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RESEARCH ARTICLE

The kinetics study of the reduction of Fast Green dye with cetylpyridinum chloride as cationic surfactant

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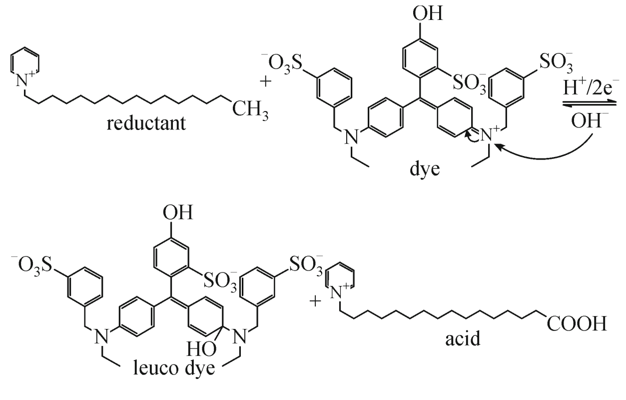
The kinetics of the reaction of Fast Green dye (FG) with cetylpyridinum chloride was studied in alkaline medium by UV-Visible spectrophotometer. Reduction of Fast Green dye was carried out by varying the fast green dye concentration, cetylpyridinum chloride concentration and concentration of sodium hydroxide. In the present study the reduction of dye was carried out in order to reduce the color content. The interaction of dye was carried out with reducing analyte (cetylpyridinum chloride). The rate of the reaction was determined by varying the above parameters at different temperatures. It was observed that the reduction followed pseudo first-order kinetics with respect to dye, surfactant, OH$^-$ ion concentration according to the following reaction pathway.



The mechanism for the photo bleaching of the dye has been proposed and well confirmed by the data simulation procedure. The activation parameters of the reaction like entropy of activation (ΔS) and free energy of activation (ΔG) showed the extremely solvated states of transient complex which was less disorderly arranged than the oxidized form of dye, whereas E_a values reflects a high amount of energy required for the reduction of dye with cetylpyridinum chloride.

Keywords Fast Green, cetylpyridinum chloride, OH$^-$ ions, decoloration, cationic surfactant

1 Introduction

Dyes are the most visible sign of water pollution as they are hazardous to health because of the toxicity of their degradation products [1,2]. The synthetic dyes are widely used in textile, food, plastic and biomedical industries. Textile manufacturers generate about 3.84×10^5 tons of waste each year [3]. There is no single conventional technology is established to remove all the classes of dyes [4,5]. The effect of various solvents on the color intensity of dyes and its decolorization in the presence of reductant was studied by many workers [6–10].

The interaction of surfactant and dye is very significant in dyeing processes such as printing ink, textile dyeing and photography [11]. These interactions also help to understand the chemical equilibra, mechanisms, kinetics of surfactants-sensitized color and fluorescence reactions [12]. In textile finishing procedures surfactants are widely used as auxiliaries [13]. The interaction of surfactants play an important role for achieving level of dyeing.

The structure of surfactant contains both hydrophilic and hydrophobic parts and the solution properties of dye lime absorption spectrum were changed by the addition of least amount of surfactant with alternating the environment of the solution. When the charge of the dye is opposite to the charge of the surfactant, attractive forces arise between the surfactant and the dye molecules and cause complex formation in the solution [14–22].

Redox reaction occurs in the presence of reactants sodium hydroxide (NaOH), Fast Green dyes (FG) and cetylpyridinum chloride (CPCl). In alkaline solution the generated hydroxyl radicals (·OH) will attack the target contaminant and degrade it. After the attack of OH$^-$ ion into the dye, the dye was reduced and decolorized to produce lecuo dye molecule and the surfactant got oxidized and produced oxalic acid [24]. A tentative mechanism for photobleaching of the dye is proposed. The hydroxyl radical is a powerful oxidant that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water [25,26]. Then it is able to degrade the pollutants effectively [27–29].

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2 Materials and methods

2.1 Chemicals

Cetylpyridinum chloride, sodium hydroxide (NaOH) and Fast Green dye.

2.2 Instrument

UV-visible spectrophotometer (Shimadzu 1601).

