KINETICS OF DECOLORIZATION OF ALIZARIN RED S IN AQUEOUS MEDIA BY FENTON-LIKE MECHANISM

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Keywords: Alizarin Red S; decolorization; kinetics; Fenton-like

The decolorization kinetics of Alizarin Red S (ARS) in aqueous solution was studied using Fenton like reaction in dark environment. The effects of dye, iron(III) ions and hydrogen peroxide concentrations were investigated. The reaction was first order in ARS, H_2O_2 and zero order in iron(III) chloride. Increasing the hydrogen peroxide concentration (2-8 x10^{-3} mol dm^{-3}) increases the rate constant from 1.05x10^{-3} to 3.2 x 10^{-3} s^{-1} and excess of hydrogen peroxide shows no effect on the rate constant. Iron(III) ions concentration shows soft retardation effect on the degradation rate of ARS. Increasing the initial ARS concentration from 1 to 4x 10^{-4} mol dm^{-3} decreases the decolorization from 85 % to 55 % within 15 minutes. Increasing temperature in the range of 298-313 K increases the rate of degradation and no optimal value detected. In addition, the influence of inorganic additives such, carbonate, nitrate and chloride on the efficiency of dye removal were examined.

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Introduction

Textile dyeing process is significant source of environmental pollution. One of the most problems of textile waste water in addition to toxic and carcinogenic nature is color effluent. It does not reflect atheistic problem because it is visible pollutant but also depletes sunlight penetration which reduces the photosynthetic activity in aquatic plants, thereby having undesirable impact on their growth. Many physical, chemical and biological methods are used to remove the dyes from waste water.[1-6]

This study is concerned with removal of Alizarin Red S from water. Alizarin Red S is widely used for dyeing textile materials.[7-9] Alizarin Red S is (1,2–dihydroxy-9,10-anthraquinonesulfonic acid sodium salt). It is synthesized by sulfonation of Alizarin which is extracted from root of madder plant. Alizarin Red S is used as stain microscopy, acid-base indicator and in determination of fluorine. The removal of anthraquinone dyes like Alizarin Red S is crucial process from both economical and environmental points of view.[10]

In recent years a great efforts has been done to remove Alizarin Red S using photocatalytic techniques.[2,7-8] In the same time less attention was given to advanced oxidation process such as Fenton and Fenton like process which could be good option to treat and remove Alizarin Red S. Fenton's reagent is an attractive reagent due to the fact that, iron is an abundant and non-toxic element, hydrogen peroxide is easy to handle and can be broken down to environmentally benign product and there is no need for special equipment.

The main object of this study is to examine the effect of the major system parameters on the decolorization kinetics of Alizarin Red S dye. Such parameters are the pH, concentration of iron (III) ions, H_2O_2, dye and temperature of ambient. Also the study gave attention to the effect some inorganic electrolytes.

Experimental

Reagents and materials

All chemicals were of pure grade and were used without further purification. Alizarin Red S purchased from LOBA Chemie PVT Mumbai: 400005 India (molecular formula, $C_{14}H_7O_7NaS$, Molecular weight = 342.26, λ_{max} = 430 nm). The chemical structure and UV-vis spectrum of ARS is given in (Figure1). $FeCl_3$, $NaNO_3$ and Na_2CO_3 were purchased from Merck. Hydrogen peroxide solution (35 %) was of analytical grade. All solutions were prepared using bidistilled water. Stock solutions of dye (1 mM), $FeCl_3$ (10 mM) were prepared in 0.01 M of HCl. All experiments were performed at pH below 3.

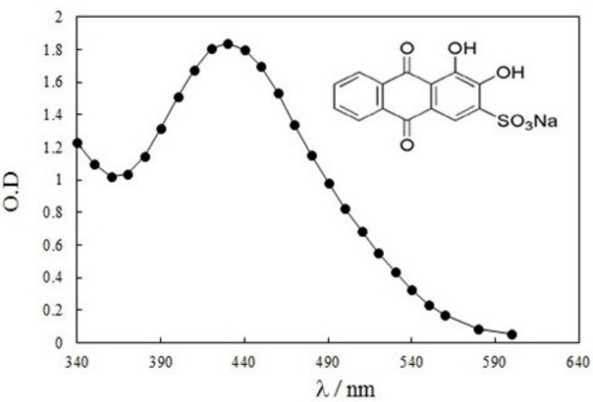

Figure 1. Chemical structure, UV-visible spectrum of ARS. [ARS] = 5 x 10^{-4} mol dm^{-3}

Kinetic experiments

Kinetic experiments were conducted by mixing the solutions of dye and hydrogen peroxide and adjusting $[H^+]$ to the required value with NaOH/HCl using a Griffin pH-meter fitted with a glass calomel electrode. The reaction initiated by adding $FeCl_3$ to thermostated solution (dye + H_2O_2). The progress of the reaction was monitored at λ_{max} = 430 nm using a thermostated 292 Cecil spectrophotometer.

