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Enhanced photo catalytic activity of Ag$_2$O nanostructures through strontium doping

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Abstract
Nanoparticles of Ag$_2$O and varying amounts of Sr-doped Ag$_2$O synthesized by basic co-precipitation method were practiced for purging of relentless organic dyes, after characterizing them using Powdered x-ray Diffraction (PXRD), Scanning electron microscopy (SEM), Energy dispersive x-ray spectroscopy (EDX) and transmission electron microscopy (TEM). Photo catalytic degradation of cationic dyes such as methylene blue (MB), rhodamine B (RhB) and anionic dye methyl orange (MO) was carried out by utilizing photosensitive silver oxide nanoparticles functionalized with various concentrations of strontium under solar irradiation with the aid of UV–vis spectroscopy. Besides the rapid de colorization, Sr/Ag$_2$O solar-driven photocatalysis was concurrently able to oxidize the dye, leading to approximate mineralization of carbon. It is proposed that prime oxidant in degradation of both kind of dyes is hydroxyl radical. Kinetic analysis reveals that photodegradation of cationic and anionic dyes follow pseudo-first order kinetics.

1. Introduction
Nanoscience has discovered the golden opportunity for the formation of new nano-sized materials that possess exceptional optical and electronic properties that are diverse from the ones of their bulk state [1]. Significant number of atoms residing on the surface and the quantum confinement effect of the electronic states has important effect on the distinct characteristics of the nanomaterials [2]. Therefore, nanomaterials have illustrated prospective applications due to their exclusive electronic, optical, magnetic and catalytic properties [1, 3] along with the enhanced properties of metal oxide nanoparticles such as mechanical hardness and thermal stability [4]. The nanostructured oxides are widely used in paints, batteries, optical devices, cosmetics, for medical diagnosis etc [5] amongst these oxides particularly silver oxide nanoparticles draw the momentous attention due to the probability of usage in several fields including synthesis of nanoscale electronics, surface improved raman properties etc. [6, 7] The various accessible compositions of silver oxide include Ag$_2$O, Ag$_2$O$_3$, AgO and Ag$_3$O$_4$ etc. Owing to their unique properties such as increased chemical stability, innocuous nature, high abundance and low cost silver oxides act as potential semiconducting materials for sensor purposes [8–12]. Ag$_2$O a p-type semiconductor exists in different morphologies with the reported band gap ranging from 1.2 eV to 3.4 eV. The cubic crystal structure of silver oxide is analogous to Cu$_2$O [13]. Due to its photosensitive nature and instability under irradiating light, Ag$_2$O is often used as a prime photo catalytic material besides acting as a co-catalyst [14]. The foremost appalling risk to the environment is contamination of water due to the regular discharge of organic dyes and the products obtained after their decomposition. Absolute removal of these dyes and their breakdown products is essential to make water fit for use as these organic dyes are highly toxic in nature which not only effects the human health but also influence the aquatic life. Recently, photo catalysis has been staunched for the elucidation of wastewater dyes, predominantly due to its capability of absolute mineralization of the contaminant. Semiconductors like titania, zinc oxide, zinc sulphide, iron oxide etc serve as light sensitizers and stimulate the redox processes owing to the electronic structure of the metallic atoms in chemical permutation, which is specified by the presence of a filled and empty valence and conduction band respectively.
Previously, the aqueous solution of an anionic dye methyl orange was successfully decolorized by Ag2O with the rate constant of 0.023 min$^{-1}$ under fluorescent light induction illustrating its photocatalytic efficiency [14]. Visible light induced degradation of dyes has attracted much interest and several research groups have reported the efficient degradation of a dye like methylene blue using metal oxides [16]. Comparative study of visible light induced photocatalytic degradation of methylene blue using different metal oxide catalysts illustrating their rate constants are enlisted (table 1).

Recently, a research group was successful in synthesizing Ag2O nanoparticles utilizing green combustion method. These NPs were then employed to assess the photocatalytic degradation of acid orange-8 dye under UV light irradiation. AO-8 dye was efficiently degraded to an extent of 70% [22].

Amreen Shah et al. examined the photocatalytic activity of synthesized Ag2O nanoparticles by applying eco-friendly scheme using extract of fresh leaves of P. emodi. NPs degraded 97.78% methylene blue dye in a time span of 180 min using UV-visible light irradiation with a rate constant of 0.0214 min$^{-1}$ [23].

