Photocatalytic Degradation of Phenol-red Over Sb_2S_3 – Graphene Oxide composite

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ABSTRACT

The photocatalytic degradation of phenol red has been studied in the presence of Sb_2S_3-graphene oxide (GO) as a composite photocatalyst. The composite was characterized using X-ray diffraction (XRD), Field emission scanning electron microscopy analysis (FESEM), Energy dispersive X-ray (EDX) and Fourier transform infrared (FT-IR) analyses. The XRD patterns indicated the formation of cubic inverse spinel structure and average particle size was found to be 14.26 nm. The photocatalytic activity of Sb_2S_3-GO was evaluated in photodegradation of phenol red dye under visible light. The effect of various parameters such as pH, the concentration of dye, amount of semiconductor and light intensity on the rate of degradation was also studied. Oxygen molecule radical anion was considered responsible for oxidative photodegradation of phenol red. A tentative mechanism has been proposed for this reaction.

GRAPHICAL ABSTRACT
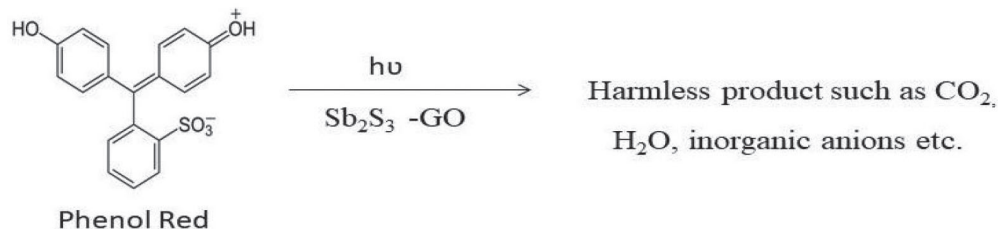
Key words : *Photocatalytic degradation, Phenol Red, Sb2S3-GO, Uv light.*

Introduction

Water pollution is a major environmental problem all are the globe and it is all due to water from less treated sewage, agricultural runoff and domestic effluents, etc. Major water pollutants are effluents from dying, printing and textile industries. Azo dyes were photocatalytically degraded in TiO2 sus-pension. It was observed that diazo dye is relatively less degradable as compared to monoazo dyes (Tanaka *et al.* 2000). The photocatalytic degradation of methyl orange (MO) and rhodamine 6G (R6G) was reported in of different semiconduters such as ZnS, TiO_2 CdS, ZnO and SnO2. The effect of process parameters such as amount of catalyst, concentration of dye and pH on photocatalytic degradation of

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MO and R6G was evaluated (Kansal *et al.,* 2007). The photocatalytic degradation of phenol red by using thiocyanate complexes of iron, copper and cobalt in presence of hydrogen peroxide was investigated (Lodha *et al.* 2008).

The $UV/TiO_2/O_2/H_2O_2$ system was used for degrading phenol red in aqueous solutions in presence of nanosized TiO_2. It was reported that photodegradation rates of phenol red followed the pseudo-first-order kinetics according to Langmuir–Hinshelwood model (Wahab and Hussain, 2016). The degradation of phenol red was also studied and it was reported that photoactivity of niobate increases in the presence of amorphous carbon by a factor 4.7, which indicated a synergy effect between these two (Lanfredi *et al.,* 2016). An enchanced photocatalytic degradation of phenol red was observed in presence of different La-substituted bismuth ferrites; Bi1-xLaxFeO$_3$ (x = 0.00, 0.05, 0.10 and 0.15) nanostructures. A rod like morphology was there with length between 12–30 nm and diameter about 1.5–3 nm. It was observed that photocatalytic activity increases upto 90.1% on increasing tha ratio (x) from 0.0 to 0.10 and then it decreases to 82.6%, where x was further increased to 0.15 (Dhanalakshmi *et al.* 2016). A composite of Bi2S3 nanorods supported by MoS_2 nanosheets was prepared via a simple hydrothermal method without using any surfactant. The highest removal percentage of phenol red (83.4% after 60 min) was observed with 80 wt% SB_2S_3 -20 wt% MoS_2 (BM-20) and its photocatalytic performance was retained even after 5 cycles (Vattikuti and Byon, 2016).

