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Solar Photocatalytic Decolorization of Direct Blue 14 Dye by Using Synthesized SrO Nanoparticles

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ABSTRACT

Direct Blue 14, a di-azo dye, generally used to stain dead tissues in laboratories and also in textile industries. Direct Blue 14 (DB14) is also called as Trypan Blue as it can kill trypanosomes, the parasites that cause sleeping sickness. In this study, the photocatalytic decolorization of DB 14 dye by using synthesized SrO (NP's) have been investigated. The SrO NP's were prepared by solution combustion method using strontium nitrate and urea as precursors. SrO NP's were characterized by using SEM, XRD and UV-absorption spectroscopic methods. The surface analysis of the NP's was obtained by BET adsorption studies. Zero point charge of the SrO was determined. The photocatalytic degradation studies carried out under natural sunlight irradiation on SrO. The obtained results have shown an almost complete degradation of the dye. The effect of pH, catalyst dosage and concentration of the dye were studied. This protocol can be effectively applied for the degradation of similar kind of di-azo dyes which are hazardous to the environment.

Key words: Dye, Direct Blue 14, Nano particles, SrO and Photocatalyst.

I. INTRODUCTION

The textile industries are the largest industrial sectors which contribute significantly to the economic growth of a country. The contribution of these sectors to the overall economy is higher than other production sectors. These industries play a major role in economic development; they are also famous for the pollution of water resources through their textile processes [1]. DB 14 a di-azo dye is used for the photocatalytic studies. DB 14 is a vital stain and a di-azo dye, generally used to color dead tissues and also, it is used in textile industries for coloring purposes. DB 14 is derived from toluidine and called as Trypan blue which causes various biological effects such as toxicity and carcinogenic effects that cause deleterious efforts on livelihood [2].

As for as photocatalytic studies of azo dyes are concerned, Yogendra *et al.* [2011] reported application of various nano particle metal oxides for the degradation of Coralene Red F3BS dye. [3]. Nevertheless, Gowthaman *et al.* [2014] worked on the doping effects of Strontium metal oxides for photocatalytic properties [4]. Similarly Madhusudhana *et al.* [2014] have also reported the various metal oxides on the photocatalytic decolorization of Textile Effluent [5]. Hence, based on the literature study and in continuation of our earlier work on Photocatalytic decolorization of azo dyes, in this study synthesis and characterization of SrO by solution combustion method using strontium nitrate and the fuel urea and is successful application of SrO NP's to Direct Blue 14 Dye have been reported by using characterization techniques - SEM, XRD, UV-absorption spectroscopy and BET methods.

II. MATERIALS AND METHODS

SrO NP was synthesized in the laboratory condition by solution combustion method using Strontium nitrate and urea as a fuels. The di-azo dye DB 14 (Fig.1) is obtained by Sisco Research Laboratories Pvt. Ltd., Taloja, Maharastra and it was used for the degradation study. The chemicals like Strontium nitrate ($Sr(NO_3)_2 . 4H_2O$) (99%, AR) is obtained by Loba Chemie Pvt. Ltd, Mumbai and urea (NH_2CONH_2) (99%, AR) were obtained from Nice chemicals Pvt. Ltd., Cochin.

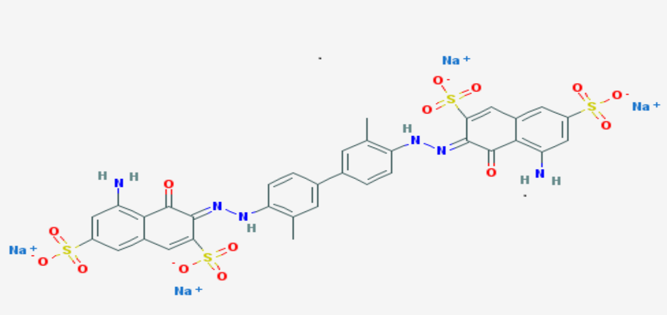

Fig 1: Chemical Structure of DB 14 di- azo dye.