Ying Wang et al. carried out photocatalysis-assisted adsorption for the removal of azo dye such as congo red by utilizing the fabricated Ag2O NPs. Results illustrating the regeneration of silver oxide after complete photodegradation of the azo dye in 35 min under irradiation of visible light. The adsorption of dye following pseudo second order kinetics in accordance to Langmuir equation [24].

Chemically highly reactive alkaline earth metal, Strontium, exhibiting chemical analogy with calcium, can be used in bone construction and in the bone loss avertion. Researchers have discovered numerous new applications of strontium, exemplifying its significance. Iwase et al. scrutinized that small size of cationic Sr$^{2+}$ resulted in the increase in photo catalytic rate of water splitting when surface of sodium tantalum oxide was modified with Sr [25]. Another group detailed that by increasing the amount of dopant Sr upto 1 mol%, the phase modification to the tetragonal shape occurred, alongside the considerable raise in the granular magnitude, evident density, the dielectric constant and piezoelectric coefficients with the decrease in the dielectric loss that make strontium modified lead zirconate titanate ceramics to be efficiently used in piezoelectric applications [26]. Buchi Suresh M. and Roy have reported that strontium doped ceria founded ceramics greatly amplified the ionic conductivity as a consequence of increase in the size of the grains. In addition to increase in the oxygen vacancy the lattice binding energy is lowered which directed the higher mobility of oxygen ion that was supported by the less activation energy displayed by the creation of Sr-GDC [27]. Yuexiang Li et al. have declared that functionalization of titania with different alkaline earth metals lead to radically enlarged photo catalytic hydrogen production by relying on the size and synthetic protocol [28]. In accordance to all affirmations, it is summarized that photo catalytic activity, grain size, total conductivity and the dielectric constant of nanoparticles can be enhanced by using strontium as a dopant.

The current research aims (1) To scrutinize the changes in size, photo catalytic efficiency and shape of silver oxide nanoparticles modified with contrasting amounts of strontium dopant. (2) Assessment of photo catalytic behavior of the produced nanoparticles against the cationic and anionic dyes due to the strong absorption band of Ag2O in the visible region (3) Mechanistic study of dye degradation (4) To evaluate the comparative rate constants (min$^{-1}$) for particular time span in order to understand the kinetics of dye degradation.

### 2. Experimental

#### 2.1. Materials and methods

Shimadzu 1800 UV–vis spectrophotometer operating in the range of 200–800 nm was used for recording the absorption spectra. The purity, phase and polycrystalline nature of the samples were initially characterized using powder x-ray diffraction (PXRD) with CuKα radiation of 0.154 nm at varying diffraction angles ranging from 20–80. The fabricated samples were dispersed in n-Hexane after sonicating them for 10 min JSM-6500F and Hitachi S-3000H suitable and powerful scanning electron microscope (SEM) was utilized to examine the surface morphology. Moreover, EDX spectra were also recorded for determining the elemental composition of all the

| Metal oxide catalysts | Rate constants | References |
|-----------------------|----------------|------------|
| TiO$_2$               | 0.0347         | [17]       |
| ZnO                   | 0.0015–0.0067  | [18]       |
| Cu$_2$O               | 0.0009         | [19]       |
| SnO$_2$               | 0.0139         | [20]       |
| In$_2$O$_3$           | 0.0063         | [21]       |
| Ag$_2$O               | 0.0379         | [16]       |

Table 1. Rate constants of different metal oxide catalysts for methylene blue degradation.
samples. JEM-1400 transmission electron microscope operating at 100 kV was employed for the structural and grain size information of all the samples.

2.2. Synthesis of strontium doped silver oxide NPs
The emblematic co-precipitation method was opted for the production of silver oxide nanoparticles doped with various concentrations of strontium in the presence of a precipitating agent mainly sodium hydroxide that was added drop wise in the reaction mixture. The first step of synthesis comprised of preparation of 0.01 M aqueous solution of the precursor silver nitrate with constant stirring at a temperature of 80 °C, afterwards different mole ratios of SrCO₃ were added in the reaction mixture to yield a series of new doped catalysts. The remaining procedure is discussed before [29].