Results and Discussion

Effect of pH

Advanced oxidation processes are powerful alternative methods of wastewater treatment. This method based on the production of powerful oxidant, $HO^{\bullet}$ (E = 2.8 V versus NHE). These radical are capable to degrade recalcitrant organic compounds under mild experimental conditions.[11] The general mechanism of Fenton reaction[12] is

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

k = 76.5 $mol^{-1}\ dm^3\ s^{-1}$

Then, Fe^{3+} ions can be reduced by excess H_2O_2 to form Fe^{2+} ions and more $HO^{\bullet}$ Radicals. Second reaction is called Fenton-like[13] allowing Fe^{2+} regeneration leading to catalytic mechanism (reactions, 2-4),

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^{+} \quad (2)$$

$K_{eq} = 3.1 \times 10^{-3}$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (3)$$

$k = 27\times10^{-3}\ s^{-1}$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (4)$$

$k < 2\times10^{3}\ mol^{-1}\ dm^3\ s^{-1}$

The perhydroxy radicals ($HO_2^{\bullet}$) are unstable and converted to hydroxyl free radicals ($HO^{\bullet}$) as in reaction 5

$$2HO_2^{\bullet} \rightarrow 2HO^{\bullet} + O_2 \quad (5)$$

$$dye + HO^{\bullet} \rightarrow product \quad (6)$$

As clear from equation (1) the amount of $HO^{\bullet}$ depends on the pH of solution. It was reported that the optimum pH value is 3.[4, 6, 14-17]

It was difficult to study the effect of pH on the rate of decolorization of ARS since it is chemical indicator and spectrum changes completely by changing the pH, (Figure 2). Consequently all experiments were performed at pH=2.87

Effect of H_2O_2 concentration

Decolorization reaction rate of ARS dye by Fenton-like process can be represented by equation 7

$$Rate = k[H_2O_2][ARS][Fe^{3+}]^0 \quad (7)$$

$$Rate = k_{obs}\ [ARS] \quad (8)$$

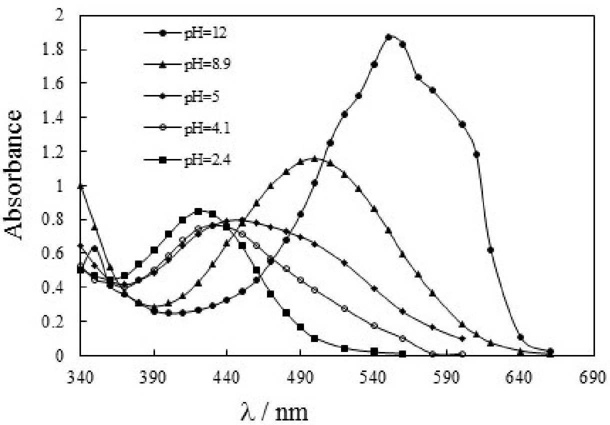

Figure 2. Effect of pH on the absorption spectrum of ARS in aqueous solution. [ARS]= 2×10^{-4} mol dm^{-3}

k_{obs} is obtained from the slope of plot of ln A_t(absorbance of ARS at time interval, t) versus time. Figure 3 showed that the decrease in dye concentration as function of time was dependent of hydrogen peroxide concentration. The data were in good agreement with pseudo first order kinetics model.[18-19] Increasing the hydrogen peroxide concentration ($2\text{-}8\times10^{-3}$ mol dm^{-3}) increases the rate constant from 1.05×10^{-3} to 3.2×10^{-3} s^{-1}, Table 1. Excess of hydrogen peroxide shows no effect on the rate constant. This attributed to production of less reactive radical ($HO_2^{\bullet}$) or consumption of $HO^{\bullet}$ radicals by self-scavenging.[4,6,11,20] Plot of ln k_{obs} versus ln $[H_2O_2]$ yields straight line with slope of unity indicates the reaction is first order in hydrogen peroxide.

