

## Influence of operational parameters on photomineralization of Evans blue by Ag-TiO<sub>2</sub> composite

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Study Ag-TiO<sub>2</sub> composite has been synthesized by photodeposition method. The prepared composite has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and diffuse reflectance spectroscopy (DRS). The effect of Ag deposition on TiO<sub>2</sub> has been tested for photocatalytic degradation of azo dye, Evans Blue (EB). The comparison of different advanced oxidation processes (AOP) such as (i) Only Ag-TiO<sub>2</sub> (ii) only UV (iii) UV + TiO<sub>2</sub> (iv) UV + Ag-TiO<sub>2</sub> (v) UV + Ag-TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> have been carried out for the photocatalytic degradation of EB. In addition, different operational parameters like initial concentration of EB and composite dose have also been studied on photocatalytic degradation of EB. The degradation is found to increase in the order only Ag-TiO<sub>2</sub> < Only UV < UV + TiO<sub>2</sub> < UV + Ag-TiO<sub>2</sub> < UV + Ag-TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> for EB.

**Keywords:** AOP, Ag-TiO<sub>2</sub>, Evans Blue, Photodeposition, Photocatalytic degradation

Synthetic dyes especially azo dyes are used in many industrial branches for dyeing of wool, cotton, nylon, leather, paper, cosmetics, pharmaceuticals, food, plastic, petroleum products<sup>1</sup>. A literature survey<sup>2</sup> shows that nearly 20% of dyes are left during the dyeing processes leading to produce a large amount of wastewaters containing these dyes as pollutant. Aromatic rings in dye molecular structure cause toxicity and mostly biodegradability resistance so that the dyes are becoming a highlighted source of non-pleasant pollutions<sup>3</sup>. The existence of very low amount of dyes is clearly detectable and considerably affects water quality<sup>4,5</sup>. Thus, years of researches have been aimed at the decolorization and mineralization of azo dye effluents. Conventional methods such as adsorption<sup>6</sup>, flocculation<sup>7</sup>, electrochemical methods<sup>8,9</sup>, membrane separation<sup>10</sup>, ozonation<sup>11</sup>, advanced oxidation using UV/H<sub>2</sub>O<sub>2</sub> or UV/TiO<sub>2</sub><sup>12-14</sup> and biological oxidation<sup>15,16</sup> for industrial wastewater can be used efficiently. Nevertheless many of them divulge some drawbacks, since traditional physical techniques just transfer organic compounds from wastewater to another phase which can cause secondary pollution easily. Biological oxidation cannot degrade dyes under aerobic condition, while can reduce dyes into potentially carcinogenic

compounds under anaerobic condition<sup>17-19</sup>. Due to the large numbers of aromatic compounds present in dye molecules and stability of modern dye, thus, there is a need to develop treatment methods that are more effective in eliminating dyes from the wastewater. Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds using semiconductor photocatalysts under light irradiation<sup>20,21</sup>. Among the various metal oxide semiconductors used; Titanium dioxide (TiO<sub>2</sub>) is one of the most important photocatalysts for the degradation of environmental contaminants. This is because of its high photocatalytic activity, non-toxicity, chemical stability under different conditions, and relative inexpensiveness<sup>22,23</sup>. However, the large band gap and low quantum yield of TiO<sub>2</sub> prevent it from practical applications. The further enhancement of photocatalytic activity of TiO<sub>2</sub> is one of the most important tasks for technical applications of heterogeneous photocatalysis in the future<sup>24-27</sup>. To enhance photocatalytic activity, noble metals such as Ag, Au, Pt and Pd are deposited on a TiO<sub>2</sub> surface, because they act as an electron trap promoting interfacial charge transfer processes in the composites<sup>28</sup>. Here, we report the synthesis of Ag-TiO<sub>2</sub> composites with Ag loading by

photodeposition method. The as synthesized composite was characterized by XRD, SEM and DRS. The photocatalytic activity of Ag-TiO<sub>2</sub> composite was tested by photocatalytic degradation of azo dye EB as a model organic contaminant. EB is extensively used in dyeing, printing and textile industries. It is considered as hazardous irritant and potential carcinogen<sup>29</sup>.

