

Degradation of Methylene Blue from Water Under Sunlight using SnO₂/Graphene Oxide Composite

P. Ranjith Reddy, Shireesha.V, V. Malapat, K. Venkateswara Rao, Y. Aparna

Abstract— Tin oxide (SnO₂) nanoparticles (NP) has been intensely investigated as photo catalyst for water purification and environment decontamination, while the photon generated electron and hole pair (EHP) recombination is one of factors limiting its efficiency. Tin oxide/Graphene oxide (SnO₂/GO) nanocomposite is very promising to overcome this limitation for photo catalytic applications. GO, with its unique electronic properties, large specific surface area and high transparency, contributes to facile charge separation and adsorptivity in this hybrid structure. The SnO₂/GO composite under sunlight photo catalytic degradation of methylene blue (MB) has been investigated in aqueous heterogeneous suspensions. It may be used either alone or in combination with H₂O₂ to enhance their performance and control of bio growth (slime). The hydrogen peroxide may also be used to speed up catalysts reactions for complete degradation. The SnO₂/GO composite showed an enhanced photo catalytic degradation activity for the organic dye methylene blue under sunlight compared to bare H₂O₂. Degradation of methylene blue under sunlight is fast with in 10min with the combination of SnO₂/GO and H₂O₂ as a photo catalyst. The study of the prepared SnO₂/GO composite under the sunlight photo catalytic activity of photo catalyst was investigated by the colorimeter by observing the optical density with reference of distilled water.

Keywords: SnO₂/GO Composite, methylene blue, Sunlight, Graphene Oxide, Photo catalyst.

I. INTRODUCTION

During the past several decades, fast and relatively uncontrolled population growth and also industrial, agricultural and technological developments have been adversely affecting the environment and human health. Especially wastewater effluents of industrial manufacturing companies contain toxic organic compounds. Additionally, the combustion of fossil fuels has caused global warming due to the increase of CO₂ concentration in the atmosphere. Moreover, with the rapid development of the printing and dye industry; the effluents of these industries have become one of the most important water pollution sources. The printing and dye industries' effluents are very complex, usually containing some remaining dyes, sizing agents, surfactants and

accessory ingredients among others. Besides, many dyes are very toxic and cause serious damage to human beings even at very low concentrations. Traditional wastewater treatments for printing and dyeing plants' effluents are mainly physical, chemical and biochemical methods [1-3]. Moreover, with the rapid development of the textile industry in recent years, more and more new types of dyes have been produced, such as Methylene blue. SnO₂ is able candidate to photo catalyze the complete oxidative mineralization of Methylene blue by O₂. Chemical contamination of water streams has become crucial issue of human life. To prevent this problem wastewater treatment plays an important role in reducing the toxic elements in wastewater. For this reason, heterogeneous photo catalysis can be applied to remove contaminants existing in the wastewater effluent catalysis under light irradiation is called photo catalysis. Heterogeneous photo catalysis includes kind of reactions such as organic synthesis, water splitting, photo-reduction, hydrogen transfer and metal deposition, disinfection, water treatment, removal of gaseous pollutants, etc. It has become an increasingly viable technology in environmental decontamination. Photo catalytic oxidation of organic compounds in the environment is derived by semiconductor materials such as TiO₂, ZnO, GaP, SiC CdS, and Fe₂O₃.SnO₂.SnO₂ is the most widely used photo catalyst, when compared with other photo catalysts due to its low cost, non-toxicity, high activity, large chemical stability, very low aqueous solubility and environmentally friendly characteristics. Tin-assisted photo catalytic oxidation is an alternative method for purification of air and water streams. Also, in water splitting, the driving force for electrons is provided by energy of the light. When SnO₂ is exposed to light, photo catalytic reaction is initiated. In fact, an electron which is in the filled valence band becomes excited and jumps to the empty conduction band upon the exposure to the light. Hence, the photon energy $h\nu$, which equals or exceeds the band gap of the semiconductor photo catalyst leaves a hole in the valence band; i.e. electrons (e⁻) and positive holes (h⁺) are produced [4-7], while the photon generated electron and hole pair (EHP) recombination is one of factors limiting its efficiency, SnO₂/GO nanocomposite is very promising to overcome the limitation for photo catalytic applications. GO, with its unique electronic properties, large surface area and high transparency, contributes to spacial charge separation and absorptivity in this hybrid structure.

