

# **Bi<sub>2</sub>S<sub>3</sub> Induced Photocatalytic Degradation of Azo Dye Reactive Red 152 Under UV light**

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## **ABSTRACT**

Researchers are interested in photocatalytic decolorization of dyes using advance oxidation process(AOP) because it provides an appealing way for decolorization of dyes and breaks them down into simple mineral form. The photocatalytic efficiency of Bi<sub>2</sub>S<sub>3</sub> was investigated in terms of Reactive Red 152 dye degradation. A thorough analysis of the photodegradation of Reactive Red 152 (RR152) utilizing Bi<sub>2</sub>S<sub>3</sub> has been conducted. The results show that dye degradation is affected by dye concentration (RR 152), photocatalyst concentration (Bi<sub>2</sub>S<sub>3</sub>), and pH of the experimental solutions. The ideal parameters for dye photobleaching had been determined. The kinetics of dye degradation in dilute aqueous solutions follow first order kinetics. The results showed that the dye was effectively treated with the Bi<sub>2</sub>S<sub>3</sub> reagent.

**Keywords:** - Reactive red 152, photocatalysis, Bi<sub>2</sub>S<sub>3</sub>.

## **INTRODUCTION**

Water pollution has been a severe environmental concern in recent decades, affecting both human health and the ecosystem. Photocatalysts could be a way for many regions to solve their long-standing freshwater problems (Pawar *et al*, 2018). The waste water from the dyes industry, especially the material initiatives, is a major source of water pollution. Most of the time, 65–75% of the common textile dyes businesses use aromatic-azo-dyes (Alinsafi *et al*, 2007). Due to their toxicity, unappealing color, high chemical oxygen demand content, and non-biodegradability, dye effluents from textile manufacturers are becoming a severe environmental issue (Yazdanbakhsh *et al*, 2010). Dye-polluted wastewater is treated using conventional wastewater treatment techniques such flocculation, biodegradable, physical adsorption, and chemical oxidation, however these techniques have several drawbacks (Iang *et al*, 2014). These procedures turn the organic components in the water into a secondary contaminant, such as sludge, which requires additional treatment.

The cost of cleanup is also increased by the additional approaches needed to remediate secondary contaminants (Huang *et al*, 2014; Gao *et al* 2015). Therefore, the environment as a whole greatly benefits from the development of efficient advanced treatment techniques for dye-containing waste water. To destroy organic and inorganic pollutants, photocatalytic methods primarily use semiconductor catalysts such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZnO when exposed to light (UV radiation or solar light) (Kuriakose *et al*, 2015; Mohamed *et al*, 2017). Various oxide and sulphide semiconductors have been employed as photocatalysts for waste water treatment, specifically dye degradation. There are two main ways that previous research in the field has been done. First, the method used wide bandgap photocatalysts (like TiO<sub>2</sub>, ZrO<sub>2</sub> SnO<sub>2</sub>, and ZnO) and changed their surface, shape, and band structure. (Zeng *et al* 2015; Chidambaram *et al* 2016; Liu *et al* 2016). Second, it aims to use new photocatalysts with a narrow bandgap (e.g.-Bi<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub>, Ce<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>) (Cao *et al* 2012; Hong *et al* 2016; Liyanage *et al* 2014).

In addition to metal oxides, a few non-oxide Metal sulphides and other substances also exhibit high ability to photodegrade effectively (Wu *et al*, 2010). Due to their high absorption coefficient, a wide range of metal chalcogenides have been investigated for the hydrogen evolution process and the degradation of organic contaminants (Suet *al*, 2018; Baiet *al*, 2016; Xuelianet *al*, 2014). Due to its appropriate narrow band gap (1.3–1.7 eV), non-toxicity, and high absorption coefficient, Bi<sub>2</sub>S<sub>3</sub> has received the most attention among the various metal sulphides (Zhu *et al*, 2017). When compared to other heavy metals, bismuth sulphide is recognized to cause less harm. Bismuth is roughly twice as plentiful as gold.

## MATERIALS AND METHODS

The photocatalyst  $\text{Bi}_2\text{S}_3$  and the widely available azo dye Reactive Red 152 were utilized in the current investigations. Structural Formula of RB152 is  $\text{C}_{52}\text{H}_{30}\text{Cl}_2\text{N}_{14}\text{Na}_6\text{O}_{20}\text{S}_6$  and molecular weight is 1752.11 gm. In order to create the stock solution, 0.1752 g of the dye Reactive Red was dissolved in 100 mL of double-distilled water, resulting in a dye solution with a  $1.0 \times 10^{-3}$  M concentration. From the stock solution, aqueous solutions of the necessary concentrations were created. The addition of previously standardized sulphuric acid and sodium hydroxide solutions changed the solution's pH to the required level. Analytical grade was used for all laboratory reagents.

