



KINETICS OF THE OXIDATIVE DECOLORIZATION OF AMARANTH RED BY ACIDIC BROMATE

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The kinetics of the oxidative decolorization of amaranth with KBrO_3 acidified by H_2SO_4 was followed up by monitoring the decrease of the absorbance of amaranth at $\lambda_{\text{max}} = 520$ nm. The reaction was carried out under pseudo-first-order conditions. The concentration of BrO_3^- was ca 300 greater than that of amaranth. The rate of reaction increased with increasing concentration of H_2SO_4 and BrO_3^- , while amaranth had no effect on the rate of reaction. The effects of the ions, Cl^- , Br^- and SO_4^{2-} were investigated and the reaction rate increased with increasing concentrations of chloride and bromide while it decreased with increasing concentration of SO_4^{2-} . A reaction mechanism has been proposed.

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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 ($\bullet\text{OH}$) ($E = 2.8\text{V}$ vs NHE) that oxidize a broad range of pollutants quickly and non-selectively. AOPs such as Fenton and Photo-Fenton catalytic reactions,⁴⁻⁶ $\text{H}_2\text{O}_2/\text{UV}$ processes.⁶

Potassium bromate is powerful oxidizing agent.⁷ It is used in oxidation of organic and inorganic compounds.⁸⁻⁹ 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*E*)-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. KBrO_3 was supplied from Merck and its initial concentration was standardized iodometrically using starch as an indicator.¹⁷ The desired concentration of KBrO_3 was obtained by successive dilutions from the standard stock solution.

Kinetic measurements

The kinetic measurements were carried out spectrophotometrically using 292 Cecil spectrophotometer was equipped with constant temperature cell holder attached to thermostatic controlled bath with temperature stability of $\pm 0.1^\circ\text{C}$.

The kinetics of reaction were carried out by mixing solutions of (KBrO_3 & H_2SO_4) 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 $\lambda_{\text{max}} = 520$ 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 KBrO_3 (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 KBrO_3 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 KBrO_3 . The absorbance of amaranth at $\lambda_{\text{max}} = 520 \text{ nm}$ decreased with time as shown in Figure 1.

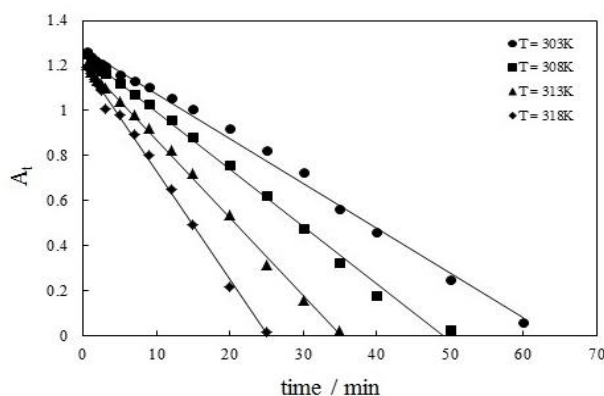


Figure 1. Zero order plots for the decolorization of amaranth by acidified KBrO_3 at different temperatures. $[\text{dye}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{KBrO}_3] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$

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, $[\text{KBrO}_3]_0$, on the reaction rate was investigated at constant [amaranth], $5 \times 10^{-5} \text{ mol dm}^{-3}$, and in the presence of 0.08 mol dm^{-3} of H_2SO_4 . Figure 2 shows linear relation between rate constant and $[\text{BrO}_3^-]_0$, which indicates that the reaction follows first-order kinetics with respect to the $[\text{KBrO}_3]$ (plotting of $\ln k_o$ versus $\ln[\text{BrO}_3^-]$ yields straight line of slope equals the unity). This is in good agreement with earlier results¹⁸⁻¹⁹ while Nasiruddin Khana et al²⁰ reported that the reaction followed zero order kinetics with respect to the $[\text{KBrO}_3]$.

