

Decolorization of Reactive Red 239 Via Heat Activated Persulfate

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Abstract: Effluents of cotton dyeing process of textile industry is considered as extremely polluted due to presence of unfixed azo dyes and auxiliary chemicals. The complex aromatic structure and non-biodegradability nature of azo dyes involved new and efficient treatment technologies to eliminate intense color from textile wastewater. In recent years, *in-situ* chemical oxidation technology (ISCO) using persulfate ($S_2O_8^{2-}$) as an oxidant has appeared to be a promising method for removal of azo dyes. $S_2O_8^{2-}$ can be activated by UV, heat or transition metals to generate sulfate radical ($SO_4^{\cdot-}$). In this study, decolorization of Reactive Red 239 (RR239) azo dye via heat activated $S_2O_8^{2-}$ was explored. Experiments were conducted in a cylindrical batch reactor equipped with a water jacket. Effect of parameters such as temperature, pH and $S_2O_8^{2-}$ concentration on decolorization of RR239 was investigated. The results show that decolorization efficiency was enhanced with increasing temperature from 45 to 55°C but further increase in temperature did not enhance decolorization. The pseudo first order rate constant values fit well Arrhenius equation, yielding an activation energy of 108.75 kJ mol⁻¹ for decolorization of RR239. The highest decolorization efficiency was obtained at pH=3 under the tested pH range. As $S_2O_8^{2-}$ concentration increased decolorization efficiency increased. 89.67% and 39.05% decolorization and aromatic degradation efficiencies were observed within 120 minutes of reaction time, respectively. These results show that heat activated $S_2O_8^{2-}$ method was a feasible method for decolorization of RR239.

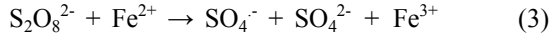
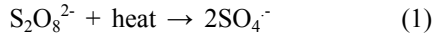
Keywords: Heat Activated Persulfate, Sulfate Radical, Azo Dye, Decolorization

1. Introduction

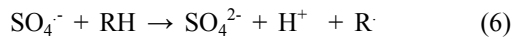
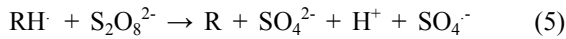
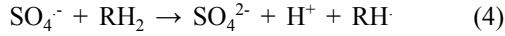
Remediation of a large volume of wastewater originating from textile industry is of basic importance for preventing water pollution. Effluents of cotton dyeing process of textile industry are characterized by having an intense color and a low BOD₅/COD ratio due to presence of unfixed reactive dyes. BOD₅/COD ratio ranges from 0.06 to 0.35, indicating a low biodegradability of textile effluents [1-2]. Since reactive dyes have a low dye-fiber fixation rate in comparison with other dyes, a considerable amount of them is lost in dyeing process. The release of them into receiving water bodies causes non-aesthetic pollution, eutrophication and reduction of light penetration [3-5]. The chromophore group of reactive dyes is mostly azo type and azo dyes are known to be toxic and mostly nonbiodegradable. Although several treatment technologies have been considered for textile wastewater so far, they are not efficient in the presence of nonbiodegradable azo dyes. Removal of azo dyes by conventional aerobic

biological treatment is not amenable and aromatic amines which show more toxic effect than dye molecules are formed under anaerobic conditions. Physical methods transfer dyes from one phase to another and cause secondary pollution [6]. Therefore, an efficient treatment technology for removal of azo dyes from textile effluents should be developed to meet stringent discharge limits. Recently, *in-situ* chemical oxidation technology (ISCO) in which hydrogen peroxide (H_2O_2), persulfate ($S_2O_8^{2-}$), permanganate (MnO_4^-) and ozone (O_3) are used as an oxidant has emerged as an alternative to conventional technologies[7]. $S_2O_8^{2-}$ is a strong oxidant with an oxidation-reduction potential of 2.01 V and offers some advantages such as high stability, high aqueous solubility, high oxidation-reduction potential and relatively low cost over other oxidants [8-9]. When $S_2O_8^{2-}$ is activated, sulfate radical ($SO_4^{\cdot-}$) with an oxidation-reduction potential of +2.5 to +3.1 V vs. NHE is generated. $SO_4^{\cdot-}$ is capable of degradation of hazardous water contaminants through electron transfer [10]. $S_2O_8^{2-}$ can be activated by UV [6, 11-14], heat [10, 15-17] and

transition metals [9, 18]. The related equations with these activation methods are given as follows [19-20]:



Once $\text{SO}_4^{\cdot-}$ is generated *in-situ* by these methods, organic compounds (R) are degraded through chain reactions as summarized in the following equations[6]:



The objective of this study was to investigate decolorization of a model azo dye, Reactive Red 239 (RR239), via heat activated $\text{S}_2\text{O}_8^{2-}$. The effect of process variables on decolorization of RR239 was evaluated.

