 18 (604.47) < C.I. Reactive Yellow 1 (714.29) < C.I. Reactive violet 2 (953.6) < C.I. Direct Blue 71 (1029.86). Generally, lower monocular weight results in a faster rate of diffusion of the adsorbate molecules for the smaller resistance force when they across the external boundary layer and the internal gap of the adsorbent. Meanwhile, the four dyes owing different structure and various active sites to be adsorbed on the adsorbent, thus the decolorization rate was C.I. Acid Red 18 > C.I. Reactive Yellow 1 > C.I. Direct Blue 71 > C.I. Reactive violet 2.

3.4 Effect of initial pH on decolorization efficiency

pH is a significant influence on both surface binding sites of adsorbents and aqueous chemistry²⁶. Figure 5 depicts the effect of pH on decolorization. It indicated that acidic and low alkaline pH was favorable for the removal of dyes by CATCS. The color removal of dye solutions were affected slightly by the pH ranging from 2 to 10. However, when pH was over 10, the decolorization efficiency decreased as pH increased dramatically. It affected decolorization efficiency significantly, as well as zeta potential. The decline of decolorization efficiency may due to the decrease of zeta potential of CATCS (see Figure S2). According to Chiou and Yoshida^{27, 28}, reduction of electrostatic attractions between negatively charged dye anions and positively charged adsorption

sites may cause decrease in dye adsorption. This explanation agrees with our data on pH effect. In low pH conditions, positive

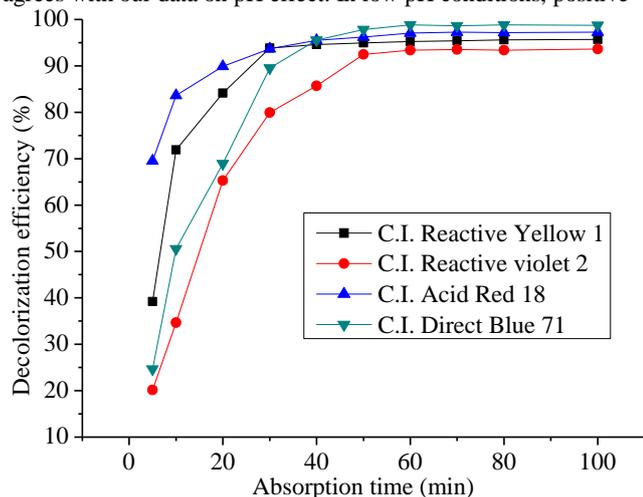


Figure 4. Effect of reaction time on decolorization efficiency (dye concentration 100 mg/L, temperature 25 °C).

charge dominates the surface of CATCS and strong electrostatic attraction exists between the positively charged surface of CATCS and negatively charged dyes. As the pH increased, the positive charge on CATCS reduced which made electrostatic attraction force decline and the existence of excess OH⁻ ions will compete with dye anions for the adsorption sites²⁹, therefore prevented the adsorption of dye anions on the adsorbent surface.

Though pH dependence showed the evidence of the electrostatic interaction, it should be noted the complex effect of pH on dissociation of dyes and protonate of the functional groups such as -OH, -SO₃, -NH₂, -NH, and -CO- in the molecule of dyes and CATCS. The complex and unpredictable effect of pH on color removal of C.I. Acid Red 18 by CATCS may be explained by this, because these functional groups were not only important for electrostatic interaction, but also played an indispensable role in forming dye-polymer-dye bridges.

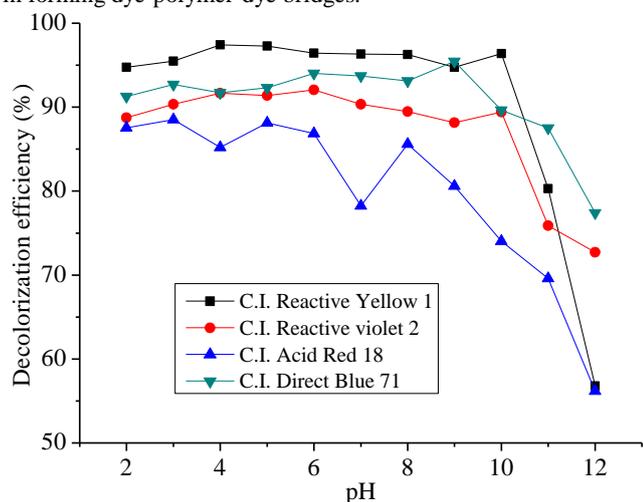


Figure 5. Effect of initial pH on the decolorization efficiency (dye concentration 100 mg/L, temperature 25 °C, adsorption time 90min.)

3.5 Effect of initial dye concentration

Adsorption capacity profiles of CATCS versus initial dye concentration are presented in Figure 6. It is observed that an increase in initial dye concentration led to increase in the amount of dye adsorbed on per unit weight of CATCS. Higher concentration resulted in higher driving force of the concentration gradient. This driving force accelerated the diffusion of dyes from the solution into the adsorbent and decreased the resistance to the uptake of solute from solution of dye²⁶. As the initial concentration increase from 30 to 180 mg/L, the amount of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 absorbed on the adsorbent increased from 354.2 to 873.9 mg/g, 193.7 to 903.6 mg/g, 384.3 to 1295.8 mg/g and 721.9 to 3005.6 mg/g, respectively.

