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Investigation of the oxidative decolorization of Acid Red 14 by peroxydisulfate with thermally activated and Ag(I) catalysis

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ABSTRACT

The present study investigates the degradation of Acid Red 14 (AR 14), commonly used as a textile dye, in aqueous medium through the process of thermally activated oxidation by peroxydisulfate under a set of variables (concentration of $S_2O_8^{2-}$, AR 14, Ag^+ and temperature). Degradation efficiency was small when the oxidation was carried out in the absence of heat. Increasing the temperature from 20 to 70 °C accelerated the oxidation rate of AR 14, which achieved complete oxidation in 10 min. Also results showed that removal of dye increased with increasing Ag^+, peroxydisulfate initial concentration, pH and dye initial concentration decreasing. Our results suggest that the oxidative treatment of AR 14 by peroxydisulfate activated with heat is a viable option for removal of the textile dyes from effluents.

Keywords: Advanced oxidation process; Acid Red 14 degradation; Peroxydisulfate; Thermal; Wastewater treatment

1. Introduction

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dyes, such as Acid Red 14 (AR 14), are widely used in the textile industry [1,2] Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation, elimination by adsorption on activated carbon, etc. are applied for color removal from textile effluents [3]. In the last decades, chemical oxidation of contaminants in the natural environment by oxidants has been increasingly studied to develop novel remediation technologies. The oxidants H_2O_2, $KMnO_4$, O_3, Fenton's reagent, peroxidisulfate ($S_2O_8^{2-}$) have been widely tested in laboratory work and field applications and used for the remediation of soil and groundwater contaminated by organic compounds. *Peroxydisulfate* has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants. The use of peroxydisulfate has several advantages; It is a strong oxidizing agent ($E^0 = 2.01$ V), non-selectively reactive, and relatively stable at room temperature. peroxydisulfate, widely used in many industrial processes (e.g., polymerization and metal surface oxidation), has been recently studied as an oxidant alternative for treating contaminants [4,5]. In addition to its oxidation power, above-mentioned advantages make the peroxydisulfate oxidation a promising choice among the advanced oxidation processes (AOPs) for site clean-up applications [4].

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Also, heat, transition metal ions (M^{n+}) and UV light can excite $S_2O_8^{2-}$ to form sulfate radical ($SO_4^{\bullet-}$), a stronger oxidant ($E^0 = 2.60$ V) than $S_2O_8^{2-}$, to significantly enhance the oxidation of contaminants.

$$S_2O_8^{2-} + \text{heat}/UV \rightarrow 2SO_4^{\bullet-} \quad (1)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\bullet-} + M^{(n+1)+} + SO_4^{2-} \quad (2)$$

In a peroxydisulfate–water system, hydroxyl radicals can be formed via following reactions, and may participate in the oxidation of contaminants

$$\text{All pHs: } SO_4^{\bullet-} + H_2O \rightarrow OH^{\bullet} + H^+ + SO_4^{2-} \quad (3)$$

$$\text{Alkaline pH: } SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \quad (4)$$

Using electron paramagnetic resonance techniques, have reported that in neutral to acidic solutions (pH 7–2) the formation of $SO_4^{\bullet-}$ is observed and in solutions with pH > 12 $OH^{\bullet}$ is the active species formed in $S_2O_8^{2-}$ systems. $S_2O_8^{2-}$ has great capability of degrading numerous organic contaminants through free radicals (e.g., $SO_4^{\bullet-}$ and $OH^{\bullet}$) generated in the peroxydisulfate system [4–6]. Sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($OH^{\bullet}$) are generated as a result of heat decomposition of $S_2O_8^{2-}$ in aqueous phases. The early studies using heat-assisted peroxydisulfate oxidation reported that the employed process effectively oxidize 59 volatile organic compounds, including benzene, tol uene, ethylbenzene, xylene, methyl *tert*-butyl ether (MtBE), trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA), etc. [4,7,8]. Also for oxidative decolorization of Acid Red 14 as an azo dye by peroxydisulfate system, the following mechanism is proposed [9].