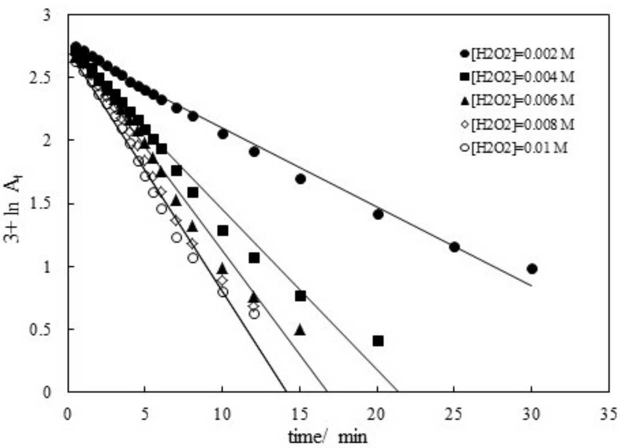

Figure 3. First order plots for the decolorization of ARS by Fenton-like reaction at various H_2O_2 concentrations. pH= 2.87, T = 30 °C, [ARS] = 2×10^{-4} mol dm^{-3}, $[Fe^{3+}]$ = 2×10^{-4} mol dm^{-3}

Efficiency of decolorization was 90% within 15 minutes at 8×10^{-3} mol dm^{-3} of hydrogen peroxide.

Effect of iron(III) chloride concentration

Although no reaction was observed between ARS and hydrogen peroxide in absence of iron(III) ions, iron(III) ions concentration shows soft retardation effect on the degradation rate of ARS. Keeping temperature at 30 °C, [ARS]= 2×10^{-4} mol dm^{-3} and $[H_2O_2]$ = 4×10^{-3} mol dm^{-3} using different concentrations of iron(III) chloride namely, 2-6 x10^{-4} mol dm^{-3}, the degradation rate dropped from 91% to 86% within 20 minutes by increasing the concentration from 2x10^{-4} to 6 x10^{-4} mol dm^{-3}. This could be attributed to the increasing in [Fe^{3+}] increases [Fe^{2+}] which scavenging the $HO^{\bullet}$.[4,6,17] Alireza et al[20] reported that increasing of iron(III) ions concentration increases the decolorization rate of brilliant blue and maximum rate was at [Fe^{3+}] =2x10^{-4} mol dm^{-3}.

Table 1. Observed first order rate constants of the decolorization of ARS by Fenton-like reagent at temperature = 30 °C, pH=2.87

Concentrations, mol dm^{-3}			k_{obs} x10^3 s^{-1}
[ARS]x10^4	H_2O_2x10^3	[Fe^{3+}]x10^4	
1	4	4	2.05
2	4	4	1.70
3	4	4	1.15
4	4	4	0.72
2	2	2	1.05
2	4	2	2.13
2	6	2	2.75
2	8	2	3.20
2	10	2	3.20
2	4	2	2.65
2	4	4	2.70
2	4	6	2.52

The values of first order rate constant, k_{obs}, are given in Table 1, no change with rise of iron(III) chloride concentrations indicates the reaction is zero order in iron(III) chloride. This could attribute to fast formation of very weak complex between iron(III) and ARS in step proceed the rate determining step. M. Tariq et al[21] observed weak complex between Cu^{2+} and ARS and Cu^{2+} retarded the photodegradation of ARS.

Effect of dye concentration

The effect of initial dye concentration of aqueous solution of ARS on Fenton-like process was investigated since pollutant concentration is important parameter in wastewater treatment. Increasing the initial ARS concentration from 1 to 4x 10^{-4} mol dm^{-3} decreases the decolorization from 85 % to 55 % within 15 minutes. Plotting ln A_t versus time, (Figure 4) showed that drop of the rate of decolorization by increasing the dye concentration. This attributed to relatively lower of $HO^{\bullet}$ results from the increasing of ARS concentration while concentration of H_2O_2 and iron(III) chloride remains the same. The obtained results was in good agreement with earlier reported.[15-17]

Effect of Temperature

The variation of the temperature in range of 298-313 K increases the rate of decolorization of ARS, (Figure 5). No optimal temperature in this study was detected as opposed to the literature reports[22-23] in which 30 °C is stated as optimal temperature for Fenton oxidation. Another optimal temperature, 50 °C was reported on decolorization of some dyes by Fenton-like reaction.[4]

The activation energy was calculated from Arrhenius plot and Eyring equation and was found to be 47.04 kJ mol^{-1}.