2.3 Methods

A solution of cetylpyridinum chloride, sodium hydroxide (NaOH) and Fast Green dye were prepared by dissolving the known amount in double distilled conductivity water. Kinetic study was made by preparing different sets of reaction mixtures in which one reactant was diversed while the other two were kept constant at given concentrations. Three reacting species were mixed together and the progress of the (inlet) reaction was monitored by recording the change in optical density during the reaction at $\lambda_{\max} = 612$ nm on a UV-visible spectrophotometer (Shimadzu 1601). Various operational and activation parameters were evaluated in order to find out the order of reaction by measuring the particular reaction rate at various temperatures and different ionic strengths [23]. Percentage removal of the dye was also calculated by using Eq. (1)

$$\text{Decrease in concentration } (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f represent the initial and final concentration respectively. The UV-visible spectrophotometer (Shimadzu 1601) was used throughout the experiments for the measurement of absorbance.

3 Results and discussion

3.1 Effects of dye

The photochemical degradation of Fast Green dye was observed at $\lambda_{\max} = 625$ nm spectroscopally. The concentration of NaOH and CPCl were kept constant and the concentrations of dye were varied from 2.0×10^{-5} to 6.0×10^{-5} $\text{mol}\cdot\text{dm}^{-3}$. The results for a typical run are given in Table 1 and shown in Fig. 1. The results show that the optical density of FG solution was decreased with the increase in the irradiation time, indicating that FG is consumed on irradiation. The plot of log $\frac{A_o - A_\alpha}{A_t - A_\alpha}$ against time is presented in Fig. 2. They are linear and follow the pseudo-first order kinetics. The rate constant was determined by the graphical method. It was obtained, $k = (1.73 \pm 0.092) \times 10^{-3}\ \text{s}^{-1}$, which shows that the dye gets reduced in the presence of reductant in alkaline medium and the reductant gets oxidized. The acidic dye will react with OH^- ion and produce colorless compounds which are called leuco dye after the reaction of OH^- ion, The electrons are localized in one of the above rings. Because of this the dye is not able to produce color and form colorless compound which are called leuco dye.

3.2 Effect of sodium hydroxide (NaOH) concentration

The kinetic investigations were carried out by changing the optical density of Fast Green dye at 625 nm wavelength. The concentration of dye and CPCl were kept constant and the concentration of NaOH was varied from $(2.0–6.0)\times 10^{-1}\text{mol}\cdot\text{dm}^{-3}$. The results for a typical run are given in Table 1 and shown in Fig. 3. The results show that the rate of reduction of dye increases with the increase in concentration

Table 1 First order kinetics of dye at different operational parameters

FG^+/ (10^5 mol·dm^{-3})	NaOH /(10^1 mol·dm^{-3})	Cetylpyridinum chloride / (10^2 mol·dm^{-3})	(dx/dt) / (10^5 mol·dm^{-3}·s^{-1})	K/ (10^3 s^{-1})	Absorption /%
2.0	2.0	2.0	−7.40	1.73	84.35
3.0	2.0	2.0	−1.20	1.61	86.19
4.0	2.0	2.0	−1.33	1.64	88.43
5.0	2.0	2.0	−1.88	1.52	90.31
6.0	2.0	2.0	−2.17	1.52	94.52
2.0	3.0	2.0	−7.16	3.00	55.33
2.0	4.0	2.0	−6.23	3.37	53.18
2.0	5.0	2.0	−7.22	4.16	51.78
2.0	6.0	2.0	−7.13	2.66	58.98
2.0	2.0	3.0	−5.26	7.71	67.74
2.0	2.0	4.0	−4.61	8.21	56.02
2.0	2.0	5.0	−3.81	7.42	55.07
2.0	2.0	6.0	−7.40	8.34	78.22