2. Method

2.1. Materials

All chemicals used in this study were of analytical grade and used without further purification. $\text{Na}_2\text{S}_2\text{O}_8$ ($\geq 99.9\%$) was acquired from Merck. A commercially available RR239 was from DyStar. HCl (37% w/w) was purchased from Merck and NaOH was purchased from Sigma-Aldrich.

2.2. Experimental Procedure

Decolorization of RR239 was performed in a cylindrical batch reactor using RR239 solution of appropriate concentration prepared by diluting 100 mg dm^{-3} stock solution. For each run, 0.5 dm^3 RR239 solution at desired concentration was put into reactor and stirred by a magnetic stirrer (IKA RH KT/C) for 10 minutes. The initial pH of RR239 solution was adjusted using either dilute NaOH or HCl solution. After addition of $\text{Na}_2\text{S}_2\text{O}_8$, the reaction was initiated. The temperature of reaction medium was hold at predetermined temperature by circulating water heated in the thermostatic water bath (Nüve BS 302) through the water jacket of the reactor.

2.3. Analysis

Samples taken from reaction medium at regular time intervals were analyzed by means of a double beam Shimadzu UV-1700 Pharmaspec UV-Visible Spectrophotometer. The concentration of RR239 was determined by measuring the absorbance at maximum wavelength of 540 nm. Decolorization efficiency of the samples was calculated as follows:

$$\text{Decolorization \%} = [\text{C}_0(540\text{nm}) - \text{C}(540\text{nm}) / \text{C}_0(540\text{nm})] \times 100 \quad (8)$$

Aromatic degradation efficiency of the samples was calculated as follows:

$$\text{Degradation \%} = [\text{C}_0(289\text{nm}) - \text{C}(289\text{nm}) / \text{C}_0(289\text{nm})] \times 100 \quad (9)$$

where C_0 and C are the initial and treated dye concentrations at corresponding wavelengths, respectively.

3. Results and Discussion

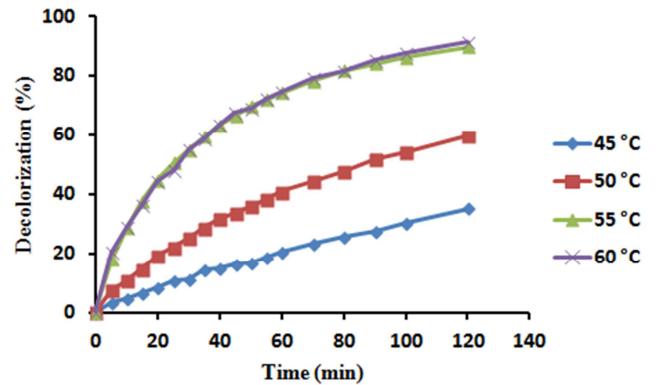
3.1. Effect of Temperature

The effect of temperature was investigated in the temperature range of 45-60 °C using $2 \text{ mM Na}_2\text{S}_2\text{O}_8$ at initial RR239 concentration of 40 mg dm^{-3} . As is evident from Figure 1, decolorization efficiency increased with increasing temperature up to 55 °C and no enhancement was observed with a further increase in temperature within 120 minutes of reaction time.

Linear plot of $\ln(\text{C}_0/\text{C})$ vs. time exhibits pseudo first order kinetic model for decolorization of RR239 via heat activated $\text{Na}_2\text{S}_2\text{O}_8$. Pseudo first order kinetic model can be expressed as:

$$\ln(\text{C}_0/\text{C}) = k_{\text{app}}t \quad (10)$$

where C_0 and C are initial and treated dye concentrations, k_{app} is pseudo first order rate constant and t is reaction time.



$$[\text{RR239}] = 40 \text{ mg dm}^{-3}, [\text{S}_2\text{O}_8^{2-}] = 2 \text{ mmol dm}^{-3}, \text{pH}=3$$

Figure 1. Effect of temperature on decolorization of RR239.

As shown in Figure 2, experimental data fit well to pseudo first order kinetic model evidenced by high correlation coefficients (R^2). The pseudo first order rate constant values were increased from 0.0035 to 0.0196 min^{-1} as temperature increased from 45°C to 60 °C. Besides, Arrhenius equation (11) was used to determine the activation energy for decolorization of RR239.

$$\ln(k_{\text{app}}) = \ln A - E_a/RT \quad (11)$$

where A is the frequency factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. Arrhenius dependency of pseudo first order rate constants obtained for decolorization of RR239 over the range of temperature studied is given in Figure 3. The activation

energy was calculated as $108.75 \text{ kJ mol}^{-1}$ from this figure.