The intercept of abscissa means that no reaction takes place at $[\text{BrO}_3^-]$ below $0.015 \text{ mol dm}^{-3}$. 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: H_2BrO_3^+ , BrO_2^- , HOBr and BrO_2^- .²¹⁻²³ These species could be competed with bromated ion in the oxidation and decolorization of organic dyes.

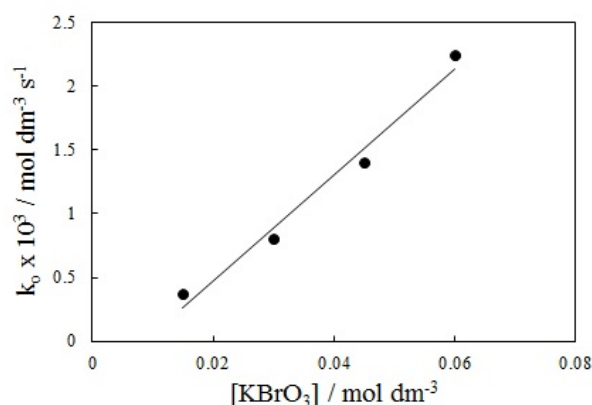


Figure 2. Variation of observed rate constant with $[\text{KBrO}_3]$. $[\text{dye}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$, at 35 °C

Effect of sulfuric acid concentration

The effect of $[\text{H}_2\text{SO}_4]$ on the reaction rate was investigated by keeping the [amaranth] and $[\text{KBrO}_3]$ constant while the concentration of the acid was varied in range of $0.04\text{-}0.4 \text{ mol dm}^{-3}$, Figure 3.

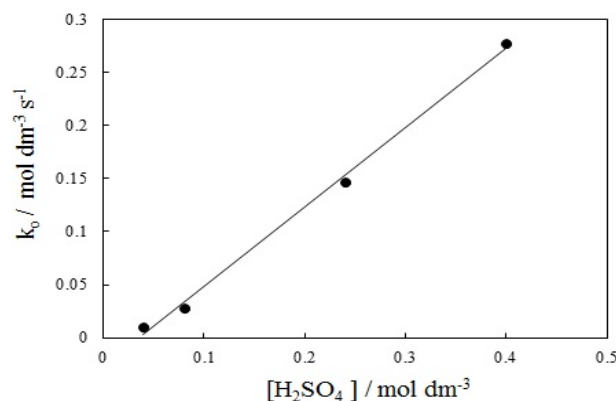


Figure 3. Variation of observed rate constant with $[\text{H}_2\text{SO}_4]$. $[\text{dye}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{KBrO}_3] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, at 35 °C

Figure 3 shows that the reaction rate is very slow at $[\text{H}_2\text{SO}_4]$ lower than about 0.04 mol dm^{-3} , and then it is gradually increased. Plot $\ln k_o$ versus $\ln [\text{H}_2\text{SO}_4]$ yields straight line with slope of unity indicates that the order of reaction with respect to the H_2SO_4 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 of dye on the reaction rate was investigated, in range of $3 \times 10^{-5} - 8 \times 10^{-5} \text{ mol dm}^{-3}$. The $[\text{KBrO}_3]$ and $[\text{H}_2\text{SO}_4]$ were kept constant at 0.03 mol dm^{-3} and 0.08 mol dm^{-3} respectively.

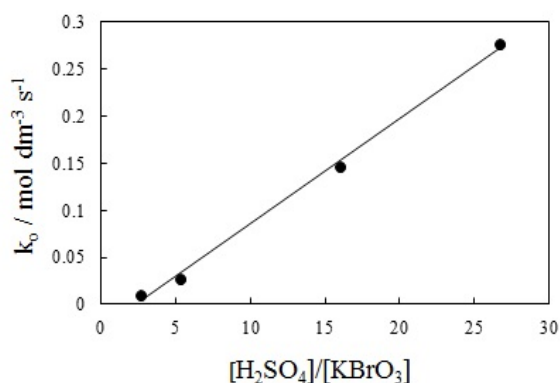


Figure 4. Variation of observed rate constant with $[H_2SO_4]/[KBrO_3]$ ratio. $[dye] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, at 35°C

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.

