Determination of Activation Energy for the Degradation of Rhodamine B in the Presence of Hydrogen Peroxide and some Metal Oxide

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Summary: In this research, degradation of rodamine B in the presence of (hydrogen peroxide), (hydrogen peroxide+aluminum oxide), (hydrogen peroxide+nano-sized aluminum oxide) and (hydrogen peroxide+iron oxide) was curried out at various temperatures (20, 25, 30, 35 and 40 $^\circ$C) to calculate activation energy. The activation energy for degradation of rodamine B in the presence of (hydrogen peroxide), (hydrogen peroxide+aluminum oxide), (hydrogen peroxide+nano-sized aluminum oxide) and (hydrogen peroxide+iron oxide) in studied rang were calculated 40.71, 33.75, 30.72 and 36.60 kJ.mol^{-1}, respectively.

Introduction

Among the many organic compounds found in wastewaters, the pollution caused by dyestuffs posed a serious environmental problem for years. Synthetic dyestuffs are used by several industries such as textile, dyeing and printing industries. Within the overall category of dyestuffs Rhodamine B, RB, is one of the most important xanthene dye, which is famous for its good stability. Thus, the treatment of effluents containing such compounds is important for the protection of waters and environment in general [1]. The treatment of dye containing wastewater by conventional methods such as flocculation, air sparging and adsorption using activated carbon are quite ineffective for the decolorization of wastewater, since dyestuffs are difficult to remove using these processes due to their low molecular weight and high water solubility [2]. Other processes, such as coagulation and adsorption, merely transfer the pollutants from the wastewater to other media that produce sludge and cause disposal problems [3]. Recently, extensive research is conducted for the degradation of RB, such as photocatalytic degradation using titanium dioxide [4-6], ultrasonic treatment [7-9], sonocatalytic degradation and photodegradation using nano-sized zinc oxide powder [10, 11]. Photodegradation of rhodamine B was also investigated by silver and indium oxide co-doped TiO$_2$ [12]. So far the work on the determination of activation energy for degradation of rhodamine B is not reported. The aim of this study is to find the activation energy for the degradation of Rhodamine B in presence of hydrogen peroxide, iron oxide, aluminum oxide and nano-sized aluminum oxide.

Results and Discussion

Degradation of RB in the Presence of Hydrogen Peroxide

The degradation of RB was carried out at various temperatures (20, 25, 30, 35 and 40 $^\circ$C) using constant concentration of RB and hydrogen peroxide in order to calculate activation energy of degradation. The absorption spectra of RB solution during degradation are illustrated in Fig. 1. The concentration of RB were calculated from the absorption in λ_{max}= 555 nm by using a calibration curve and Beer's Law. Then unreacted fractions of RB, α, were evaluated. The relationship between $Ln(\alpha)$ and degradation time shows a linear relationship which suggest that the degradation of RB is a pseudo-first-order reaction. Thus the rate equation for degradation of RB in the presence of hydrogen peroxide can be written as:

$$\frac{d[RB]}{dt} = -k[H_2O_2]^n[RB] = -k'[RB]$$

$$Ln\frac{[RB]}{[RB]_0} = Ln(\alpha) = -k't$$

where $k' = k[H_2O_2]^n$ is the apparent rate constant. The apparent rate constants were obtained from the

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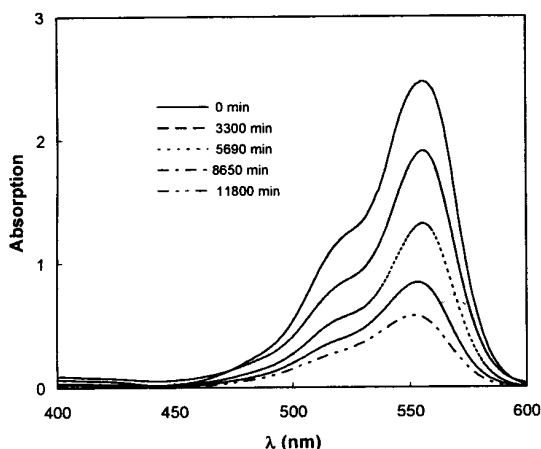*To whom all correspondence should be addressed.