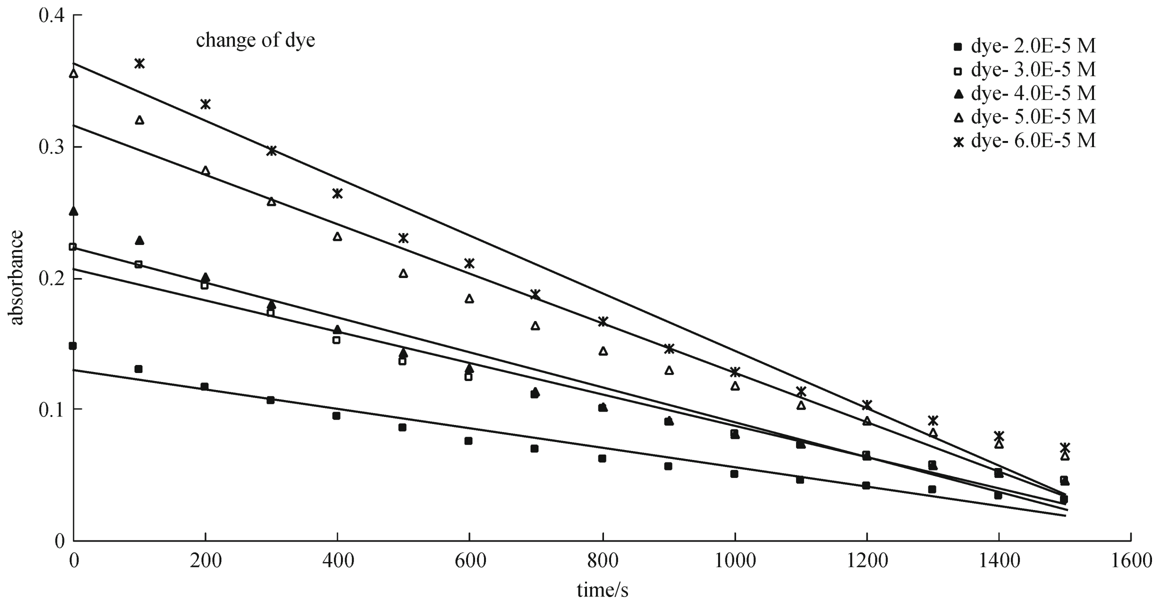

Figure 1 A plot of absorbance vs. time of reduction of FG with different concentration of FG [(2.00–6.00)$\times 10^{-5}$ mol·dm^{-3}].

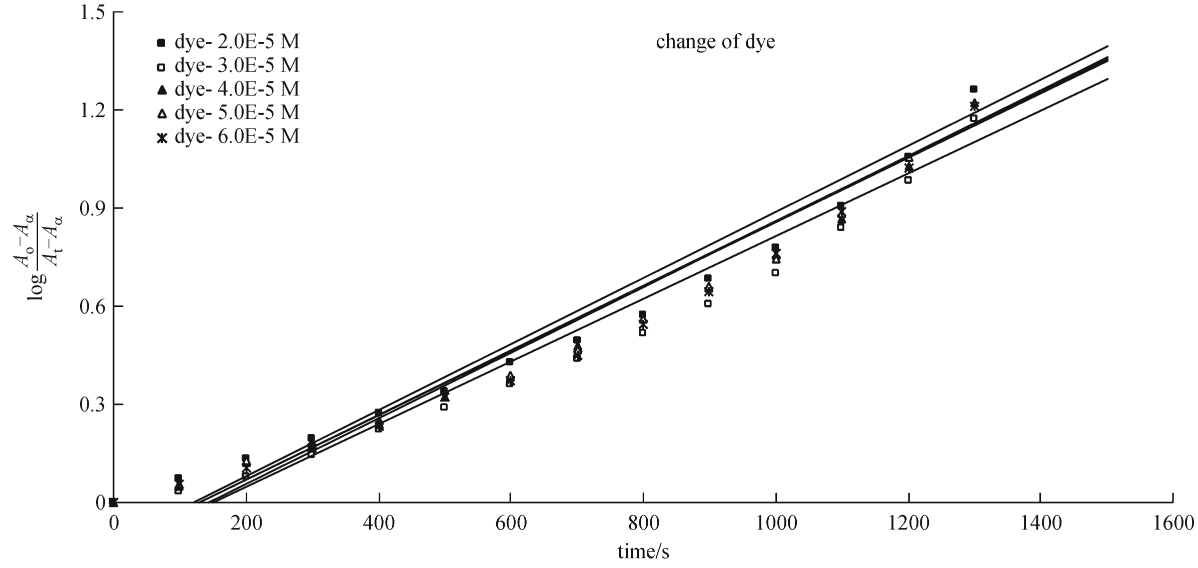

Figure 2 A plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ vs. time of reduction of FG with different concentration of FG [(2.00–6.00)$\times 10^{-5}$ mol·dm^{-3}].

of Sodium hydroxide. The plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ against time represented in Fig. 4 is linear and follows the pseudo-first order kinetics, and the rate constant was obtained, $k = (3.00 \pm 0.082) \times 10^{-3}$ s^{-1}.