The ZnO@Cr core/shell nanoparticles were synthesized via modified Pechini method. Photocatalytic activity of as-prepared ZnO@Cr nanoparticles was studied using phenol red. It was observed that as-prepared nanoparticles exhibited 1.24 times higher degradation in acid medium than in basic medium (Silveira *et al*. 2016). The N-TiO_2/WO_3 nano-composite material was prepared and it was observed that photocatalytic degradation of adsorbed phenol red was only about 6.32% while assynthesized photocatalyst could degrade 93.87% under visible irradiation as compared to UV irradiations (75.74%) (Hagos, 2014). The Co (II) tetraaminophthalocyanine (Co (II)TAPc) was prepared and it was reported that photocatalytic activity of ZnO-Co (II) TAPc for phenol red degradation was better than that of ZnO. It is stable and can be reused several times without much loss in activity

(Patilpik and Meshram, 2021). An urchin-like Sb_2S_3 nanostructure was synthesized without using any surfactant via a wet chemical method. It was claimed that as-prepared Sb_2S_3 exhibited higher catalytic activity towards the degradation of methylene blue under visible light and it could achieve 99.32% degradation in 130 min (Zhou *et al.* 2018).

Graphene-Sb_2S_3 (G-Sb_2S_3) composites were synthesized via a facile solvothermal method. The highest photodegradation activity for degradation of rhodamine B was observed with the photocatalyst where GO concentration was 0.1 mg mL^{-1} (Tao *et al.* 2013). Graphene oxide was used as a support for manganese oxide to prepare a nanocomposite catalyst. It was then used for degradation of reactive black 5 (RB5). It was revealed that GO-MnO_2 nanocomposite exhibited higher catalytic activity for the degradation of RB5 even at ambient conditions, which was much higher than as compared to MnO_2 (Saroyan *et al.* 2019). The silicotungstic acid (SiW) decorated reduced graphene oxide (rGO) formed nanocomposite (rGOSiW). It was used as a heterogeneous nanocatalyst for degrading methylene blue (MB) and rhodamine B (RhB). It was reported that degradation could be achieved in 34 min for MB and 81 min for RhB using rGO-SiW in presence of NaBH4 (Ucar *et al.* 2017).

Synthesized graphene oxide grafted titanium dioxide nanoparticles (TiO_2-GO nanocomposite) was prepared via a solvothermal method. The photocatalytic activity of as-prepared TiO_2-GO nanocomposite was evaluated on the degradation of methylene blue and methyl orange in presence of UV light. It was observed that a maximum degradation efficiency of 100 and 84% could be achieved in case of MB and MO within 25 and 240 min, respectively on exposure to UV light in presence of TiO_2-GO (Atchudan *et al.* 2017). A new method was developed to prepare Sb_2S_3/TiO_2 heterostructure photocatalyst. The photocatalytic activity of as-prepared catalyst was investigated for photocatalytic degradation of azo dyes in presence of visible light. It was reported that highest efficiency was observed, when the sample was calcined at 673 K keeping 60 wt % Sb_2S_3 (Sun *et al.* 2012).

Experimental

Preparation of Sb_2S_3 – graphene oxide (GO) composite

Antimony trisulfide is a colored compound and ab-

sorb in visible range. It is a semiconductor in nature. Graphene oxide has also a conducting behaviour. A composite of Sb_2S_3 and graphene oxide was prepared by mechanochemical method. The composite was characterised with the techniques like Field emission scanning electron microscopy, X-ray diffraction and energy dispersive X-ray spectrum.

A stock solution of phenol red ($1.0 \times 10{-}3$ M) (Fig. 1) was prepared in double distilled water. Working solution of $1.0 \times 10{-}5$ M solution of phenol red was prepared by diluting the stock solution and 0.10 g of Sb_2S_3-GO was added to it. The pH of reaction mixture was kept 8.0 and then this solution was exposed to a 200 W tungsten lamp. The absorbance of phenol red solution was determined with the help of a spectrophotometer (Systronics Model 106) at λmax = 450 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL Model SM 201). Absorbance of the solution at various time intervals was measured with the help of spectrophotometer. It was observed that the absorbance of the solution decreases with increasing time of exposure, which indicates that the concentration of phenol red dye decreases with increasing time.
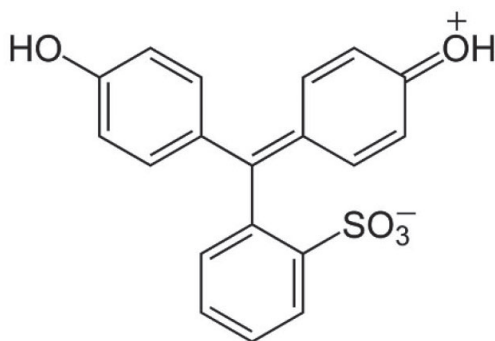