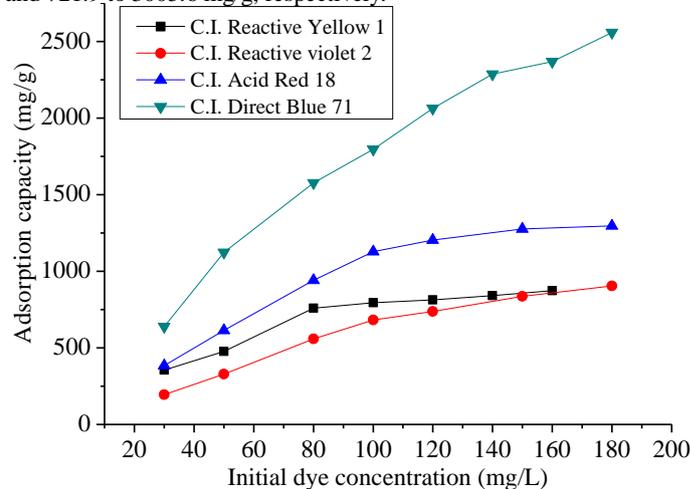


Figure 6. Effect of initial dye concentration (temperature 25 °C, adsorption time 90min, dosage of CATCS was 0.33, 0.23, 0.06, 0.04g/L for C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71, respectively.)

3.6 Effect of salt (NaCl) concentration on decolorization efficiency

The effect of salt (NaCl) are shown in Figure 7. The NaCl concentration used was in typical range of for salt tested³⁰. It shows that raise of NaCl resulted in an increase in decolorization efficiency when the concentration of NaCl ranged in 0 ~ 0.02 mol/L, but decreased when the concentration increased from 0.02 to 0.2 mol/L. The increase in decolorization efficiency after NaCl addition may be attributed to an increase in dimerization of reactive dyes in solution. Because cause intermolecular forces such as vander Waals forces, ionedipole forces and dipole-dipole forces occurring between adsorbent and adsorbate increased upon the addition of salt to the dye solution³¹⁻³³. The decrease of color removal by NaCl addition may be explained by effect of NaCl on zeta potential of CATCS flocculant (see Figure S3). The zeta potential declined with the increase of NaCl concentration, which reduced the electrostatic interactions between the adsorbent and dyes and therefore led to the decrease of decolorization efficiency. Moreover, the existence of Cl⁻ will compete with negative groups such as -SO₃⁻ for the electropositive adsorption sites and large amount of Na⁺ may hinder the ionization of -SO₃Na, thus, the adsorptive force between dyes and CATCS decline and decolorization efficiency decreased.

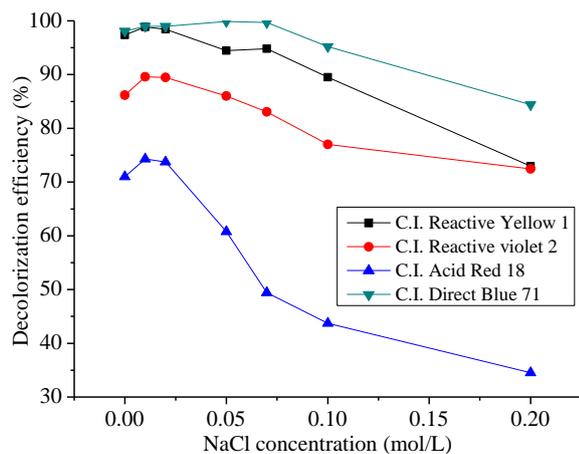


Figure 7. Effect of NaCl concentration on the decolorization efficiency (dye concentration 100 mg/L, temperature 25 °C, adsorption time 90 min).

3.7 Decolorization for real dye wastewater

The property of the real dye wastewater is shown in Table 1. The decolorization of real dye wastewater by CATCS was studied. Commercial activated carbon which has been widely used and investigated by a number of researchers as a relatively efficient adsorbent for color removal³¹ was studied as comparison.

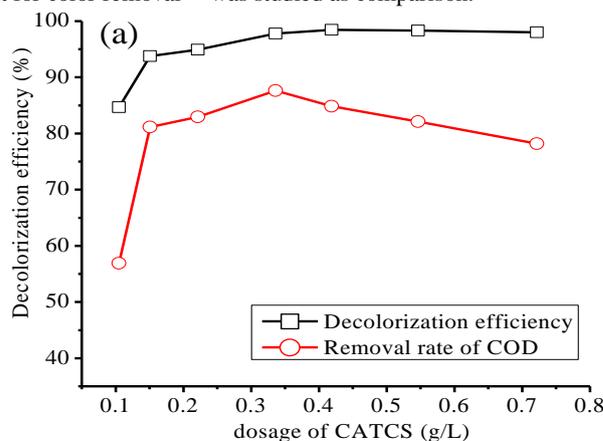


Table 1 Property of the real dye wastewater

pH	COD(mg/L)	Maximum adsorption wavelength (nm)	Absorbance	color
6.89	3307.58	612	0.385	atrovirens

According to Figure 8 (a), decolorization efficiency of the real dye wastewater increased with the dosage of CATCS increased until and reached a peak value of 98.3%. When dosage of CATCS was 0.15 g/L, the decolorization efficiency of the dye wastewater over 93%. The removal rate of COD increased as amount of CATCS increase from 0.10 g/L to 0.34 g/L and the peak value was 87.6%. When the amount of CATCS was over 0.42 g/L, the removal rate of COD declined with increase in dosage of CATCS. This may attribute to excessive CATCS dissolved in the solution, which contributed to the increase of COD. The experimental results by commercial activated carbon are shown in Figure 8 (b). The removal rate of COD increased with the increase of commercial activated carbon until it reached a peak value of 97.1% at the concentration of 11.5 g/L. To get a decolorization efficiency of 90%, over 2 g/L commercial activated carbon is needed which is ten times that of CATCS. Thus, the flocculant CATCS is ultrahigh efficient in decolorization for the real dye wastewater.