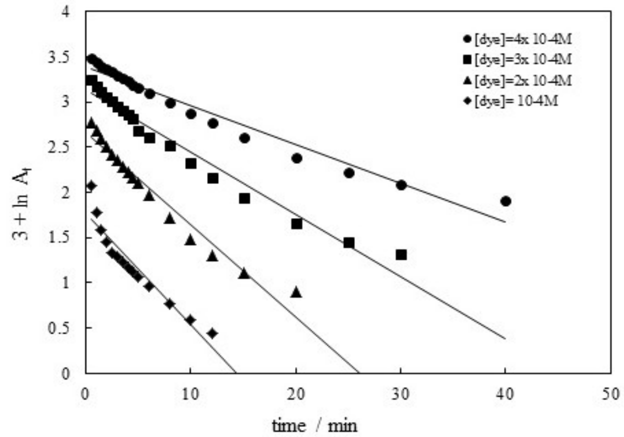

Figure 4. First order plots for the decolorization of ARS by Fenton-like reaction at various ARS concentrations. pH= 2.87, *T* = 30 °C, [H_2O_2] = 4x10^{-3} mol dm^{-3}, [Fe^{3+}] = 4x10^{-4} mol dm^{-3}

Effect of inorganic anions

Inorganic anions occur naturally in wastewater (e.g. NO_3^-) or may be added to facilitate the dyeing (e.g. Cl^- and CO_3^{2-}). The presence of inorganic anions in textile wastewaters plays an important role in the oxidation kinetics of different dyes. Inorganic anions may induce or reduce the rate of photooxidation. For example, formation of $HO^{\bullet}$ radicals during the radiation of nitrate ion may induce the rate of photooxidation[24-25] while scavenging of hydroxyl radicals by chloride and carbonate ions[26-27] reduces the reaction rate.

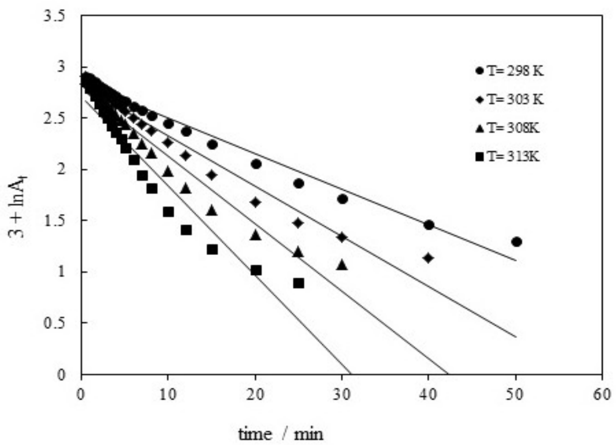

Figure 5. First order plots for the decolrization of ARS by Fenton-like reaction at various temperatures. [ARS] =2x10^{-4} mol dm^{-3}, [Fe^{3+}] =2x10^{-4} mol dm^{-3}, [H_2O_2] =2x10^{-3} mol dm^{-3}, pH=2.87

Effect of $NaNO_3$

Figure 6, shows pseudo first order decolorization of ARS at different concentrations of $NaNO_3$. Addition of 5 g L^{-1} $NaNO_3$, rate constant increased from 1.95x10^{-3} s^{-1} (in absence of nitrate) to 2.53 x 10^{-3} s^{-1}. Increasing the concentration of nitrate up to 20 g L^{-1} had no effect. According to that reported in literature[24-25] increasing the rate was attributed to generation of $HO^{\bullet}$ radicals by rapid protonation of $^{-}O^{\bullet}$ as follow

$$NO_3^- + h\nu \rightarrow NO_3^{-\bullet} \rightarrow NO_2^- + O^{-\bullet}$$

$$O^{-\bullet} + H_2O \rightarrow HO^- + HO^{\bullet}$$

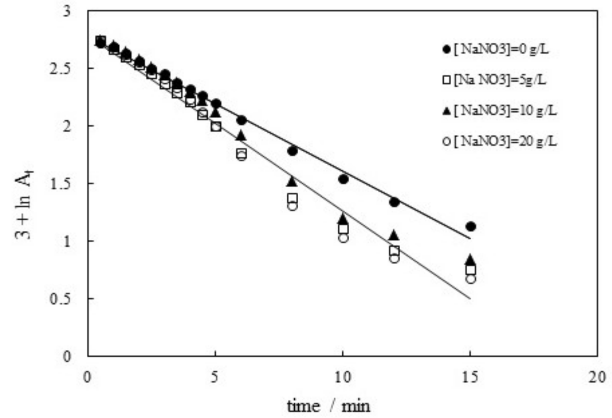

Figure 6. First order plots for decolorization of ARS by Fenton-like reaction at various $NaNO_3$ concentrations. [ARS]=$2x10^{-4}$ mol dm^{-3}, [H_2O_2] = $2x10^{-3}$ mol dm^{-3}, [Fe^{3+}] =$2x10^{-4}$ mol dm^{-3}, *T*= 35 °C, pH= 2.87

In this study the reason was not clear since the reaction occurred in absence of light.