II. EXPERIMENTAL

A. Materials & Methods

Tin (II) chloride dehydrate (SnCl₂.2H₂O), Sodium Hydroxide (NaOH), Graphite Fine Powder was used for synthesizing Graphene oxide (GO). Sulphuric acid (H₂SO₄, 98%), potassium permanganate KMnO₄ (99.9%),

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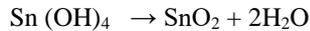
hydrogen peroxide (H₂O₂ 30%), polyvinyl pyrrolidone (PVP), ethylene glycol (98%) were used for Methylene blue organic dye.

B. Synthesis of Tin oxide (SnO₂)

The process of co-precipitation method involves the use of tin (II) chloride dehydrate (SnCl₂.2H₂O) 0.1M and sodium hydroxide (NaOH). The solution of tin chloride is prepared by dissolving granules of SnCl₂.2H₂O in de-ionized water. Now NaOH is gradually added to the prepared solution of tin chloride with continuous stirring. After some time white precipitate of tin hydroxide [Sn(OH)₄] appears in the form of reaction product is given below:



In this reaction, excess sodium hydroxide is added to convert all tin chloride into tin hydroxide. After this, the precipitate is washed several times with de-ionized water and ethanol, so as to remove excess sodium chloride and sodium ion. Now, the precipitate is filtered and dried in an oven at about 150°C for an hour. The product obtained is tin hydroxide which is calcinated at 600°C for four hours to get the tin oxide particles. The chemical reaction is as follows.



Tin dioxide obtained by this Co-precipitation method is in white color.

C. Preparation of Graphene Oxide (GO)

Graphene oxide was synthesized from graphite powder by modified Hummer’s method. Concentrated H₂SO₄ (50 ml) was added to mixture of graphite powder (1 g). The mixture was stirred under ice bath and then KMnO₄ (3 g) was added slowly about to an hour to the above mixture, reaction temperature was maintained below 5°C, while adding KMnO₄. The mixture was magnetically stirred for about 4 to 6hrs and added (100 ml) of distilled water slowly, during oxidation process the colour change was observed from dark purplish-green to dark brown and further stirrer for 30min after that, to stop the oxidation process distilled water of 100 ml is added. H₂O₂ (25 ml) was added to the solution, and then the colour of mixture was changed to bright yellow colour indicating a high oxidation level of graphite. The solution was filtered and washed several times with water until PH shows the neutral value, results in thickening of the Graphene oxide solution. The washing process was carried out by a simple decantation of the supernatant with centrifugation technique at 1000 rpm for 30 minutes which results the formation of final product Graphene oxide (GO).

D. Preparation of Tin Dioxide & Graphene oxide composite (SnO₂/GO)

SnO₂/GO composite material was prepared using ultra-sonication by dissolving SnO₂ in 0.2 ml of Hcl in 20ml of distilled water and sonicated for 1hr, similarly 0.1gm of GO in 20ml distilled water sonicated for 1hr in two separate beakers. After adding both solutions into one beaker and again sonicated for 4hrs final product was washed with distilled water and filtered end product was dried at 90°C for 12hrs the outcome is Tin dioxide and Graphene oxide composite.