Fig. 1: Absorption spectra of Rhodamine B aqueous solution during degradation time with $[RB]_0=5.69\times10^{-5}$ mol.L^{-1} and $[H_2O_2]_0=5.815$ mol.L^{-1} at 20°C.

slope of *Ln(α)* versus time. The relationship between *Ln(α)* and degradation time is shown in Fig. 2. According to usual Arrhenius treatment, plot of *Ln(k')* versus 1/T gave a linear relation with slope - E_a/R. Thus the activation energy was calculated from the slope of plot of *Ln(k')* versus 1/T. The relationship between *Ln(k')* and 1/T for the degradation of RB in the presence hydrogen peroxide was shown in Fig. 3. The activation energy in this case was obtained 40.71 kJ.mol^{-1}.

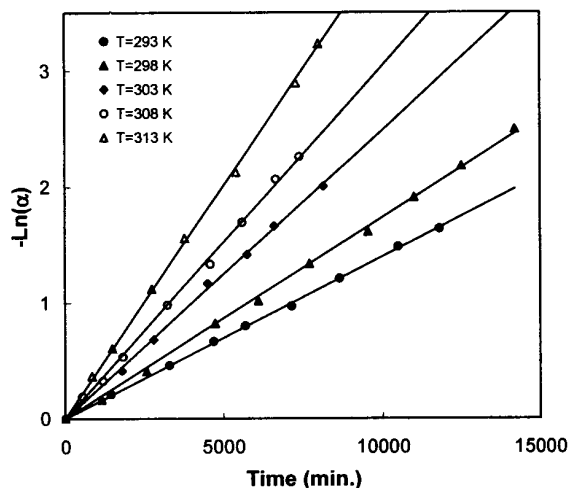Fig. 2: Relationship between *Ln(α)* and degradation time in different temperatures with $[RB]_0=5.69\times10^{-5}$ mol.L^{-1} and $[H_2O_2]_0=5.815$ mol.L^{-1}.

Degradation of RB in the Presence of Aluminum Oxide and Hydrogen Peroxide

The degradation of RB was carried out at various temperatures (20, 25, 30, 35 and 40 °C) using constant concentration of RB in the presence of hydrogen peroxide and aluminum oxide in order to calculate activation energy of degradation. The relationship between *Ln(α)* and degradation time shows a linear relationship which suggest that the degradation of RB is a pseudo-first-order reaction. Thus the rate equation for degradation of RB in the presence of hydrogen peroxide and aluminum oxide can be written as:

$$\frac{d[RB]}{dt} = -k[H_2O_2]^n[Al_2O_3]^m[RB] = -k'[RB]$$

$$Ln\frac{[RB]}{[RB]_0} = Ln(\alpha) = -k't$$

where $k' = k[H_2O_2]^n[Al_2O_3]^m$ is the apparent rate constant. The apparent rate constants, k', were obtained from the slope of *Ln(α)* versus time. The relationship between *Ln(α)* and degradation time was shown in Fig. 4. The activation energy was calculated from the slope of plot of *Ln(k')* versus 1/T. The relationship between *Ln(k')* and 1/T for the degradation of RB in presence hydrogen peroxide and aluminum oxide was shown in Fig. 3. The activation energy in this case was obtained 33.75 kJ.mol^{-1}.
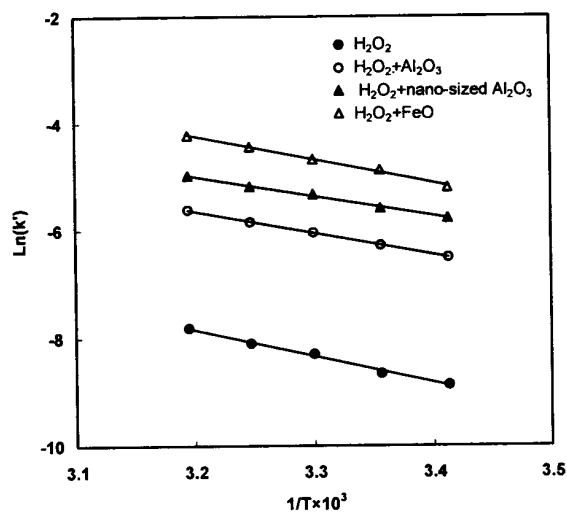