## Experimental Section

### Materials

TiO<sub>2</sub> (Merck, Germany), AgNO<sub>3</sub> (Spectrochem Pvt. Ltd. India), EB (s d fine – chem Ltd., India) were used as received. The structure of EB is shown in Fig. 1. Double distilled water was used throughout all experiments. The setup of the photo-catalytic reaction was used for the evaluation of the prepared Ag-TiO<sub>2</sub> composite by comparing their photocatalytic activity with that of bare TiO<sub>2</sub>.

### Preparation of Ag-TiO<sub>2</sub> composite by photodeposition method (PD)

In the PD method TiO<sub>2</sub> doped with Ag metal was prepared by photoreducing Ag<sup>+</sup> ions to Ag metal on the TiO<sub>2</sub> surface according to the following steps. First, 500 mg TiO<sub>2</sub> was added to 50 mL deionized water. Then the required amount of AgNO<sub>3</sub> for doping was added to the TiO<sub>2</sub> suspension. The mixture was then irradiated with UV light (Four 8W low pressure mercury vapor lamps) for 3 h and then dried in an air oven at 110°C for 2 h.

### Characterization of Ag-TiO<sub>2</sub> composite

Ag-TiO<sub>2</sub> composite was characterized by X-Ray Diffraction, Scanning Electron Microscopy and Diffuse Reflectance Spectroscopy (DRS). The Scanning Electron Microscopy was carried out by using Scanning Electron Microscope (Jeol JSM-6360) and was used to characterize the morphology of the Ag-TiO<sub>2</sub> composite. The analysis of X-Ray diffraction was used to determine the crystal structure of the composite. It was carried out by using the Powder X-Ray Diffractometer (XRD) (Phillips PW1729) which was equipped with Cu anode and graphite

monochromator and the diffractograms were recorded by using CuK $\alpha$  radiation over a range 20° to 80°. UV-Visible absorbance spectra of solid material was recorded between range 200nm and 800 nm using a UV visible spectrometer (JASCO V-670) equipped with DRS and BaSO<sub>4</sub> was employed as reference substance. UV-Visible absorbance spectra of solutions were recorded using Shimadzu (UV-1800) double beam UV -Visible spectrophotometer.

### Photoreactor setup

Photocatalytic experiments were carried out with 100 mL, 5.0  $\times 10^{-5}$  M EB aqueous solution using 40 mg Ag-TiO<sub>2</sub> composite as photocatalyst under exposure to UV irradiation in a multilamp photoreactor constituting four 8W low pressure mercury vapor lamps at 30 $\pm$ 1°C. Air was bubbled through the reaction solution from the bottom using aerator with constant speed. The whole reactor assembly was mounted on magnetic stirrer for mixing the aqueous solution during the reaction in order to ensure that the solution was well-mixed and the catalysts did not settle down inside the container as depicted in Fig. 2. During photocatalytic experiment, the slurry containing aqueous EB solution and photocatalyst was magnetically stirred for 10 min in dark to attain adsorption desorption equilibrium between EB molecule and catalyst, then it was irradiated and aliquot (1 mL) was withdrawn at specific time intervals and filtered to separate the catalyst through 0.2  $\mu$ m, 13 mm diameter millipore disc. Changes in absorption spectra were recorded at 605 nm using Shimadzu (UV-1800) UV-visible spectrophotometer.

