

## Enhanced Oxidation of Azo Dye Using Ag-SiO<sub>2</sub> Nanoparticle and Peroxydisulfate and Kinetic Study

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### Abstract

Present work investigates the capability of oxidative treatment process in the presence of nano silver doped on silicate particles for decolorization of a widely used azo dye, C.I. Direct Blue 129 (DB129) in water samples. Solutions with initial concentration of 20 mgL<sup>-1</sup> of dye, within the range of generic concentration in textile wastewaters, were treated under ambient conditions of initial pH of 6.7 and temperature of 25°C. The operational parameters evaluation including dye and peroxydisulfate concentration, initial pH, nanoparticles dosage and reaction time was studied in an endeavor to reach the higher dye removal efficiency. Subsequently, a removal more than 90% of dye was attained by applying the optimal operational conditions as follow: 0.4 g of catalyst, 20 mgL<sup>-1</sup> of dye, 5 mM of peroxydisulfate and initial pH of 6.7 in 35 min. Moreover, kinetic study for various parameters in several conditions for treatment process was investigated. Pseudo- first-order reaction rate constants were calculated for the systems. The morphology and crystal structure of Ag-SiO<sub>2</sub> nanoparticles were characterized by means of Transmission Electron Microscope (TEM).

**Keywords:** Nano silver; Direct Blue 129; Peroxydisulfate; Kinetic; Degradation.

### Introduction

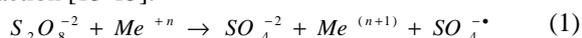
In the era of water scarcity, excessive discharge of pollutants by various industries along with their untreated or partially treated wastewater into the water bodies is a great concern [1]. Many of these pollutants are toxic and recalcitrant in nature and tend to bio accumulate [2]. Colored wastewater emanating from various color manufacturers and color consuming industries is one of the greatest concerns because of its high visibility and recalcitrant nature [3, 4]. Azo dyes are the largest class of synthetic dyes used worldwide for textile dyeing because of their cost effectiveness property and variety of colors available. Particularly,

azo dyes caused special concern because some azo dyes, azo dye precursors, and their degradation products such as aromatic amines are carcinogenic [4].

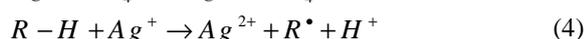
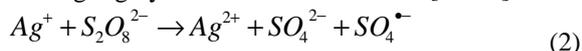
Conventionally, azo dyes treated with various chemical, physical and biological techniques which greatly reduce the pollutant, but not enough to comply with current standards which are becoming stricter more and more [5, 6]. These methods are not destructive and mainly concentrate pollutants which need further processing before disposal. One of the most promising techniques for treatment is Advanced Oxidation Processes (AOP) because it is a simple and easy way to completely mineralize organic compounds to carbon

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dioxide and lead to a clean and green purification technique for treatment of dyestuff effluents [4, 7]. Peroxydisulfate ( $S_2O_8^{2-}$ ) is a strong oxidant ( $E_0 = 2.05$  V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator [8, 9]. It has also been reported to be an effective sacrificial reagent in degrading organics in hazardous acidic or basic wastewaters through direct chemical oxidation [10-12]. During oxidation, the peroxydisulfate is reduced to sulfate ions. If there are enough ion metal ( $Me^{n+}$ ) as oxidizing, peroxydisulfate can change to radical form as it is shown in the below reaction [13-15].



One of the transition metals that has a catalytic effect and has been used with peroxydisulfate for degradation of contaminants is silver [16]. Silver in electron transferring reactions could activate peroxydisulfate for generating highly reactive sulfate radicals [16-18].



Nano silver due to high surface area, suitable size, optical property, electron donor and catalytic properties that depends on Ag nanoparticles structure, has been used in the degradation process of Reactive Blue 129 (RB129).