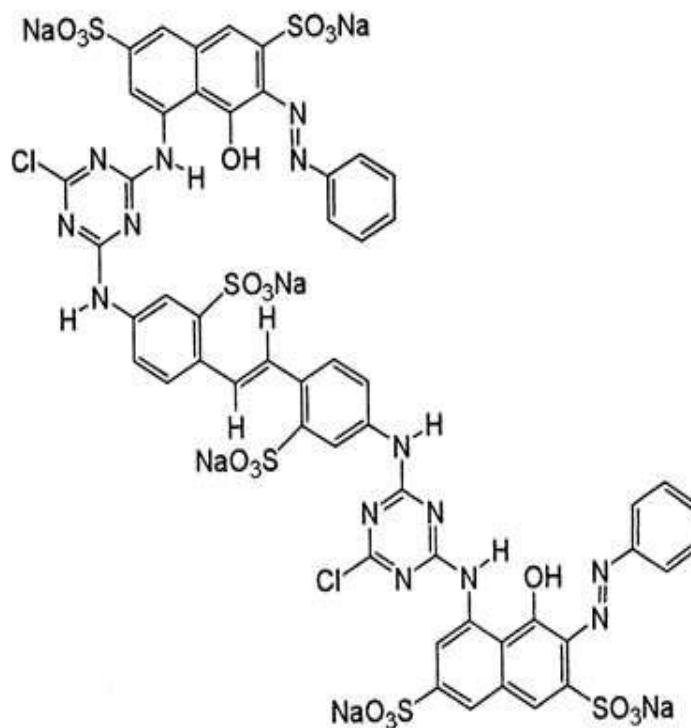


Fig: 1 Structure of Reactive Red 152

### Procedure and Analysis

To carry out the photochemical reaction, 100 mL of acceptable concentration dye solution ( $3 \times 10^{-5}$  M) was collected and an adequate amount of solid  $\text{Bi}_2\text{S}_3$  catalyst (0.25 g) was added. The initial absorbance of dye solutions was measured using a UV-VIS Spectrophotometer. The studies were carried out in a photochemical reactor using UV tubes of 254 nm to give energy to stimulate  $\text{Bi}_2\text{S}_3$ . A spectrophotometer was used to determine the maximum absorbance of the dye sample, which was 550 nm for reactive red 152. The rate of responsiveness of color decline with time was continually measured. The pace at which the color faded over time was constantly measured. The presence of inorganic ions such as sulphate and nitrate was measured using a conventional technique after full mineralization (Mehta *et al*, 2011; Sharma *et al*, 2011).

## RESULTS AND DISCUSSION

Table: 1 shows the result of photocatalytic degradation of Reactive Red 152.

Time	Abs	1 + log(Abs)
0	0.553	0.742
10	0.479	0.680
20	0.420	0.624
30	0.367	0.565

40	0.319	0.504
50	0.277	0.442
60	0.240	0.382
70	0.211	0.324
80	0.183	0.263
90	0.160	0.204

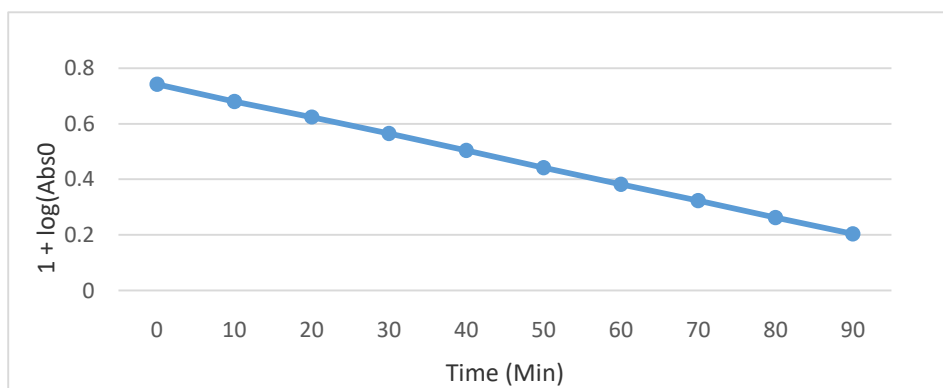


Figure 2 depicts the visual result of RR152's photodegradation

$$k = 2.32 \times 10^{-4} \text{ sec}^{-1}$$

#### Effect of amount of photocatalyst:

The quantity of semiconductor powder may also influence the dye degradation process. Keeping all other variables constant, photocatalyst concentrations ranging from 0.10 to 0.50 g/100 mL were used. Observations indicate that the rate of dye decolorization rises with increasing catalyst concentration up to 0.25 g, after which the rate of reaction stays nearly constant. This may be because an increase in the quantity of catalyst first increases the number of  $\text{Bi}_2\text{S}_3$  active sites on the surface, which in turn increases the number of  $\cdot\text{OH}$  and  $\text{O}_2\cdot$  radicals. Consequently, the rate of deterioration increases. Above a certain level (saturation point), the amount of substrate molecules is insufficient to occupy the active sites of  $\text{Bi}_2\text{S}_3$ , and a rise in solution turbidity lowers the solution's light transmission. Therefore, additional addition of catalyst has no effect on the degradation rate, which remains constant.