2.3. Photo catalytic Activity
The photo catalytic activity was carried out in accordance of two important facts firstly, stability and secondly strong absorption of the organic dyes in the visible region like methylene blue (MB) and rhodamine B (RhB) and anionic dye such as methyl orange (MO) under different pH conditions. Photo catalytic activity was successfully performed under direct sunlight (outdoor lightening) against three different dyes. The photo catalytic activity of the doped and pristine silver oxide nanoparticles was evaluated independently with the usage of the aqueous solution of 25 ml of 10⁻⁵ M of dye in the existence 10 mmol (0.01 g) for the complete dye degradation. A decrease in the characteristic absorption peaks of all dyes was observed with the irradiation of solar energy that resulted in efficient photo degradation. For the evaluation of the self-degradation ability of all the dyes under the irradiating sunlight, blank experiments were carried out under the same reaction conditions.

3. Result and discussion

3.1. Characterization of NPs
Nanoparticles of diverse size, shape, physical and chemical properties of silver oxide and strontium modified silver oxide of different concentrations were produced as a result of co-precipitation method. The synthesized nanoparticles were characterized using several physical techniques available such as PXRD, EDX, SEM and TEM. The acquired XRD pattern was indexed as a pure cubic crystal system of Ag₂O having Pm-3m space group no. 00-001-1041. The prevalence of assorted strong diffraction peaks at (111) (200) (220) and (311) planes corresponding to 32.90, 38.10°, 54.93°, 65.70° respectively at an angle 2 theta indicate the atom’s preferential growth along with these surfaces of primordial cubic system. XRD indicates high phase purity of the sample as there is no reflection present in the pattern other than silver oxide. Reflections in the pattern appear to be slightly broad that is related to the nano size of the particles. Overall slight shifting of diffraction peaks towards higher angle was observed due to tensile stress in strontium doped silver oxide NPs. The crystallinity of fabricated nanoparticles is confirmed by the XRD analysis (figure 1).

Scherrer’s equation was used for the calculation of average crystallite size of nanoparticles which can be determined from the peak width at varying 2θ values. \( D = \frac{k \lambda}{\beta \cos \theta} \) where D symbolizes the average diameter perpendicular to the reflecting surfaces, K is a constant whose value is (0.94), \( \lambda \) is wavelength of x-rays (1.5406 Å), \( \beta \) represents FWHM i.e., full width at half maximum in radians and \( \theta \) is the diffraction angle.

The reaction conditions and method utilized for synthesis of nanoparticles results in the production of various morphologies of Ag₂O such as cubic, hexapod and octapod. SEM analysis gave an insight of the catalyst’s surface topography. The results disclosing that shape and morphology of Ag₂O changes with increase in Sr concentration. The image of pure Ag₂O nanoparticles shows uniform allocation of grown nanoparticles throughout the catalyst surface. Nanoparticles with 1,3.5% Sr doping possess spherical consistency, with further increase in Sr concentration upto 7% and 9% particles seem to be more agglomerated. (figure 2).

The EDX results depict that the catalyst is enriched with silver, oxygen and strontium hence eliminating the possibility of presence of any other kind of elemental impurity. Peak of Silver Ag L\( \alpha \) appears at 2.984 KeV and Sr L\( \alpha \) emerges at 1.806 KeV while O K\( \alpha \) appears at 0.525 KeV (figure 3).

The subsistence of extensive variety in size and shape of nanoparticles is illustrated through TEM images. The diameter of Sr doped Ag₂O nanoparticles is comparatively small to pure Ag₂O, with the abundance of structurally spherical and circular disc shaped nanoparticles having defined boundaries. Although, with elevating concentration of strontium dopant a steady decline in the size of nanoparticles is evident (figure 4).

3.2. Photo catalytic degradation of dye molecules
Generally, the dependency of the two prime mechanisms on each other is responsible for controlling the photo catalytic activity that includes the formation of holes and electrons as a consequence of light and photo catalyst
interaction and the other being the influence of the surface of the catalyst. In accordance with the reported literature, the electrons and holes produced as a result of the light interaction would be held captive and then transferred to the catalytic surface where these get involve with the dye molecules through redox reactions, that enhances the photo degradation efficacy by restraining the recombination of electrons and holes. The definite surface area, size of particles and the band gap of the catalyst are the other factors which affect the photo catalytic

Figure 1. XRD pattern illustrating phase purity of synthesized Ag₂O and Sr/Ag₂O nanoparticles.