To the best of our knowledge, this is the first time that Ag-SiO<sub>2</sub>/ peroxydisulfate process has been employed in decolorization of the textile dye C.I. (RB129). Therefore, in this work the effect of

operational parameters on treatment of a dye solution containing RB129 by Ag-SiO<sub>2</sub>/peroxydisulfate process were investigated. Factors affecting the treatment procedure, including dye and persulfate concentration, pH and Ag-SiO<sub>2</sub> nanoparticle dosage were assessed. Kinetic study for various parameter were investigated as well. To this end, we investigated the complemented oxidation of RB129 by monitoring the absorbance changes in the UV-vis region of the dye spectrum during the treatment process.

## Material and Methods

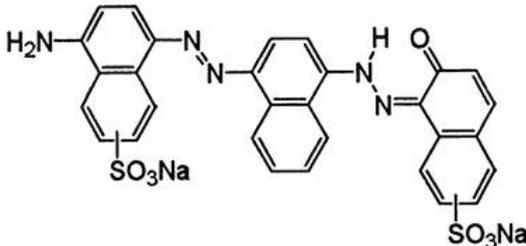
### Reagents

Potassium peroxydisulfate ( $K_2S_2O_8$ ), sulfuric acid and sodium hydroxide were of laboratory reagent grade (Merck Co., Germany) and used without further purification. Immobilized silver nanoparticles on SiO<sub>2</sub> was obtained from Lotus Nano chemistry Pars Company (Iran). C.I. Reactive Blue 129, commonly used as a textile dye, was obtained from Alvansabet Company, Iran. The Dyes characteristic are given in Table 1. The pH of the solution was controlled by adding H<sub>2</sub>SO<sub>4</sub> (0.1 M) and NaOH (0.1 M).

### Experimental procedure

The batch experiments were carried out with 100mL dye solutions. The temperature of the reaction medium was kept constant at  $25 \pm 0.2^\circ\text{C}$ . Before adding Ag-SiO<sub>2</sub> powder, the absorbance of dye concentration was measured by spectrophotometer (Shimadzu UV-160, German). Subsequently a suitable amount of persulfate for oxidation process was added. Then dye-catalyst

Table 1. Characteristics of Direct Blue 129

Color Index	Direct Blue 129
Chemical Name	Sodium 8-amino-5-((E)-(4-((Z)-2-(2-oxo-6-sulfonatophthalcn-1(2H)-ylidenc)hydrazinyl)naphthalene-1-yl)diazanyl)naphthalene-2-sulfonate
Type	Dianionic
Azo Group	Two
Chemical Structure	
max	610 nm
Molecular Formula	C <sub>30</sub> H <sub>19</sub> N <sub>5</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>
Molecular Weight (g mol <sup>-1</sup> )	671.61
Solubility in Water	15g/L(20 C)

suspension was stirred for 35 min. During the runs, 3mL samples of suspension were withdrawn at regular intervals and were immediately centrifuged at 3500 rpm to remove catalyst particles. Consequently, dye solution absorbance was determined in  $\lambda_{\max}=610$  nm and color removal was calculated using Eq (1)

$$\% \text{Removal percentage} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where  $C_0$  is the initial concentration of dye in ppm and  $C_t$  is dye concentration in ppm at any time  $t$ .

For effective parameter assessment in one at a time condition, all parameters were in a constant level except one which was supposed to be investigated.

## Results and Discussion

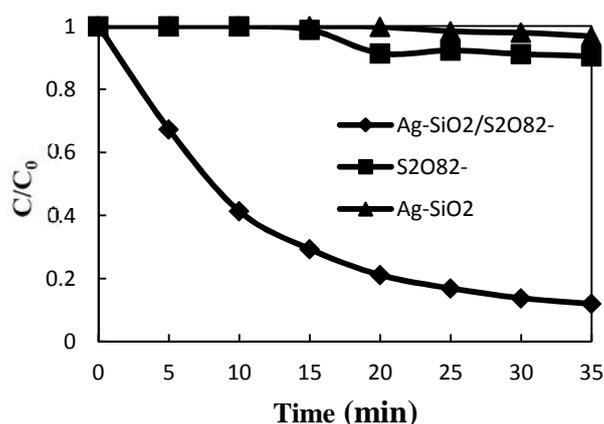
### *Effect of nano Ag-SiO<sub>2</sub> catalysis; Absence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in comparison with S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/Ag-SiO<sub>2</sub> on DB129 decay*