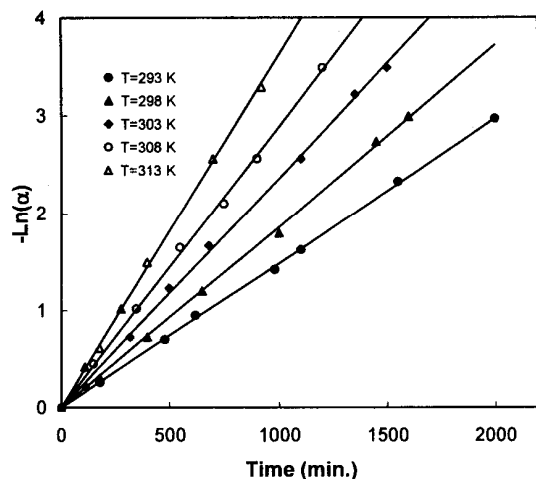Fig. 3: Plot of *Ln(k')* versus 1/T in various conditions.

Fig. 4   Relationship between $Ln(\alpha)$ and degradation time in different temperatures with $[RB]_0=5.69\times10^{-5}$ mol.L^{-1}, $[H_2O_2]_0=5.815$ mol.L^{-1} and $[Al_2O_3]=30$ g.L^{-1}.
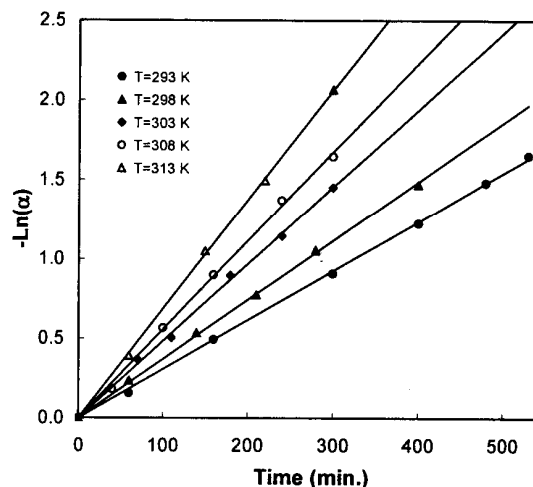
Fig. 5:   Relationship between $Ln(\alpha)$ and degradation time in different temperatures with $[RB]_0=5.69\times10^{-5}$ mol.L^{-1}, $[H_2O_2]_0=5.815$ mol.L^{-1} and [nano-sized Al_2O_3]$=30$ g.L^{-1}.

Degradation of RB in the Presence of Nano-sized Aluminum Oxide and Hydrogen Peroxide

The degradation of RB was carried out at various temperatures (20, 25, 30, 35 and 40°C) using constant concentration of RB in the presence of hydrogen peroxide and nano-sized aluminum oxide in order to calculate activation energy of degradation. The relationship between $Ln(\alpha)$ and degradation time shows a linear relationship which suggest that the degradation of RB is a pseudo-first-order reaction. Thus the rate equation for degradation of RB in the presence of hydrogen peroxide and nano-sized aluminum oxide can be written as:

