

Investigation of Immobilized Silver Nanoparticles –Catalyzed in Eliminating Trace amount of Acid Red 87 Dye with Peroxydisulfate from Contaminated Water

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Abstract

The present study was carried out to investigate the effect of silver nanoparticles to catalyzed peroxydisulfate in order to removal of Acid Red 87 from contaminated water, the simultaneous use of peroxydisulfate and nanosilver significantly increased the removal efficiency. The effects of various parameters such as Peroxydisulfate concentration, contaminant concentrations and dosage of silver nanoparticles on the dye removal were evaluated. Results showed that increasing the concentration of peroxydisulfate and nano-silver catalyst can increase the rate of pollutants removal. The optimal amount of nanosilver and the optimum concentration of peroxydisulfate were estimated 0.125g.L⁻¹ and 10 mM, respectively.

Keywords: advanced oxidation, Nano technology, Peroxydisulfate, Acid Red 87, nanosilver

1. Introduction

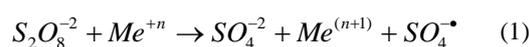
Effluent from the textile, leather, food processing, dyeing, cosmetic, paper and dye manufacturing industries are major sources of dye pollution [1]. Pollution from dyeing industries contains small amounts of organic materials that require special management [2]. The release of contaminants into the environment through wastewater is one of serious concerns; therefore, the removal of these compounds

from textile industry wastewater and adopting methods with the highest removal efficiency and the lowest cost is a necessity [3]. Commonly applied treatment methods for color removal from dye-contaminated effluents consist of various processes involving biological, physical and chemical decolorization methods [4]. Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents [5], [6]. These processes generally, involve UV/H₂O₂ UV/O₃,

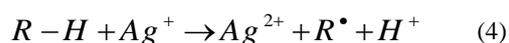
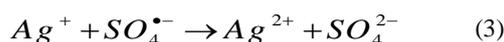
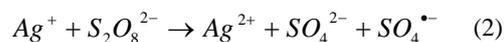
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UV/S₂O₈²⁻ or UV/Fenton's reagent for the oxidative degradation of contaminants [7], [8].

This process is usually utilized by UV radiation accompanied by an oxidizer or Fenton's reagent to reduce pollution [9],[10]. However, the potential of alternative AOPs to improve the removal performance is always of interest and the photochemical oxidant, peroxydisulfate, could be a good candidate for such a purpose. Peroxydisulfate (S₂O₈²⁻ ion) is a strong oxidant (E₀=2.05V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator. In addition it seems that peroxydisulfate ions are more satisfactory for following reasons: (1) Peroxydisulfate can perform better in reactions that are difficult to control. (2) Peroxydisulfate is a solid oxidant that is better than a liquid oxidant such as H₂O₂ for use in the industry. (3) The use of Peroxydisulfate is more affordable in comparison with ozone and hydrogen peroxide. (4) Due to high activity and solubility, its application in the water treatment plant is recently taken into consideration. (5) High oxidation power, non-selective performance and safe by-products are of its advantages [11-14]. The process does not involve toxic catalysts or the cogeneration of secondary wastes. Peroxydisulfate ions convert organic materials to water, carbon dioxide and inorganic material. During this oxidant, the peroxydisulfate is reduced to sulfate ions. If there are enough metal (Meⁿ⁺) as electron giving ion, peroxydisulfate can change to radical form as it shown in the below reaction [15].



One of the transition metals that has a catalytic effect and has used with peroxydisulfate for degradation of contaminates is silver [16]. Silver in electron transferring reactions could active peroxydisulfate for generating highly reactive sulfate radicals [17].



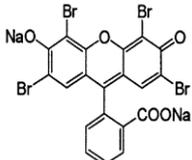
Nanosilver due to having efficient surface for catalytic property, suitable size, optical property, having electron donor properties and catalytically that has depend on their structure, has been using in degradation of Acid Red 87(AR87).

2. Materials and methods

2.1. Chemicals and procedures

Potassium peroxydisulfate 98%, nitric acid 98%, sodium peroxide, from (Merck Company), nanosilver immobilized on silica 100% from (Lotus Company), from (Acid Red 87 alvan sabet company) has been obtained. Dyes characteristic are given in (Table 1). peroxydisulfate oxidants was immediately prepared before the measurement to avoid the change in its concentration due to self-decomposition. Dilute solution of sodium hydroxide and nitric acid has been used for adjusting pH.

Table 1. Characteristics of Acid Red 87.