Fig. 1. Structure of phenol red

Characterization of Composite

EDX Spectrum

The element composition was confirmed through an energy–dispersive X-ray spectroscopy system connected to Tecnai T-20 instrument. EDX spectrum of Sb_2S_3- GO composite is given in Fig. 2.
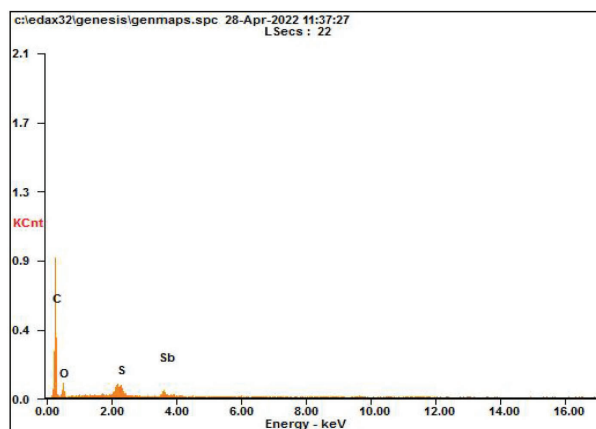

Fig. 2. EDX spectrum

FESEM Images

The field emission scanning electron microscopy analysis (FESEM) was performed using a Quanta 200-3D FEI instrument. FESEM images of different resolutions are given in Fig. 3.
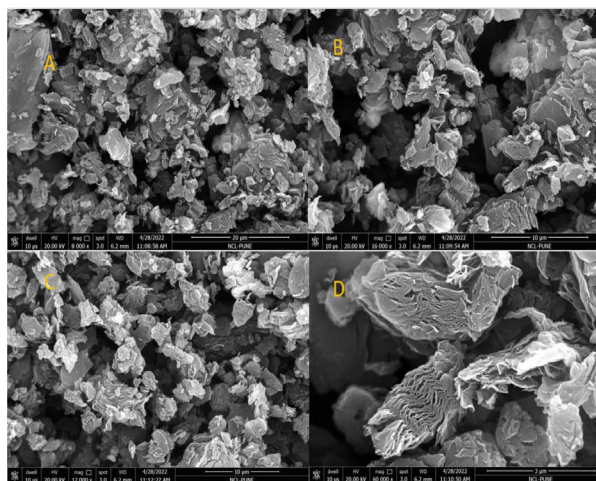

Fig. 3. FESEM images of Sb_2S_3-GO (a) 20 m (b) 10 m (c) 10 m (d) 3 m

XRD

A Bruker d8 ADVANCE X-ray diffractometer was used for XRD analysis. It gives sharp peaks indicating crystalline nature of component. The crystal size of the composite was determined by Debye-Scherrer equation and average crystalline size was found to be 14.26 nm.
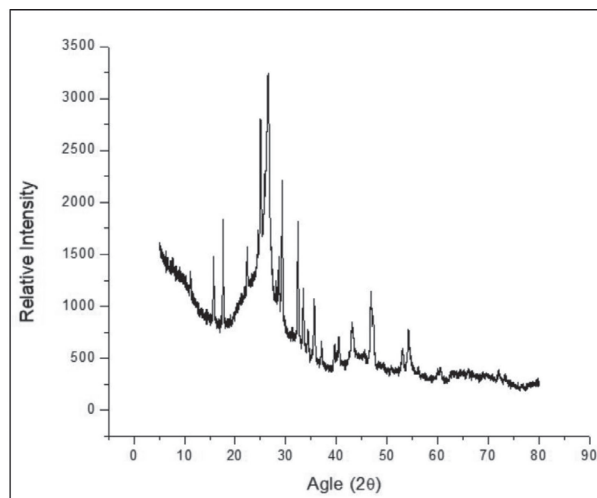
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Fig. 4. XRD spectrum

Typical Run

A typical run is given in Table 1 and graphically presented in Fig. 5.

pH = 8.0   [Phenol red] = 4.0×10^{-5} M
Amount of composite = 0.10 g
Light intensity = 60 mW cm^{-2}