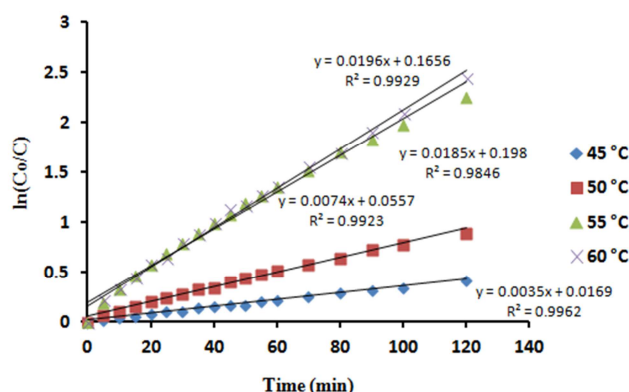


Figure 2. Kinetics of decolorization of RR239.

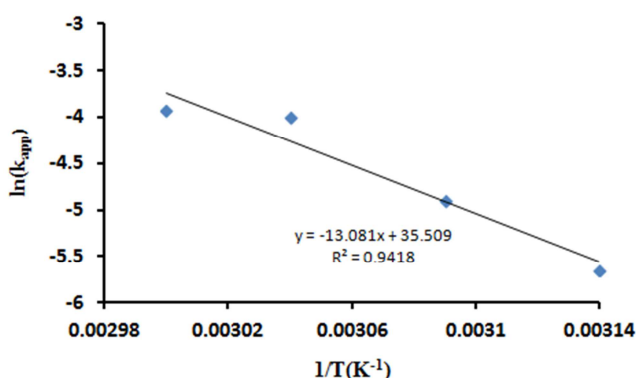
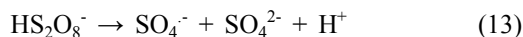
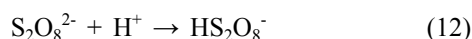


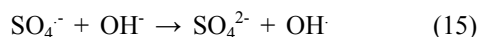
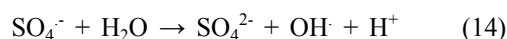
Figure 3. Arrhenius plot of pseudo first order rate constants.

3.2. Effect of pH

The effect of pH on decolorization of RR239 was investigated in the range of 3-9 at 55°C using $2 \text{ mM Na}_2\text{S}_2\text{O}_8$ with initial RR239 concentration of 40 mg dm^{-3} . As can be deduced from Figure 4, an appreciable decolorization was observed at $\text{pH}=3$ in compared to that in neutral and basic conditions. In acidic condition $\text{S}_2\text{O}_8^{2-}$ can be decompose into SO_4^\cdot through following equations [14]:



In neutral and basic conditions, SO_4^\cdot is transformed to hydroxyl radical (OH^\cdot) by equations 14 and 15 [16].

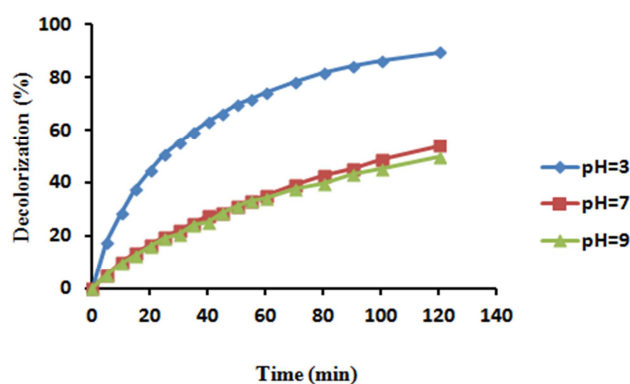


OH^\cdot is another strong radical with an oxidation-reduction potential of $+1.8$ to $+2.7 \text{ V}$ vs. NHE. SO_4^\cdot is preferable because of its higher oxidation-reduction potential, longer half life and ability of oxidizing organic compounds selectively [21-22]. The pH of solution considerably influences presence of predominant radical in the reaction medium. In this study, decolorization efficiency followed the order of $\text{pH}=3 > \text{pH}=7 > \text{pH}=9$. Similar result was reported by Jiang et al. [10] for

oxidation of fluoroquinolone antibiotics via heat activated $\text{S}_2\text{O}_8^{2-}$.