Figure 2. SEM images of (a) Ag₂O (b) 1% Sr/Ag₂O (c) 3% Sr/Ag₂O (d) 5% Sr/Ag₂O (e) 7% Sr/Ag₂O (f) 9% Sr/Ag₂O nanoparticles possessing spherical consistency.
Figure 3. EDX images of (a) Ag₂O (b) 1% Sr/Ag₂O (c) 3% Sr/Ag₂O (d) 5% Sr/Ag₂O (e) 7% Sr/Ag₂O (f) 9% Sr/Ag₂O showing presence of Ag, Sr and O.

Figure 4. TEM images of (a) Ag₂O (b) 1% Sr/Ag₂O (c) 3% Sr/Ag₂O (d) 5% Sr/Ag₂O (e) 7% Sr/Ag₂O (f) 9% Sr/Ag₂O nanoparticles.
activity. Taking these facts into consideration, nanoparticles of Ag₂O along with the varying concentrations of the Sr dopant were synthesized for scrutinizing the photo catalytic activities in opposition to the three diverse organic dyes. This work illustrates that the efficiency of photo catalytic activity depends upon the size of the nanoparticles, lesser the dimension more will be the active sites on the enlarged surface area hence greater will be the photo degradation efficiency of the catalysts. The average crystallite size of the nanoparticles was calculated using Debye–Scherrer’s equation.

\[ d = \frac{0.94 \lambda}{FWHM(2\theta) \cos \theta} \]  

The band gap energy of these particles is derived on account of the maximum absorption band of the doped and pristine nanoparticles using the subsequent equation.

\[ E_{bg}(eV) = 1240 / \lambda_{max} \]  

Here \( E_{bg} \) corresponds to the energy of the band gap in electron volts and \( \lambda_{max} \) is the maximum absorption at a particular wavelength that varies according to the respective nanoparticle under consideration. The average crystallite size along with the band gap energies of different synthesized nanoparticles with varying dopant concentrations are listed (table 2).

The photo degradation of the organic dyes was carried out by irradiating the 25 ml of dyes solution containing the small concentration of the catalyst i.e.10 mg in the reactor with the direct light from the Sun in July 2017 between 10 am and 3 am (GPS coordinates N = 33° 43' 7'', E = 73° 3' 35''). The extent of the dye degradation by the nanoparticles was examined with the transient irradiation time causing the successive decline in the distinct absorption peak. UV–vis absorption spectra were recorded on Shimadzu 1800 spectrophotometer ranging from 200 to 800 nm. The cationic dyes such as Methylene Blue (MB) and Rhodamine B (RhB) degraded relatively more rapidly than the anionic dye such as Methyl Orange (MO). It can be inferred from the degradation plots of doped and pristine silver oxide nanoparticles that the most active species responsible for the degradation are the negative charges mainly hydroxyl ions inherited on the surface of the catalyst. The electrostatic forces of attraction between the anionic catalytic surface and the cationic molecules of the dye assist in the transference of the electrons which is impossible when the dye is neutral in nature. The only case of neutral dyes in which transference of the electron is facilitated to small extent is when the molecules are larger in size and flexible and develop polarizability owing to their skeletal sprawling. The smaller size and the larger surface area of the catalyst result in the effective degradation of the dye as it offers greater number of the unsaturated coordination positions.

### 3.3. Mechanism of dye degradation

Considering the case of cationic dyes particularly MB and RhB the active mediators, negatively charged hydroxyl ions residing on the catalytic surface have various origination sources, the first being the translation of adsorbed molecular oxygen bounded to the surface into the oxygen radicals and the second in which water molecules are oxidized. So in this fashion, in the incidence of the Sunlight electron transfer is aided with oxygen radicals that are reactive in nature. The hydroxyl ion radical and the photo generated holes are considered to be the prime oxidative agents that take part in the photo catalytic reactions actively. The photo generated carriers, the electrons and holes are formed as a result of solar light interaction with the catalyst as this light possess the adequate amount of energy that cast out the electrons which then react with the oxygen molecules dissolved in the material to form oxygen radical O₂⁻ and holes then give rise to OH⁻ which then oxidize the dyes.