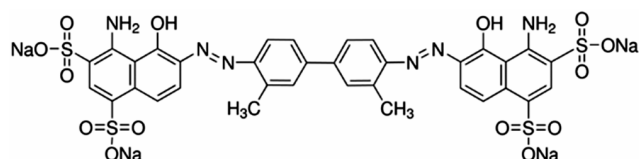


Fig. 1 — Structure of Evans Blue



Fig. 2 — Experimental setup of photoreactor

## Results and Discussion

### Characterization of Ag-TiO<sub>2</sub> composite

The XRD of Ag-TiO<sub>2</sub> is shown in Fig. 3. The clear and well-defined peaks at 25.3°, 37.8°, 48°, 53.9° (JCPDS card No. 21-1272) appeared in the nanocomposite which confirm the anatase phase of TiO<sub>2</sub> in the XRD pattern of Ag-TiO<sub>2</sub> composite. Besides, the diffraction peaks corresponding to silver oxide species, for example Ag<sub>2</sub>O at 32.97° are not detected, so it can be concluded that there is no silver oxide species in the samples as well<sup>30</sup>. Ag-TiO<sub>2</sub> shows a strong absorption peak at  $\lambda < 400$  nm which corresponds to UV region with maximum absorbance around 350 nm which indicates that Ag-TiO<sub>2</sub> is highly active under UV light. The SEM studies were used to investigate the surface morphology of Ag-TiO<sub>2</sub> composite. The SEM micrograph obtained for Ag-TiO<sub>2</sub> is shown in Fig. 4, clearly indicates that spherical Ag nanoparticles are doped into TiO<sub>2</sub> nanoparticles.

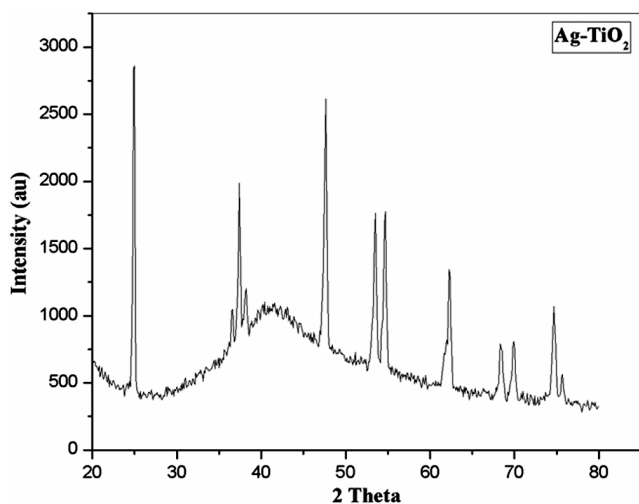


Fig. 3 — XRD pattern of Ag-TiO<sub>2</sub> composite

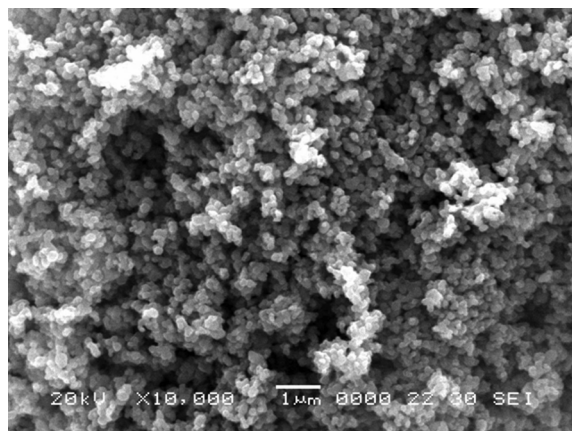


Fig. 4 — SEM of Ag-TiO<sub>2</sub>

### Optimization of Ag-TiO<sub>2</sub> concentration

The effect of Ag-TiO<sub>2</sub> concentration was studied. Experiments were performed with various amounts of composite (20-60 mg/50 mL) at  $1.0 \times 10^{-5}$  mol/L initial concentration of EB. The results obtained are depicted in Fig. 5 which shows that as the concentration of catalyst is increased, the number of photons absorbed and the number of EB molecules adsorbed are increased owing to an increase in the number of Ag-TiO<sub>2</sub> particles. The density of particles in the area of illumination also increases and so the rate is enhanced. Maximum degradation was obtained at Ag-TiO<sub>2</sub> dose of 40mg/50mL. Beyond this the substrate molecules available are not sufficient for adsorption by the increased number of Ag-TiO<sub>2</sub> particles. Hence, the additional catalyst powder is not involved in catalyst activities and the rate does not increase with an increase in the amount of catalyst beyond a certain limit<sup>31</sup>. Also, at high Ag-TiO<sub>2</sub> concentrations particles aggregate and reduce the interfacial area between the reaction solution and the photocatalyst. Thus the number of active sites on the catalyst surface decreases. The increase in opacity and light scattering by the particles may be the other reasons for the decrease in the degradation rate.