Figure 1 shows the decolorization of DB129 with only Ag-SiO<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> without catalyst and Ag-SiO<sub>2</sub> in presence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in dye concentration of 20 mgL<sup>-1</sup> and initial pH. The results revealed that there was no remarkable decolorization observed in the absence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> or Ag-SiO<sub>2</sub> but oxidant treatment in presence of Ag-SiO<sub>2</sub> nanoparticles resulted in considerable removal of dye. Figure 2 illustrates the TEM image of favorable immobilization of nano Ag on SiO<sub>2</sub>. It is clear that Ag nanoparticles were distributed among SiO<sub>2</sub> particles.

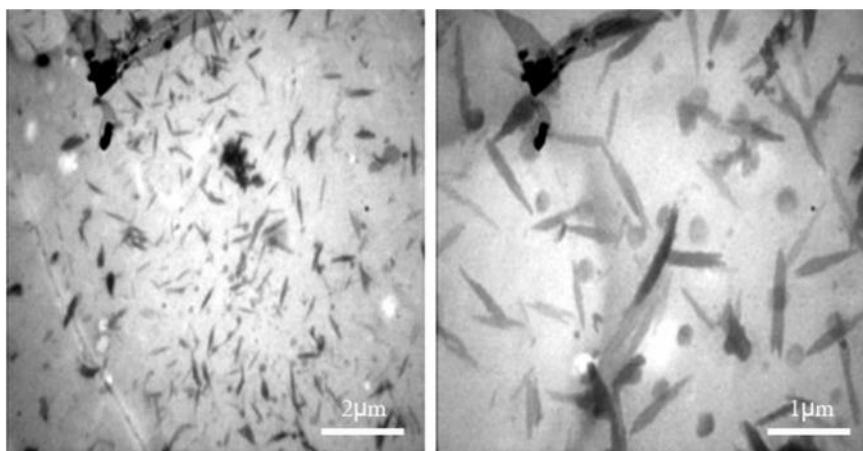
### *Effect of initial C.I. Direct Blue 129 concentration*

It is important both from the mechanistic and application standpoint, to study the effect of initial dye concentration on the degradation efficiency. Therefore, experiments were carried out with different initial dye concentrations (5-40 mgL<sup>-1</sup>) to study their effect of the degradation that presented in Figure 3a.

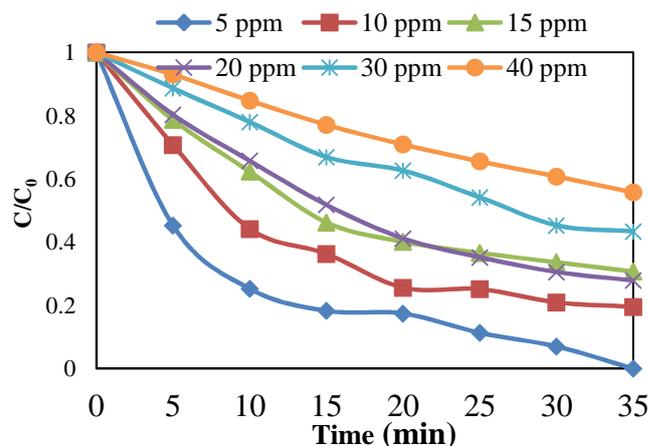
As shown in Figure 3a the decrease in removal rate