But in the case of the MO which is categorized as an anionic dye upon the irradiation of the solar light the photo generated electron in the conduction band is transported to the silver ions Ag⁺ present in the lattice owing to its high positive potential as it is considered to be an efficient sacrificial reagent that imprisons the electron for the progression of oxygen in coarse of water splitting. Initially, the concentration of Ag⁺ is reduced by the formation of metallic silver by trapping the photo generated electrons. These electrons are then migrated to the Ag sites which are then taken up by the oxygen via multi-electron transfer routes. The holes present in the

| Catalysts | \( \lambda_{max} \) (nm) | Average crystallite size (nm) | Band gap energy (eV) |
|-----------|-------------------------|----------------------------|----------------------|
| Ag\(_2\)O | 662                     | 48.37                      | 1.87                 |
| 1% Sr/Ag\(_2\)O | 425                     | 43.44                      | 2.91                 |
| 3% Sr/Ag\(_2\)O | 533                     | 36.92                      | 2.32                 |
| 5% Sr/Ag\(_2\)O | 612                     | 33.95                      | 2.02                 |
| 7% Sr/Ag\(_2\)O | 562                     | 38.20                      | 2.20                 |
| 9% Sr/Ag\(_2\)O | 454                     | 35.65                      | 2.73                 |
valence band are then involved in the oxidation of the organic molecular dyes \[12\]. For further evaluation of the self degradations of various dyes the blank samples were monitored keeping the conditions constant without the addition of the catalyst and it was found out that all the organic dyes possessed stability under solar light irradiation. Therefore, it can be concluded that the photo generation of the carriers is essential for the decolorization along with the dye adsorption as they facilitate the transportation of the electrons from the catalyst to the organic dyes \[30\] (figure 5).

The decolorization of dye was screened with the successive decline in the absorption peak, characteristic of every dye with the passage of time due to interaction of the solar light with the catalytic surface. Efficiency of the dye degradation was estimated by using the subsequent equation.

\[
(1 - \frac{A_0}{A_t}) \times 100
\]

\(A_0\) signifies the absorbance of dye initially and \(A_t\) is the instantaneous absorption at the time \(t\) \[14\].

Taking into consideration the cationic dye methylene blue, photodegradation activity was examined following the maximum absorption peak at 664 nm. There was a steady decline in the absorption peak with the passage of time when the dye together with the catalyst were exposed to the Sunlight. Almost 96.63% of the degradation occurred using 5% \(\text{Sr}/\text{Ag}_2\text{O}\) just in 60 min proving it to be the most effective among the other catalysts. Approximately 65% of the dye was degraded in 110 min using undoped silver oxide catalyst. The efficacy and the time taken for the decolorization of the dye completely by the various catalysts are enlisted (table 3).

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The absorption spectra of all the catalysts utilized for the methylene blue decolorization were recorded under similar conditions using UV–vis spectrophotometer (figure 6).

Table 3. Efficiency of catalysts for methylene blue degradation.

| Catalysts | Time (min) | % Degradation |
|-----------|-----------|---------------|
| Ag₂O      | 110       | 65.41         |
| 1% Sr/Ag₂O| 120       | 52.83         |
| 3% Sr/Ag₂O| 110       | 96.06         |
| 5% Sr/Ag₂O| 60        | 96.63         |
| 7% Sr/Ag₂O| 80        | 95.12         |
| 9% Sr/Ag₂O| 100       | 92.68         |

Comparative study on the efficacy of the catalysts on the degradation of methylene blue in a time span of 60 min was also carried out as the 5% \(\text{Sr}/\text{Ag}_2\text{O}\) was found to be the most efficient one which decolorized the dye completely in such short time. The decolorizing efficiency of the catalysts at this particular time is summed up in the table accordingly (table 4.)

In order to investigate the degradation efficacy of the fabricated catalysts on the anionic dye like methyl orange the most intense peak at 457 nm was chosen which went through a firm decrease in its absorption as the time passed. The maximum degradation that is almost 69% was achieved for 5% \(\text{Sr}/\text{Ag}_2\text{O}\) nanoparticles with the

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**Figure 5.** Schematic study of (a) cationic (b) anionic dye degradation.
irradiation of the solar light during the time length of 80 min. The efficiency of methyl orange degradation by using different catalysts is given as (table 5).

The absorption spectra of dye degradation with various catalysts under similar conditions were recorded. A blue shift was monitored in the peak that resulted due to the demethylation of the dye with the most possibility of replacement with the H$_3$O$^+$ (figure 7).

Comparative study on the efficacy of the catalysts on the degradation of methyl orange in a time span of 60 min was also carried out as the 5%Sr/Ag$_2$O was found to be the most efficient one which decolorized the dye effectively in such short time. The decolorizing efficiency of the catalysts at this particular time is summed up in the table accordingly (table 6).