$$S_2O_8{}^{2-} \rightarrow 2SO_4^{-} \quad (5)$$

$$\underset{\text{(I)}}{-N{=}N-} + SO_4^{-} \rightarrow \underset{\text{(I')}}{-\overset{+}{N}-N-} + SO_4{}^{2-} \quad (6)$$

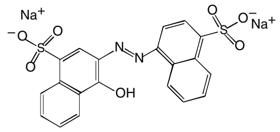
$$-\overset{+}{N}-N- + SO_4^{-} \rightarrow -\overset{+}{\underset{\underset{OSO_3^-}{|}}{N}}{=}N- \quad (7)$$

$$-\overset{+}{\underset{\underset{OSO_3^-}{|}}{N}}{=}N- + H_2O \rightarrow -\underset{\underset{O}{\downarrow}}{N}{=}N + H^+ + HSO_4^- \quad (8)$$

The formation of the azoxy product in Eq. (8), has been previously reported for the oxidation of azo-containing compounds, e.g., 4-(phenylazo)diphenylamine and some direct dyes [10,11] –N=N–(I) and $-N^+ -N^{\bullet}-$ (I′) are referred to as the azo centre of the compounds and their radical intermediate species, respectively.

In the present study, the thermally oxidation of AR 14 (the properties of the Acid Red 14 presented in Table 1) by peroxydisulfate was investigated via batch experiments. The effect of concentration of $S_2O_8^{2-}$, Ag^+, dye and temperature on the AR 14 degradation was examined. The findings of this study could be helpful for the treatment of wastewater.

Table 1
Properties of Acid Red 14

Color index	Acid Red 14
Azo group	One
Type	Anionic
Structure	
λ_{max} (nm)	514
Molecular weight (g/mol)	502.4

2. Materials and methods

2.1. Materials

The dye Acid Red 14 was provided by Sigma–Aldrich, and used without further purification. Silver nitrate was obtained from Applichem and amonium peroxydisulfate from Merck. Its solution was immediately prepared before the measurements to avoid the change of concentration due to self-decomposition. Other chemicals were of analytical reagent grade and were used without further purification, and all solutions were prepared in distilled water.

2.2. Methods

First of all, 50 ml synthetic solution containing the desired initial concentration of $S_2O_8^{2-}$ and dye solution in a glass bottle were mixed using a magnetic stirrer and was placed inside thermostat for temperature control under isothermal condition. The reaction temperature was in the range of 20–70 ± 0.1 °C. During the experiments the temperature controlled by Lauda RE 104 thermostat varied within ± 0.1 °C from its set point. The dye solution samples were taken at the desired time intervals and were analyzed by a UV/vis spectrophotometer (shimadzu UV-160) at λ_{max} = 514 nm. The operating conditions of all experimental test runs are summarized in each figure legend. The efficiency of color removal was expressed as the ratio of A_t to A_0 (Eq. (9)), where A_0 is the initial absorbance value of AR 14 and, A_t is the absorbance value of AR 14 at time t.

$$X = \frac{A_t}{A_0} \quad (9)$$

3. Results and discussion

3.1. Effect of heat on AR 14 oxidation by peroxydisulfate

Fig. 1 shows the decay of AR 14 vs. time for experiments carried out with and without heat in concentration of dye 20 ppm, 80 mm of $S_2O_8^{2-}$, natural pH in ambient temperature (25 °C) and other 5 °C. There was no observable loss of the color when the $S_2O_8^{2-}$ was applied in the absence of heat but, in elevated temperature, the oxidation rate of AR 14 accelerated, which achieved complete oxidation. The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was oxidizing by $S_2O_8^{2-}$ and heat.