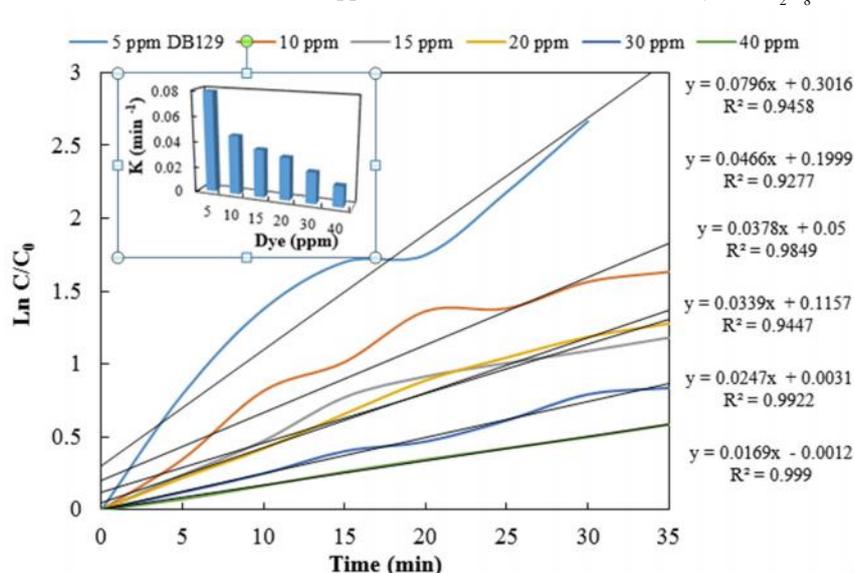
**Figure 1.** Effect of nano Ag-SiO<sub>2</sub> and peroxydisulfate on oxidative decolorization of DB129 [DB129]<sub>0</sub>=20 ppm, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub>=5mM, X=C/C<sub>0</sub>, T=25±1 °C



**Figure 2.** TEM image of Ag-SiO<sub>2</sub> with 20 nm of size



**Figure 3a.** Effect of initial concentration of DB129 (ppm) on oxidative decolorization of dye.  $[S_2O_8^{2-}]_0 = 5 \text{ mM}$ ,  $T = 25 \pm 1 \text{ }^\circ\text{C}$ .



**Figure 3b.** Kinetics of DB129 decolorization ( $\ln ([Dye]_0/[Dye])$ ) in oxidative experiments using nanoparticles of Ag-SiO<sub>2</sub> for different concentration of DB129.

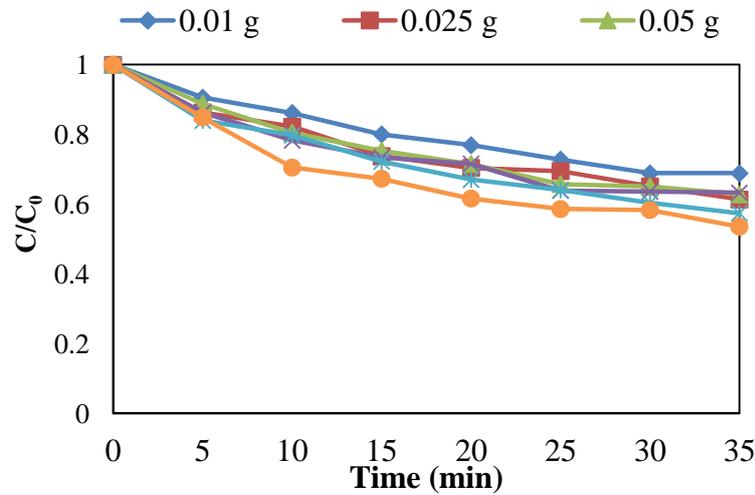
with increasing initial DB129 concentration was observed. At higher concentrations of  $S_2O_8^{2-}$ , the generated intermediates become scavengers of  $HO^\bullet$  and  $SO_4^{\bullet-}$  radicals that may be a possible of all reasons cited already [12, 17]. Although the rate of degradation decrease at higher dye concentrations, total dye degraded at the end of the process is comparable with that at lower dye concentrations. Kinetic study of degradation systems derived from variance concentration of DB129 illustrated in Figure 3b. In order to calculate K values,  $\ln(C/C_0)$  was plotted as a function of the DB129 concentration. The rate constant values, K ( $\text{min}^{-1}$ ), are calculated from the straight-line slope of the first-order lines [19].