Another cationic dye Rhodamine B (Rhb) was also used for the investigation of effectual catalytic dye degradation. The peak at 553 nm with the maximum absorption intensity was selected and a regular trend in the reduction of its peak intensity was observed. Almost 96% degradation was achieved in the time duration of 70 min. In this case, 9%Sr/Ag$_2$O was found to be the most efficient one. Different catalytic efficiencies at different time periods are given in the table (table 7).

Following the similar reaction conditions the absorption spectra of several catalysts were obtained (figure 8).

Relative efficacies of the catalysts in the time span of 70 min are shown (table 8).

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**Table 4.** Efficiency of catalysts for methylene blue degradation in a time span of 60 min.

| Catalysts   | % Degradation |
|-------------|---------------|
| Ag$_2$O     | 42.85         |
| 1% Sr/Ag$_2$O | 43.39        |
| 3% Sr/Ag$_2$O | 55.90        |
| 5% Sr/Ag$_2$O | 96.63        |
| 7% Sr/Ag$_2$O | 81.30        |
| 9% Sr/Ag$_2$O | 64.22        |

**Table 5.** Efficiency of catalysts for methyl orange degradation.

| Catalysts   | Time (min) | % Degradation |
|-------------|------------|---------------|
| Ag$_2$O     | 60         | 36.15         |
| 1% Sr/Ag$_2$O | 90         | 44.37         |
| 3% Sr/Ag$_2$O | 160        | 60            |
| 5% Sr/Ag$_2$O | 80         | 69.23         |
| 7% Sr/Ag$_2$O | 60         | 55.88         |
| 9% Sr/Ag$_2$O | 120        | 47.28         |
Figure 7. UV–vis spectra for Methyl Orange Degradation in the incidence of (a) Ag2O (b) 5% Sr/Ag2O.

Table 6. Efficiency of catalysts for Methyl Orange Degradation in a time span of 60 min.

| Catalysts  | % Degradation |
|------------|---------------|
| Ag2O       | 36.15         |
| 1% Sr/Ag2O | 34.32         |
| 3% Sr/Ag2O | 36.52         |
| 5% Sr/Ag2O | 64.61         |
| 7% Sr/Ag2O | 55.88         |
| 9% Sr/Ag2O | 16.15         |

Table 7. Efficiency of catalysts for rhodamine B degradation.

| Catalysts  | Time (min) | % Degradation |
|------------|------------|---------------|
| Ag2O       | 85         | 82.64         |
| 1% Sr/Ag2O | 120        | 96.59         |
| 3% Sr/Ag2O | 160        | 71.24         |
| 5% Sr/Ag2O | 70         | 94.89         |
| 7% Sr/Ag2O | 100        | 95.90         |
| 9% Sr/Ag2O | 70         | 96.89         |

Figure 8. UV–vis spectra of Rhodamine B Degradation by (a) Ag2O (b) 9% Sr/Ag2O.
3.4. Kinetics of photo catalytic degradation of dyes

The activity of catalysts against three dyes was examined by channeling a steady decline in the absorption peak that is peculiarity for every dye. The comparison between relative concentrations and irradiation time showed that the degradation was of pseudo first order in nature and the kinetics of dye degradation can be represented by the subsequent modified form of the Lambert Beer’s equation.

\[ A = \varepsilon CL \]  

Where \( \varepsilon \) is molar absorptivity coefficient that is specific to the nature of material, \( L \) is the path length and \( C \) is the concentration. The rearranged and modified form of the equation is:

\[ C = A/\varepsilon L \]  

\[ \ln \left( \frac{C_0}{C_t} \right) = kt \]  

\[ k = \frac{\ln \left( \frac{C_0}{C_t} \right)}{t} \]  

From this equation rate constant can be calculated where \( C_0 \) accounts for the initial and \( C_t \) represents the instantaneous concentration at time \( t \) [31].

The kinetics of methylene blue showed that the dye followed pseudo first order degradation reaction with the usage of the different catalysts. 5% Sr/Ag\(_2\)O took the least time to degrade the dye completely so, the rate constant for this dye is found to be the maximum. As the average crystallite size of 5% Sr doped nanoparticles was found to be the least hence offering greater surface area and the active sites, therefore accountable for the enhanced efficiency (figure 9).

The rate constants of methylene blue degradation by the utilization of varying catalysts are summarized in the given table. The rate constants show that all the catalysts degraded the cationic methylene blue dye effectively (table 9).

