



Evaluation of Photocatalytic Activity of Ag^I and Sr^{II} co-doped TiO₂ Nanoparticles for the Degradation of Reactive Blue-160 (RB-160) Textile Dye

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Abstract — The focus of the work is on the synthesis of Ag^I and Sr^{II} co-doped TiO₂ nanoparticles, which exhibit superior photo catalytic activity to that of Ag^I doped TiO₂ on UV and visible light illumination. The physicochemical parameters such as pH of solution, intensity of light, dosage of photo-catalyst, concentration of dye, effect of sensitizers, etc., were studied to optimize the conditions for photocatalysis. The nanoparticles are characterized by XRD, HR-TEM, EDAX, BET, and UV-Visible DRS techniques. The surface doping of Ag^I and Sr^{II} on the lattice of TiO₂ are found to bring the isolated energy levels near the conduction and valence bands resulting in the narrowing of the energy band gap (Eg). The XRD analysis demonstrated that both silver and strontium nanoparticles are dispersed finely on the surface of titania framework. TEM studies showed particle size of 8-20 nm for Ag-doped TiO₂ and 11-25 nm for Ag^I and Sr^{II} co-doped TiO₂ nanoparticles. The synthesized materials were effective as photocatalysts for the degradation of a textile dye, namely, RB-160. The superior photo-catalytic activity of Ag^I and Sr^{II} co-doped TiO₂ nanoparticles is attributed to the interactive effect caused by the narrowing of band gap and also the enhancement in charge separation.

Keywords: photo catalytic activity, nanoparticles, textile dye, TiO₂

I. INTRODUCTION

Titanium dioxide (TiO₂) is a well known photo-catalytic material due to its high stability, non-toxicity, low cost and high performance in the mineralization of organic pollutants present in air and water [1–4]. However, the photo-catalytic processes with TiO₂ catalysts is effective under UV light irradiation, due to its high band gap (~3.2 eV), restricting the use of TiO₂ in practical applications, as the UV region makes up to only about 5% of total solar light spectrum.

Doping of transition and alkaline earth elements into TiO₂ lattice, by physical and chemical processes, have been found to be useful to improve the light sensitized catalysis [5]. However, these metal dopants have to be used in small quantities to avoid the recombination of

photo-generated electrons and holes, which is bolstered by the large amount of these dopant species [6]. Simultaneous doping of two different atoms into TiO₂/ZnO photo-catalysts has attracted significant interest since it can exhibit higher photo-catalytic activity and unique characteristics compared to doping with a single element and several reports are available in the literature on co-doped photo-catalysts [7-15]. However, it is interesting to note that not many studies have been carried out to degrade the textile dyes, which are a serious environmental threat particularly towards water pollution.

Most of the chemical pollutants, which are soluble in water, are harmful not only for the humans but also for the environment. It has been estimated that about 1.1 billion people lack clean water and about 35% of people in the developing world die from various water-related problems. Usage of synthetic organic (azo) dyes has grown significantly in textile, cosmetic, paper, drug and food processing industries. These contain synthetic colorants that are not easily degradable by biological treatment methods, owing to their complex structure and high stability. Most of these dyes are carcinogenic, harmful and have potential to reduce the light penetration in the aqueous systems; thus causing a negative effect on the photosynthesis, apart from affecting human health [16]. The dye containing effluents are characterized by their fluctuating pH, suspended particles, high oxygen demand, non-biodegradability and resistance to oxidation, moreover conventional water decontamination methods are often chemically, energetically and operationally intensive and suitable only for large systems [17, 18] thereby necessitating development new materials for effective dye removal. Various physico-chemical methods are available for the removal of dyes from waste water and in particular through photo-catalysis, which can be used to cause redox transformations and complete degradation of dye molecule. TiO₂ mediated photo-degradation has attracted extensive interest, owing to its unique opto-electronic properties, low-price, chemical

stability and non-toxicity [19-20]. A simple synthetic approach for the preparation of two novel nanoparticles photo-catalysts, a) Ag doped TiO₂ & b) Sr and Ag co-doped TiO₂ was attempted and the composites were used for the degradation of a commonly used textile dyes, RB-160, in the presence of UV light. The synthesized TiO₂ based nanoparticles were found to exhibit superior photo-catalytic behavior and faster degradation kinetics, in comparison to the available photo-catalyst reports, over a wide range of dye concentration even in the presence of limited amount of photo-catalysts.