3.3 Effect of reductant

Kinetic investigations were carried out by changing the optical density of Fast Green dye at 625 nm wavelength. The concentration of NaOH and dye were kept constant and the concentration of CPCl were varied from (2.0–6.0)$\times 10^{-2}$ mol ·dm^{-3}. The results for a typical run are given in Table 1 and shown in Fig. 5. The results show that the rate of reduction of dye got increased with the increase in the concentration of reductant. The plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ against time shown in Fig. 6 are linear and follow the pseudo-first order kinetics. The rate constant determined by the linear regression method was $k = (2.66 \pm 0.082) \times 10^{-3}$ s^{-1}.

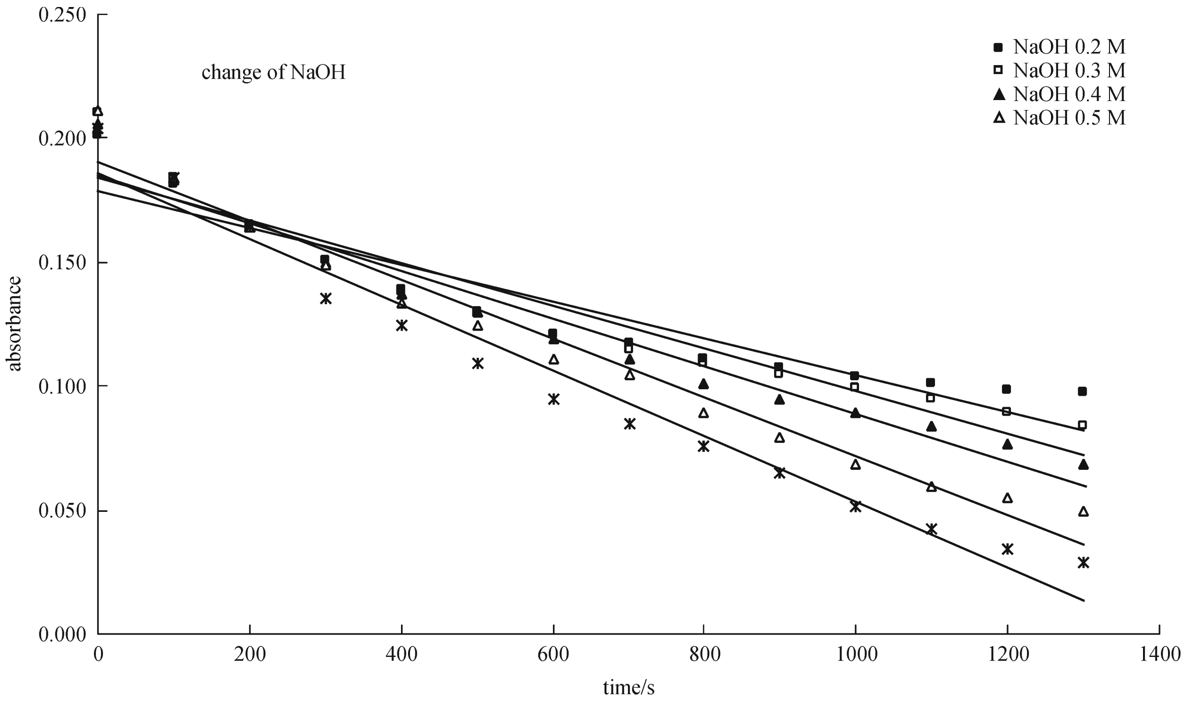

Figure 3 A plot of absorbance vs. time of reduction of FG with different concentration of NaOH [$(2.0\text{–}6.0)\times10^{-1}$ mol·dm^{-3}].