Relative rate constants considering catalysts at a time span of 60 min were also recorded which are given in the table. At this particular time Ag\(_2\)O has the lowest rate constant showing that the strontium doping has enhanced the photo degradation of the dye due to the decrease in size (table 10).

The extent of anionic dye degradation such as methyl orange was found less in comparison to the two other cationic dyes. Relative concentration alteration, at various time intervals, revealed the nature of degradation

| Catalysts     | % Degradation |
|---------------|---------------|
| Ag\(_2\)O     | 78.51         |
| 1% Sr/Ag\(_2\)O| 71.96         |
| 3% Sr/Ag\(_2\)O| 23.52         |
| 5% Sr/Ag\(_2\)O| 94.89         |
| 7% Sr/Ag\(_2\)O| 77.86         |
| 9% Sr/Ag\(_2\)O| 96.89         |

Table 8. Efficiency of catalysts for rhodamine B degradation in a time span of 70 min.

| Catalysts       | % Degradation |
|-----------------|---------------|
| Ag\(_2\)O       | 78.51         |
| 1% Sr/Ag\(_2\)O| 71.96         |
| 3% Sr/Ag\(_2\)O| 23.52         |
| 5% Sr/Ag\(_2\)O| 94.89         |
| 7% Sr/Ag\(_2\)O| 77.86         |
| 9% Sr/Ag\(_2\)O| 96.89         |

Figure 9. Photo Degradation of Methylene Blue following pseudo first order kinetics in the presence of (a) Ag\(_2\)O (b) 5%Sr/Ag\(_2\)O.
which came out to be of pseudo first order. 5% Sr/Ag$_2$O showed the maximum efficiency in decolorizing this dye due to its smaller dimensions comparative to others (figure 10).

Different rate constants of catalysts exhibiting contrasting efficiencies depending upon their size are given in the table (table 11).

Comparative efficiencies of dye degradation at particular time of 60 min are depicted in the following table. All the results obtained are in accordance to the ones that are previously mentioned (table 12).

Table 9. Rate constants of catalysts for methylene blue degradation.

| Catalysts   | Rate constant min$^{-1}$ | Rate constant (Blank) |
|-------------|---------------------------|------------------------|
| Ag$_2$O     | 9.5 × 10$^{-3}$          | 1.6 × 10$^{-3}$        |
| 1% Sr/Ag$_2$O | 6.2 × 10$^{-3}$          | 1.6 × 10$^{-3}$        |
| 3% Sr/Ag$_2$O | 2.8 × 10$^{-2}$          | 1.6 × 10$^{-3}$        |
| 5% Sr/Ag$_2$O | 5.6 × 10$^{-2}$          | 1.6 × 10$^{-3}$        |
| 7% Sr/Ag$_2$O | 3.7 × 10$^{-2}$          | 1.6 × 10$^{-3}$        |
| 9% Sr/Ag$_2$O | 2.5 × 10$^{-2}$          | 1.6 × 10$^{-3}$        |

Table 10. Rate constants of catalysts for methylene blue degradation in a time span of 60 min.

| Catalysts   | Rate constant min$^{-1}$ |
|-------------|--------------------------|
| Ag$_2$O     | 9.0 × 10$^{-3}$          |
| 1% Sr/Ag$_2$O | 9.3 × 10$^{-3}$          |
| 3% Sr/Ag$_2$O | 1.3 × 10$^{-2}$          |
| 5% Sr/Ag$_2$O | 5.6 × 10$^{-2}$          |
| 7% Sr/Ag$_2$O | 2.7 × 10$^{-2}$          |
| 9% Sr/Ag$_2$O | 1.6 × 10$^{-2}$          |

Table 11. Rate constants of catalysts for methyl orange degradation.

| Catalysts   | Rate constant min$^{-1}$ |
|-------------|--------------------------|
| Ag$_2$O     | 7.3 × 10$^{-3}$          |
| 1% Sr/Ag$_2$O | 6.2 × 10$^{-3}$          |
| 3% Sr/Ag$_2$O | 5.9 × 10$^{-3}$          |
| 5% Sr/Ag$_2$O | 1.7 × 10$^{-2}$          |
| 7% Sr/Ag$_2$O | 1.3 × 10$^{-2}$          |
| 9% Sr/Ag$_2$O | 5.3 × 10$^{-3}$          |

Figure 10. Pseudo first order kinetics of Methyl Orange Degradation when (a) Ag$_2$O (b) 5% Sr/Ag$_2$O was added.
The kinetics of rhodamine B showed that the dye followed pseudo first order degradation reaction by utilizing different catalysts of the same concentration under similar reaction conditions. 9% Sr/Ag₂O took the least time to degrade the dye completely so, the rate constant for this dye is found to be the maximum (figure 11).