$$\frac{d[RB]}{dt} = -k[H_2O_2]^n[nano-sized\ Al_2O_3]^m[RB] = -k'[RB]$$

$$Ln\frac{[RB]}{[RB]_0} = Ln(\alpha) = -k't$$

where $k'=k[H_2O_2]^n[nano-sizedAl_2O_3]^m$ is the apparent rate constant. The apparent rate constants, k', were obtained from the slope of $Ln(\alpha)$ versus time. The relationship between $Ln(\alpha)$ and degradation time was shown in Fig. 5. The activation energy was calculated from the slope of plot of $Ln(k')$ versus 1/T. The relationship between $Ln(k')$

and 1/T for the degradation of RB in the presence hydrogen peroxide and nano-sized aluminum oxide was shown in Fig. 3. The activation energy in this case was obtained 30.72 kJ.mol^{-1}.

Degradation of RB in the Presence of Iron Oxide and Hydrogen Peroxide

The degradation of RB was carried out at various temperatures (20, 25, 30, 35 and 40 °C) using constant concentration of RB in the presence of hydrogen peroxide and iron oxide in order to calculate activation energy of degradation. The relationship between $Ln(\alpha)$ and degradation time shows a linear relationship which suggest that the degradation of RB is a pseudo-first-order reaction. Thus the rate equation for degradation of RB in the presence of hydrogen peroxide and iron oxide can be written as:

$$\frac{d[RB]}{dt} = -k[H_2O_2]^n[FeO]^m[RB] = -k'[RB]$$

$$Ln\frac{[RB]}{[RB]_0} = Ln(\alpha) = -k't$$

where $k'=k[H_2O_2]^n[FeO]^m$ is the apparent rate constant. Therefore the apparent rate constants, k', were obtained from the slope of $Ln(\alpha)$ versus time.

The relationship between $Ln(\alpha)$ and degradation time was shown in Fig. 6. The activation energy was calculated from the slope of plot of $Ln(k')$ versus $1/T$. The relationship between $Ln(k')$ and $1/T$ for the degradation RB in the presence of hydrogen peroxide and iron oxide was shown in Fig. 3. The activation energy in this case was obtained 36.60 $kJ.mol^{-1}$.
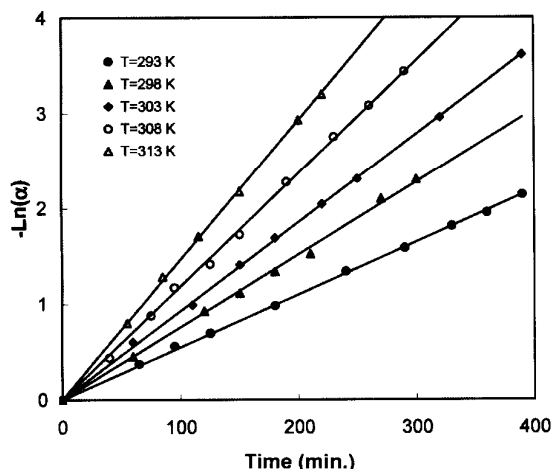

Fig. 6: Relationship between $Ln(\alpha)$ and degradation time in different temperatures with $[RB]_0=5.69\times10^{-5}$ $mol.L^{-1}$, $[H_2O_2]_0=5.815$ $mol.L^{-1}$ and $[FeO]=5$ $g.L^{-1}$.

Experimental

Materials

Rhodamine B (purity 99 %), hydrogen peroxide (30 %), iron oxide (99.5 %), potassium hydroxide (99 %), hydrochloric acid (37 %) and aluminum oxide (99.5 %) were supplied by Merck. Fig. 7 shows the chemical structure of rhodamine B. All materials were used without further purification. Distilled water was used for preparation of solutions.