III. RESULT AND DISCUSSION

The XRD pattern of GO sheet (Figure 1(a)) shows the diffraction peak (0 0 2) at diffraction angle 2θ~ 9° indicates the formation of Graphene oxide. XRD patterns of SnO₂ nanoparticles (Figure1 (b)) shows the diffraction peaks of

(110), (101), (200), (211), (220), (002), (311), (112), (301), (202) and (321) at 2θ of 26.8, 33.9, 37.9, 51.8, 54.8, 57.7, 61.8, 64.8, 66.0, 71.2and 78.6o, respectively. Which matches well with JCPDScard # 41-1445 and structure of the crystal is found to be Cassiterite type tetragonal of SnO₂ crystal. The average crystallite size of the tin dioxide is estimated from Debye-Scherrer and its value is found to be ~12nm. The XRD pattern of SnO₂/GO nanocomposite (Figure1(c)) shows only SnO₂ peaks without Graphene oxide peak in XRD pattern of SnO₂/GO nano composite have been observed, but the intensity of the peaks are reduced when compared with XRD pattern of individual GO and SnO₂.

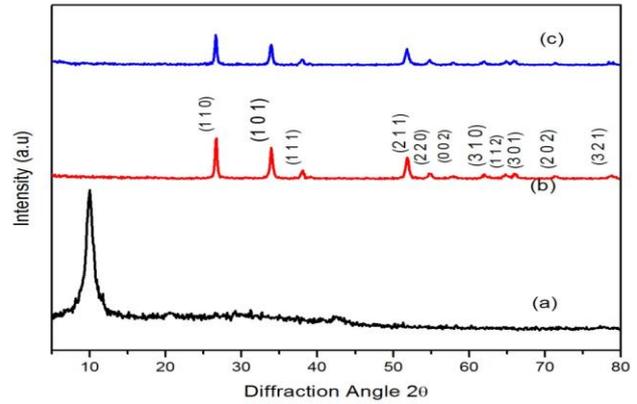


Fig 1: (a) XRD pattern of GO (b) XRD pattern of SnO₂ nanoparticles (c) XRD pattern of SnO₂ /GO nanocomposite

UV-visible spectroscopy is an important tool for probing optical properties of materials. It provides useful information of band gap energy of the semiconductors. The room temperature absorption spectrum of SnO₂ in the wave length range 200 -400 nm is shown in Figure 2(a). The highest absorption is achieved at wavelength 218 nm with absorption edge at 275 nm. Graphene oxide (GO) has an absorption maxima at 232nm for a well oxidized material is shown in Figure 2(b). The SnO₂ /GO composite that is formed has maximum absorption at 213nm is shown in Figure 2 (c). The energy band gap of the SnO₂, GO and SnO₂/GO estimated by Tauc’s relation. The estimated energy band gap of these materials have values 3.4 eV, 4.2eV and 3.2eV indicated from hv vs (αhv)² plots as shown in Figure 3(a), (b), (c). The conductivity of SnO₂ is enhanced by adding Graphene oxide in the SnO₂, in turn shows the decrease in energy band gap of SnO₂/GO nanocomposite.

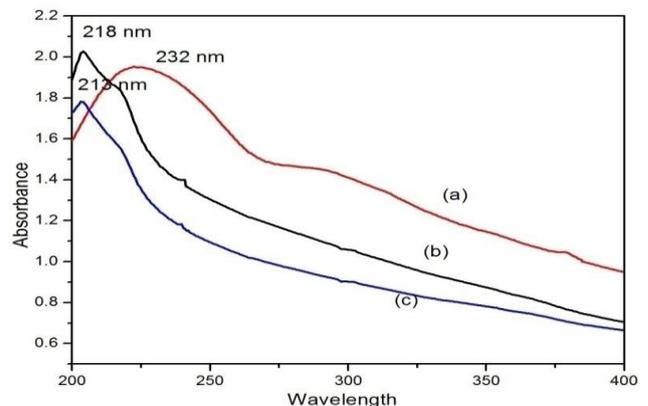


Fig 2: Room temperature absorption spectra of (a) GO (b) SnO₂(c) SnO₂-GO nanocomposite