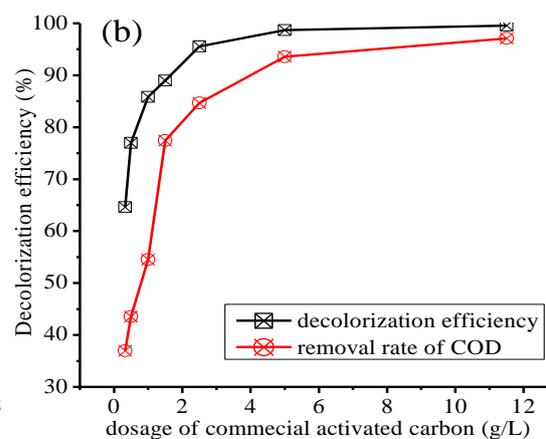


Figure 8. Decolorization efficiency of real dye wastewater by (a) CATCS flocculant and (b) commercial activated carbon (temperature 30 °C, decolorization time 90min).

3.8 Adsorption isotherm

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. The adsorption isotherms of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 by CATCS at various temperature are shown in Figure 9 (a), (b), (c) and (d), respectively.

Isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Redlich - Peterson isotherm models were tested for equilibrium description³⁴. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogenous sites within the adsorbent and has found successful application in many adsorption processes of monolayer adsorption³⁵. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{Q_L} + \left(\frac{1}{Q_L K_L}\right) \frac{1}{C_e} \quad (1)$$

Where q_e (mg/g) is the amount of dyes adsorbed on per unit weight of CATCS, C_e (mg/L) is the equilibrium concentration of dyes, Q_L (mg/L) is the maximum monolayer adsorption capability, K_L (L/mg) is a constant related to the free energy of adsorption.

The well-known Freundlich isotherm, which is often used for heterogeneous surface energy systems, can also be used to describe the equilibrium data. It states that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution is not constant at different concentrations³⁶. A linear form of the Freundlich equation is

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Where K_F (L/mg) and n (dimensionless) are constants related to adsorption capacity and intensity. The values of K_F and n can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$. The larger n value is, the more heterogeneous the system is.

The Dubinin-Radushkevich (D-R) isotherm is more general isotherm because it does not assume a homogeneous surface or constant adsorption potential³⁷. It was applied to distinguish between the physical and chemical adsorptions of dye. The linear form of D-R isotherm equation is

$$\ln q_e = \ln Q_D - \beta \varepsilon^2 \quad (3)$$

where β (mg^2/kJ^2) is a constant related to the mean free energy of adsorption per mole of the adsorbate. Q_D (mg/g) is the theoretical saturation capacity and ε is the Polanyi potential, which is equal to $\varepsilon = -RT \ln(1 + 1/C_e)$, where R ($R = 8.314 \text{ J/mol/K}$) is the gas constant and T (K) is the absolute temperature. Thus, by plotting $\ln q_e$ versus ε^2 , the value of Q_D is obtained from the intercept and the value of β from the slope.

Temkin isotherm⁴ considered the effects of some indirect adsorbate-adsorbate interactions on adsorption isotherms. This isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Temkin isotherm is represented by following equation:

$$q_e = \frac{RT}{b} \ln(K_i C_e) \quad (4)$$

It can be expressed in its linear form as:

$$q_e = \frac{RT}{b} \ln K_i + \frac{RT}{b} \ln C_e \quad (5)$$

$$q_e = B_1 \ln K_i + B_1 \ln C_e \quad (6)$$

Where $B_1 = \frac{RT}{b}$

The adsorption data can be analysed according to Eq. (6). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_i and B_1 . K_i is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption.

The Redlich-Peterson (R-P for short) isotherm equation is expressed as³⁸:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln b_R + \alpha \ln C_e \quad (7)$$

where K_R is R-P isotherm constant (L/mg), b_R is R-P isotherm constant (L/mg) and α is the exponent which lies between 1 and 0. Plotting the left-hand side of Eq. (7) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, K_R , α and b_R . Therefore, a minimization procedure is adopted to solve Eq. (7) by maximizing the correlation coefficient between the theoretical data for q_e predicted from Eq. (7) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with the solver add-in function of the Microsoft excel.

In order to compare the validity of the isotherm equations, a normalized standard deviation Δq_e (%) is calculated:

$$\Delta q_e (\%) = 100 \sqrt{\frac{\sum [(q_e - q_{e,cat}) / q_e]^2}{N - 1}} \quad (8)$$

