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Kinetic and thermodynamic studies for oxidation of rosaniline hydrochloride dye by persulfate in ambient temperatures

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ABSTRACT

The kinetics of the oxidative decolorization of rosaniline hydrochloride by potassium persulfate was studied spectrophotometrically over a pH range of 3.5–9.5 at 30–45˚C. The reaction was of second order with respect to dye and half order with respect to persulfate. Increasing the pH of the medium increased the rate of decolorization drastically in alkaline medium. Activation parameters were found to be 62.11 kJ mol^{-1}, 90.33 kJ mol^{-1}, and −98.44 J K^{-1} mol^{-1}, with respect to activation energy, free energy, and entropy, respectively. The addition of sodium chloride and sodium sulfate had no effect on the rate of decolorization.

Keywords: Kinetics; Mechanism; Degradation; Rosaniline; Persulfate

1. Introduction

Textile dyeing process is a significant source of environmental pollution. It produces large amounts of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Many physical and chemical processes such as adsorption [1], electrochemical [2], and photocatalytic [3] are used to remove the dyes from wastewater. Chemical oxidative processes seem to provide an opportunity for future use in industrial wastewater. Examples of such potentially effective chemical oxidants for oxidative processes include Fenton reagent [4–5], $KBrO_3$ [6–7], and $KClO_3$ [8].

Recently, the use of persulfate has received attention as an alternative oxidant in the chemical oxidation of pollutants [9–12]. Persulfate (KPS) is one of the strongest oxidants known in aqueous solution and has higher potential ($E_o = 2.01$ V) than H_2O_2 ($E_o = 1.76$ V) [13], Table 1. It offers some advantages over other oxidants as a solid chemical at ambient temperature with ease of storage and transport, high stability, high aqueous solubility, and relatively low cost. The reaction of persulfate with organic pollutants is generally slow at ambient temperature and activation of persulfate is necessary to accelerate the process. Upon activation, persulfate can produce highly oxidative species, sulfate-free radicals, which are capable of degrading numerous organic pollutants and dyes [9–12]. Persulfate can be activated to generate sulfate-free radicals by thermal [9], transition metal complex [14], electrochemical [15], photochemical [16], microwave [17–18], and nanoparticles [19] techniques.

Basic dyes such as crystal violet, malachite green, and rosaniline hydrochloride (RAH), are used in cotton tannin, mordant printing, and dyeing in textile. Rosaniline is a triphenylmethane dye with an amino group on each phenyl ring. Its structure is easily reducible where the chromophore group is destroyed and the compound loses its color. The redox reaction of RAH by sulfite and nitrite ions are reported earlier [20–22].

This work focused on the kinetic study of oxidation of RAH with persulfate at ambient temperature

Table 1
Standard potentials of some oxidants used in advanced chemical oxidation [13]

Oxidant	BrO_3^-/Br_2	ClO_3^-/Cl_2	IO_3^-/I_2	H_2O_2/H_2O	O_3/O_2	$S_2O_8{}^{2-}/SO_4^{2-}$
E_o/V	1.51	1.46	1.19	1.76	2.07	2.01

spectrophotometrically. The effects of pH, dye, persulfate concentrations, and temperature were studied. Also, the mechanism as well as rate law equation for the reaction was proposed.

2. Experimental

2.1. Reagents and materials

All chemicals were of pure grade and were used without further purification. The chemical structure of RAH (BDH, molecular weight = 337.8, $\lambda_{max} = 540$ nm) is given in Fig. 1. NaCl and Na_2SO_4 were purchased from Merck. All solutions were prepared using bi-distilled water. Stock solutions of dye (1 mM) and $K_2S_2O_8$ (100 mM) were prepared. The pH is adjusted by HCl and NaOH solutions.

2.2. Kinetic experiments

All kinetic measurements were carried out using a Cecil 292 spectrophotometer equipped with a water-jacketed cell holder. The reactants (dye and $K_2S_2O_8$ + NaOH) were thermostated for 15 min, then mixed thoroughly and quickly transferred to an absorption cell. The progress of the reaction was monitored at 540 nm. The pH of the reaction was adjusted using Griffin pH-meter fitted with a combined glass-calomel electrode.

3. Results and discussion

Kinetic study for oxidation of RAH by KPS was followed at $\lambda_{max} = 540$ nm. Fig. 2 shows the decrease in absorbance with time. Fig. 2 also shows that about 85% of rosaniline is removed in 60 min at a temperature of 25°C.