3.2. Effect of initial peroxydisulfate concentration

The concentration of $S_2O_8^{2-}$ was found to be an important parameter for the degradation of AR 14 by $S_2O_8^{2-}$ oxidation. The decay of AR 14 was indicated in Fig. 2 in concentration of 5, 10, 20, 40, 80, 100, 150, 200 mm and initial AR 14 concentration of 20 ppm at 50 °C. For different $S_2O_8^{2-}$ concentrations, from 10 to 200 mm, oxidative reaction increased. This is likely because sulfate radicals are generated simultaneously and improved the oxidative decolorization of AR 14. Oxidizing species (mostly likely $SO_4^{\bullet-}$ under the experimental conditions) might dominate the reaction with AR 14 although numerous oxidizing species (e.g., $SO_4^{\bullet-}$, $OH^{\bullet}$ and $S_2O_8^{2-}$) could exist in the system and react with dye [12,13].

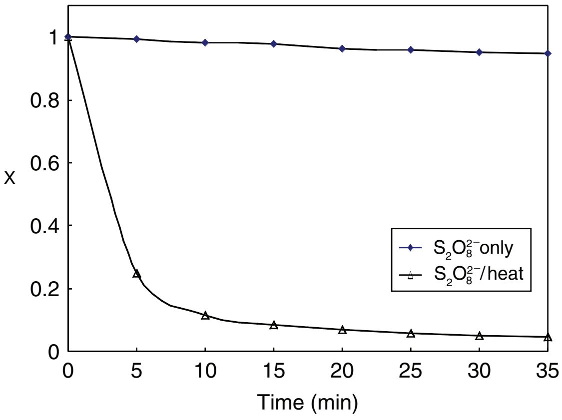


Fig. 1. Effect of heat on peroxydisulfate oxidation in decolorization of AR 14. $[AR\ 14]_0$ = 20 ppm, $[S_2O_8^{2-}]_0$ = 80 mm, pH_0 = natural (6.3), T = 25, 50 °C.

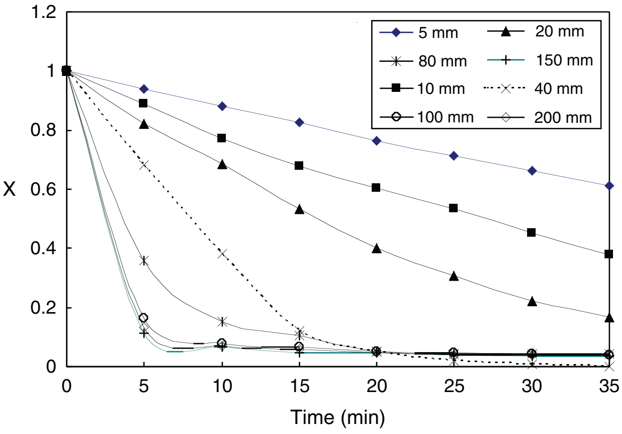


Fig. 2. Effect of initial concentration of $S_2O_8^{2-}$ (mm) in oxidative decolorization of AR 14. $[AR\ 14]_0$ = 20 ppm, pH_0 = natural (6.3), T = 50 °C.

3.3. Effect of initial dye concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of dye. The results in Fig. 3 shows the dye degradation with 80 mm of $S_2O_8^{2-}$ at natural pH (6.3) and 50 °C. It is observed that the dye removal increases rapidly at low AR 14 concentrations and then changes slowly as the initial concentration increases at the same concentration of $S_2O_8^{2-}$ [14].

3.4. Effect of temperature

The results in Fig. 4 that shows the percent AR 14 degradation at 35 min at 20, 30, 40, 50, 60 and 70 °C elucidate the temperature effect on the reactions of peroxydisulfate with AR 14. Comparison of the data reveals that the reaction rates increased with increasing reaction temperature. In addition, the activation energy of the degradation reaction could be obtained based on the experimental data using the Arrhenius equation, $k = A \exp(-E_a/RT)$, where A is the frequency factor, E_a is the activation energy, R is the universal gas constant and T is the temperature in Kelvin indicating that heat energy can activate peroxydisulfate to sulfate radicals more effectively [4,7].