$$-\ln \frac{C}{C_0} = Kt \quad (2)$$

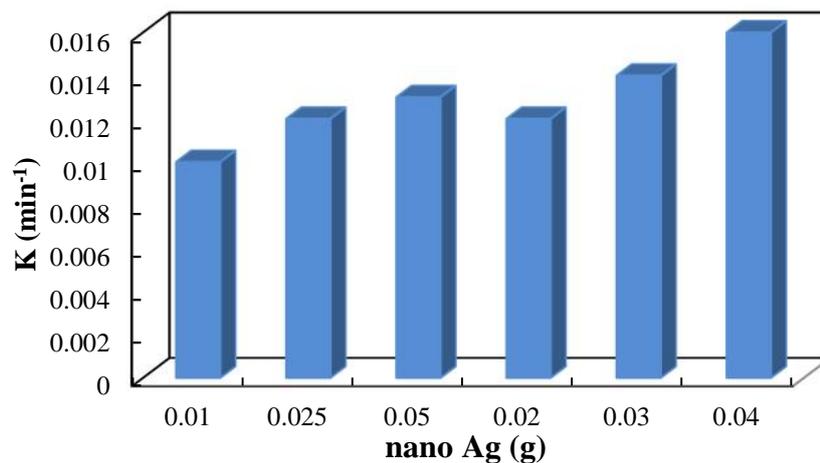
As can be seen from the chart the increase in dye concentration from 5 ppm to 40 ppm causes the decrease in rate constant from 0.0796 to 0.0169  $\text{min}^{-1}$ .

#### *Effect of catalyst dosage*

The initial rate of oxidation of many organic compounds is a function of the catalyst dosage [20]. To avoid the excess uses of catalyst, it is essential to find the optimum dosage of catalyst for the efficient degradation. The effect of the amount of nano Ag-SiO<sub>2</sub> on dye decolorization efficiency versus time is illustrated in Figure 4. The concentration of direct blue 129 dye ( $30 \text{ mgL}^{-1}$ ) was kept in the same level in all these experiments. The decolorization rate enhanced



**Figure 4a.** Effect of nano Ag-SiO<sub>2</sub> dosage on oxidative decolorization of dye. [ $S_2O_8^{2-}$ ]<sub>0</sub>=2mM, [DB129]<sub>0</sub>=20mg/L, T=25±1 °C

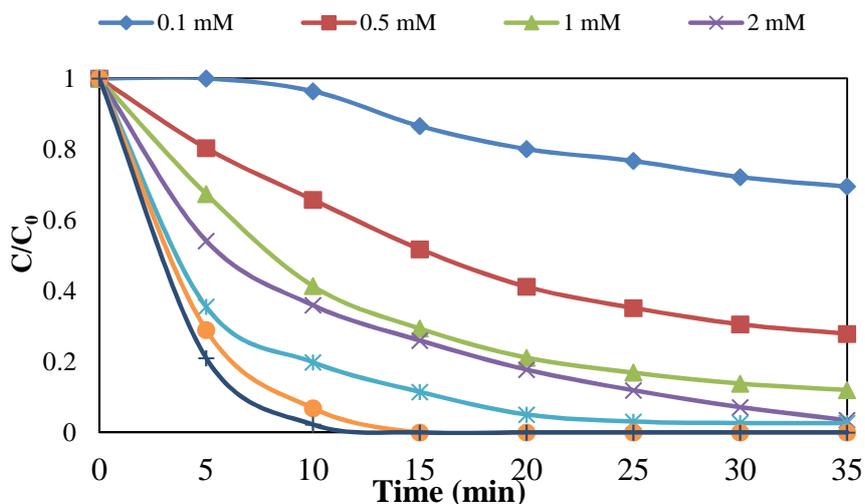


**Figure 4b.** The effect of nano Ag-SiO<sub>2</sub> on k<sub>app</sub>; [DB129]<sub>0</sub>= 20 mg/L, [ $S_2O_8^{2-}$ ]<sub>0</sub>=2mM, T=25±1 °C

