KINETICS OF THE OXIDATIVE DECOLORIZATION OF AMARANTH RED BY ACIDIC BROMATE

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The kinetics of the oxidative decolorization of amaranth with KBrO₃ acidified by H₂SO₄ was followed up by monitoring the decrease of the absorbance of amaranth at λₘₐₓ = 520 nm. The reaction was carried out under pseudo-first-order conditions. The concentration of BrO₃⁻ was ca 300 greater than that of amaranth. The rate of reaction increased with increasing concentration of H₂SO₄ and BrO₃⁻, while amaranth had no effect on the rate of reaction. The effects of the ions, Cl⁻, Br⁻ and SO₄²⁻ were investigated and the reaction rate increased with increasing concentrations of chloride and bromide while it decreased with increasing concentration of SO₄²⁻. A reaction mechanism has been proposed.

Introduction

Wastewater treatment is one of the major problems facing the chemical, petrochemical, pharmaceutical, and textile industries. These industries generate large quantities of organic pollutants that cause environmental and health problems. Biological (biodegradation),¹ physical² and chemical methods (chlorination, ozonation)³ are the most frequently used methods for removal of dyes from effluent water streams. But, these traditional processes for treatment of the effluents prove to be insufficient to purify waste water after the different operations of waste waters dyeing and washing.

Advanced oxidation processes (AOPs) are alternative methods for the complete degradation of dye. The usage of the advanced oxidation processes (AOPs) have improved during the last decade since they are able to eliminate the problem of dye destruction in aqueous systems. AOPs were based on the generation of very reactive species such as hydroxyl radicals (·OH)(E = 2.8V vs NHE) that oxidize a broad range of pollutants quickly and non-selectively. AOPs such as Fenton and Photo-Fenton catalytic reactions,⁴⁶ H₂O₂/UV processes.⁶

Potassium bromate is powerful oxidizing agent.⁷ It is used in oxidation of organic and inorganic compounds.⁸⁹ Literature survey shows that bromate is used as an oxidizing agent for various dyes. The oxidation of dyes received attention for last decade.¹⁰⁻¹² Although previous studies have taken important steps forward in generating empirical rules for oxidation, further intensive study is still required to understanding the mechanism of oxidation by bromate.

Azo dyes are used extensively in textile industry. Amaranth as example for azo dyes is used as cosmetic dye and can applied for natural and synthetic fibers, leather, paper, phenol formaldehyde resins.¹³ Number of studies is published on oxidation of amaranth by various oxidizing agents.¹⁴⁻¹⁶ Quick look in literature oxidation of amaranth by bromate has not yet reported.

The aim of this study is investigation of the kinetic aspects of the oxidative decolorization of amaranth with acidic bromate solution. It also describes the effect of temperature, and foreign ions on the oxidation of amaranth by bromate.

Experimental

Materials

All chemicals were of high grade quality, they were used as received. The standard solutions and dilution were made using bidistilled water. Amaranth, trisodium(4-ethyl-3-oxo-4-[(4-sulfonato-1-naphthyl)-hydrazono]-naphthalene-2,7-di-sulfonate, was obtained from Aldrich. For the daily kinetic runs a stock solution of dye (10⁻³ mol dm⁻³) was prepared. The flask containing the dye solution was wrapped in aluminium foil and stored in the dark to minimize exposure to light. KBrO₃ was supplied from Merck and its initial concentration was standardized iodometrically using starch as an indicator.¹⁷ The desired concentration of KBrO₃ was obtained by successive dilutions from the standard stock solution.

Kinetic measurements

The kinetic measurements were carried out spectrophotometrically using 292 Cecil spectrophotometer equipped with constant temperature cell holder attached to thermostatic controlled bath with temperature stability of ± 0.1°C.