where N is the number of data, q_e (mg/g) is the experimental value and $q_{e,cat}$ (mg/g) is the calculated value by isotherm equations. The isotherm parameters of adsorption of dyes onto CATCS under different temperature conditions calculated from plots of these linear isotherm equations are given in Table 2-5 and in supporting information Table S1-S4, respectively. Meanwhile, the experimental data have been analyzed by non-linear fitting of these isotherm equations. The results are shown in Table S5- S8 in supporting information. It is evident from these results that the surface of CATCS was made up of homogeneous and heterogeneous adsorption patches. For C.I. Reactive Yellow 1, Langmuir isotherm models fit best when the R^2 values were compared (Table 2). The value of Q_L was almost equal to the experimental equilibrium adsorption capacity (Figure 9a) and it increased as temperature increased. The linear correlation coefficients of Langmuir model was in a range of 0.981-0.998. Meanwhile, in comparison with the non-linear R^2 values (Table S5 in supporting information), Langmuir isotherm (R^2 value was in a range of 0.978-0.990) also represented a better fit of experimental data than other isotherm models. Moreover, Δq_e (%) values (Table 6) by Langmuir model were lowest and narrow distributed (3.99 % - 9.44 %), which also showed Langmuir isotherm models fit best. It indicated adsorption took place at specific homogenous sites within the adsorbent. It also showed that as the adsorption proceeded, the surface of adsorbent became crowded with adsorbed molecules of dye attached to its active spots and as a result it became increasingly difficult for free dye molecule in solution to find a vacant site. Moreover, it implied that the adsorbed dye molecules were not vertically oriented or there did not exist strong competition from the solvent³⁹. The results showed that the adsorption of C.I. Reactive violet 2 onto CATCS was best fitted to D-R isotherm model, as indicated by the R^2 and adsorption capacity values in Table 3. Further, Δq_e (%) values (Table 6) were much less than other isotherm models. The increasing value of the parameter β suggested that higher temperature benefited the removal of C.I. Reactive violet 2 by the flocculant CATCS. The results by non-linear method (Table S6 in supporting information) showed R^2 values of D-R isotherm model were over 0.980, indicating D-R isotherm model described the decolorization process of C.I. Reactive violet 2 very well. It paralleled the above results of the linear method. Comparing the results of Table 4, Table 5 and Table 6, it suggested that the experimental data collected for C.I. Acid Red 18 and C.I. Direct Blue 71 were both fitted very well by Freundlich isotherm, which exhibited the highest coefficient at various temperature (R^2 in range of 0.97 - 0.99) and lowest and narrow Δq_e (%) values (5.22% - 12.62% for C.I. Acid Red 18 and 2.14% - 4.57% for C.I. Direct Blue 71). To confirm the results, the experimental data

have been analyzed by non-linear fitting of these isotherm equations. According to Table S7 and Table S8, C.I. Acid Red 18 and C.I. Direct Blue 71 both followed Freundlich isotherm best (the non-linear R^2 value was in range of 0.970 – 0.998). It is the same as predicted by above linear analysis. Application of the Freundlich model confirmed that dye adsorption capacity by CATCS increased with the temperature, because the value of K_F increased with temperature raised. The value of n indicates the type of isotherm to be favorable ($n > 1$), unfavorable ($n < 1$), linear ($n = 1$). The high values of n ($n > 2$) at equilibrium at all the temperature conditions indicated that biosorption of the dyes

onto the CATCA flocculant were favorable processes. Temkin isotherm and the R-P isotherm constants and the correlation coefficients are listed in Table S1-S4 (in supporting information). It was observed that Temkin isotherm ($0.89 < R^2 < 0.93$) and the R-P isotherm ($0.88 < R^2 < 0.93$) did not adequately fit the experimental values. The low correlation coefficients indicated that decolorization data of the dyes was not well fitted to both Temkin isotherm and the R-P isotherm. The high and wide distributed Δq_e (%) values in Table 6 also showed both Temkin isotherm and the R-P isotherm did not fit the decolorization progress of the dyes.

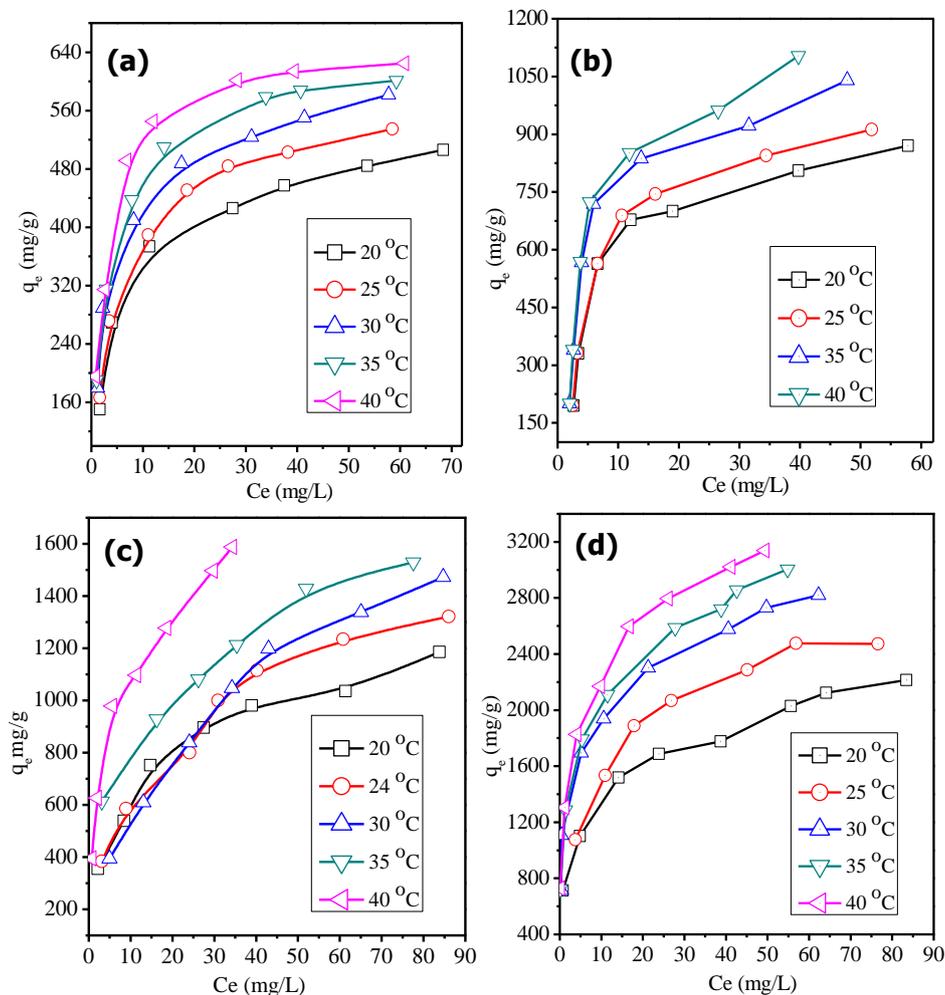


Figure 9. Adsorption isotherms of dye at various temperatures by CATCS. (a) C.I. Reactive Yellow 1, (b) C.I. Reactive violet 2, (c) C.I. Acid Red 18 and (d) C.I. Direct Blue 71.