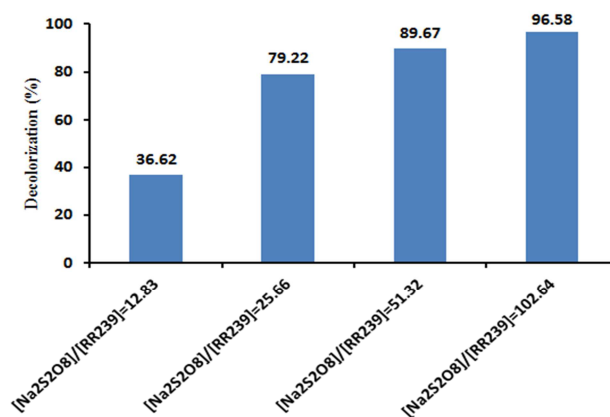
3.3. Effect of $\text{S}_2\text{O}_8^{2-}$ Concentration

In order to investigate the effect of $\text{S}_2\text{O}_8^{2-}$ concentration a series of experiments was conducted. $[\text{S}_2\text{O}_8^{2-}]_0/[\text{RR239}]_0$ mole ratios was obtained by fixing $[\text{RR239}]_0$ to 40 mg dm^{-3} (0.03897 mM) and varying $[\text{S}_2\text{O}_8^{2-}]_0$ from 0.5 mM to 4 mM . As shown in Figure 5, decolorization efficiency increased with increasing $[\text{S}_2\text{O}_8^{2-}]_0/[\text{RR239}]_0$ ratio. As expected, increasing $\text{S}_2\text{O}_8^{2-}$ concentration resulted in generation of more SO_4^\cdot in the solution, thus leading to higher decolorization efficiency. Based on these results a higher $\text{S}_2\text{O}_8^{2-}$ concentration would provide high decolorization efficiency. This result was in agreement with the studies reported by Tan et al. [15] and Ghauch et al. [16].



$[\text{RR239}] = 40 \text{ mg dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = 2 \text{ mmol dm}^{-3}$, $T=55^\circ\text{C}$

Figure 4. Effect of pH.



$[\text{RR239}] = 40 \text{ mg dm}^{-3}$, $\text{pH}=3$, $T=55^\circ\text{C}$

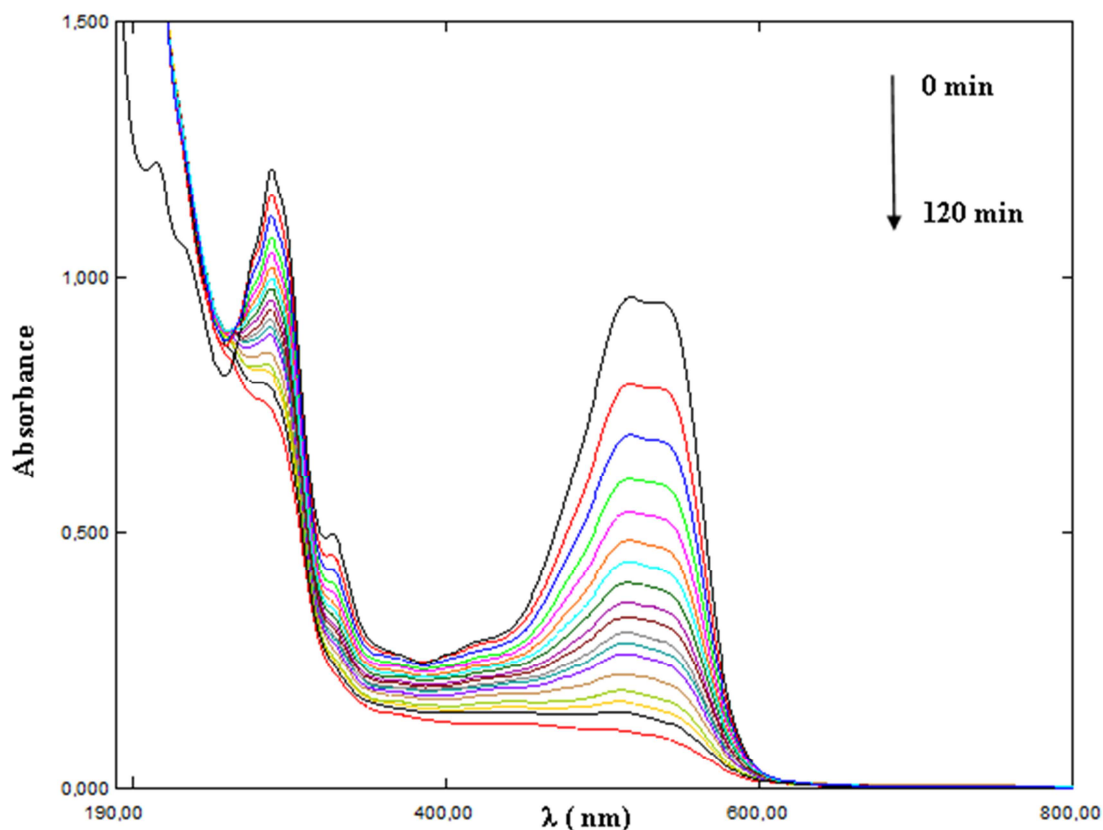
Figure 5. Effect of $\text{S}_2\text{O}_8^{2-}$ Concentration.