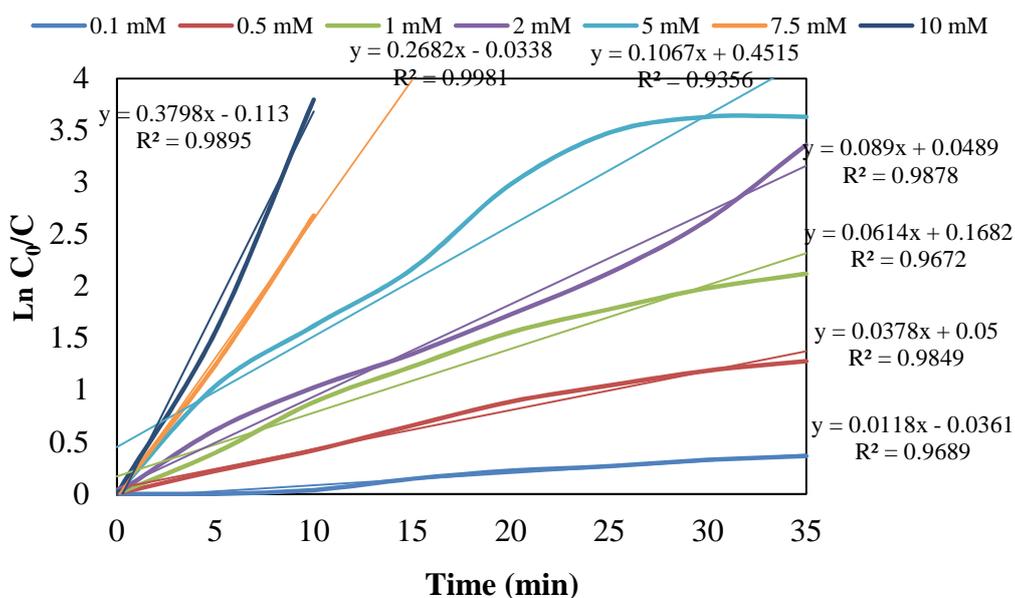
with increasing the amount of catalyst, reaching the highest value of the catalyst (0.4 g). The reason of this observation is thought to be the fact that when the concentration of the catalyst increments, the production of overall number of OH radicals increases in shorter time [21]. As results show, maximum decolorization (47.5%) of DB129 was observed after 35 min with the maximum rate constant ( $1.6 \times 10^{-2} \text{ min}^{-1}$ ) in the presence of 0.4 g of the catalyst which is in accordance with previous literature [16-17]. Therefore, 0.4 g of the catalyst was used as optimum value.

#### *Effect of peroxydisulfate concentration on the dye degradation*

To disquisition the dependency of oxidant on the dye degradation, different concentrations of peroxydisulfate from 0.1 mM to 10 mM with determined concentration of DB129 were prepared under natural pH and room temperature of 25±1 °C in 35 minutes (Figure 5a). Considerable increase of the peroxydisulfate from 0.1 to 10mM led to increasing decolorization efficiency from 30.52% to 100%, respectively. It is reasonable since as the concentration of  $S_2O_8^{2-}$  is increased, more sulfate and hydroxyl radical are available to attack the dye



**Figure 5a.** Effect of initial concentration of peroxydisulfate (mM) on oxidative decolorization of DB129. [DB129]<sub>0</sub>=20 mg/L, Ag-SiO<sub>2</sub>=0.3g, T=25±1 °C.



**Figure 5b.** Relation between first-order rate constant (k) with peroxydisulfate by S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/ Ag-SiO<sub>2</sub> process; [DB129]<sub>0</sub>=20 mg/L, Ag-SiO<sub>2</sub>=0.3g, T=25±1 °C.

structure and as a result rate increases [14, 20, 22] according to equations 1-4. Applying the pseudo-first-order kinetics to DR129 photo-oxidation, the degradation rate can be calculated. As it demonstrated in Figure 5b the more sulfate and hydroxyl radicals the more dye removal rate would be.

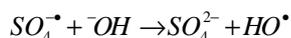
**Effect of pH**

pH of solution is one of the ascertainment factors

during DB129 degradation by the oxidation process. To clarify the effect of pH, dye solution with initial pH of 2.3, 4.2, 6.1, 9.4 and 11.1 were prepared. As it is clear from this Figure 6, decolorization efficiency reached to the highest value (72.4%) when initial pH was about 6.1.

According to equation 5 and 6 persulfate is more active in acidic solutions in fact the production of sulfate radical increased along with increasing the

acidity of solution [23].