The kinetics of reaction were carried out by mixing solutions of (KBrO₃&H₂SO₄) and placed in a thermostatic bath at desirable temperature. The reaction started by adding thermostatted dye solution. The progress of the reaction was monitored at λₘₐₓ = 520 nm. Pseudo first-order conditions were maintained in all runs by using a large excess of bromate over amaranth.
Results and discussion

In the present study the oxidizing property of the acidified KBrO₃ (redox potential of 1.5 V at 25 °C) was considered as a tool for color removal of organic dyes in the industrial wastewater stream.

When amaranth was added to the acid-free KBrO₃ solution no changes in the absorbance spectra have been observed. The reaction was initiated when the dye solution was allowed to react with the acidified KBrO₃. The absorbance of amaranth at λ_max = 520 nm decreased with time as shown in Figure 1.

![Figure 1. Zero order plots for the decolorization of amaranth by acidified KBrO₃ at different temperatures. [dye] = 5x10⁻³ mol dm⁻³, [KBrO₃] = 1.5x10⁻² mol dm⁻³, [H₂SO₄] = 8x10⁻² mol dm⁻³](image)

The plot of the absorbance vs. time was linear as shown in Figure 1. This indicates the zero-order kinetics of the reaction with respect to the amaranth concentration.

Effect of potassium bromate concentration

The effect of the initial concentration, [KBrO₃]₀ on the reaction rate was investigated at constant [amaranth], 5x 10⁻⁵ mol dm⁻³, and in the presence of 0.08 mol dm⁻³ of H₂SO₄. Figure 2 shows linear relation between rate constant and [KBrO₃]₀ which indicates that the reaction follows first-order kinetics with respect to the [KBrO₃]. (plotting of ln k_o versus ln [KBrO₃]₀ yields straight line with slope of unity). This is in good agreement with earlier results while Nasiruddin Khana et al.⁹ reported that the reaction followed zero order kinetics with respect to the [KBrO₃].

![Figure 2. Variation of observed rate constant with [KBrO₃]. [dye] = 5x10⁻³ mol dm⁻³, [KBrO₃] = 1.5x10⁻² mol dm⁻³, at 35 °C](image)

The intercept of abscissa means that no reaction takes place at [BrO₃⁻] below 0.015 mol dm⁻³. This means that the concentration of the generated active species is very small and unable to oxidize the amaranth. It has been reported that the system involved various acidified oxybromo species such as: H₃BrO₄⁺, BrO₂⁻, HOBr and BrO₂⁻. These species could be competed with bromated ion in the oxidation and decolorization of organic dyes.

Figure 3 shows that the reaction rate is very slow at [H₂SO₄] lower than about 0.04 mol dm⁻³, and then it is gradually increased. Plot ln k_o versus ln [H₂SO₄] yields straight line with slope of unity indicates that the order of reaction with respect to the H₂SO₄ is first order.

Again, the slower rate obtained at lower concentrations of the acid can be attributed to the formation of the intermediates active species contributed in the oxidation reaction needed a high acid concentrations, i.e., the acid/bromate ratio should be equal to or more than 3 as can be seen from Figure 4.

Effect of amaranth concentration

The influence of the initial concentration, [amaranth] on the reaction rate was investigated, in range of 3x10⁻⁵ - 8x10⁻⁵ mol dm⁻³. The [KBrO₃] and [H₂SO₄] were kept constant at 0.03 mol dm⁻³ and 0.08 mol dm⁻³ respectively.
Under this condition, the reaction obeyed zero-order kinetics with respect to [amaranth]. As shown in Figure 5, increasing the [amaranth] led to soft increase in the reaction rate.