3.4. UV-Visible Spectral Changes of RR239

As is evident from Figure 6, two main peaks at 289 and 540 nm were appeared in UV-visible spectra of RR239 measured over the wavelength range of $190\text{-}800 \text{ nm}$ during 120 minutes of reaction time. The absorbance peak at 540 nm in visible region is attributed to chromophoric group of RR239 and peak in the UV region at 289 is attributed to

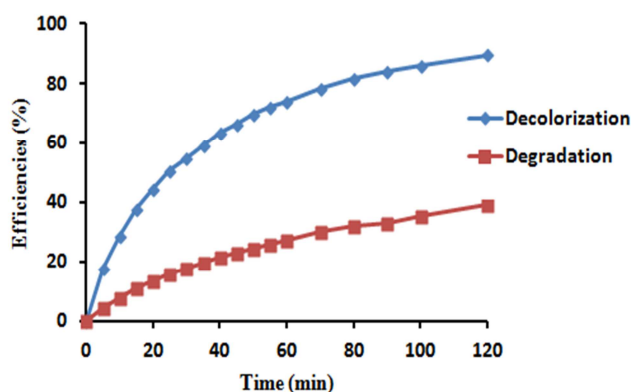
benzene ring. Accordingly, decolorization of RR239 via heat activated $S_2O_8^{2-}$ was monitored by measuring the absorbance at 540 nm, while aromatic degradation was followed by measuring the absorbance at 289 nm. Decolorization and aromatic degradation efficiencies obtained using 2 mM $Na_2S_2O_8$ with initial RR239 concentration of 40 mg dm^{-3} at 55°C and $\text{pH}=3$ were given in Figure 7. 89.67% of decolorization and 39.05% of degradation efficiency levels

were reached at the end of 120 minutes. Decolorization occurred via cleavage of $-N=N-$ bond and almost complete decolorization was achieved within 120 minutes of reaction time. However, decolorization does not mean the removal of RR239 completely. Colorless intermediates are expected to be formed during reaction. Therefore, aromatic degradation required longer time than decolorization.



$[RR239] = 40 \text{ mg dm}^{-3}$, $[S_2O_8^{2-}] = 2 \text{ mmol dm}^{-3}$, $T=55^\circ\text{C}$, $\text{pH}=3$

Figure 6. UV-visible spectra of RR239.



$[RR239] = 40 \text{ mg dm}^{-3}$, $[S_2O_8^{2-}] = 2 \text{ mmol dm}^{-3}$, $T=55^\circ\text{C}$, $\text{pH}=3$

Figure 7. Decolorization and degradation efficiencies of RR239.

4. Conclusion

In the present study, decolorization of RR239 azo dye via

heat activated persulfate was investigated. A series of experiments was carried out to evaluate the effect of temperature, pH and $S_2O_8^{2-}$ concentration. Decolorization efficiency increased with increasing temperature up to 55°C and further increase in temperature did not enhance decolorization. Activation energy was calculated as $108.75 \text{ kJ mol}^{-1}$ using Arrhenius equation. 89.67% of decolorization was observed at $\text{pH}=3$, whereas 54.04% and 49.58% decolorization efficiency values were obtained at $\text{pH}=7$ and $\text{pH}=9$, respectively. When $[S_2O_8^{2-}]_0/[RR239]_0$ mole ratio was increased from 12.83 to 102.64 decolorization efficiency was improved from %36.62 to %96.58. Since $SO_4^{\cdot -}$ firstly attacked to $-N=N-$ bond of dye degradation efficiency was lower than decolorization efficiency at the end of 120 minutes, thus requiring longer time for complete degradation. Experimental results confirmed that decolorization of RR239 was achieved effectively via heat activated $S_2O_8^{2-}$.

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