Table 1. A typical run

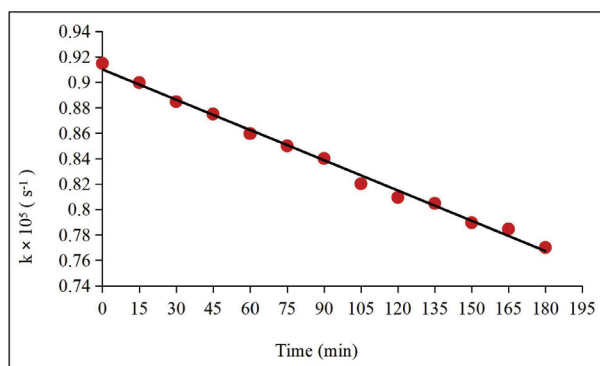| Time (min)	Absorbance	1+ log A
0.0	0.822	0.9149
15.0	0.794	0.8998
30.0	0.764	0.8848
45.0	0.750	0.8751
60.0	0.724	0.8597
75.0	0.708	0.8500
90.0	0.692	0.8401
105.0	0.661	0.8202
120.0	0.645	0.8095
135.0	0.638	0.8048
150.0	0.616	0.7896
165.0	0.609	0.7846
180.0	0.589	0.7701

Fig. 5. Typical run

Effect of pH

The effect of variation of pH was studied in the range 5.5-8.5 and the results are reported in Fig. 6.
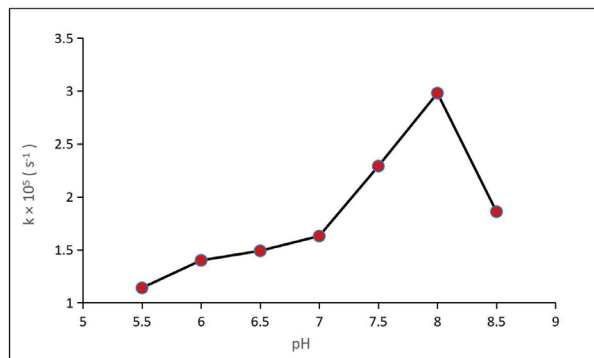

Fig. 6. Effect of pH

It was observed that the rate increases with an increase in pH up to 8.5, but the rate of degradation decreases with a further increase in pH. An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\bullet-}$. An increase in the rate of photocatalytic degradation of dye with the increase in pH may be due to the availability of more $O_2^{\bullet-}$ radicals. A decrease in the rate of photocatalytic degradation of the dye may be due to the fact that phenol red is present in its anionic form, which will experience a force of repulsion with the negatively charged surface of the semiconductor due to absorption of more OH> ions on the surface of the photocatalyst.

Effect of phenol red concentration

The effect of dye concentration on the photocatalytic degradation of phenol red was observed in the range of 2.0×10^{-5} to 4.0×10^{-5} M and the results are summarized in Fig. 7.
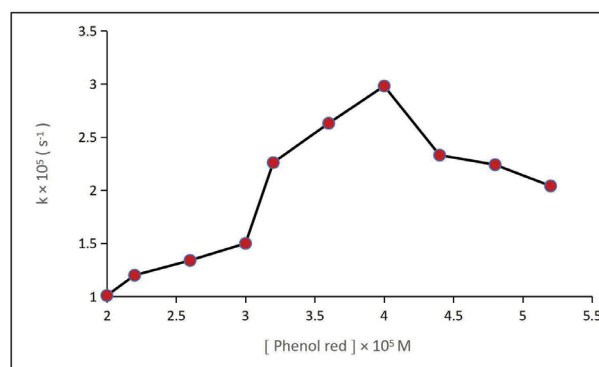

Fig. 7. Effect of dye concentration

It was observed that as the concentration of the dye was increased, the dye degradation increases but after 4.0×10^{-5} M (optimum condition), the rate of dye degradation decreases.