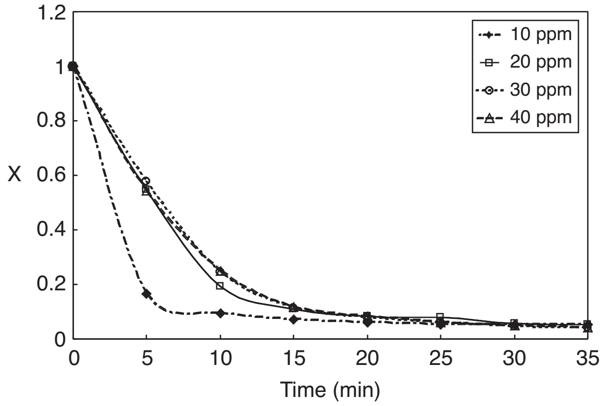


Fig. 3. Effect of initial dye (ppm) concentration in oxidative decolorization of AR 14. $[S_2O_8^{2-}]_0$ = 80 mm, pH_0 = natural (6.3), T = 50 °C.

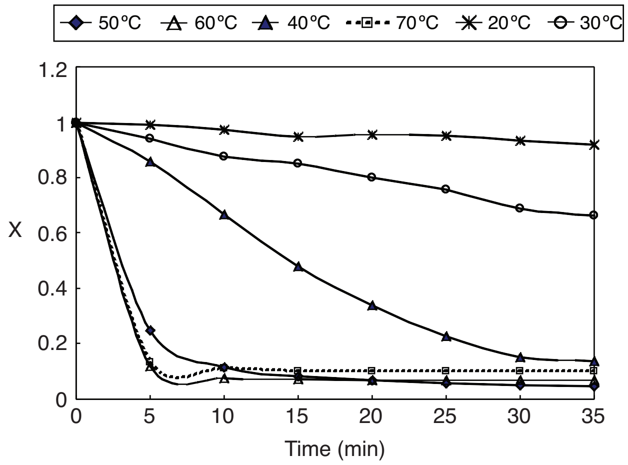


Fig. 4. Effect of temperature in oxidative decolorization of AR 14. $[S_2O_8^{2-}]_0 = 80$ mm, $[AR\ 14]_0 = 20$ ppm, pH_0 = natural (6.3).

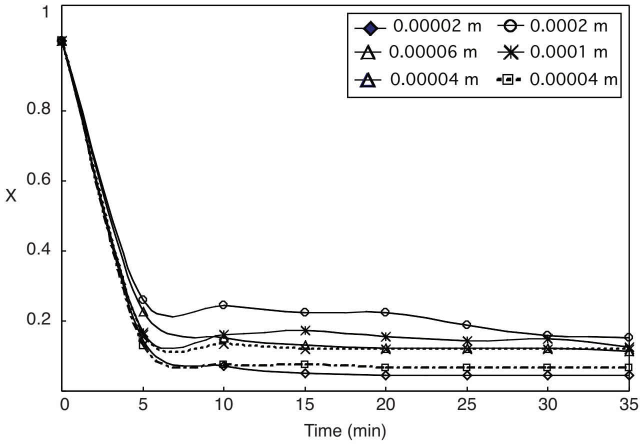


Fig. 5. Effect of initial concentration of Ag^+ (M) in oxidative decolorization of AR 14. $[S_2O_8^{2-}]_0 = 80$ mm, $[AR\ 14]_0 = 20$ ppm, pH_0= natural (6.3), $T = 50$ °C.

3.5. Effect of thermally oxidation of AR 14 by peroxydisulfate in presence of Ag^+

The results from the degradation of the AR 14 (20 ppm) using different concentration of Ag^+ in concentration of 80 mm $S_2O_8^{2-}$ and at 50 °C were summarized in Fig. 5. The removal efficiency increased with improving in Ag^+ concentration. It was reported that Ag^+ was the most efficient metal ion for the activation of peroxydisulfate among nine transition metals tested by Anipsitakis and Dionysiou [15]. It can be seen from Fig. 5 that in 10 min a large amount of the dyes are disappeared. About this result can be explained in terms of that increasing in Ag^+ concentration accelerate the conversion of $S_2O_8^{2-}$ to $SO_4^{\bullet-}$ to oxidize AR 14 rapidly.