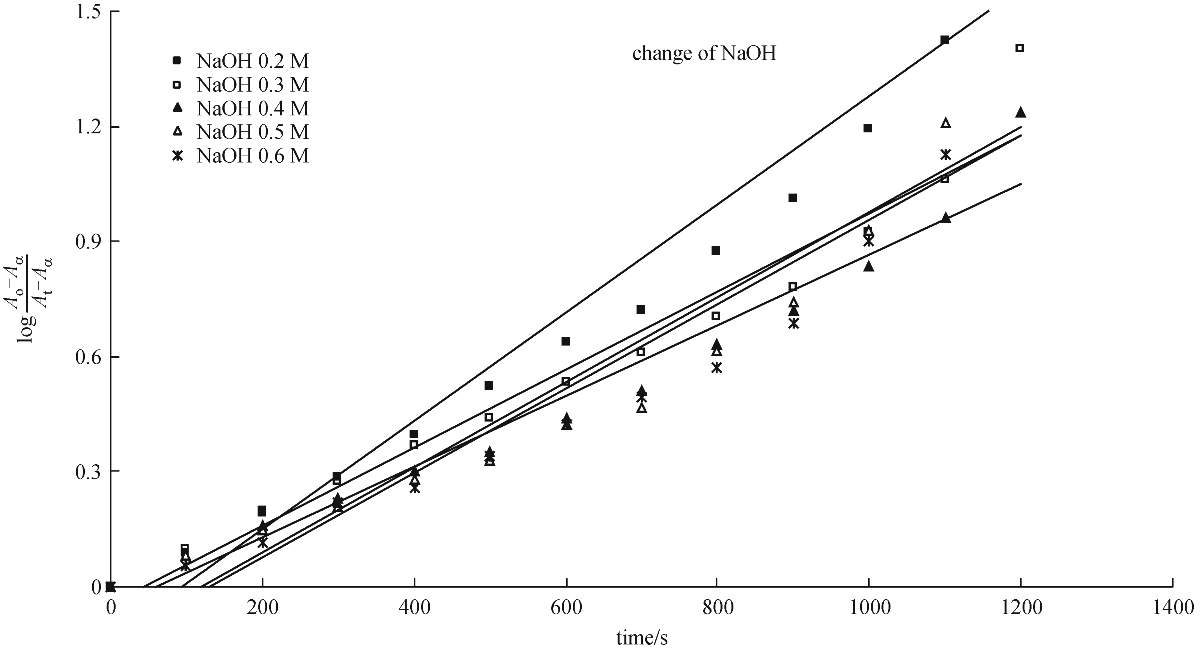

Figure 4 A plot of $\log\frac{A_o - A_\alpha}{A_t - A_\alpha}$ vs. time of reduction of FG with different concentration of NaOH [$(2.0\text{–}6.0)\times10^{-1}$mol·dm^{-3}].