II. MATERIALS AND METHODS

A. Chemicals

Titanium (IV) isopropoxide (Sigma-Aldrich), Silver nitrate (Merck limited), Strontium nitrate (SD Fine chemicals), 2-propanol (SD Fine chemicals), Tween 20 (Hi-Media), Sodium borohydrate (SD Fine chemicals), Chloroacetic acid (SRL Chemicals), Sodium acetate (SRL Chemicals), Ammonium acetate (SRL Chemicals), used in the present work were Analytical grade reagents and used without further purification. Millipore water was used in all experiments.

B. Synthesis of Ag^I and Sr^{II} co-doped TiO₂ nanoparticles

A mixture of 5 mL of titanium (IV) isopropoxide in 50 mL isopropanol was added drop-wise to 200 mL of distilled water at pH 1.5 under stirring. To this solution, calculated amount of aqueous solutions of AgNO₃ and Sr(NO₃)₂ (0.2 mol% to 1.0 mol %) were added drop-wise while stirring for an additional 45 min. A small aliquot of distilled water and 0.05 M hydrazine hydrate were added to it followed by 5 mL of tween 20 (capping agent to prevent agglomeration of particles) and the stirring was continued for an additional 30 min. The resultant sol was sonicated at 80 MHz for 90 min and then dried at 100°C in a hot air oven for 24 h to get the dry gel which was calcinated at 450°C to get the desired nanoparticles powder.

C. Characterization of nanoparticles

Powder XRD pattern was recorded using X-ray BRUKER D8 Advance X-ray diffractometer with Cu K_α source ($\lambda=1.5406$ Å). Major peak positions were compared with the standard JCPDS files to identify the crystalline phase of the synthesized nanoparticles. JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) was used for imaging, SAED pattern and energy dispersive X-ray with an accelerating voltage of 200 KV at different magnifications. Diffuse reflectance spectra were recorded using JASCO V-670 UV-Vis spectrophotometer. Specific surface area of the sample was arrived at through nitrogen adsorption at 77 K using BET, Micromeritics ASAP2020 V4.01 (V4.01 H).

D. Photodegradation studies

The photo-catalytic activity was assessed by measuring the decomposition of the aqueous solution of RB-160 dyes under UV and visible light irradiation using an annular model multi-lamp photo-reactor (Heber Scientific). For carrying out the photo-catalysis experiments, 50 mL of the dye solution containing appropriate quantity of the catalyst suspensions was used.

The suspension was stirred for 30 min in dark to obtain equilibrium after which the solution was aerated continuously by pumping oxygen supply for complete mixing of the reaction solution. After irradiation, 2 mL of the dye sample from the reaction tube was withdrawn at different time intervals and the change in the dye concentration was measured through absorbance values 610 nm for RB-160 after centrifugation. The absorbance at 610 nm for RB-160 represents the aromatic part of the dyes and its decrease indicates the dissipation of the aromatic unit. All the absorption measurements were carried using JASCO V-670 UV-Vis spectrophotometer. The pH of the solution was measured on HANNA Phep (Model H 198107) digital pH meter after adjusting it with 0.2 M chloroacetic acid, 0.2 M sodium acetate and 0.2 M ammonium acetate.

III. RESULTS AND DISCUSSION

A. Optical properties

UV-Vis absorption spectra of pure TiO₂, Ag doped TiO₂ & Sr and Ag co-doped TiO₂ showed in in Fig. 1 (a). A well defined band edge in the UV region of 300–350 nm seen could be attributed to the photo-excitation taking place from valence band to conduction band.

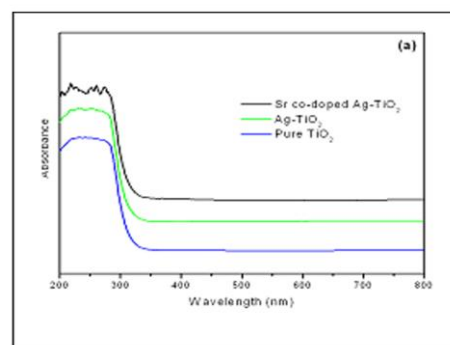


Fig. 1(a). UV-Vis absorption spectra of pure TiO₂, Ag doped TiO₂ & Sr and Ag co-doped TiO₂

It is interesting to note that TiO₂ doped with silver has lower shift in comparison to strontium and silver (1.0 mol %) co-doped TiO₂ nanoparticles, which showed a significant red shift. The extent of red shift was found to increase with increasing levels of strontium and silver, which signifies the improvement in the optical activity of the photo-catalyst towards visible light. The energy gap (E_g) is calculated from the following equation,

$$(ah\nu)^2 = A (h\nu - E_g)^n \quad (1)$$

Where α is the absorption coefficient, A is a constant and $n = 2$ for direct transition; $n = 1/2$ for indirect transition [21]. An extrapolation of Kubelka Munk plot of $h\nu$ vs. $(\alpha h\nu)^2$ was used to get the value of the optical energy gap (E_g) as shown in Fig. 1 (b).