### Optimization of initial concentration of EB

The effect of initial concentration of EB on the photocatalytic degradation rate was investigated over the concentration range of 0.000005 M - 0.00005 M, since the pollutant concentration is a very important parameter in water treatment. Experimental results are presented in Fig. 6, which show that the degradation

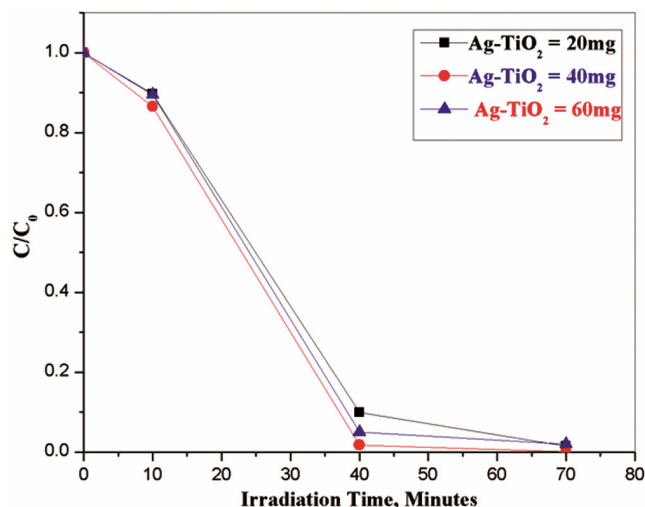


Fig. 5 — Optimization of Ag-TiO<sub>2</sub> concentration

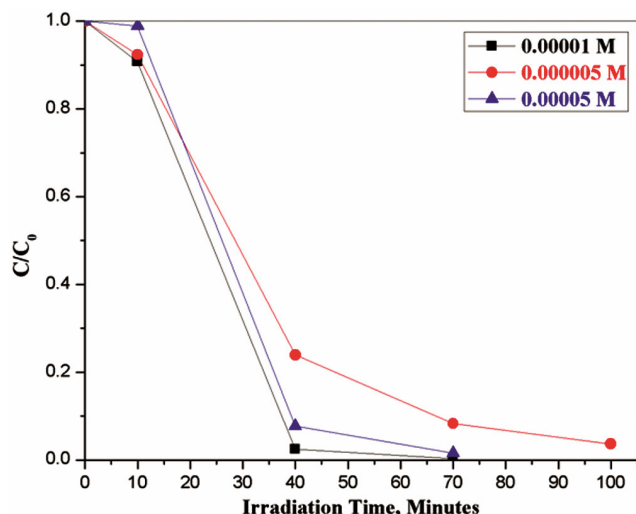


Fig. 6 — Optimization of initial concentration of EB

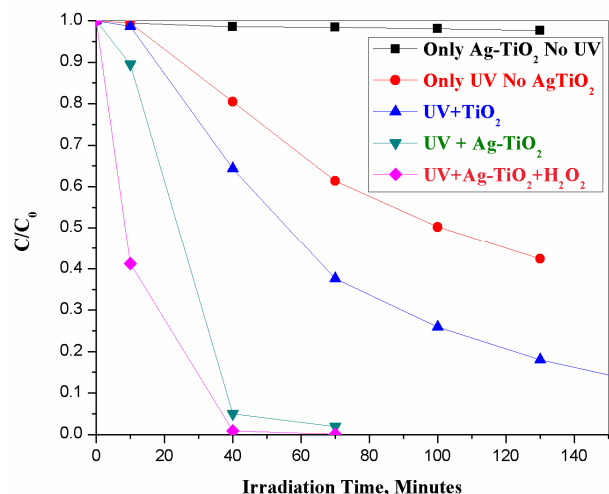


Fig. 7- Comparison of different AOPs for the degradation of EB rate depends on the initial concentration of EB. Degradation rate decreases at low initial EB concentration of 0.000005 M. It may be attributed to the fact that, the life time of  $\cdot\text{OH}$  radicals is very short (only a few nano seconds), and they can only react at or near the location where they are formed. The increased concentration enhances the probability of collision between the  $\cdot\text{OH}$  radicals and EB molecules. But when the initial concentration of EB is increased further to 0.00005 M, the % reduction in the initial concentration of EB decreases, it may be due to the reaction occurring between the  $\cdot\text{OH}$  radicals which are generated at the active OH sites on the surface of Ag-TiO<sub>2</sub> particles and EB molecule from the

solution<sup>32</sup>. Maximum degradation of EB was obtained at 0.00001M concentration.

#### Effect of addition of H<sub>2</sub>O<sub>2</sub>

The addition of H<sub>2</sub>O<sub>2</sub> to the heterogeneous system increases the concentration of  $\cdot\text{OH}$  radicals<sup>33</sup>. The experimental results for the UV+Ag-TiO<sub>2</sub>+H<sub>2</sub>O<sub>2</sub> system are depicted in Fig. 7 for EB, which showed a drastic increase in the rate of degradation of EB due to the increased concentration of  $\cdot\text{OH}$  radicals. The percentage rate of degradation was found to be 99% after irradiating for 15 min. As an electron acceptor, H<sub>2</sub>O<sub>2</sub> does not only generate  $\cdot\text{OH}$  radicals but inhibits the electron-hole recombination process<sup>34</sup>.