Effect of Na_2CO_3

Different concentrations of Na_2CO_3 were used to study the effect of carbonate ions on the oxidation of Alizarin red S. Carbonate ions were present mainly as H_2CO_3, since the experiments were performed at pH $\leq$ 3. Presence of bicarbonate ions in the course of oxidation may decrease the decolorization rate due to scavenging of $OH^{\bullet}$ by HCO_3^- ($HCO_3^- + HO^{\bullet} \rightarrow CO_3^{-\bullet} + H_2O$). Production of $CO_3^{-\bullet}$ which is less reactive than hydroxyl radical[27] lowered the levels of $HO^{\bullet}$ during the course of the reaction hence decreasing the decolorization rate as shown in (Figure 7). It was observed that the decolorization rate constant (1.78 x 10^{-3} s^{-1}) in the absence of carbonate ions decreased to 1.12 x 10^{-3} s^{-1} due to the presence of 8×10^{-3} mol dm^{-3} Na_2CO_3.

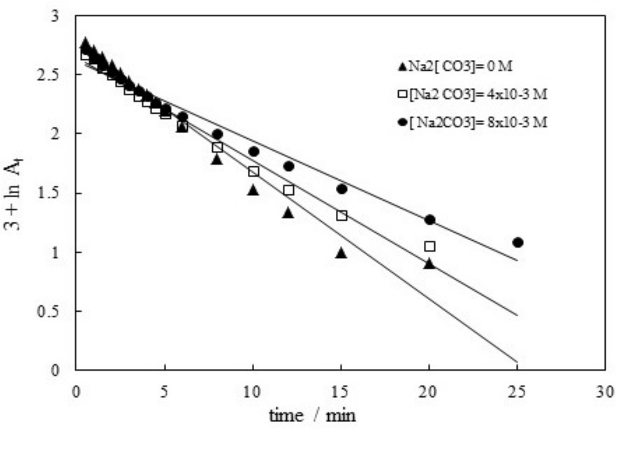

Figure 7. First order plots for the degradation of ARS by Fenton-like reaction at various Na_2CO_3 concentrations. [ARS] =$2x10^{-4}$ mol dm^{-3}, [H_2O_2] =$2x10^{-3}$ mol dm^{-3}, [Fe^{3+}] = $2x10^{-4}$ mol dm^{-3}, T=35 °C, pH=2.87

Effect of NaCl

In absence of chloride, the dye decolorization was 90% in 20 minutes. The addition of 5 g L^{-1} to the dye solution caused 15% increase in decolorization in first 5 minutes after that the decolorization rate decreased in comparison in absence of chloride. Figure 8 shows pseudo first order decolorization of ARS at different concentrations of NaCl. High chloride concentration had no effect on the rate of dye decolorization.

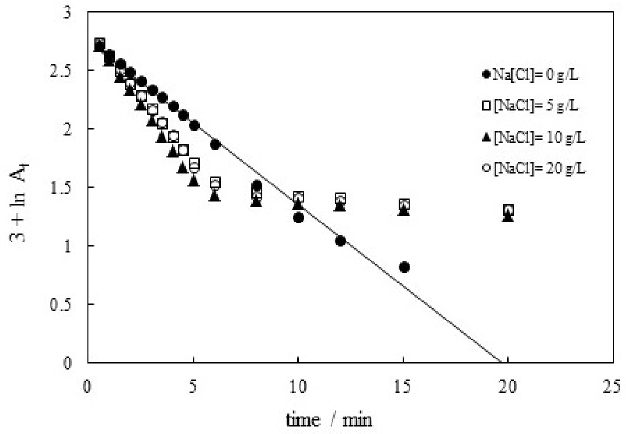

Figure 8. First order plots for degradation of ARS by Fenton-like reaction at various NaCl concentrations. [ARS] =$2x10^{-4}$ mol dm^{-3}, [H_2O_2] = $2x10^{-3}$ mol dm^{-3}, [Fe^{3+}] =$2x10^{-3}$ mol dm^{-3}, T= 35 °C, pH = 2.87

Conclusion

The decolorization kinetics of Alizarin Red S in aqueous solution was studied using Fenton like reaction in dark environment. The results showed that the Fenton like is powerful method for decolourization of ARS. The rate of decolorization is decreased by increasing the concentration of dye and addition of carbonate. The rate of decolorization is increased by increasing the concentration of hydrogen peroxide and addition of nitrate. The reaction was first order in ARS, H_2O_2 and zero order in ferric chloride.

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Received: 21.10.2013.
Accepted: 10.12.2013.