Apparatus and Procedure

For preparing nano-sized aluminum oxide, the aluminum oxide was suspended in hot aqueous solution of KOH. Then the suspension was sonocated (Dr. Hielscher UP400 S ultrasonic processor) and neutralized by hydrochloric acid and the sediment was washed to remove the sodium chloride. Transmission electron microscopy (TEM) (Leo 906)
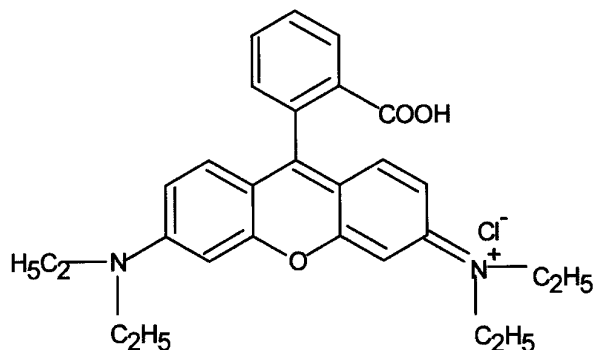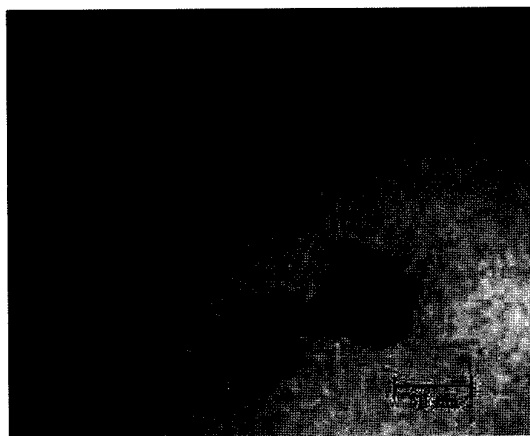

Fig. 7: The chemical structure of RB.

Fig. 8: TEM of nano-sized Al_2O_3.