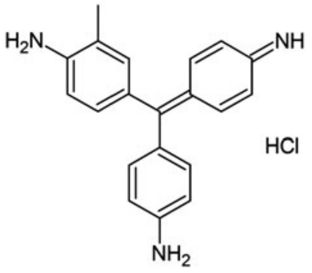

Fig. 1. Chemical structure of RAH.

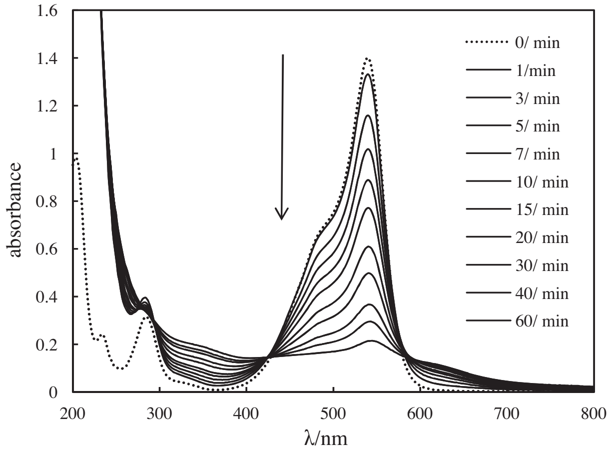

Fig. 2. UV–visible spectra of RAH after the addition of persulfate at different time intervals. [RAH] = 2×10^{-5} mol dm^{-3}, $[K_2S_2O_8] = 2 \times 10^{-2}$ mol dm^{-3}, pH 9, $T = 25$°C.

3.1. Kinetic study

In the present study, zero-, first-, and second-order reaction kinetics were used to study the decolorization kinetics of RAH by KPS. The individual expressions are represented below

$$C_t = C_o - k_o t \tag{1}$$

$$\ln C_t = -k_1 t + \ln C_o \tag{2}$$

$$1/C_t = 1/C_o + k_2 t \tag{3}$$

where C_t is the concentration of RAH at reaction time t.

Regression analysis based on the zero-, first-, and second-order reaction kinetics for the decolorization of RAH by KPS was conducted and the results are shown in Fig. 3. Since plotting of A_t vs. time (Fig. 3(a)) did not give straight line, zero-order kinetics is excluded. Comparing the regression coefficients (R^2)

obtained from Fig. 3(b) and (c), it can be seen that R^2 of the second-order reaction kinetics (Fig. 3(c)) was 0.9995, which is obviously much better than that based on the first-order reaction kinetics ($R^2 = 0.9394$). The results indicated that the decolorization kinetics of RAH followed the second-order kinetics well.