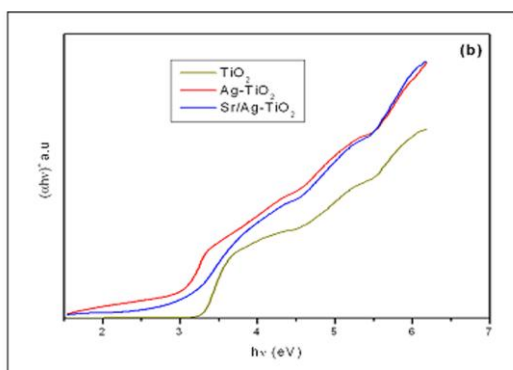


Fig. 1(b). Optical energy gap value

The energy band gap values for the pure TiO_2 , Ag^{I} doped TiO_2 & Ag^{I} and Sr^{II} co-doped TiO_2 nanoparticles were found to be approximately 3.17 eV, 2.71 eV and 2.62 eV respectively. It was observed that the doping of titanium dioxide with transition metals (silver and strontium) was accompanied with a decrease in the band energy and an increase in the wave length (red shift).

B. X-ray diffraction

Fig.2 (a) shows the X-ray diffraction pattern of the Ag^{I} and Sr^{II} co-doped TiO_2 nanoparticle samples. In all the samples, anatase phase was confirmed by the 2θ peaks at 25.3 $^\circ$, 37.9 $^\circ$, 47.9 $^\circ$, 55.0 $^\circ$ and 62.8 $^\circ$, all of them are in complete agreement with peaks corresponding to the anatase phase TiO_2 . Phases related to Ag and Sr were not significantly detected in any of the samples due to their low concentration levels and hence their doping did not result in any significant changes in the phase crystallinity. However, a marginal shift in the d-spacing with discernible change in the cell volume suggests the incorporation of dopants into TiO_2 . Ag^{I} and Sr^{II} did not show any phase changes suggesting that aggregates might have been formed on the crystal borders and on the surface of the photo-catalyst.

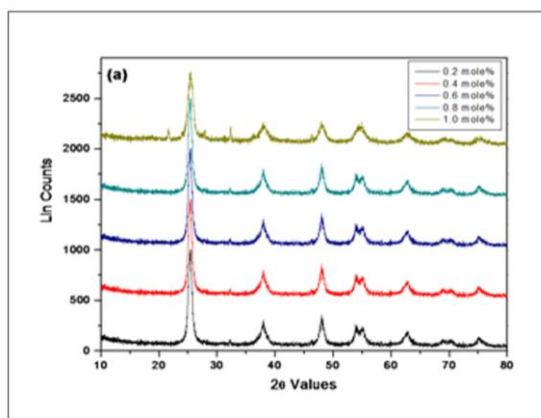


Fig. 2. XRD patterns of Ag^{I} and Sr^{II} co-doped TiO_2

C. TEM and EDX analysis

The morphologies of the nanoparticles were analyzed under TEM. Fig 3(a) show images of $\text{Ag}^{\text{I}}/\text{Sr}^{\text{II}}$ co-doped TiO_2 sample with highly uniform nano-crystalline microstructures and a uniform grain size, as indicated by the XRD data. From the images, it could be inferred that the uniformly distributed particles range from 7 to 22 nm with irregular sized spherical morphologies and slight agglomeration. The SAED pattern of this sample are shown in Fig.3 (b), in which the dark rings on the right correspond to the standard polycrystalline diffraction rings for the anatase phase (indexed). Interestingly, no signs of diffraction rings related to other phases were observed. EDX mapping HR-TEM images were Fig. 3(c) used to obtain more discernible microstructure information to enable accurately analyze the single grains and grain boundaries. Fig. 3(d) of the photo-catalysts showed uniform dispersion of the dopant metals onto the support, which are in agreement with the XRD results. The BET (Brunauer–Emmet–Teller) surface area of the Ag-doped and Sr/Ag co-doped TiO_2 were measured as 984.62 and 1296.21 m^2/g .