Chemical structure	$\lambda_{(max)}$ (nm)	Molecular formula	Mw (g mol ⁻¹)
	517	C ₂₀ H ₆ Br ₄ Na ₂ O ₅	691.85418

In this investigation, solutions with the desired concentrations of the dye and peroxydisulfate were prepared in a volume of 100 ml. It is noteworthy that the concentration of the test solution changes with regard to

parameters of the test. In the first step, the concentration of the oxidizer and the amount of absorption in the specified time periods has been measured. Then in the second step, the concentration of the catalyst and re-

measured the absorbance at the same conditions as the previous step. In the next step, the dye concentration was changed. For all prepared solutions, initial absorption of the solution was measured before addition of nanosilver. During the test, samples were taken at time intervals of 5 minutes and transmitted into the UV-Vis cells. The amounts of remaining dye adsorption in solution were read by spectrophotometer. AR87 removal percentages can be calculated in order Equation (1) Where the A_0 and A_t were the dye absorbance of the sample at time 0 and t, respectively.

$$\% = [(A_0 - A_t) / A_0] \times 100 \quad (1)$$

3. Results

3.1. The role of nano-Ag in AR87 oxidation by peroxydisulfate

To evaluate the roles of Ag^+ in the Ag-peroxydisulfate system, a pre-determined amount of Ag and $S_2O_8^{2-}$ were added separately to ambient solution under identical conditions. The dosage of Ag used in this experiment was 125 mg L^{-1} . Upon addition of 125 mg L^{-1} of Ag, $S_2O_8^{2-}$ was activated and rapidly oxidized 95% of the AR87 (Fig. 1). These results suggest that Ag^+ released from Ag was most likely responsible for $S_2O_8^{2-}$ activation and AR87 oxidation. The results reveal that, there was no observable loss of the color when the Ag was applied in the absence of $S_2O_8^{2-}$.

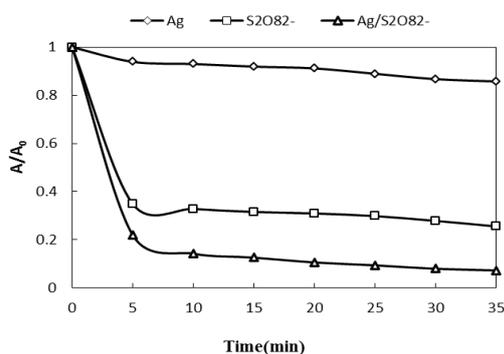


Figure 1. The role of nano-Ag in AR87 oxidation by peroxydisulfate. 3.2. Effect of initial peroxydisulfate concentration

The concentration of $S_2O_8^{2-}$ was found to be an important parameter for the degradation of AR87 by $S_2O_8^{2-}$

oxidant. The results (Fig.2) indicated that by increasing the concentration of $S_2O_8^{2-}$ from 0.5 to 30mM, the rate of removal increases. This increase with regard to increase in production of hydroxyl radical and sulfate radical is justifiable due to increase in concentration of $S_2O_8^{2-}$. By increasing the concentration of $S_2O_8^{2-}$ to more than 10mM, the amount of AR87 removal did not show much difference in compare with higher values. This could be explained as if the increase in concentration of $S_2O_8^{2-}$ will increase the production of hydroxyl radicals due to photolysis process. According to the blow equations, increase in concentration of hydroxyl radicals would lead to reproduction of hydrogen peroxide and as the result, a decrease in hydroxyl radicals would lead to decrease in AR87 removal rate. The optimal amount of $S_2O_8^{2-}$ was determined 10mM.

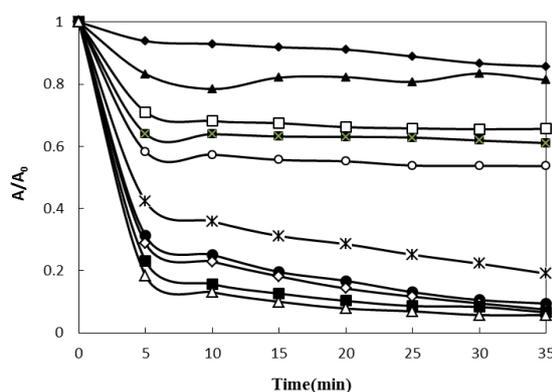
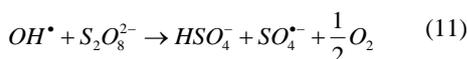
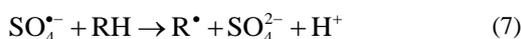
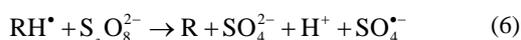
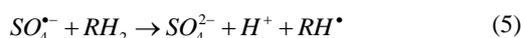


Figure 2. Effect of initial peroxydisulfate concentration. $[DYE]_0 = 20 \text{ mg L}^{-1}$, $T = 25^\circ \text{C}$, $[Ag^+] = 0.125 \text{ g L}^{-1}$



3.3. Effect of silver nanoparticles dosage

The results from the degradation of AR87 (20 mg L^{-1}) using different amount of silver nanoparticles were summarized in (Fig.3). The removal efficiency increased

with improving in nano-Ag dosage. About this result can be explained in terms of that increasing in nano-Ag dosage accelerate the conversion of $S_2O_8^{2-}$ to $SO_4^{\cdot-}$ to oxide AR87 rapidly.