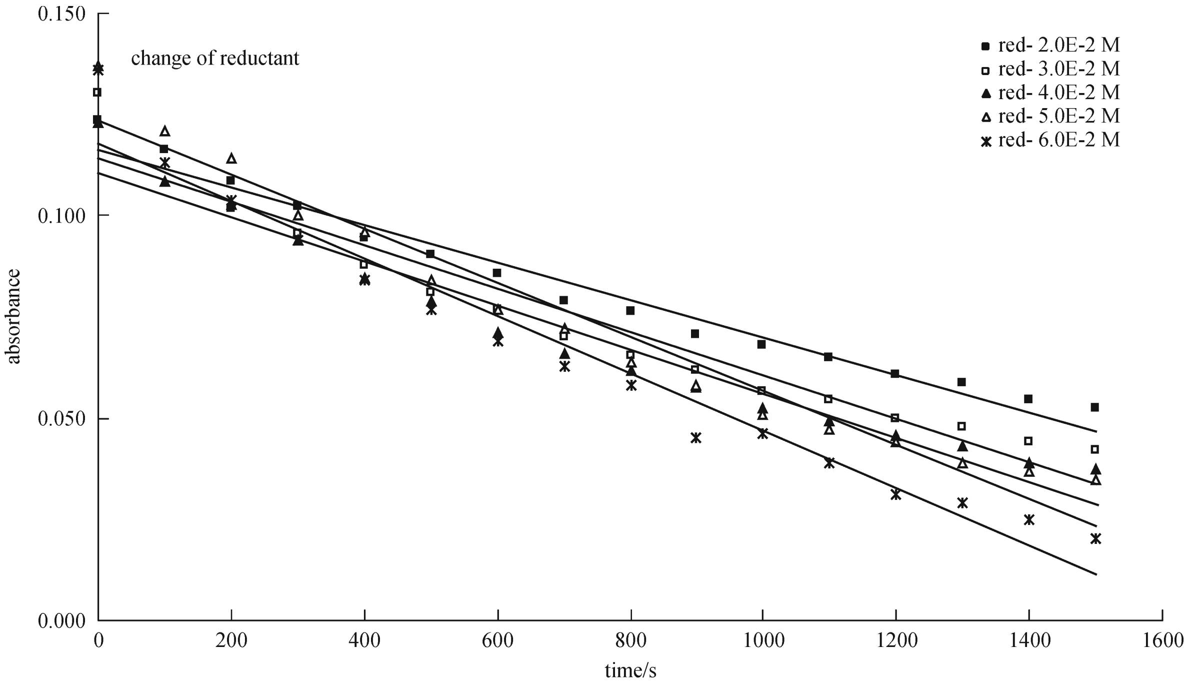

Figure 5 A plot of absorbance vs. time of reduction of FG with different concentrations of cetylpyridinum chloride [(2.0–6.0)× 10^{-2} mol·dm^{-3}].

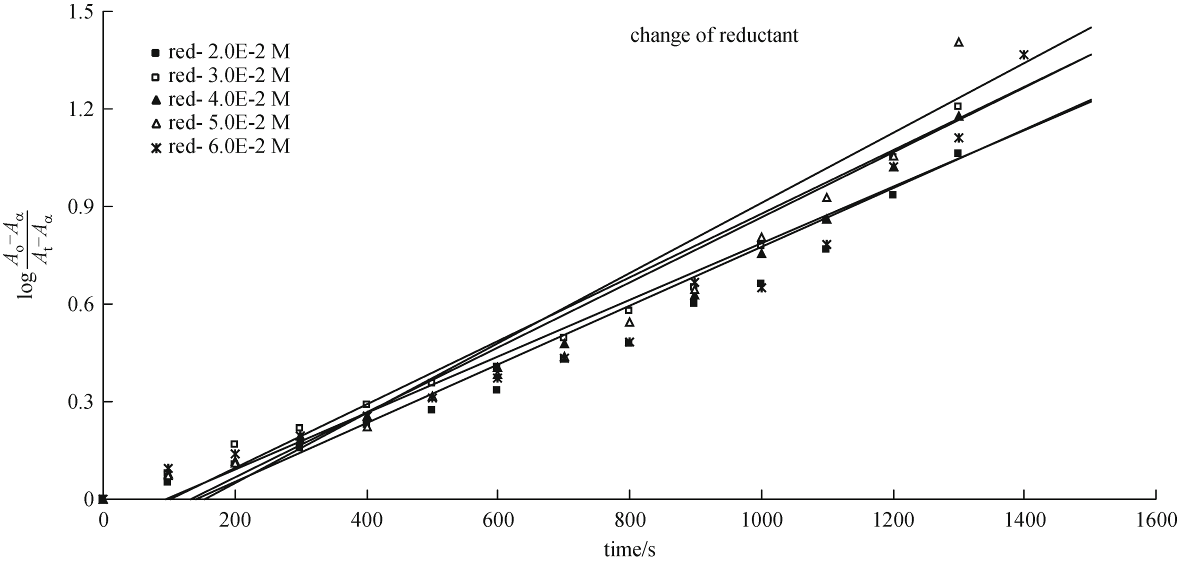

Figure 6 A plot of $\log\frac{A_o-A_\alpha}{A_t-A_\alpha}$ vs. time of reduction of FG with different concentrations of cetylpyridinum chloride [(2.0–6.0)× 10^{-2} mol·dm^{-3}].

3.4 Effect of temperature

The effect of temperature for the reduction of Fast Green dye is shown in Figs. 7 and 8 and Table 2. The results show that decolorization of dye got increased with the increase in temperature. Thermodynamic activation parameters like E_a is 10.52 kJ/mol which supports that the initial reaction proceeded slowly. The value of entropy of activation (ΔS) for the reduction of Fast Green with cetylpyridinum chloride, 223.76 J/(mol·K), showed a highly solvated state of activated complex, which indicates an increase in the degree of freedom due to the formation of an activation complex. And this increase results in an extensive reorientation of solvent molecules and the solvent molecules release OH^- ion which