Table 2. Linear fitting parameters of isotherms of C.I. Reactive Yellow 1 by CATCS at various temperatures.

T(K)	Langmuir			Freundlich			D-R isotherm		
	Q_L (mg/g)	K_L (/mg)	R^2	K_F (L/mg)	n	R^2	Q_D (mg/g)	β (mg^2/kJ^2)	R^2
293.15	500	0.426	0.998	155.21	3.35	0.923	434.89	0.82	0.901
298.15	555	0.429	0.997	166.09	3.07	0.940	460.77	0.81	0.903
303.15	588	0.623	0.987	202.86	3.59	0.936	503.16	1.03	0.922
308.15	588	0.739	0.992	219.14	3.62	0.936	533.68	0.36	0.844
313.15	625	0.842	0.981	239.85	3.70	0.903	544.46	0.26	0.838

Table 3. Linear fitting parameters of isotherms of C.I. Reactive violet 2 by CATCS at various temperatures.

T(K)	Langmuir			Freundlich			D-R isotherm		
	Q _L (mg/g)	K _L (L/mg)	R ²	K _F (L/mg)	n	R ²	Q _D (mg/g)	β (mg ² /kJ ²)	R ²
293.15	1250	0.081	0.909	189.43	2.39	0.813	778.68	2.28	0.985
298.15	1428	0.073	0.920	186.90	2.22	0.831	810.70	2.08	0.981
308.15	2000	0.067	0.890	235.31	2.34	0.778	930.94	1.44	0.990
313.15	2500	0.054	0.871	230.95	2.13	0.788	985.84	1.37	0.990

Table 4 Linear fitting parameters of isotherms of C.I. Acid Red 18 by CATCS at various temperatures.

T(K)	Langmuir			Freundlich			D-R isotherm		
	Q _L (mg/g)	K _L (L/mg)	R ²	K _F (L/mg)	n	R ²	Q _D (mg/g)	β (mg ² /kJ ²)	R ²
293.15	1250	0.24	0.963	172.14	2.15	0.985	979.1	5.09	0.738
298.15	1250	0.14	0.952	249.49	2.58	0.987	1017.5	2.20	0.728
303.15	1250	0.24	0.939	349.60	2.92	0.977	1157.9	1.17	0.726
308.15	1429	0.24	0.931	427.82	3.41	0.99	1233.9	1.42	0.737
313.15	1429	0.54	0.969	482.27	2.92	0.986	1204.2	0.22	0.782

Table 5. Linear fitting parameters of isotherms of C.I. Direct Blue 71 by CATCS at various temperatures.

T(K)	Langmuir			Freundlich			D-R isotherm		
	Q _L (mg/g)	K _L (L/mg)	R ²	K _F (L/mg)	n	R ²	Q _D (mg/g)	β (mg ² /kJ ²)	R ²
293.15	1825	0.80	0.894	764.79	4.12	0.995	1757.5	0.22	0.704
298.15	2500	0.19	0.969	778.06	3.53	0.974	2164.6	2.12	0.794
303.15	2242	1.24	0.920	804.40	3.78	0.988	2155.5	0.10	0.708
308.15	2500	4	0.898	1163.98	4.18	0.998	2296.8	0.045	0.723
313.15	2500	2	0.907	1223.54	3.97	0.995	2375.8	0.045	0.731

Table 6. Normalized standard deviation Δq_e (%) of the linear isotherm equations.

dyes	T (K)	Langmuir Δq _e (%)	Freundlich Δq _e (%)	D-R isotherm Δq _e (%)	Tempkin Δq _e (%)	R-P isotherm Δq _e (%)
C.I.Reactive yellow 1	293.15	9.23	12.89	14.46	26.94	19.74
	298.15	9.39	13.42	14.18	15.72	18.63
	303.15	9.44	10.22	28.17	17.23	18.27
	308.15	7.91	13.86	20.27	20.99	18.06
	313.15	3.99	15.61	21.63	18.80	18.96
C.I. Reactive violet 2	288.15	19.12	25.03	6.54	21.5	23.96
	293.15	18.31	24.69	7.71	19.75	23.42
	298.15	26.84	30.17	7.78	27.17	30.53
	308.15	26.57	30.57	6.34	26.82	34.38
C.I. Acid Red 18	288.15	29.38	9.16	41.84	17.29	19.04
	293.15	13.16	5.22	25.76	28.57	13.77
	298.15	40.20	12.62	45.35	23.05	35.8
	308.15	29.38	9.16	31.85	20.49	25.05
	318.15	11.97	5.89	25.5	14.33	37.9
C.I. Direct Blue 71	288.15	16.35	2.65	49.23	7.29	19.04
	298.15	5.55	4.57	31.51	28.57	13.77
	303.15	17.14	2.49	50.72	23.05	35.84
	308.15	21.7	2.14	43.46	20.49	25.05
	313.15	21.05	3.7	42.85	14.33	9.04

3.9 Thermodynamic parameters

The thermodynamic equilibrium constant K_a for the sorption reaction has thermodynamic properties. Its dependence with temperature can be used to estimate thermodynamic parameters, such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). These parameters were determined by using following equations (Eq. (9) and Eq. (10)).

$$\Delta G = -RT \ln K_a \quad (9)$$

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

The constant K_a was determined by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating zero q_e . The plot of $\ln K_a$ as a function of $1/T$ yields a straight line from which ΔH and ΔS were calculated from the slope and intercept, respectively. R in Eq (10) is universal gas constant, 8.314 (J/mol/K). The results are given in

Table 7.