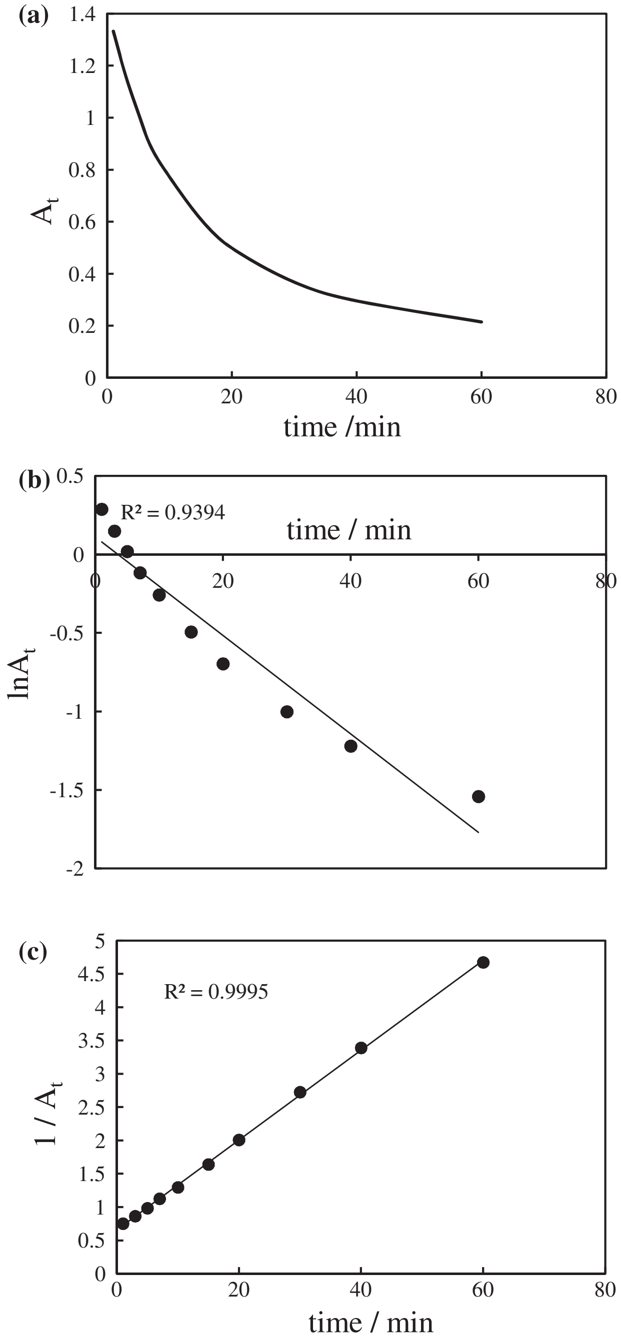

Fig. 3. Pseudo order of RAH degradation by persulfate, (a) zero order, (b) first order, and (c) second order. [RAH] $= 2 \times 10^{-5}$ mol dm^{-3}, $[K_2S_2O_8] = 2 \times 10^{-2}$ mol dm^{-3}, pH 9, $T = 25$℃.

Based on the above analysis, the second-order kinetic rate constants for the decolorization of RAH at different reaction conditions are listed in Table 2.

3.2. Effect of pH

A thermally activated persulfate oxidation system is known to involve $SO_4^{-\cdot}$ and $HO^{\cdot}$ radicals depending on the pH of the medium. According to literature survey, $SO_4^{-\cdot}$ is a predominant oxidant radical at pH < 7, both $SO_4^{-\cdot}$ and $HO^{\cdot}$ are present at neutral pH and $HO^{\cdot}$ is a predominant radical at pH > 9 [9]. Keeping the concentration of RAH, KPS, and temperature constant and increasing the pH in range of 3.5–9.5, the rate of the reaction increased, Fig. 4. Increasing the pH in the range 3.5–9.5 increased observed rate constant (k_{obs}) from 6.7×10^{-4} to 6.8×10^{-3} mol^{-1} dm^3 s^{-1}, Table 2. This is probably attributed to the effect of hydroxyl ion on RAH which converts it to a carbinol base with no conjugation structure. All studies were done at pH 9, since cotton dyeing is performed in alkaline medium [23].

3.3. Effect of dye concentration

The effect of initial concentration of RAH on the oxidation process by persulfate was investigated since pollutant concentration is an important parameter in wastewater treatment. The observed rate constant decreases linearly with an increase in the initial concentration of RAH, Fig. 5. This is attributed to the relative increase in rosaniline concentration while the

Table 2
Kinetic data for degradation of RAH by persulfate

pH	T(℃)	[RAH] × 10^5 (M)	$[K_2S_2O_8] \times 10^2$ (M)	$k_{obs} \times 10^3$ ($M^{-1}s^{-1}$)
3.5	40	2	2	0.67
6.3				1.99
8.3				3.94
9.5				6.79
9	40	1	2	11.72
		2		7.76
		3		5.10
9	40	2	0.4	3.13
			0.8	6.18
			1.6	8.50
			2.4	9.92
9	30	2	2	1.99
	35			4.14
	40			5.23
	45			6.68

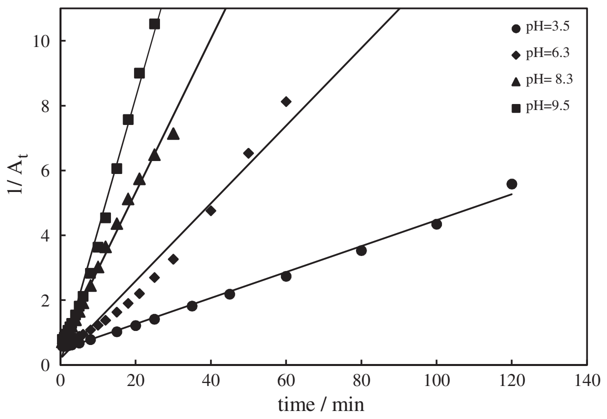

Fig. 4. Effect of pH on the reaction between RAH and persulfate. [RAH] = 2 × 10^{-5} mol dm^{-3}, [$K_2S_2O_8$] = 2 × 10^{-2} mol dm^{-3}, T = 40˚C.