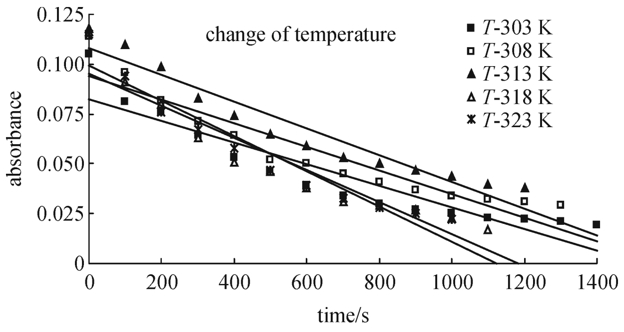

Figure 7 A plot of absorbance vs. time of reduction of Fast Green with different temperature (303–323 K)

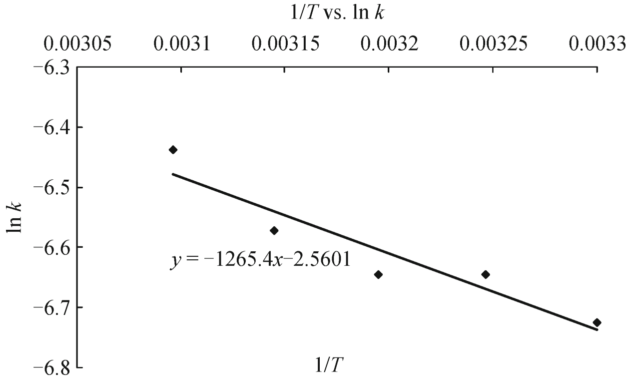

Figure 8 Effect of temperature on photodecoloration of Fast Green with cetylpyridinum chloride

Table 2 Influence of temperature on rate constant of photochemical reduction of dye.

Temperature /K	$-\nu$ (dx/dt) /(10^5 mol·dm^{-3}·s^{-1})	Apparent rate constant (k_{app}) /10^3	Specific rate constant (k_{sp}) /(10^3·s^{-1})	Decoloration/%	Decoloration at fixed time/%
303	5	1.2	1.2	81.90	76.19
308	6	1.0	1.3	74.56	70.15
313	7	1.0	13	67.79	62.71
318	8	1.6	1.4	85.34	80.17
323	9	1.7	1.6	80.86	80.86

Th = 5.54×10^{-5} mol·dm^{-3};
Concentration of reductant = 1.43×10^{-2} mol·dm^{-3};
Concentration of NaOH = 1.27 mol·dm^{-3}.

causes the reduction of dye. The fairly high values of enthalpy of activation ΔH, free energy of activation ΔG and energy of activation E_a indicate that the transition state is highly saturated. It also reveals that the rate determining state is less orderly oriented relative to the reactants. The value of ΔH = 8.00 J shows that enthalpy was not the driving force for the formation of complex, while the entropy value ΔS = 223.76 J/(mol·K) was responsible for the formation of the complex that involves one charged species and solvent molecules for the reduction of dye. The values of other parameters like ΔH and ΔG also support the reduction kinetics of dye. The value of ΔG is 7.58 kJ/mol and the results are summarize in Table 3.

3.5 Mechanism

It was observed that the basic medium facilitates the attack of OH^-, so the rate constant was increased. It was observed that at low pH and higher concentrations of reductant the change in absorbance is not observed and having a constant rate at pH 6, while at higher pH change in rate constant was observed, as reported in Tables 2 and 3. The OH^- nucleophile having large size and high charge density makes it less solvated, hence it is more reactive. The reduction of dye was followed by the attack of OH^- on the N^+ atom of dye. The values of rate constant increased with the increase of the concentration of sodium hydroxide and also with the increase of the reductant concentration. The increase of reaction rate between dye and reductant with the increase in sodium hydroxide concentration shows that in the polar solvent the formation of activated complex is more favorable. The mechanism between dye and reductant can be written as

$$H_2O + h\overset{*}{\nu} \rightarrow \overset{*}{O}H + H^+$$

Table 3 Thermodynamic activation parameters of reduction of Fast Green with cetylpyridinum chloride