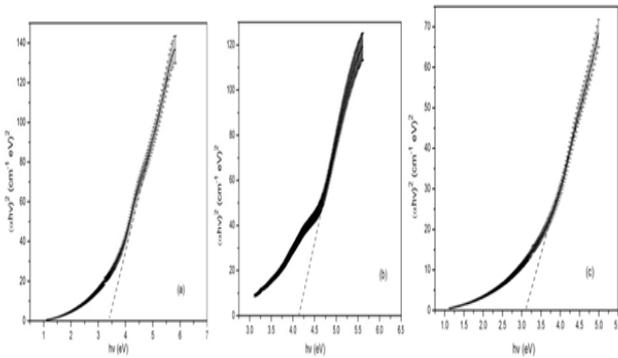


Fig 3: $h\nu$ vs $(\alpha h\nu)^2$ plots of (a) SnO₂ (b) GO (c) SnO₂-GO nanocomposite.

In Figure 4(a) shows the TG curve of SnO₂ with weight loss of 29% from room temperature to 1100°C and further continued till 600°C show weight loss of 10% for complete decomposition. DTA measures the temperature and heat flow during transition (change) in the material as a function of time and temperature in controlled atmosphere, there is a peak at 30-500°C known as exothermic peak. The chemical process related to the exothermic peak is due to cross-linking reaction. Figure 4(b) depicts the TGA plot of Graphene oxide. Obviously there are two weight loss stages; the first stage is from room temperature to 480°C with 20% wt loss, which can be attributed to the dehydration process of water molecules and the interlayer of Graphene oxide. The second stage is from 480°C to 600°C with 40% wt loss, is due to the burning decomposition of oxygen-containing groups attached to Graphene oxide layers and above 600°C GO is stable. TGA curve of SnO₂/GO nanocomposite shown in Figure 4 (c) with three stages of weight loss, the first stage is from room temperature to 200°C has 20% wt loss might be due to dehydration process of water molecules in the interlayer of Graphene oxide. The second stage varies from 200°C to 420°C with 75% wt loss, could be due to the burning decomposition of oxygen-containing groups attached and in third stage for SnO₂ to Graphene oxide layers is in the temperature range from 420°C to 570°C is 10% due to burning decomposition of carbon skeleton.

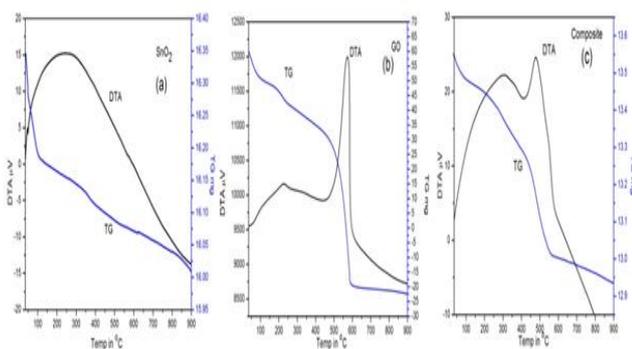


Fig 4: TG-DTA plots of (a) SnO₂, (b) GO and (c) SnO₂/GO nanocomposite.

TEM images of SnO₂/GO composite structure with different magnifications are shown in Figure (5), which presented a uniform spread of SnO₂ nanoparticles over Graphene oxide sheets. It is noticed that the SnO₂ nanoparticles that cover GO surface in a reasonable uniform fashion.