III. EXPERIMENTAL

3.1 Synthesis of SrO nanoparticle

Strontium nitrate (12.6g) and Urea (6g) dissolved in a minimum quantity of water in a silica crucible (100 mm size). The dish containing the solution was introduced in to a muffle furnace (L = 28cm, B = 17cm maintained at 600±10 °C for 5-10 minutes. The product of combustion is a voluminous foamy SrO particles.

$$6\ Sr(NO_3)_2 + 10\ NH_2CONH_2 \rightarrow 6\ SrO + 10\ CO_2 + 20\ H_2O + 16N_2$$

Photo 1: Synthesis of SrO by solution combustion method

3.2 Sample Characterization

The XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The band gaps measured using UV-VIS spectrophotometer (Ocean Optics DH-2000) over the wavelength range 200-1000 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. The surface area of the NPs was measured by BET nitrogen gas adsorption method using NOVA-1000 version 3.70 surface area analyzer. The surface morphology of SrO were studied by SEM analysis using S-3400N at vijnana bhavan, Mysore university.

3.3 Nature of Surface Charge

Point of zero charge or the isoelectric point is the pH of the solution at which the total charge on the surface of NP's becomes zero (neutral). The point of zero charge of SrO(urea) NPs were measured by pH drift method. In this method 50ml of 0.01M NaCl solution was taken in six separate beakers and bubbled it with Nitrogen gas to expel the dissolved CO_2 for few minutes at room temperature till it attains a stable pH reading. Then the pH of the solution in each beaker was adjusted between 2 and 12 by adding HCl or NaOH after which 50mg of SrO(urea) NPs were added to this system was kept till the exact pH was taken. The final pH measured and a graph of initial pH $^{v}/_{s}$ final pH was plotted. The straight line drawn passes through the origin and through the points where the initial pH = final pH. The zero point charge is the intersection point of this straight line is the point of zero charge.

3.4 Photo catalytic activity

Photocatalytic efficiency of SrO NP's was evaluated for DB 14 dye under visible irradiation. 0.2g/100ml of catalyst was added to the 100ml of 30PPM of aqueous DB14. The mixture was stirred and exposed to solar irradiation for 120min. The dye concentration was monitored spectrophotochemically at 711nm, where the absorbance is maximum for DB 14.

IV. RESULT AND DISCUSSION

4.1 X-Ray Diffraction (XRD)

The XRD analysis of the prepared SrO NP's is presented in Figure 2. According to the Debye-Scherrer's formula $D = K\lambda/(\beta \cos\theta)$, where, K is the Scherrer's constant, λ the X-ray wavelength, β is the full width at half-maximum, and θ is the Bragg diffraction angle calculated using the Debye-Scherrer's formula. The average crystallite size of the SrO was found to be 51 nm.

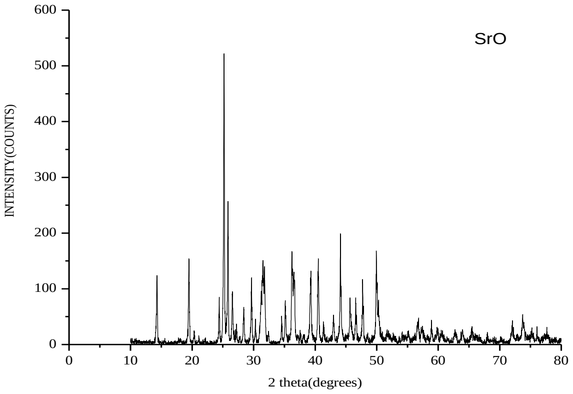

Fig 2: X-ray Diffraction of SrO

4.2 Scanning Electron Micrograph (SEM)

The SEM study shows thickly arranged layers of the nano particles. Which looks like sandwiched over one another. Also a plate like structures can be seen with irregular shapes and sizes (Fig. 3).