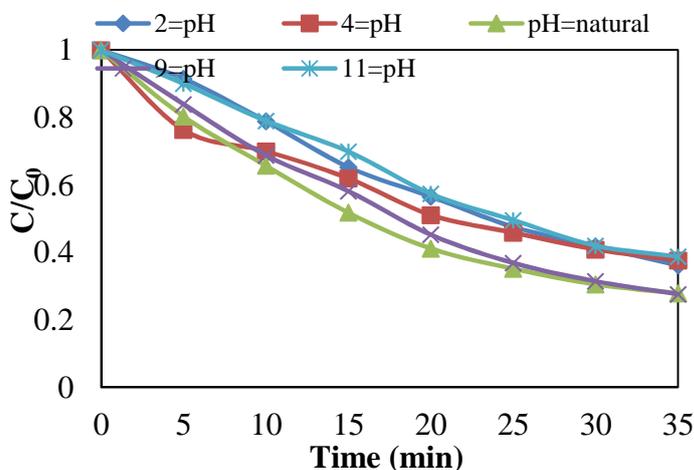
**UV-vis spectra**

Figure 7 shows a typical time-dependent UV-Vis spectrum of DB129 solution during persulfate activated Ag-SiO<sub>2</sub> nanoparticles oxidation process at the optimized conditions ([Dye]<sub>0</sub> = 20 mgL<sup>-1</sup>, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub> = 5 mM, Ag = 0.4 g and pH = 6.7). The absorption peaks in the UV and visible region at }<sub>max</sub> = 210, 237, 322 and 610 nm corresponding to dye, diminished and finally disappeared without the appearance of new absorption peaks under reaction which indicated that the dye was

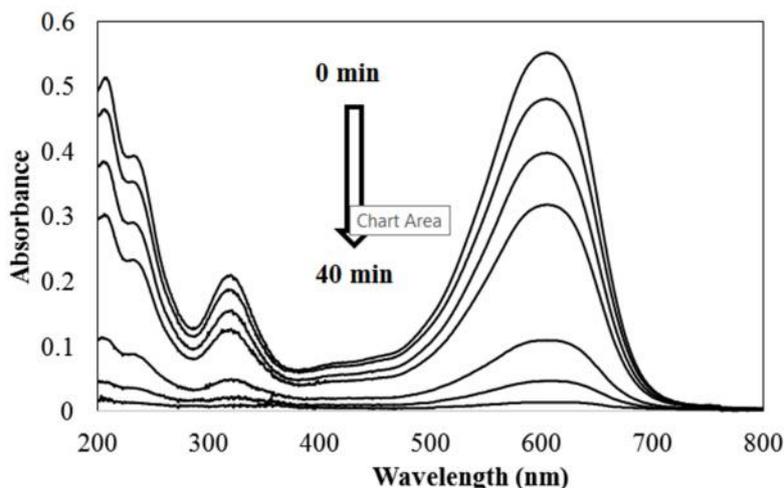
completely removed and mineralized.

**Conclusion**

This study elucidates the degradation of DB129 by Ag-SiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidation process. It was observed that DB129 could be removed from water by only oxidant (proxidysulfate), with no ultraviolet or visible light radiation however, the combination of oxidant with nano Ag-SiO<sub>2</sub> catalyzer significantly accelerated the degradation process. It is noteworthy that only 10% of catalyst is Ag nanoparticles. The degradation of dye by the Ag-SiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process exhibited pseudo-first-order kinetics. In order to achieve the high degradation efficiency, the moderate and the suitable conditions are: catalyst dosage: 0.4 g, pH 6.73 (natural pH) and 5 mM



**Figure 6.** The effect of pH on dye removal; [DB129]<sub>0</sub> = 20 mg/L, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub> = 2mM, T = 25 ± 1 °C



**Figure 7.** UV-vis absorption spectrum of DB129 at optimal condition, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub> = 4 mM, [DB129]<sub>0</sub> = 20 mgL<sup>-1</sup>, pH = 6.73, nano Ag-SiO<sub>2</sub> = 0.3g

of  $S_2O_8^{2-}$ . Under these conditions, more than 90% of 20 ppm of dye was degraded after 20 min. The COD result proved 65% mineralization of contaminant during oxidation process.

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