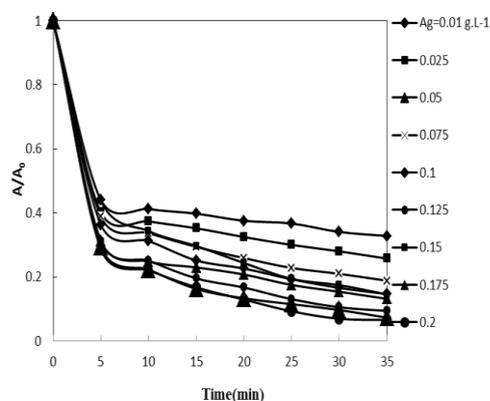


Figure 3. Effect of silver nanoparticles dosage. $[DYE]_0 = 50 \text{mgL}^{-1}$ (ppm), $[S_2O_8^{2-}] = 10 \text{mM}$, $T = 25^\circ\text{C}$

3.4. Effect of initial dye concentration

It is important from an application point of view to study the degradation of removal efficiency on the initial concentration of dye. Dye concentration varied from 10mgL^{-1} to 50mgL^{-1} at constant dosage of nano-Ag and $S_2O_8^{2-}$ concentration (10mM). Degradation of 100% observed in 10mgL^{-1} while only 32% of degradation achieved in 50mgL^{-1} concentration of AR87. Fig.4 shows based on increasing on concentration of contaminant the removal of reduces. One possible reason may be that the increase in dye concentration decrees the ratio of sulfate radical to dye and percentage of decolorization reduces in result.

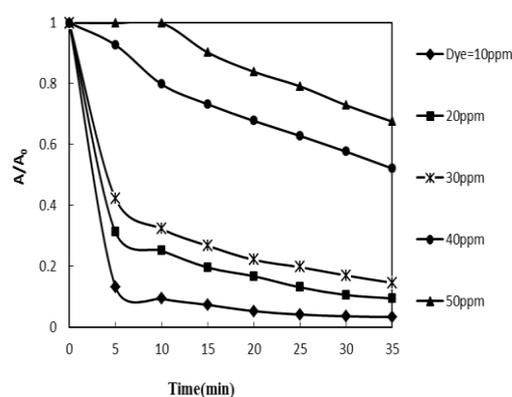


Figure 4. Effect of initial dye concentration. $[S_2O_8^{2-}]_0 = 10 \text{mM}$, $T = 25^\circ\text{C}$, $[Ag^+] = 0.125 \text{g.L}^{-1}$.

3.5. Spectral changes of AR87 during degradation

The changes in the absorption spectra of AR87 solutions during the oxidation process at different

reaction time are shown in Fig.5. The decrease of the absorption peak of AR87 at 517nm in Fig.5 indicated a rapid decolorization of dye.

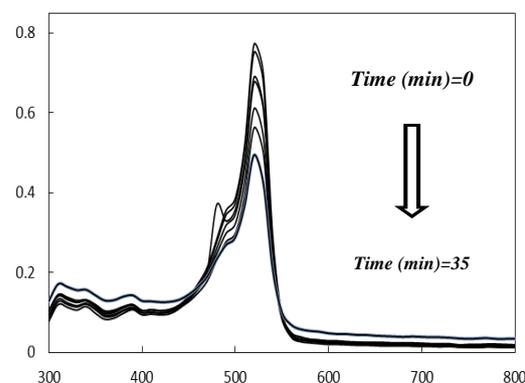


Figure 5. Spectral changes of AR87 during degradation.

4. Conclusion

The application of peroxydisulfate along with immobilized silver nanoparticles as an advanced oxidation process introduces an effectual and safe method to remove AR87. Almost no dye removal was achieved using nano-Ag alone. Degradation rate of AR87 was dependent on dye concentration, peroxydisulfate concentration and nano-Ag dosage. The more the concentration of dye is, the less the decolorization percentage would be. Optimum concentration of peroxydisulfate and nano-Ag dosage found to be 10mM and 125mgL^{-1} respectively. The main conclusion to be drawn is that using nano-Ag and peroxydisulfate provides a effective method of wastewater treatment.

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