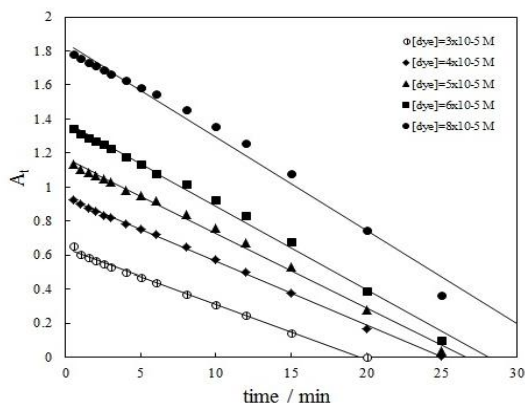


Figure 5. Zero order plots for the decolorization of amaranth by acidified $KBrO_3$ at different dye concentrations. $[KBrO_3] = 3 \times 10^{-2} \text{ mol dm}^{-3}$, $[H_2SO_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$ at 35°C

It was reported earlier that the reaction obeyed first order kinetics,¹⁸⁻¹⁹ while other study showed that reactions obeyed third order kinetics.²⁰

Effect of some additive ions

It is well known in the textile industry that in order to accelerate or increase the fixation of dyes onto the fibers, it is necessary to use high electrolyte concentration in dye bath to decrease the negative charged barrier between the cellulose and anionic dyes.²⁴ Therefore, the textile industry wastewaters are almost heavily charged with unconsumed dyes, different types of electrolytes and other chemicals. Taking into consideration that in effluents of textile dye industry, chloride and sulfate ions are naturally occurring anions, the oxidative decolorization reaction of amaranth was monitored in the presence of NaCl, NaBr and Na_2SO_4

Effect of sodium chloride concentration

The influence of chloride ions, NaCl, on the reaction rate was studied. The $[NaCl]$ was varied in range of the 0.4×10^{-2} - $2 \times 10^{-2} \text{ mol dm}^{-3}$, whereas the concentrations of the other reactants were kept constant. A plot of k_0 vs. $[NaCl]$ gave

straight line which indicates the first-order kinetics with respect $[Cl^-]$. Furthermore, the increase k_0 with increasing $[Cl^-]$, Figure 6, indicates that the reaction is catalyzed by Cl^- . Increasing the concentration of NaCl increases the ionic strength which indicates the reaction between species of the same charge. Also the great increase in rate constant as the $[Cl^-]$ increased can be attributed to the formation of active chloride species such as: Cl^- , Cl_2 , $HOCl$ and ClO^- , which could work as powerful oxidizing species.¹⁸

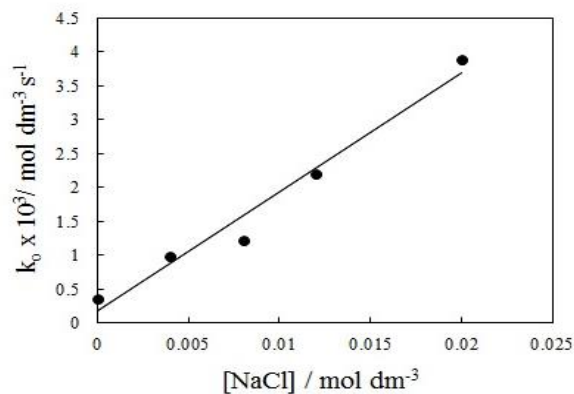


Figure 6. Variation of observed rate constant with $[NaCl]$. $[dye] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[KBrO_3] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[H_2SO_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$, at 40°C