was used to see the nano-sized aluminum oxide which is shown in Fig. 8. From Fig. 8, it is found that the treated aluminum oxide has a nano-meter scale with the size around 50 nm. Stock solution of RB (60 mgL^{-1}) was prepared gravimetrically by weighing it using an analytical balance (Sartorius CP224 S) with a precision of $\pm1\times10^{-4}$ g. Others dilutions of RB were prepared from stock solution. The UV-Vis absorption was monitored with T80 UV/Vis spectrophotometer (PG Instruments Ltd). The temperature of solutions was kept constant by a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co.) with a precision of ±0.1 K. The degradation of RB was studied by using GC-MS (6890 Network GC system, 5973 Network Mass selective Detector) after deodorization. The GC-MS profile is shown in Fig. 9. It is found that 1, 2-benzenedicarboxylic acid diethyl ester is the major degraded end product of RB.
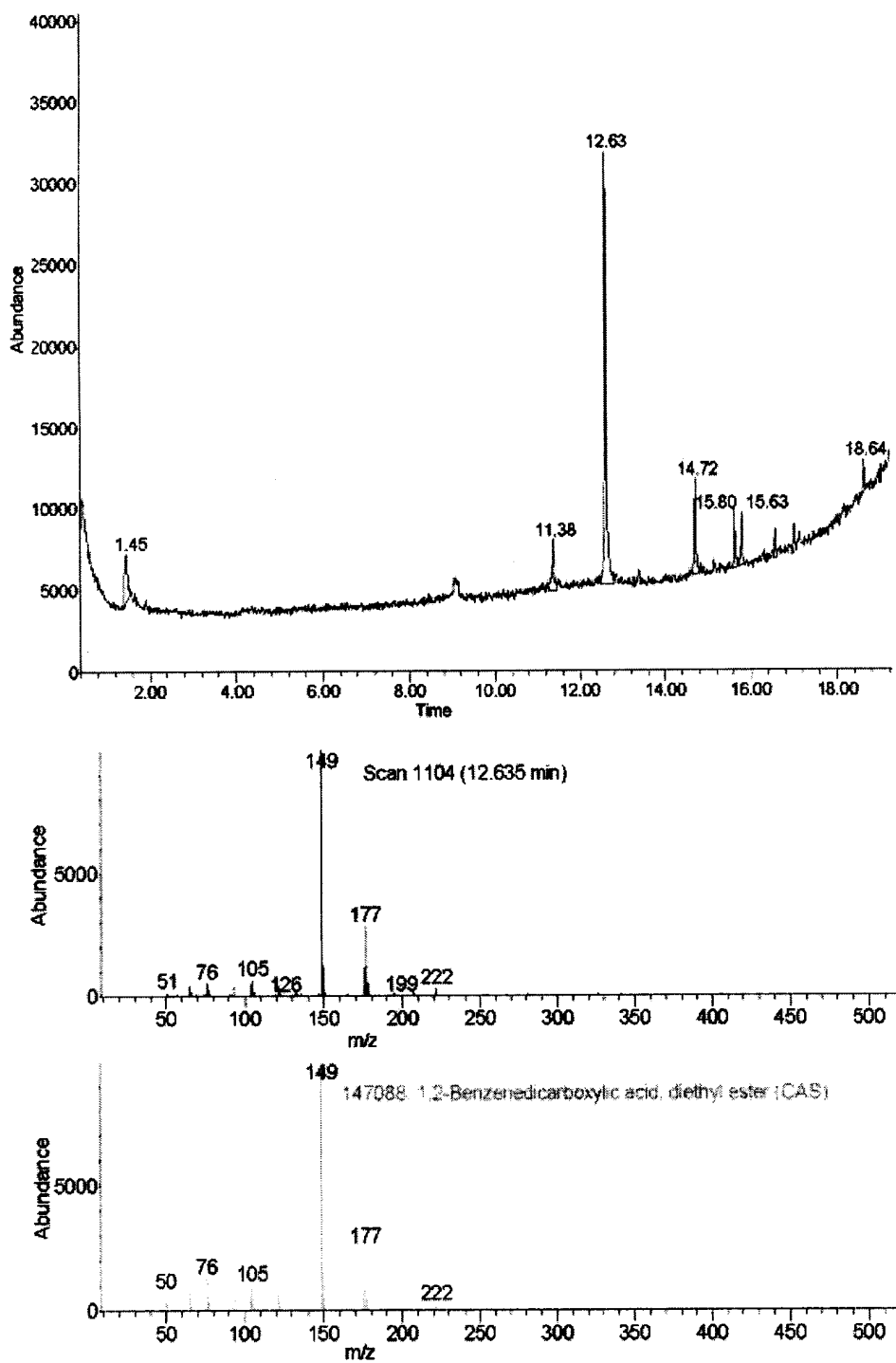
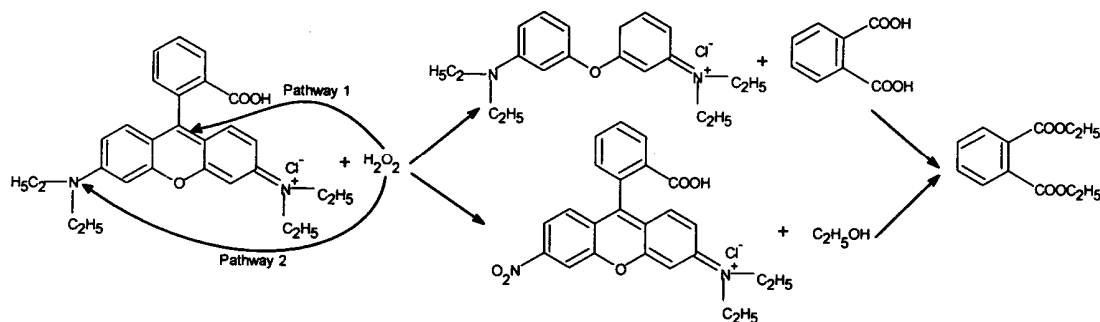Fig. 9:   GC-MS spectra of degraded RB.

Fig. 10:   The proposed mechanism for the degradation of RB.

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