Effect of sodium chloride concentration

The effect of the initial concentrations of bromide ion as common ion effect on the reaction rate was also studied. The [KBrO₃], [H₂SO₄], and [amaranth] were kept constant at 0.015 mol dm⁻³, 0.08 mol dm⁻³, and 5x10⁻⁵ mol dm⁻³, respectively, while the [NaBr] was varied from 1.2x10⁻³ to 4x10⁻⁴ mol dm⁻³, Figure 7. Figure 7 shows that the oxidation rate of amaranth is greatly accelerated with increasing [Br⁻]. This is good evidence that the [Br⁻] catalyzed the decolorization of amaranth. The experimental value of observed rate constant in absence of bromide (0.43x10⁻⁵ s⁻¹) is coincident with the intercept of Figure7 (0.391x10⁻⁵ s⁻¹). It has been reported that the addition of [Br⁻] in the reaction medium containing acidified KBrO₃ facilitated the generation of bromine and hypobromous acid species, which work as powerful oxidizing species.¹⁸
Effect of sodium sulfate concentration

The effect of the initial concentrations of sulfate ions was also investigated. The concentration of the reactants was held constant, while the concentration of Na$_2$SO$_4$ was varied from 0.004 to 0.024 mol dm$^{-3}$. The value of $k_1$ in absence sulphate (8.62x10$^{-4}$ mol dm$^{-3}$ s$^{-1}$) decreased to 4.1x10$^{-4}$ mol dm$^{-3}$ s$^{-1}$ in presence of 0.024 mol dm$^{-3}$ of Na$_2$SO$_4$. This could be ascribed to the decreasing hydrogen ions concentration in the reaction medium through the decrease of ionization constant of H$_2$SO$_4$ with increasing [SO$_4^{2-}$].

Effect of temperature

The kinetic measurements of the reaction were carried out at various temperatures in 303-318 K range. A plot of Arrhenius equation was applied and the activation energy, $E_a$ was deduced. The other activation parameters were determined and are listed in Table 1. The $\Delta H^\circ$ positive value indicates that the oxidative decolorization of amaranth is endothermic.

Table 1. Thermodynamic parameters for decolorization of Amaranth by bromate

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>71.5 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>68.94 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta S^\circ$</td>
<td>-85.24 J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G^\circ$</td>
<td>95.22 kJ mol$^{-1}$</td>
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</table>

Reaction mechanism

Based on the above results and discussion, the proposed mechanism of the oxidation of amaranth red, (D), by acidified bromate is

$$\text{H}^+ + \text{BrO}_3^- \xrightarrow{k_1} \text{HBrO}_3$$  \hspace{1cm} (1)

$$\text{HBrO}_3 + \text{D}_{\text{red}} \xrightarrow{k_2} \text{Br}^- + \text{D}_{\text{ox}}$$ \hspace{1cm} (2)

$$\text{BrO}_3^- + \text{Br}^- + \text{H}^+ \xrightarrow{k_3} \text{Br}_2 + \text{H}_2\text{O} + \text{O}_2 \text{(slow)}$$ \hspace{1cm} (3)

$$\text{Br}_2 + \text{D}_{\text{red}} \xrightarrow{k_{\text{red}}} 2\text{Br}^- + \text{D}_{\text{ox}}$$ \hspace{1cm} (4)

where (red) and (ox) are reduction and oxidation reactions respectively.

The rate of reaction can be written as

$$\text{Rate}=k_2[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]$$ \hspace{1cm} (5)

Applying steady state approximation principle for HBrO$_3$ and Br$^-$, Eqn. 5 becomes

$$\text{Rate} = k_3[\text{H}^+][\text{BrO}_3^-]$$ \hspace{1cm} (6)

This is in good agreement with the experimental findings that the reaction follows first-order kinetics with respect to BrO$_3^-$, H$^+$ and zero-order kinetics with respect to the [dye].

Conclusion

The oxidative decolorization of amaranth red dye by potassium bromate acidified with H$_2$SO$_4$ was studied. The reaction followed zero-order kinetics with respect to amaranth and first order with respect to both KBrO$_3$ and H$_2$SO$_4$. The decolorization rate was enhanced with increasing the concentrations of Br and Cl while it decreases with increasing SO$_4^{2-}$ concentration.

References

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