The overall free energy change (ΔG) during the adsorption process was negative (Table 7) for the experimental range of temperatures corresponding to a spontaneous process without requiring large activation energy. The positive value (over 40 kJ/mol) of ΔH indicated that the decolorization process by CATCS was endothermic. Generally, an adsorption process is considered as physical if absolute magnitude $\Delta H < 25$ kJ/mol and as chemical when $\Delta H > 40$ kJ/mol⁴¹. Therefore, chemical reaction was involved in the decolorization process. The entropy change (ΔS) in adsorption process of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71, was 224.48 J/(mol K), 206.55 J/(mol K), 347.27 J/(mol K), respectively. The positive entropy change (ΔS) value for adsorption corresponded to an increase in the degree of freedom of the adsorbed species.

Table 7 Thermodynamic parameters for C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 by CATCS

Dyes	T(K)	K_a (L/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
C.I. Reactive Yellow 1	293.15	308.68	-13.97		
	298.15	380.51	-14.73		
	303.15	732.60	-16.63	52.17	224.48
	308.15	980.24	-17.65		
	313.15	1057.12	-18.13		
C.I. Reactive violet 2	293.15	2530.57	-19.10		
	298.15	3743.96	-20.39	41.34	206.55
	308.15	6043.27	-22.31		
	313.15	7700.96	-23.10		
C.I. Acid Red 18	293.15	110.73	-11.47		
	298.15	222.87	-13.40		
	303.15	469.84	-15.51	90.18	347.27
	308.15	612.96	-16.44		
C.I. Direct Blue 71	313.15	1277.30	-18.63		
	293.15	1596.55	-17.98		
	298.15	1752.33	-18.51		
	303.15	5864.66	-21.87	89.35	365.03
	308.15	10231.23	-23.66		
	313.15	12298.1	-24.52		

3.10 Adsorption kinetics

The kinetics of adsorption is one of the most important characteristics in defining the efficiency of adsorption. It

describes the rate of uptake of dye onto CATCS flocculent and the rate controls the equilibrium time. Figure 10 illustrates plots of the amount of dyes adsorption versus reaction time for different temperatures. The reaction in 60 min was rapid at a