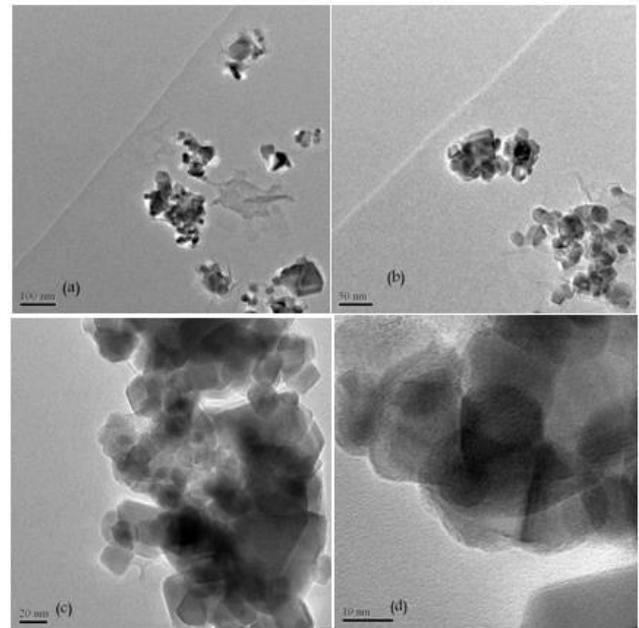


Fig 5: TEM image of SnO₂/GO composite (a) at 100 nm (b) 50 nm (c) 20nm (d) 10 nm

EDAX studies are generally carried out to test the elemental composition and purity of the sample by giving us the details of all the elements present in the given sample. The EDAX spectra and elemental composition of Tin dioxide, Graphene oxide, and SnO₂/GO composite is shown in Figure (6).

Figure 7(a) shows the room temperature Raman spectra of Graphene oxide exhibited two major peaks at 1172 cm⁻¹ (the D-band) and 1640 cm⁻¹ (G-band) are observed. On other Figure 7(b) shows Raman spectra with two major peaks at 1363 cm⁻¹ (the D-band) and 1592 cm⁻¹ (G-band) are observed in Graphene oxide. The G-band signature shows that the GO exhibit a graphite structure and the D-band signatures indicate defects on the edges or surfaces of the GO. In the Raman spectrum G band is broadened and shifted to 1592 cm⁻¹ whereas the D band at 1363 cm⁻¹ becomes the prominent feature in the spectrum testifying to indicating the creation of sp³ domains due to the extensive oxidation in SnO₂/GO nanocomposite.

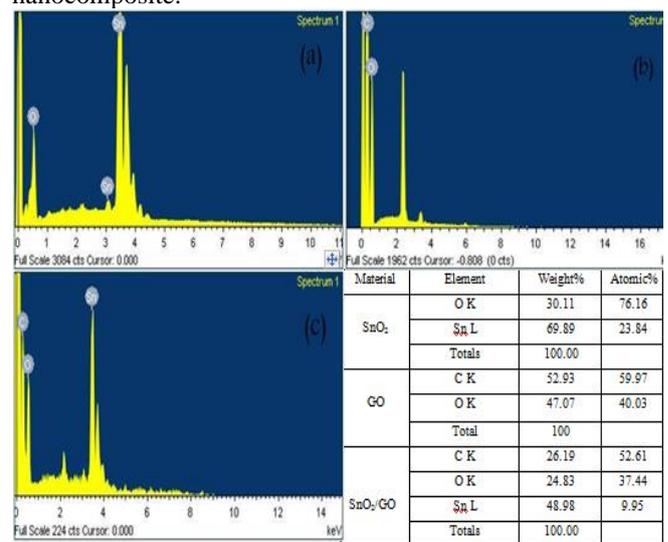


Fig 6: EDAX spectra of (a) SnO₂ (b) GO and (c) SnO₂/GO Composite with elemental composition.



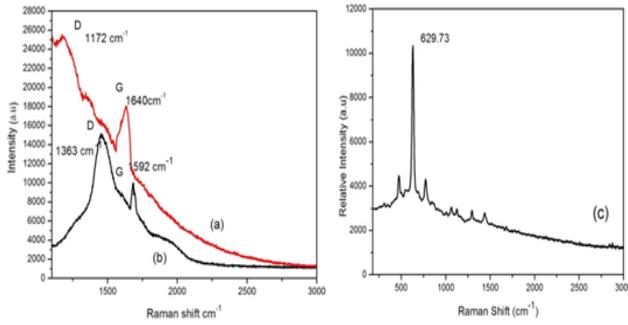


Fig 7: Raman spectra of (a) Graphene oxide (b) SnO₂/GO nanocomposite (c) SnO₂

Raman spectrum of SnO₂ powder of very small grain size show in figure 7(c). The mode A_{1g} peak at;629cm⁻¹, Modes B_{2g} peak at;756 cm⁻¹, and E_g peak at 490 cm⁻¹, are also included in the intensity and position of these bands also depend on the nanoparticles size. These bands shift toward higher wave numbers, are less intense, and broaden as the average nanoparticles size decreases. For particles larger than 7 nm these bands are not observed by simple visual inspection.