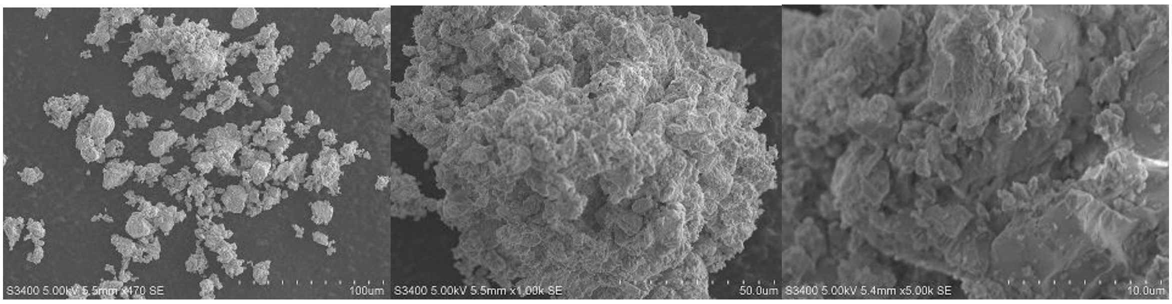

Fig 3: SEM images of SrO

4.3 UV absorbance spectroscopy

Absorption spectra of the SrO metal oxide NP was recorded using UV-VIS spectrophotometer (Ocean Optics DH- 2000) over the wavelength range 200-1000 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. From this spectrum, it has been inferred that, the NP have sufficient transmission in the entire visible and IR region. The band gap energy of the SrO NP was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

$$\text{Band Gap Energy } E = h \times C/\lambda$$

h= Planck's constant, C= Velocity of light (speed of light), λ=wavelength of light

$$h=4.135\times 10^{-15}\text{ eV},\ C= 3\times10^{8}\text{ m/s},\ \lambda= \text{---------}\times 10^{-9}\text{ nm}$$

$$\text{Band gap energy (eV)} = 4.135 \times 10^{-15}\text{ eV} \times 3 \times 10^{8} \times 10^{9}$$

$$\text{Band gap energy (eV)} = (1240/\ \text{wavelength (nm)})$$

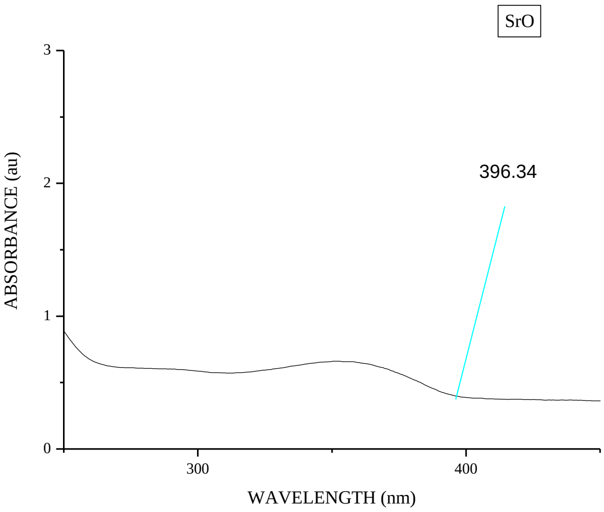

Fig 4: UV-absorption spectra of synthesized SrO Nanoparticle

The band gap energy of SrO is found to be 3.1 eV. With this we can say that the band gap of the semiconductors has been found to be particle size dependent.

4.4 BET surface area analysis

The catalytic activity of the NP's is closely related to their porus structure facilitating the contact with the pollutant which favors positively to the photocatalytic efficiency. Using the BET surface area analysis the specific surface area and pore volume are reported for obtained for SrO NP's which furnished the photoelectric conversion efficiency which is directly proportional to surface area available. The surface area for SrO (urea) is comparable to the photocatalysts prepared by other method [6].

Table 1: The properties of the nanoparticles.