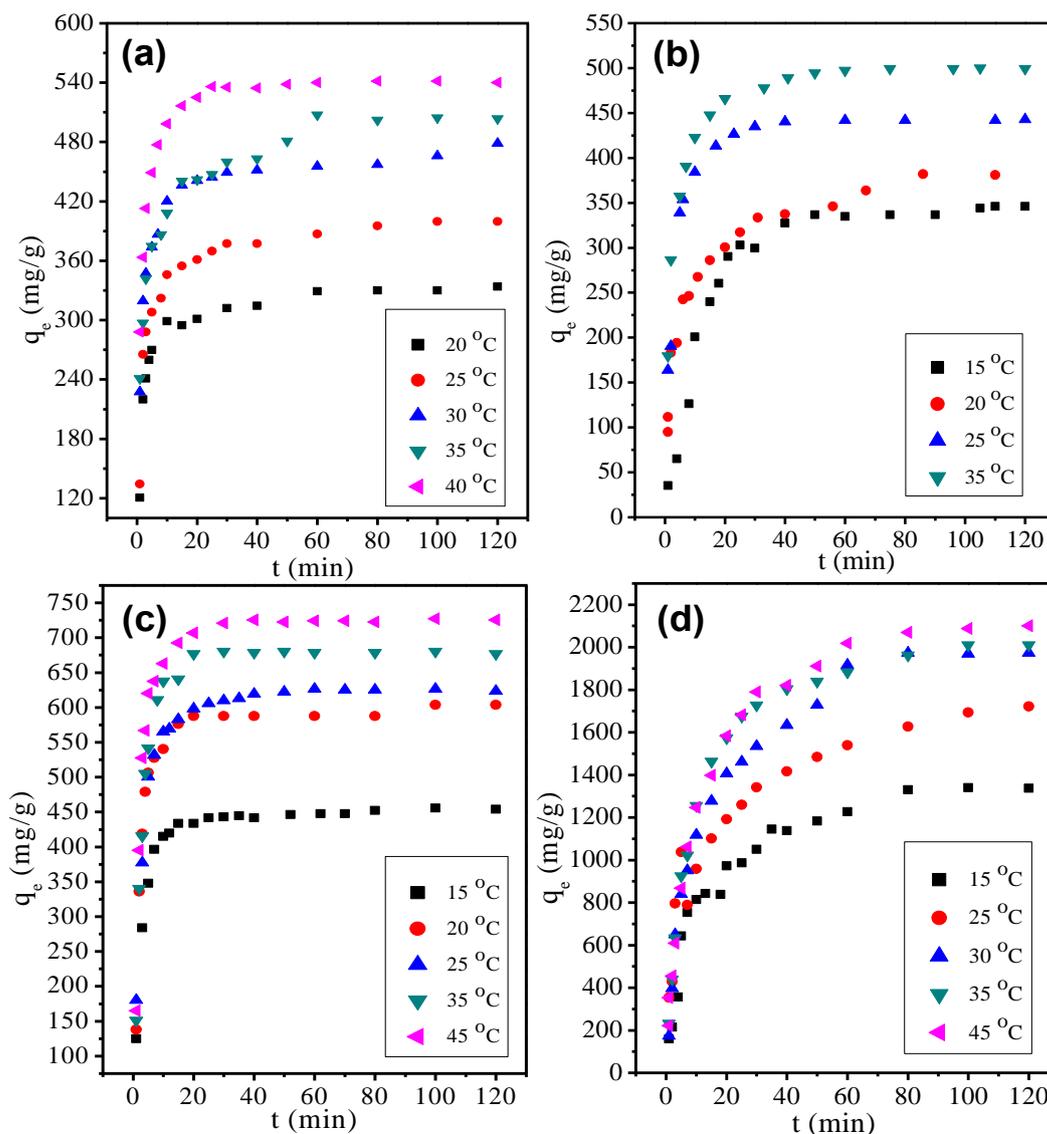


Figure 10. Kinetic curves of dyes flocculated by CATCS, (a) C.I. Reactive Yellow 1, (b) C.I. Reactive violet 2, (c) C.I. Acid Red 18 and (d) C.I. Direct Blue 7.

higher temperature and all the curves finally reached the equilibrium in 80 min. In order to determine the adsorption kinetics of dyes onto the flocculant, a kinetic investigation was carried out with the pseudo-first-equation, pseudo-second-order equation and the Elovich Equation. The conformity between experimental data and the equations predicted values was expressed by the correlation coefficient (R^2) as shown in Table 7 and in supporting information Table S5.

The pseudo-first-order rate model of Lagergren³⁵ is based on solid capacity and as described by Eq. (11):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant.

The pseudo-second-order equation can be represented as Eq.(12).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where k_2 (g/mg.min) is the second order rate constant and q_t is the amount adsorbed at time t . Constant k_1 , k_2 and corresponding correlation coefficients (R^2) have been calculated and summarized in Table 8.

The Elovich Equation is generally expressed as¹⁵:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (13)$$

To simplify the Elovich, $\alpha\beta > t$ and by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, Eq (13) becomes

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (14)$$

The plot of q_t versus $\ln t$ should yield a linear relationship with a slope $1/\beta$ and an intercept of $1/\beta \ln(\alpha\beta)$. The α initial adsorption rate (mg/(g min)) and β desorption constant (g/mg)

values, the correlation coefficients R^2 were given in supporting information Table S9.

The R^2 values showed that the adsorption of dyes onto CATCS didn't follow the pseudo-first-order kinetics ($0.56 < R^2 < 0.95$).

5 Meanwhile, it was observed that the Elovich kinetic model did not adequately fit the experimental values ($0.7691 < R^2 < 0.9244$). However, the pseudo second-order kinetic model, described all the adsorption processes very well according to the correlation coefficients, of which the correlation coefficients are
10 generally above 0.990. The calculated q_e value agreed very well with the experimental value (Figure 10) also confirmed that the adsorption phenomena followed the pseudo-first-order kinetics. The well fitting of the pseudo-second-order equation suggested the adsorption process was interaction controlled with
15 chemisorptions, which involves valance force through sharing or exchange of electrons between the adsorbent and dyes^{42, 43}.

Physical and chemical are two main types of adsorption. The insight of activation energy may give an idea about the type of adsorption. Generally, the activation energy in a physical
20 adsorption is below 4.2 kJ/mol and chemical adsorption involves

forces much stronger than that of physical adsorption⁴⁴. Activation energy of dyes absorbed onto CATCS was determined using the Arrhenius equation Eq. (15):⁴⁵

$$\ln k = \frac{-E_a}{RT} + \ln A \quad (15)$$

25 Where E_a is activation energy, R the gas constant (8.314 J/(mol K)), T is the temperature in Kelvin, k is adsorption rate constant and A is frequency factor. The value of E_a can be determined from the slope of $\ln k$ versus $1/T$ plot.

The adsorption rate constants according to pseudo-second order
30 kinetic model at various temperatures were used to calculate the activation energy value. The activation energy (E_a) of the adsorption process of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 onto CATCS was calculated as -27.74 kJ/mol, -51.71 kJ/mol, -19.3 kJ/mol and -
35 14.31 kJ/mol, respectively, which also indicated the existence of chemisorptions mechanism.

Table 8 Kinetic parameters for C.I. Reactive yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 by CATCS.

dyes	pseudo-first-order equation				pseudo-second-order equation			
	T K	k_1 min ⁻¹	q_e mg/g	R^2	$k_2 (\times 10^3)$ g/(mg min)	q_e mg/g	R^2	
C.I. Reactive yellow 1	293.15	0.037	333.97	0.8632	1.91	333.3	0.9998	
	298.15	0.042	399.77	0.8961	1.30	400	0.9998	
	303.15	0.073	478.79	0.5671	1.34	476.2	0.9995	
	308.15	0.055	503.69	0.9404	0.77	526.3	0.9992	
	313.15	0.10	540.01	0.6204	2.16	555.6	1.0000	
C.I. Reactive violet 2	288.15	0.044	345.92	0.9039	0.26	384.6	0.9924	
	293.15	0.037	381.97	0.9246	0.59	384.6	0.9977	
	298.15	0.057	443.00	0.8248	1.38	454.6	0.9999	
	308.15	0.053	500.10	0.9086	1.08	500	0.9999	
C.I. Acid Red 18	288.15	0.039	455.56	0.8326	1.49	460.2	0.9998	
	293.15	0.037	603.67	0.5674	1.13	608.6	0.9996	
	298.15	0.048	626.66	0.7738	1.11	635.7	0.9998	
	308.15	0.049	680.6	0.5335	1.05	690.1	0.9995	
C.I. Direct Blue 71	318.15	0.048	727.29	0.7534	1.06	736.9	0.9997	
	288.15	0.057	1339.5	0.9338	0.072	1428.6	0.9966	
	298.15	0.034	1721.5	0.9703	0.082	1666.7	0.995	
	303.15	0.056	1973.4	0.9583	0.056	2000	0.9974	
	308.15	0.043	2010.7	0.959	0.074	2000	0.9998	
	313.15	0.049	2100.2	0.9899	0.044	2500	0.9993	