The rate constants of rhodamine B degradation in the presence of varying catalysts are summarized in the given table. The rate constant show that all the catalyst degraded the cationic rhodamine B dye effectively (table 13).

Table 12. Rate constants of catalysts for methyl orange degradation in a time span of 60 min.

| Catalysts     | Rate constant min⁻¹ |
|---------------|---------------------|
| Ag₂O          | 7.3 × 10⁻³          |
| 1% Sr/Ag₂O    | 5.0 × 10⁻³          |
| 3% Sr/Ag₂O    | 7.5 × 10⁻³          |
| 5% Sr/Ag₂O    | 1.7 × 10⁻²          |
| 7% Sr/Ag₂O    | 1.3 × 10⁻²          |
| 9% Sr/Ag₂O    | 2.6 × 10⁻³          |

Table 13. Rate constants of catalysts for rhodamine B degradation.

| Catalysts     | Rate constant min⁻¹ | Rate constant (Blank) |
|---------------|---------------------|-----------------------|
| Ag₂O          | 2.0 × 10⁻²          | 3.4 × 10⁻⁴            |
| 1% Sr/Ag₂O    | 2.8 × 10⁻²          | 3.4 × 10⁻⁴            |
| 3% Sr/Ag₂O    | 7.7 × 10⁻³          | 3.4 × 10⁻⁴            |
| 5% Sr/Ag₂O    | 4.0 × 10⁻²          | 3.4 × 10⁻⁴            |
| 7% Sr/Ag₂O    | 3.1 × 10⁻²          | 3.4 × 10⁻⁴            |
| 9% Sr/Ag₂O    | 4.9 × 10⁻²          | 3.4 × 10⁻⁴            |

Table 14. Rate constants of catalysts for rhodamine B degradation in a time span of 70 min.

| Catalysts     | Rate constant min⁻¹ |
|---------------|---------------------|
| Ag₂O          | 2.1 × 10⁻²          |
| 1% Sr/Ag₂O    | 2.8 × 10⁻²          |
| 3% Sr/Ag₂O    | 3.7 × 10⁻³          |
| 5% Sr/Ag₂O    | 4.0 × 10⁻²          |
| 7% Sr/Ag₂O    | 2.1 × 10⁻²          |
| 9% Sr/Ag₂O    | 4.9 × 10⁻²          |

The kinetics of rhodamine B showed that the dye followed pseudo first order degradation reaction by utilizing different catalysts of the same concentration under similar reaction conditions. 9% Sr/Ag₂O took the least time to degrade the dye completely so, the rate constant for this dye is found to be the maximum (figure 11).
Comparative efficiencies of dye degradation at particular time of 70 min are depicted in the following table. All the results obtained are in accordance to the ones that are previously described (table 14).

4. Conclusion

Photo catalytic activity of Ag2O nanoparticles with different strontium dopant concentrations was effectively performed under irradiating sunlight (outdoor lightening) against three different dyes proving all the synthesized nanoparticles to be highly photo catalytically active after careful characterization by PXRD, TEM, SEM and EDX. The nanomaterials show improved and enhanced dye degradation efficiency in the presence of strontium dopant as they facilitate the configuration of photogenerated electron hole pairs. All the nanomaterials degrade cationic dyes more efficiently than the anionic one. In conclusion, amongst all other fabricated NPs 5% Sr/Ag2O proved to be the most efficient photo catalyst by degrading methylene blue and methyl orange to an extent of 96.63% and 69.23% with highest rate constant of $5.6 \times 10^{-2}$ min$^{-1}$ and $1.7 \times 10^{-2}$ min$^{-1}$ respectively, due to smaller dimensions and optimum band gap energy. 9% Sr/Ag2O degraded rhodamine B to an extent of 96.89% highest among the others with a rate constant of $4.9 \times 10^{-2}$ min$^{-1}$ showing it’s high and improved photo catalytic efficiency in comparison to pristine Ag2O nanoparticles.

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