Catalyst	**Surface area**	**Pore volume**	**PZC**
SrO (urea)	3.147 m2/g	0.003 cc/g	11.6

4.5 Zero Point Charge

To understand the behavior of adsorption or photocatalysis with respect to pH, it is important to determine the point of zero charge (pzc) of the NPs. For determination of pzc of SrO NP the graph of initial pH against final pH as plotted and the values of pH_{PZC} was found to be 11.6. The values increases with increasing pH and comes in neutral at 11.6 basic media, below the pzc the surface is positively charged and above pzc it's negatively charged. The pH of the DB 14 (10) is below the pH_{PZC} of the materials, which favors the adsorption of anionic DB 14.

4.6 Degradation Procedure

The UV results shows, λ_{max} value of DB 14 was found to be 711nm and the degradation of dye was carried out in presence of sunlight. The known concentration of dye solution was prepared by dissolving 0.03g of DB 14 in 1000ml double distilled water and investigated for its decolorization in the presence of SrO NP at different catalyst dosages and pH levels. After the photocatalytic decolorization, the extent of decolorization was determined by recording absorbance of the dye solution using UV-VIS spectrophotometer in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for 100ml of dye solutions with the optimum catalyst dose.

The percentage was determined by using equation

$$D = (C0 - Ct / C0 \times 100)$$

Where, **C0** is the initial absorbance of the dye solution **Ct** is absorbance at time interval „t‟ *i.e.,* after 120 minutes.

4.7 Mechanism of the photocatalytic degradation

$$SrO + h\nu \rightarrow (e^-_{CB} + h^+_{VB}) \qquad \text{(Eq. 1)}$$

Step 1: NP molecules get excited and transfer electrons to the conduction band.

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -} \qquad \text{(Eq. 2)}$$

Step 2: An electron in the conduction band of the NPs can reduce molecular oxygen and produce the super oxide radical.

$$H_2O + O_2^{\bullet -} \rightarrow OOH^{\bullet} + OH^- \qquad \text{(Eq. 3)}$$

$$2OOH^{\bullet} \rightarrow O_2 + H_2O_2 \qquad \text{(Eq. 4)}$$

$$O_2^{\bullet -} + \text{Direct Blue 14} \rightarrow \text{Direct Blue 14 -}OO^{\bullet} \qquad \text{(Eq. 5)}$$

Step 3: The oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process [7]. Recombination of hole-electron pair decreases the rate of photocatalytic degradation. This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule.

$$O\ OH^{\bullet} + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^- \qquad \text{(Eq.6)}$$

Step 4: Hydrogen peroxide can be generated in another path

$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^-$ (Eq. 7)

$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + OH^- + O_2$ (Eq. 8)

Step 5: Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents.

$OH^\bullet / O_2^{\bullet -} / SrO^{\bullet +}$ + Direct Blue 14 → Direct Blue 14 degradation (Eq. 9)

Step 6: The radicals produced are capable of attacking dye molecules and degrade them.

4.8 Effect of catalyst concentration on direct blue 14

The effect of catalyst concentration on the degradation was studied for different catalyst dosage from 0.1 to 1g/100ml for DB 14. The synthesized NP has shown appreciable results.

The SrO with the NP size 51nm has shown 96.34% degradation. Since, the photo degradation was most effective at 0.2g/100ml in 120 minutes for SrO NP dosages showed in (Fig. 5) (Photo 2), further experiments were continued with same dosages. This results in creation of more number of H^+ ions and e^-(CB) with the formation of $OH^\cdot$ radicals which acts as primary oxidizing agents. The increase in degradation rate can be ascertained in terms of availability of active sites on the catalyst surface and sunlight penetration into the suspension. Further increase in the catalyst amount beyond 0.2g/100ml decreases the photo degradation by a little margin. This may be due to overlapping of adsorption sites as a result of overcrowding owing to collision with ground state catalysts [8].