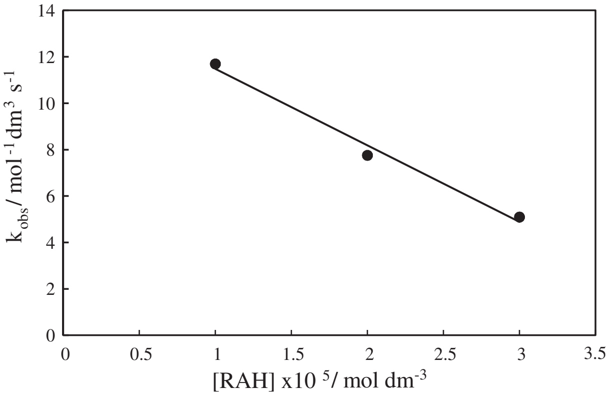

Fig. 5. Effect of dye concentration on the rate constant of the reaction between RAH and persulfate. [$K_2S_2O_8$] = 2 × 10^{-2} mol dm^{-3}, T = 40˚C, pH 9.

concentration of $SO_4^{-\cdot}$ radicals remains the same. The obtained results are in good agreement with those reported earlier [24,25].

3.4. Effect of persulfate concentration

Increasing the persulfate concentration in the range of 4 × 10^{-3}–2.4 × 10^{-2} mol dm^{-3} increased the rate constant from 3.13 × 10^{-3} to 9.92 × 10^{-3} mol^{-1} dm^3 s^{-1} at pH 9 and a temperature of 40˚C, Table 2. Plotting log k_{obs} vs. log [$K_2S_2O_8$] gave a straight line of slope 0.63 indicating the order of reaction with respect to persulfate is half, Fig. 6. This is similar to the results obtained by Mushinga and Jonnalagadda [26]. Also the fraction order (n = 0.779) with respect to persulfate is obtained by Ahmadi et al. [25].

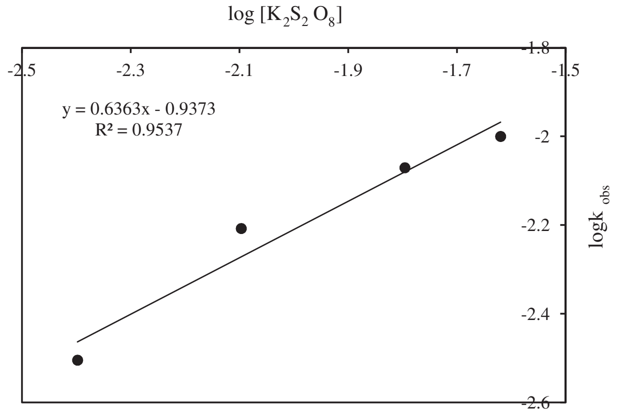

Fig. 6. Variation of log k_{obs} with log [$K_2S_2O_8$]. [RAH] = 2 × 10^{-5} mol dm^{-3}, T = 40˚C, pH 9.

3.5. Effect of temperature

The variation of temperature in the range of 303–318 K increased the rate of decolorization of rosaniline, Fig. 7. The activation energy was calculated from Arrhenius plot and Eyring equation and was found to be 62.11 kJ mol^{-1}. A low value of activation energy indicates that the reaction proceeds with a low energy barrier. The activation energy for the decolorization of RY84 was 45.84 kJ mol^{-1} [25], while for the decolorization of CV by persulfate was 28.9 kJ mol^{-1} [24]. Chen-Ju Liang and Shun-Chin Huang demonstrated that the activation energy of MB with persulfate was 87 and 90 kJ mol^{-1} in acidic and alkaline media, respectively [9]. The other activation parameters were calculated and were found to be 90.33 kJ mol^{-1} and −98.44 J mol^{-1} K^{-1} for free energy

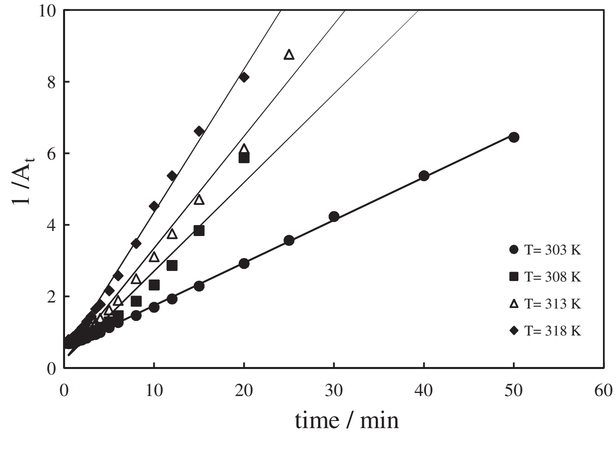

Fig. 7. Effect of temperature on the reaction of RAH and persulfate. [RAH] = 2 × 10^{-5} mol dm^{-3}, [$K_2S_2O_8$] =2 × 10^{-2} mol dm^{-3}, pH 9.

and entropy, respectively. The low negative value of entropy indicates the reaction is favorable.