#### Comparison of different AOPs for the degradation of EB

The photocatalytic activity of Ag-TiO<sub>2</sub> was studied by degradation of EB under UV irradiation. The blank study without catalysis indicated that degradation due to photolysis was only 57% after being illuminated for 130 min. Only Ag-TiO<sub>2</sub> had no effect on degradation of EB. The results are depicted in Fig. 7. The doping of Ag on TiO<sub>2</sub> increases the photocatalytic activity. The rate of degradation was found to be 97% when Ag-TiO<sub>2</sub> composite was used after being illuminated for 50 min. The enhanced photocatalytic activity can be attributed to suppression of the recombination of photogenerated electron-hole pair in the semiconductors. Therefore, Ag-TiO<sub>2</sub> exhibits an enhanced photocatalytic performance. Rate of degradation of EB was found to be in the order UV+Ag-TiO<sub>2</sub>+H<sub>2</sub>O<sub>2</sub>>UV+Ag-TiO<sub>2</sub>>UV+TiO<sub>2</sub>>Only UV No AgTiO<sub>2</sub>> Only Ag-TiO<sub>2</sub> No UV.

#### Conclusion

- Ag-TiO<sub>2</sub> composite has been successfully prepared by photodeposition method.
- The percentage degradation of EB is found to be 97% for Ag-TiO<sub>2</sub> composite after irradiating in UV for 50 min, whereas only 62% degradation of EB is achieved with bare TiO<sub>2</sub> under the same conditions.
- The optimized concentration of Ag-TiO<sub>2</sub> composite is found to be 40 mg/50 mL for photodegradation of EB.
- Maximum degradation of EB has been achieved for the initial concentration of 0.00001 M.
- The photocatalytic degradation of EB is found to be in the order UV+ Ag-TiO<sub>2</sub> +H<sub>2</sub>O<sub>2</sub> > UV+ Ag-TiO<sub>2</sub> > UV+TiO<sub>2</sub> > Only UV > Only Ag-TiO<sub>2</sub>.

- The results obtained in the present study show the great efficiencies of advanced oxidation processes in removing refractory organic compounds which are resistant to other conventional treatment processes.

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