A. Photocatalytic activity of SnO₂ /GO nanocomposite

Methylene blue dye (5 x 10⁻³ M) was diluted in 50ml distilled water. The photo catalytic degradation of methylene blue dye was studied after addition of 1g of SnO₂/Graphene oxide composite in 3ml H₂O₂ to the 50 ml dye solution using sonication. Irradiations was carried out in glass vessel under the sunlight to examine mineralization of the MB solution removal was studied using colorimeter reference with distilled water. It was used to measure Optical density of the dye solution at regular time intervals. Controlled experiments were also carried out to confirm that the degradation of Methylene blue by colorimeter. The experiments were carried out simultaneously for all the solutions in bright sunlight. Experiments were repeated for catalyst, with H₂O₂, only H₂O₂, and without H₂O₂ and without catalyst simultaneously in order to confirm the consistency of results. The optical density of the Methylene blue solutions was determined at 650 nm wavelength.

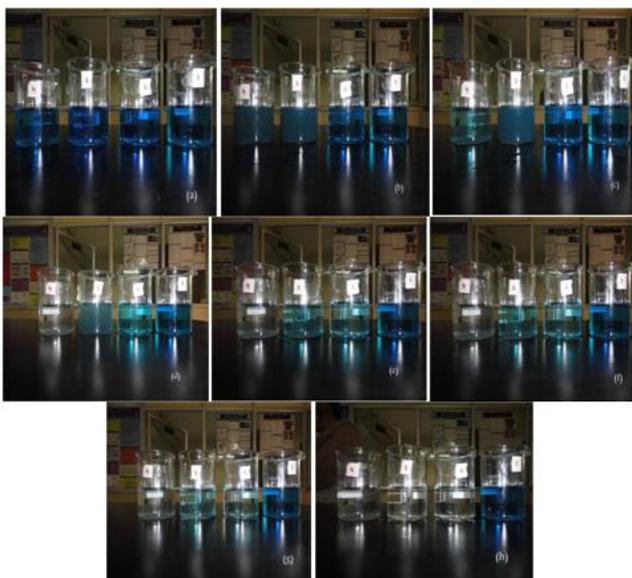


Fig 8: Diluted methylene blue water (a) before adding catalyst (b) after adding catalyst (c) after 5min under sunlight (d) after 10min under sunlight (e) after 15min under sunlight (f) after 20min under sunlight (g) after 25min under sunlight (h) after 35min under sunlight

Beakers with label 1(Right side): Diluted methylene blue water, label 2: SnO₂/GO nanocomposite as a catalyst, label 3:H₂O₂as a catalyst, label 4: SnO₂/GO nanocomposite and H₂O₂ as catalyst

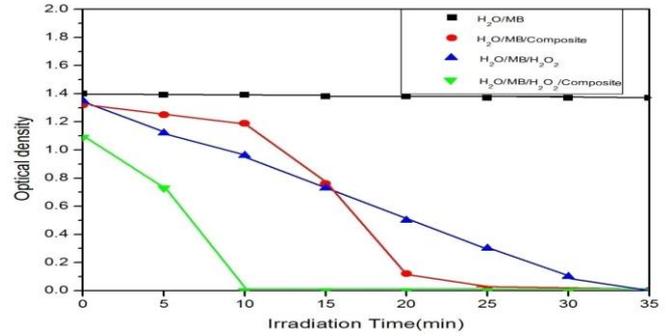


Fig 9: Photo catalytic degradation profiles of the H₂O/MB, H₂O/MB/nanocomposite,H₂O/MB/H₂O₂, and H₂O/MB/nanocomposite/H₂O₂