3.6. Effect of inorganic anions

The potent effect of persulfate as oxidizing agent in destroying organic pollutants is by the virtue of high redox potential of sulfate free radical. The presence of other species in wastewater such as chloride, sulfate, and phosphate could reduce its oxidation efficiency. It is reported earlier [27] that chloride can react with sulfate free radicals according to the following mechanism:

$$SO_4^{-\cdot} + Cl^- \leftrightarrow SO_4^{2-} + Cl^\cdot \tag{4}$$

$$Cl^\cdot + Cl^- \leftrightarrow Cl_2^{-\cdot} \tag{5}$$

$$Cl_2^{-\cdot} + Cl_2^{-\cdot} \leftrightarrow Cl^- + Cl_3^- \tag{6}$$

Chloride concentrations had an insignificant effect in the studied range 0.008–0.08 mol dm^{-3}. Also, the presence of sulfate did not reduce the decolorization rate. Similar results were observed earlier [27–29].

4. Reaction mechanism and rate law

The probable mechanism of reaction involves the break of conjugation of RAH. Since the fraction order of persulfate is observed, it is likely that the initial reaction is thermal decomposition of persulfate,

$$S_2O_8^{2-} \overset{K}{\leftrightarrow} 2SO_4^{-\cdot} \tag{7}$$

$$2RAH + SO_4^{-\cdot} \xrightarrow{k} I + SO_4^{2-} \quad \text{(slow)} \tag{8}$$

where I is an intermediate

$$I \xrightarrow{\text{fast}} \text{product} \tag{9}$$

$$\text{rate} = k[RAH]^2\,[SO_4^{-\cdot}] \tag{10}$$

Applying equilibrium approximation and assuming an equilibrium between the reactant and product of Eq. (7)

$$[SO_4^{-\cdot}] = K^{1/2}[S_2O_8^{2-}]^{1/2} \tag{11}$$

Substituting Eq. (11) into Eq. (10)

Table 3
Summary of kinetic data for oxidation of rosaniline by persulfate

$[S_2O_8{}^{2-}] \times 10^2$ (M)	$k_{obs} \times 10^3$ ($M^{-1}s^{-1}$)	$k \times 10^2$ ($M^{-1.5}\ s^{-1}$)
0.4	3.13	4.95
0.8	6.18	6.94
1.6	8.50	6.72
2.4	9.92	6.46

Mean $k = 0.0627\ M^{-1.5}\ s^{-1}$
$k = k_{obs}\ /\ [S_2O_8{}^{2-}]^{1/2}$

$$\text{rate} = K^{1/2}k[RAH]^2[S_2O_8^{2-}]^{1/2} \tag{12}$$

From experimental data

$$\text{rate} = k_{obs}[RAH]^2 \tag{13}$$

From Eqs. (12) and (13)

$$K_{obs} = K^{1/2}k[S_2O_8^{2-}]^{1/2} \tag{14}$$

The proposed mechanism and rate law are probable, so plotting of k_{obs} vs. $[S_2O_8{}^{2-}]^{1/2}$ should yield straight line passing through the origin and the slope should equal $k \times K^{1/2}$. Using the data in Table 3, the plot gave a straight line (Fig. 8) passing through the origin with slope = 0.065 (R^2 = 0.9557) ≅ calculated k (Table 3), which supports the proposed mechanism and rate equation.

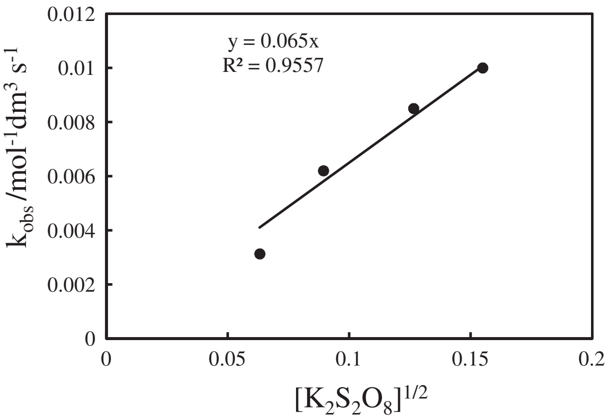

Fig. 8. Plot of k_{obs} vs. $[K_2S_2O_8]^{1/2}$. [RAH] = 2×10^{-5} mol dm^{-3}, T = 40°C, pH 9.

5. Conclusion

In this study, RAH was successfully degraded in aqueous solution by the persulfate. The RAH degradation follows the second-order kinetic model with respect to RAH and half order with respect to persulfate. The activation energy of RAH degradation by the persulfate was 62.11 kJ mol^{-1}. The presence of inorganic ions such as NaCl and Na_2SO_4, had no effects on RAH degradation.

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