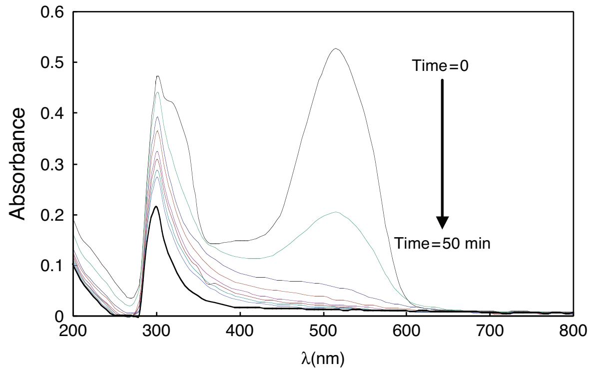


Fig. 6. Spectral changes of AR 14 solution during illumination in the presence of $S_2O_8^{2-}$ and heat. $[S_2O_8^{2-}]_0 = 80$ mm, $[AR\ 14]_0 = 20$ ppm, pH_0 = natural (6.3), $T = 50$ °C.

3.6. Spectral changes of AR 14 solution during illumination in the presence of $S_2O_8^{2-}$ and heat

The changes in the absorption spectra of AR 14 solutions during the heat assisted oxidation process in concentration of 80 mm $S_2O_8^{2-}$ in natural pH (6.3) and 50 °C at different times are shown in Fig. 6. The color of an azo dye is the result of the interaction between an azo function (–N=N–) and two aromatic species: the dyes carry an acceptor group which is an aromatic nucleus frequently containing a chromophoric group, e.g., $-SO_3^-$, and a donor group, e.g., an aromatic nucleus containing an auxochromic group such as OH group [16]. The decrease of the absorption peak of AR 14 at 514 nm in Fig. 6 indicated a rapid decolorization of the dye. The decrease is also meaningful with respect to the nitrogen-to-nitrogen double bond (–N=N–) of the azo dye, as the most active site for oxidative attack. Decrease in absorption intensity of the band at λ_{max} during the oxidation also expresses the loss of conjugation, e.g., especially the cleavage near the azo bond of the organic molecule. The weak band at 310–330 nm could be attributed to the π–π* transition related to the aromatic ring attached to the –N=N– group in the dye molecule. Absorbance decrease at 310–330 nm indicates the degradation of aromatic part of the dye.

The degradation pathway of the AR 14 could be explained as follows: the fragile group in this dye is the NH group, which results from an equilibrium between two tautomeric forms where an H atom is exchanged between O and N as shown in Fig. 7. Indeed, the abstraction of H atom (carried by an oxygen atom in the azo form and by a nitrogen atom in the hydrazone form) by sulfate or hydroxyl radicals is the main degradation pathway of this dye [17].

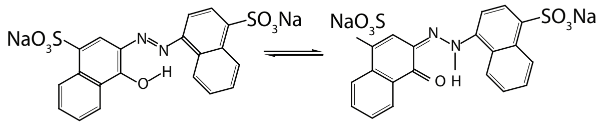


Fig. 7. Equilibrium between the two tautomeric forms in C. I. Acid Red 14.

4. Conclusion

In summary, our results show that AR 14 is effectively oxidized by peroxydisulfate activated with heat and Ag^+. Complete oxidation of AR 14 by peroxydisulfate in the presence of heat energy or Ag^+ was obtained within 10 min under optimal conditions. Our results suggest that (pre) treatment of AR 14 by heat- or Ag(I)-activated peroxydisulfate may be an option for improving the degradability of AR 14 in natural and engineered systems.

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