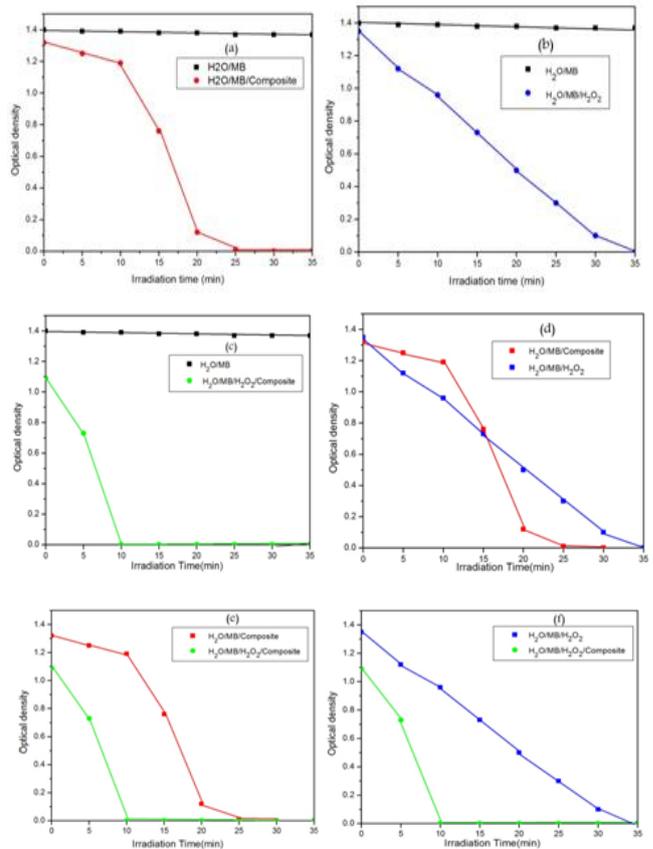


Fig 10: Photo catalytic degradation profiles of the (a) H₂O/MB and H₂O/MB/nanocomposite (b) H₂O/MB and H₂O/MB/H₂O₂ (c) H₂O/MB and H₂O/MB/H₂O₂/nanocomposite (d)H₂O/MB/nanocomposite and H₂O/MB/H₂O₂ (e) H₂O/MB/nanocomposite and H₂O/MB/H₂O₂/nanocomposite (f) H₂O/MB/H₂O₂ andH₂O/MB/H₂O₂/nanocomposite

It is clear from the Figure (9) and Figure (10) that, the catalyst SnO₂/ GO nanocomposite as expected showed highest photo catalytic activity compared to that of H₂O₂.However both the H₂O₂ as well as SnO₂/ GO showed lower photo catalytic activity than the SnO₂/ GO nanocomposite with H₂O₂. Similar observations were made for time intervals at 5min ,10min, 15min, 20min,25min,30min,35min the higher rate degradation of methylene blue when irradiation under sunlight.Higher the oxidation rate when SnO₂/ GO nanocomposite with H₂O₂added to the MB solution.



SnO₂/GO nanocomposite is a catalyst for MB degradation and also H₂O₂ itself is a catalyst for MB degradation it takes 35min for total degradation and SnO₂/GO nanocomposite as catalysts individually take 25min time to complete degradation of MB, but combination of both H₂O₂ and SnO₂/GO composite will take 10min to complete degradation of MB under sunlight.

IV. CONCLUSION

Degradation of methylene blue under sunlight with SnO₂/GO nanocomposite as a catalyst takes 25min for total degradation. It may be used either alone or in combination with H₂O₂ to enhance their performance and control of biogrow (slime). The hydrogen peroxide to activate the SnO₂/GO nanocomposite and May also is used to speed up catalysts reactions for complete degradation. Degradation of methylene blue under sunlight is fast with in 10min with the combination of SnO₂/GO and H₂O₂ as a photo catalyst. By increasing the catalyst quantity degradation time less under sunlight. SnO₂/GO nano composite shows efficient photodegradation for high concentrated MB dye under UV sunlight. We can take only H₂O₂ as catalyst under sunlight but it takes 35min to degrade total methylene blue from water.

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