Effect of amount of composite

The effect of variation of the amount of composite on the rate of dye degradation has been studied in the range from 0.02 to 0.11 g and the results are presented in Fig. 8.
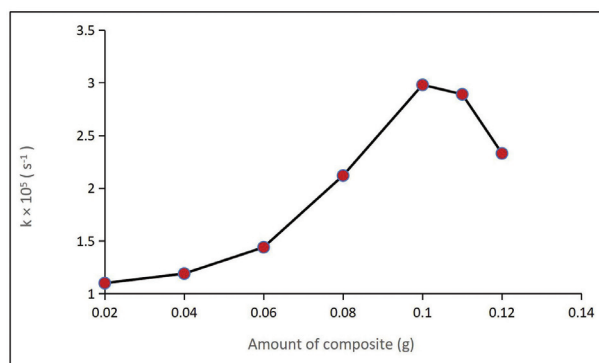

Fig. 8. Effect of amount of composite

It was observed that as the amount of composite was increased, the rate of photocatalytic activity increases. The rate of degradation was optimum at 0.10 g of the composite. After 0.10 g, the rate constant decreases slightly. Because after this value, an increase in the amount of composite will only increase the thickness of the photocatalyst layer and not the exposed surface area.

Effect of light intensity

The distance between the light source and exposed surface area of photocatalyst was varied to determine the effect of light intensity on the photocatalytic degradation. The light intensity was varied
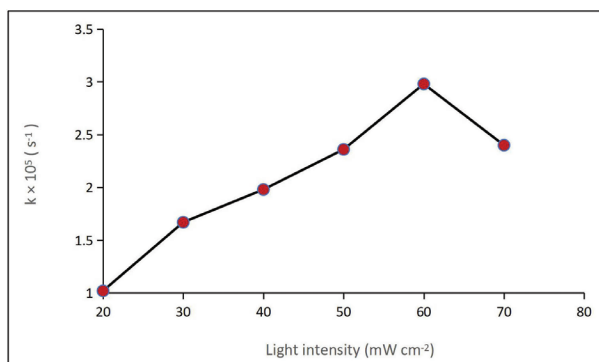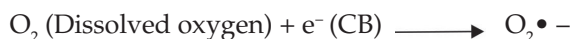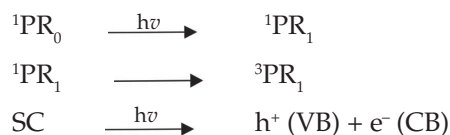

Fig. 9. Effect of light intensity

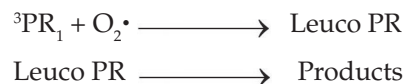from 20.0 to 70.0 mW cm^{-2}. The results are reported in Fig. 9.

The results show that rate of degradation was enhanced as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit time per unit area of composite. The maximum rate for degradation of phenol red was observed at 60.0 mW cm^{-2} for degradation of phenol red. On further increasing the intensity above 60.0 mWcm^{-2}, there was a slight decrease in the rate of photodegradation.

Mechanism

On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of phenol red (PR) in the presence of antimony trisulfide - graphene oxide composite. Phenol red absorbs radiations of suitable wavelength and exited to its singlet excited state and then it goes to its triplet excited state through intersystem crossing (ISC). The semiconductor also absorbs light to excite an electron from its valence band (VB) to conduction band (CB), which will be abstracted by dissolved oxygen to generate $O_2{}^{\bullet-}$ (in basic media). These radicals can degrade dye to its leuco form and ultimately to products.

$$^1PR_0 \xrightarrow{\ h\nu\ } {}^1PR_1$$

$$^1PR_1 \xrightarrow{\hspace{1cm}} {}^3PR_1$$

$$SC \xrightarrow{\ h\nu\ } h^+\,(VB) + e^-\,(CB)$$

$$O_2\,(\text{Dissolved oxygen}) + e^-\,(CB) \xrightarrow{\hspace{1cm}} O_2{}^{\bullet}-$$

In basic medium

$$^3PR_1 + O_2{}^{\bullet} \xrightarrow{\hspace{1cm}} \text{Leuco PR}$$

$$\text{Leuco PR} \xrightarrow{\hspace{1cm}} \text{Products}$$

It was found that the reaction rates were unaffected in the presence of •OH radical scavenger, 2-propanol, which means that there was no involvement of •OH radicals in this reaction as an active oxidizing species.

Conclusion

Sb$_2$S$_3$-GO was synthesized mechanochemically by mixing antimony trisulfide and graphene and used for photocatalytic degradation of phenol red. The particle size of synthesized catalyst was determined as 14.26 nm. The effect of different rate affecting

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parameters like pH, dye concentration, composite amount and light intensity were studied. These observations revealed that phenol red could be degraded successfully by using Sb_2S_3- GO under visible light irradiation. This photocatalytic water treatment is likely to improve the quality of polluted water.

Acknowledgements

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