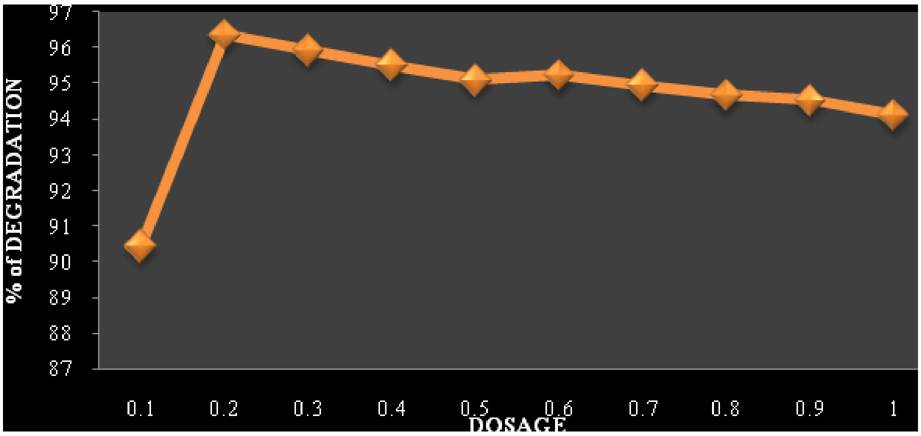

Fig. 5: Effect of catalyst concentration DB 14 at 120 minutes [DB 14=30 ppm, pH=7]

Photo 2: Effect of catalyst concentration on DB 14 at 120 minutes [DB 14=30 ppm, pH=7]

4.9 Effect of ph on direct blue 14:

pH plays a major role in photocatalytic process [9], hence, the different experiments were carried out to find the optimal pH of reaction mixture for degradation of DB 14. The examined range of pH was from 2 to 11. The results are shown in Fig. 7. It is noticed that the best results are obtained in alkaline solutions after 2 hours of irradiation and best degradation results were obtained at pH 10.

The degradation rate of DB 14 for SrO the degradation of the DB 14 increased from 91.70% to 97.74% from pH 2 to 10 and decreased to 96.90% at pH 11 in 120 minutes for 0.2g/100ml. The maximum degradation rate for the NP was achieved 97.74% at pH 10 [10].

The effect of pH explained in term of point zero charge, where the pzc of SrO is 11.6. The surface of SrO NP's is positively charged below the 11.6 pH, the result shows that, the percentage of degradation is effective in alkaline pH, where in acidic medium and the percentage of degradation shows minimum. This is due to two reasons (i) at low pH value SrO particle agglomeration reduces the dye adsorption as well as photon absorption. (ii) in DB 14 dye, the azo linkage (–N=N–) is particularly susceptible to electrophilic attack by hydroxyl radical. But, at low pH the concentration of H^+ is in excess and H^+ ions interact with azo linkage decreasing the electron densities at the azo group. From the experimental results the photocatalytic degradation efficiency of SrO is observed to be higher at alkaline pH range even though the adsorption of dye molecules are low at alkaline pH. The possible reason for this behavior is that alkaline pH range favors the formation of more $^{\cdot}OH$ due to the presence of large quantity of OH^- ions and these are the main species responsible for the oxidizing agents, which will enhance the photocatalytic degradation of dye significantly. [11,12]