Effect of sodium bromide concentration

The effect of the initial concentrations of bromide ion as common ion effect on the reaction rate was also studied. The $[KBrO_3]$, $[H_2SO_4]$, and [amaranth] were kept constant at $0.015 \text{ mol dm}^{-3}$, 0.08 mol dm^{-3} , and $5 \times 10^{-5} \text{ mol dm}^{-3}$, respectively, while the $[NaBr]$ was varied from 1.2×10^{-5} to $4 \times 10^{-5} \text{ mol dm}^{-3}$, 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 ($0.43 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$) is coincident with the intercept of Figure 7 ($0.391 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$). It has been reported that the addition of $[Br^-]$ in the reaction medium containing acidified $KBrO_3$ facilitated the generation of bromine and hypobromous acid species¹¹ which work as oxidizing species.²⁵

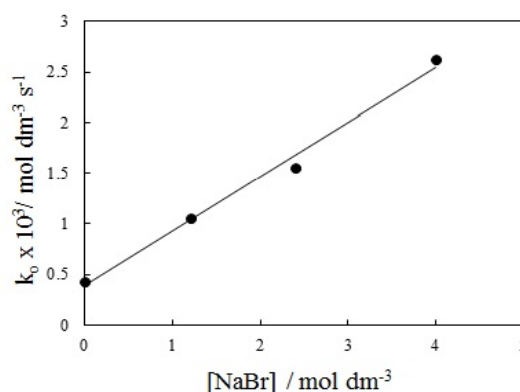


Figure 7. Variation of observed rate constant with $[NaBr]$. $[dye] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[KBrO_3] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[H_2SO_4] = 8 \times 10^{-2} \text{ mol dm}^{-3}$, at 40°C

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 Na₂SO₄ was varied from 0.004 to 0.024 mol dm⁻³. The value of *k*_o 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 Na₂SO₄. This could be ascribed to the decreasing hydrogen ions concentration in the reaction medium through the decrease of ionization constant of H₂SO₄ with increasing [SO₄²⁻].¹⁸

Effect of temperature

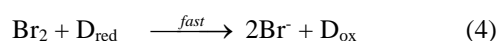
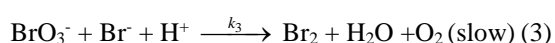
The kinetic measurements of the reaction were carried out at various temperatures in 303-318 K range. A plot of Arrhenius equation was applied and the activation energy, *E*_a was deduced. The other activation parameters were determined and are listed in Table 1. The Δ*H*^{*} positive value indicates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

Table 1. Thermodynamic parameters for decolorization of Amaranth by bromate

Parameters	Value
<i>E</i> _a	71.5 kJ mol ⁻¹
Δ <i>H</i> [*]	68.94 kJ mol ⁻¹
Δ <i>S</i> [*]	-85.24 J mol ⁻¹ K ⁻¹
Δ <i>G</i> [*]	95.22 kJ mol ⁻¹

Reaction mechanism

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



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

The rate of reaction can be written as

$$\text{Rate} = k_3[\text{Br}^-][\text{BrO}_3^-][\text{H}^+] \quad (5)$$

Applying steady state approximation principle for HBrO₃ and Br⁻, Eqn. 5 becomes

$$\text{Rate} = k_1[\text{H}^+][\text{BrO}_3^-] \quad (6)$$

This is in good agreement with the experimental findings that the reaction follows first-order kinetics with respect to BrO₃⁻, H⁺ and zero-order kinetics with respect to the [dye].

Conclusion

The oxidative decolorization of amaranth red dye by potassium bromate acidified with H₂SO₄ was studied. The reaction followed zero-order kinetics with respect to amaranth and first order with respect to both KBrO₃ and H₂SO₄. The decolorization rate was enhanced with increasing the concentrations of Br⁻ and Cl⁻ while it decreases with increasing SO₄²⁻ concentration.

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