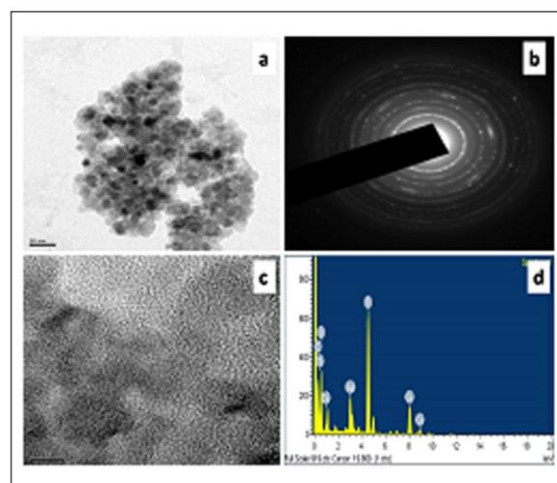


Fig. 3. TEM & EDX images of Ag^{I} and Sr^{II} co-doped TiO_2

D. Catalytic activity

Photo-catalytic activity of Ag doped TiO_2 & Ag and Sr co-doped TiO_2

Higher photo-catalytic activity of Ag^{I} doped TiO_2 & Ag^{I} and Sr^{II} co-doped TiO_2 catalyst have been observed during the degradation of RB-160 under visible light [Fig. 4(a & b)] as well as in the UV light [Fig. 4(c & d)], in comparison to pure TiO_2 nanoparticles. From the figure, it is clear that the Ag^{I} and Sr^{II} co-doped TiO_2 has shown higher photo-catalytic degradation for both the dyes, which could be attributed to the synergetic co-doping effects of Ag^{I} and Sr^{II} with TiO_2 [7-15]. The photonic efficiency of the catalyst was observed to increase with increasing Ag^{I} and Sr^{II} loading up to 1.0 mole %. However, higher amounts of Ag^{I} and Sr^{II} doping were found to be detrimental to the photonic efficiency of the catalysts. It was observed that up to the

optimum level of metal doping, the Ag^I and Sr^{II} particles get deposited on the TiO_2 surface, thereby acting as electron-hole separation centers [22, 23]. The transfer of electron from the TiO_2 conduction band to metallic silver particles at the interface is thermodynamically possible since the Fermi level of TiO_2 is higher than that of silver metal [24]. This results in the formation of Schottky barrier at the metal-semiconductor contact region, which improves the charge separation and thus enhancing the photo-catalytic activity of TiO_2 . In contrast, at higher concentrations, the Ag^I particles can act as electron hole recombination centers, thereby decreasing the photo-catalytic activity of TiO_2 . It was reported that the probability of electron-hole recombination increases with increasing Ag^I doping in TiO_2 , thereby reducing the overall photo-catalytic efficiency [24].

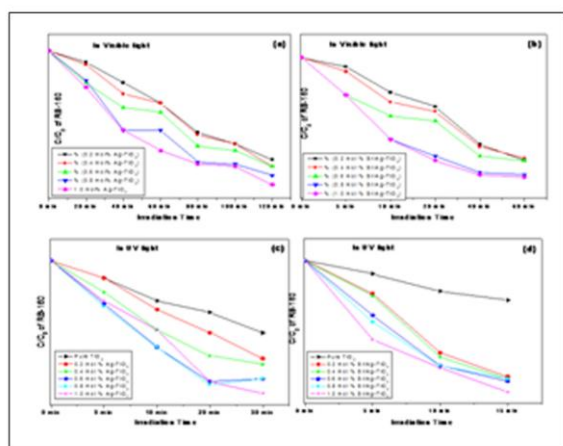
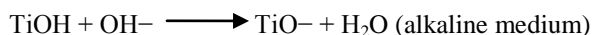
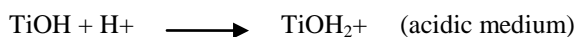


Fig. 4. Comparison of degradation patterns of Ag doped TiO_2 and Ag/Sr co-doped TiO_2 with TiO_2