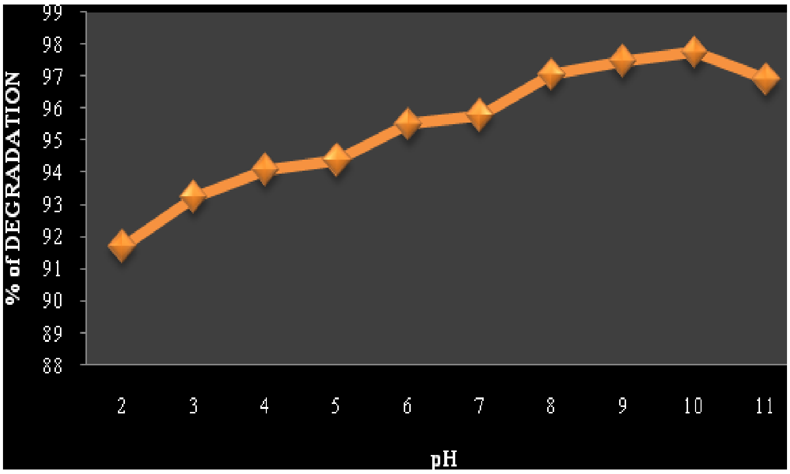

Fig 6: Effect of pH on DB 14 at 120 minutes [DB 14 =30 ppm, SrO= 0.2g/100ml]

Photo 3: Effect of pH on DB 14 at 120 minutes [DB 14 =30 ppm, SrO= 0.2g/100ml]

4.10 Effect of initial dye concentration

The experiments were performed to study the effect of initial dye concentration by varying the DB 14 concentration from 30, 40 and 50 ppm respectively (Photo 4). The results obtained for SrO is 97.74% for 30ppm, 87.62% for 40ppm and 82.55% for 50ppm respectively (Fig 7). These experiments illustrated that, the degradation efficiency was directly affected by the concentration. The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites [15]. According to Beer Lambert's law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in the lower photon absorption of the catalyst and consequently decrease photocatalytic reaction rate [16].

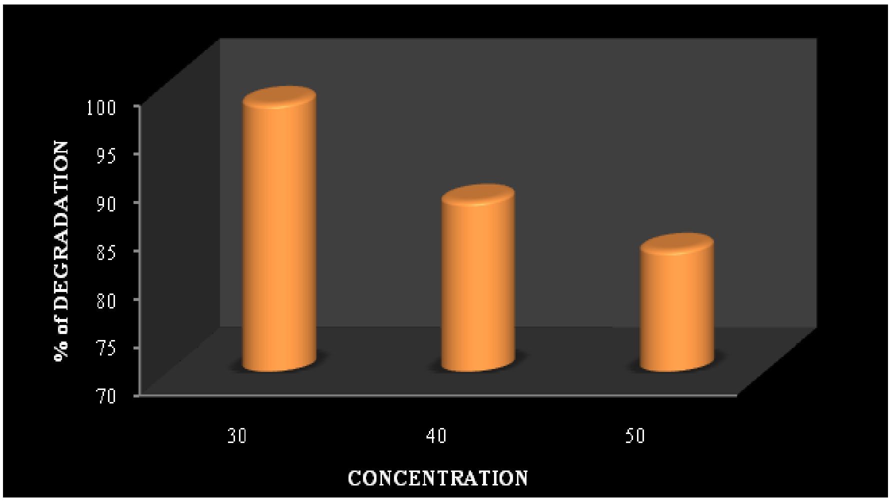

Fig 7: Effect of initial dye concentration on the photocatalytic degradation of DB 14 [SrO g/pH=0.2/10 and DB 14 = (30, 40 and 50) ppm]

V. CONCLUSION

In the present study, SrO a new photocatalyst was prepared by solution combustion method. SrO was characterized by using techniques like XRD, SEM and UV-Vis absorbance spectroscopy. The di-azo dye DB 14 was used for the photocatalytic degradation studies. The synthesized photocatalyst has shown a maximum decolorization of the selected dye solution under solar irradiation. This photocatalyst was found to be very efficient in decolorizing the azo dye and achieving 96.34% in 120 minutes at pH 7. Similarly, when the pH was altered, 97.74% at pH 10 for 0.2 g/100ml was achieved for the metal oxide NP. Hence, the results revealed that, the photocatalytic decolorization of DB 14 is mainly dependent on the pH of the dye solution and catalyst dosage and the SrO NP (size 51nm) is an effective media to decolorize the DB 14 solution.

IV. ACKNOLEDGEMENT

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