4 Conclusion

40 A high quality copolymer flocculant CATCS was synthesized and applied in enhanced decolorization for four dye solutions and a real dye wastewater. The flocculant was characterized by SEM and FT-IR spectra. The decolorization efficiency was found to depend on initial pH, dosage of CATCS, initial dye concentration,

45 salt (NaCl) concentration and reaction time. The flocculant CATCS had very high capacities to remove dyes. Ultrahigh decolorization efficiency (97.1% ~ 99.7%) for the dye solutions was observed by CATCS. It was effective in a wide pH rang (2 to 10) and could stand a high salt concentration. A decolorization
50 efficiency of 98.3% for the real dye wastewater was reached by 0.34 g/L CATCS. To remove 90% dyes in real dye wastewater,

the required amount of CATCS was less than one tenth that of commercial activated carbon. Thermodynamics and kinetics of decolorization process was investigated in details and the decolorization mechanism was determined. Thermodynamics study showed Langmuir isotherm described the decolorization process of C.I. Reactive Yellow 1 well and D-R isotherm model fitted C.I. Reactive violet 2 very well. C.I. Acid Red 18 and C.I. Direct Blue 71 both followed Freundlich isotherm (R^2 value was in range of 0.97–0.99). The overall negative free energy change (ΔG) during the adsorption process indicated it was a spontaneous process. The enthalpy change was over 41 kJ/mol in decolorization process of dye solutions by CATCS indicating that dyes adsorption onto the flocculant CATCS is an endothermic reaction and chemical reaction was involved in. The entropy change in adsorption process of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71, was 224.48 J/(mol K), 206.55 J/(mol K), 347.27 J/(mol K), respectively. The removal of dyes by CATCS followed the pseudo second-order kinetic. It suggested the decolorization process was interaction controlled with chemisorptions, which involves valance force through sharing or exchange of electrons between the adsorbent and dyes. The activation energy (E_a) of the adsorption process of C.I. Reactive Yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 onto CATCS was -27.74 kJ/mol, -51.71 kJ/mol, -19.3 kJ/mol and -14.31 kJ/mol, respectively. Charge neutralization mechanism and strong adsorption dye-CATCS-dye bridging interaction contributed to the high quality decolorization of the flocculant CATCS.

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Notes and references

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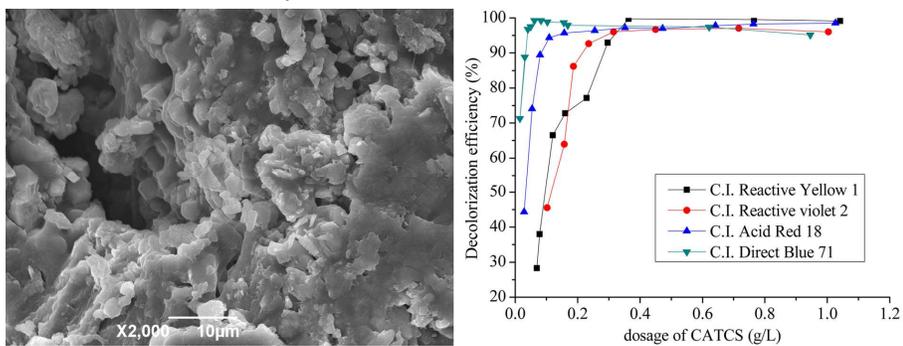
† Electronic Supplementary Information (ESI) available: [Scheme 1. Schematic representation for the synthesis of CATCS; Figure S1. Chemical formula of dyes used in this study; Figure S2. pH effect on zeta potential of CATCS; Figure S3. Effect of NaCl on zeta potential of CATCS; Table S1. Linear fitting parameters of isotherms of C.I. Reactive Yellow 1 by CATCS at various temperatures; Table S2. Linear fitting parameters of isotherms of C.I. Reactive violet 2 by CATCS at various temperatures; Table S3. f Linear fitting parameters of isotherms of C.I. Acid Red 18 by CATCS at various temperatures; Table S4. Linear fitting parameters of isotherms of C.I. Direct Blue 71 by CATCS at various temperatures; Table S5. Non-linear fitting parameters of isotherms of C.I. Reactive Yellow 1 by CATCS at various temperatures. Table S6. Non-linear fitting parameters of isotherms of C.I. Reactive violet 2 by CATCS at various temperatures. Table S7. Non-linear fitting parameters of isotherms of C.I. Acid Red 18 by CATCS at various temperatures. Table S8. Non-linear fitting parameters of isotherms of C.I. Direct Blue 71 by CATCS at various temperatures; Table S9. Kinetic parameters for C.I.

Reactive yellow 1, C.I. Reactive violet 2, C.I. Acid Red 18 and C.I. Direct Blue 71 by CATCS.]. See DOI:10.1039/b000000x/

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Table of contents entry



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