Effect of pH

Photo-catalytic degradation of dyes is greatly influenced by solution pH [25, 26]. The effect of pH on the photo-catalytic degradation of RB-160, under UV and Visible light irradiation, is shown in Fig. 5. The zero point of charge for TiO_2 is at pH 6.8 [27], hence under acidic or alkaline conditions, the surface of the titania can be protonated or deprotonated respectively, according to the following reaction [28]



At lower pH, the degradation of dyes is greatly influenced by the electrons in the conduction band for the reductive cleavage of the azo ($-\text{N}=\text{N}-$) bonds associated with the organic dyes [29-31]. In the present study, the degradation percentage of and RB-160 is found to decrease with increasing pH from 3 to 8 [Fig. 5]. RB-160, being a dianionic dyes, exists as ions in aqueous solution. This could be explained by the electrostatic forces acting between positively charged TiO_2 and highly ionized sulfonic groups present in the

dye molecule which enhances the dye removal efficiency in acidic medium.

Moreover, presence higher amount of H^+ at these pH values could mask the surface of the catalyst thereby preventing the photo-excitation of semiconductor particles and subsequent reduction in the generation of free radicals. The same phenomenon has already been reported earlier [32]. When the pH is above 6.8, the surface of the TiO_2 is negatively charged thereby repelling the anionic form of the dye molecules, which subsequently reduces the degradation efficiency.

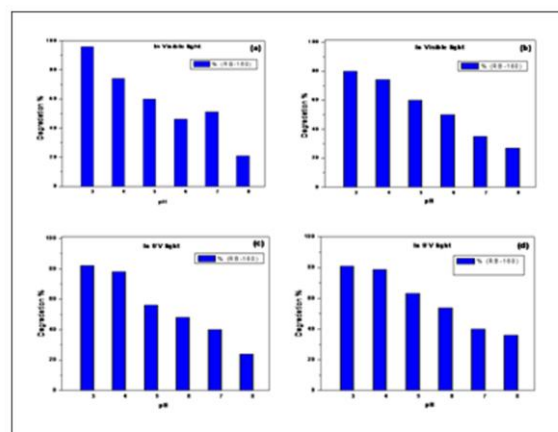
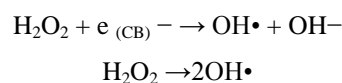
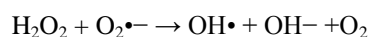


Fig. 5. pH studies of Ag/Sr co-doped TiO_2 particles
Effect of H_2O_2 (photo-sensitizer)

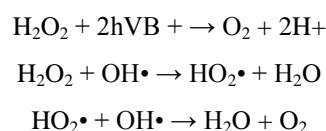
Different concentrations of hydrogen peroxide have been tried out for the assessment of photo-catalytic degradation of and RB-160 and the results are shown in Fig. 6a & b. From the figure, it could be noticed that the degradation rate of RB-160 increase with increasing H_2O_2 concentration up to 20 mM, and then thereafter it decreases. The higher reaction rates after the addition of H_2O_2 could be attributed to the increase in production of hydroxyl radical according to the following equations [33].



The H_2O_2 molecule reacts with the superoxide anion to form hydroxyl radical thereby enhancing the photo-catalytic degradation of the dyes.



However, at higher concentrations, because of the scavenging action of H_2O_2 , formation of $\text{OH}\cdot$ and hVB^+ is found to get reduced particularly above 20 mM of H_2O_2 , as observed in the experiments conducted. Since hVB^+ and $\text{OH}\cdot$ are powerful oxidants for both the dyes, the photo-catalytic oxidation would be suppressed at higher concentrations of H_2O_2 [33].



Effect of dye concentration

The study of initial dye concentration is very important in photo-catalytic reactions, in terms of both mechanistic and application point of view. The effect of dye concentration on the degradation of RB-160 was studied at different initial concentrations of the dye from 5 ppm to 30 ppm under UV [Fig. 6 (c)] as well as visible light [Fig. 6 (d)]. It is observed from the figures that the percentage of removal/degradation of RB-160 has been found to decrease rapidly with increasing initial concentration of the organic dyes. The dependence of photo-degradation rates on the initial concentrations of RB-160 could be due to the following reasons. At higher dye concentrations, the amount of dye adsorbed on the catalytic surface increases and these adsorbed dye molecules effectively hinder the light absorption characteristic of the photo-catalysts thereby affecting the overall catalytic activity. The increase in dye concentration also decreases the path length of the photon entering into the dye solution. At higher dye concentrations, the dye molecules may absorb a significant amount of light rather than the catalyst and this is likely to reduce the catalytic efficiency.