Temperature /K	E_a/(kJ·mol^{-1})	ΔH/(kJ·mol^{-1})	$-\Delta S$/(J·mol^{-1}·K^{-1})	ΔG/(kJ·mol^{-1})
303	10.52	8.00	223.76	7.58
308		7.95	223.90	7.69
313		7.91	224.03	7.80
318		7.87	224.16	7.91
323		7.83	224.29	8.02

$$\mathrm{H_2O} + h\overset{*}{\nu} \rightarrow \overset{*}{\mathrm{O}}\mathrm{H} + \mathrm{H}^+$$

$$\cdot\mathrm{OH} + \mathrm{dye} \rightarrow \mathrm{dye\ intermediate}$$

$$\cdot\mathrm{OH} + \mathrm{dye\ intermediate} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{MP}$$

$$(\mathrm{MP} = \mathrm{mineralization\ products})$$

Reaction mechanism involves the interaction between the protonated form of Fast Green and cetylpyridinum chloride molecule [14,22]. Since OH^- is present in plentiful amount and oxidation of cetylpyridinum chloride may take place at the same time. Protonation of FG may also take place and leuco FG was formed.

$$D \overset{k_1}{\longleftrightarrow} \mathrm{FG}$$

$$K_1 = \frac{\mathrm{FG}}{D}$$

where K_1 is the equilibrium constant between the two forms of Fast Green. Protonation of the dye may take place in the solvent.

$$\mathrm{FG} + \mathrm{H}^+ \overset{k_2}{\longleftrightarrow} \mathrm{FG}^+ \tag{2}$$

Protonated form of the Fast Green may interact with the reductant molecule to form leuco dye

$$\mathrm{FG}^+ + \mathrm{RH} \overset{k_3}{\longleftrightarrow} \mathrm{FG} + \mathrm{R}^- \tag{3}$$

$$k_3 = \frac{(\mathrm{FG})R^-}{(\mathrm{FG}^+)RH}$$

$$RH + \mathrm{FG}^+ \xrightarrow[\mathrm{Fast}]{} \mathrm{FG} + R + \mathrm{H}^+ \tag{4}$$

The rate law for the reaction

$$\frac{-\mathrm{d(FG)}}{\mathrm{d}t} = r = k_2(\mathrm{FG}^+)RH \tag{5}$$

For the triplet transition state of the dye

$$(\mathrm{FG})_T = D + M + \mathrm{FG} \tag{6}$$

$$(\mathrm{FG})_T = k_1 + M + \mathrm{FG}^+ \tag{7}$$

or in the form of protonated state FG^+ of the dye or

$$(\mathrm{FG})_T = \mathrm{FG} + \frac{\mathrm{FG}^+}{k_2\mathrm{H}^+} + \frac{\mathrm{FG}^+}{k_1k_3\mathrm{H}^+} \tag{8}$$

or

$$(\mathrm{FG})_T = T\mathrm{H}^+\frac{1 + k_1 + k_3k_1\mathrm{H}^+}{k_3k_1\mathrm{H}^+} \tag{9}$$

The protonated form of the dye will take place.

$$\mathrm{FG}^+ = \frac{k_1k_3\mathrm{H}^+(\mathrm{FG})_T}{1 + k_1 + k_1k_3\mathrm{H}^+} \tag{10}$$

The rate law for the above reaction after substitution of FG^+ in Eq. (5) is shown as

$$\frac{-\mathrm{d(FG)}}{\mathrm{d}t} = \frac{k_2k_1k_3\mathrm{H}^+(\mathrm{FG})_T(RH)}{1 + k_1 + k_1k_3\mathrm{H}^+}$$

The rate law shows the first order dependence on RH and fractional order with respect to H^+, which also verified the first order kinetics. This shows the dependence on the concentration of cetylpyridinum chloride. The above equation can be written for the dimeric form of Fast Green in solution:

$$K'' = \frac{k_2k_1k_3\mathrm{H}^+}{1 + k_1 + k_3k_1\mathrm{H}^+}$$

where

$$K'' = \frac{\frac{-\mathrm{d(FG)}_T}{\mathrm{d}t}}{(RH)(\mathrm{FG})_T}$$

or inverse of the equation

$$\frac{1}{K''} = \frac{1}{\mathrm{H}^+}\cdot\frac{1}{k_2k_1k_3} + \frac{1}{k_2k_3} + \frac{1}{k_2}$$

The plot $1/k$ vs. $1/H^+$ was found to be linear with a positive slope having R^2 and the value of $1/k_2 = s^{-1}$, showing the first order kinetics dependence on reductant concentration.

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