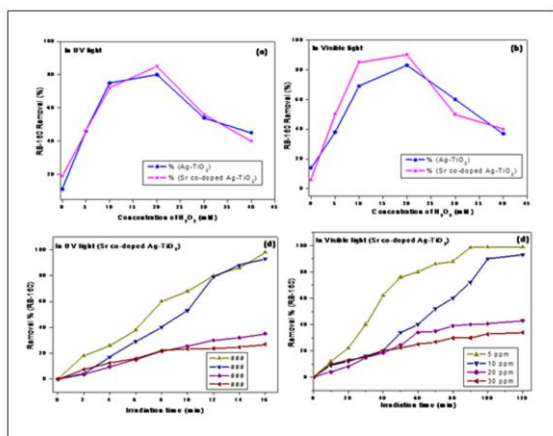


Fig. 6. Comparison of different dye concentrations and H_2O_2 (photosensitizer) on Photocatalytic degradation

Effect of catalyst amount

The extent of dye degradation is also influenced by the quantity (amount) of photo-catalyst material and their relative particle aggregation at high quantities. As the amount of catalyst increases, the degradation percentage also increases, which are the characteristic behavior, observed in heterogeneous photo-catalysis [34]. The degradation rate increases with increase in catalyst amount because of the increase in the number of active sites on the photo-catalyst surface thus causing an increase in the number of $OH\cdot$ radicals taking part in actual degradation of dye solution. The amount of Ag^I doped TiO_2 & Ag^I and Sr^{II} co-doped TiO_2 on photo-degradation RB-160 has been studied. From the data, it could be noticed that the degradation rate got enhanced when the amount of catalyst was increased from 10 mg/50 mL to 35 mg/50mL and then above 35 mg/50 mL, the degradation showed significant decrease. This

could be because of the fact that after a certain limit of catalyst the solution turns turbid, which would block the light radiation for the photo-catalytic reaction to proceed thereby the percentage degradation, starts decreasing [35].

Effect of light intensity

The intensity of light also affects the dye degradation [36]. The effect of light intensity on photo-degradation of RB-160 is shown in Table 1(A) & (B). It could be seen that with increasing intensity of light (150–500 W/cm^2 in the case of Visible, 125–400 W/cm^2 in the case of UV), the degradation rate was found to increase linearly. This could be because of the fact that as the light intensity increases, the reactions involving electron-hole formation become predominant and the recombination effects become negligible [37, 38].

TABLE 1 (A). EFFECT OF LIGHT INTENSITY ON % DEGRADATION OF RB-160 IN VISIBLE LIGHT (CONCENTRATION OF DYE 10 PPM, IRRADIATION TIME = 60 MIN, pH= 3.1)

Light intensity (W/cm^2)	% degradation of RB-160 using Sr and Ag co-doped TiO_2
150	41
340	71
500	78

TABLE 1 (B). EFFECT OF LIGHT INTENSITY ON % DEGRADATION OF RB-160 IN UV LIGHT (CONCENTRATION OF DYE 10 PPM, IRRADIATION TIME = 60 MIN, PH= 3.1)

Light intensity (W/cm^2)	% degradation of RB-160 using Sr and Ag co-doped TiO_2
125	41
250	71
400	78

IV. CONCLUSION

Ag^I doped TiO_2 & Ag^I and Sr^{II} co-doped TiO_2 nanoparticles were synthesized by a modified sol-gel route. The influence of various physio-chemical parameters on the photo-degradation characteristics of the composite photo-catalysts was studied to find out the optimal conditions for the effective degradation of the dyes. The results of photo-degradation of RB-160 indicate that the effective degradation of dye molecules is possible in the presence of both UV and visible light while using the doped catalysts. The synergetic effects of Ag^I and Sr^{II} co-doping have been found to make the catalysts electron and hole traps, leading to higher photo-catalytic activity for Ag^I and Sr^{II} co-doped TiO_2 catalyst. These results are found to be in good agreement with the UV-Vis diffuse reflectance spectra which showed higher red shift for Ag^I and Sr^{II} co-doped TiO_2 compared to Ag^I doped TiO_2 . The determination of TOC has also confirmed the complete mineralization of the dye molecules in the presence of the doped catalysts.

V. ACKNOWLEDGMENTS

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