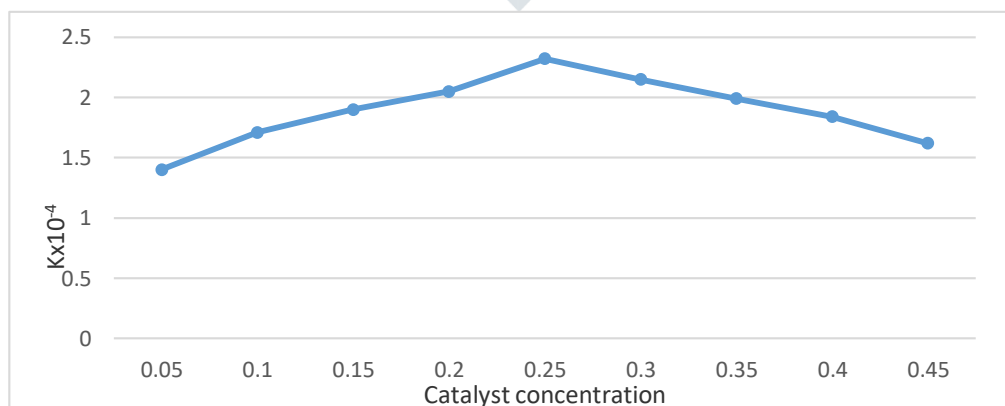


Fig 3:a graph illustrating the effect of catalyst amount variation on the photodegradation of RR152 by  $\text{Bi}_2\text{S}_3$ .

### Variation in dye concentration has the following effects: -

At constant concentrations of  $\text{Bi}_2\text{S}_3 = 0.25\text{g}$ ,  $\text{pH} = 8$ , the influence of substrate concentration on the degradation of Reactive Red 152 was investigated at various concentrations ranging from  $1.0 \times 10^{-5}\text{ M}$  to  $5.0 \times 10^{-5}\text{ M}$ . The efficiency was best at  $3.0 \times 10^{-5}$  concentration, and it degrades when substrate concentration rises from  $3.0 \times 10^{-5}\text{ M}$  to  $5.0 \times 10^{-5}\text{ M}$ . This could be as a result of the fact that as the initial dye concentration increases, more dye molecules are adsorbed onto the surface of  $\text{Bi}_2\text{S}_3$ , while the irradiation time and catalyst dose remain constant. The catalyst's activity is then inhibited by a rise in the number of substrate ions accommodated in the interlayer gap, which lowers the quantity of reactive  $\cdot\text{OH}$  and  $\text{O}_2\cdot$  free radicals attacking the dye molecules and the effectiveness of photodegradation.

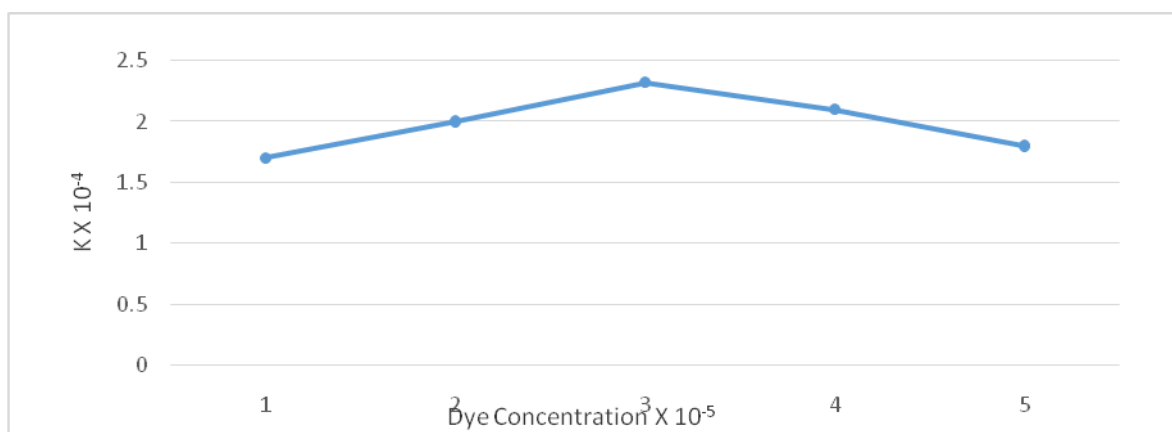


Fig 4: a plot demonstrating the effect of dye concentration variation on the photodegradation of RR 152 by  $\text{Bi}_2\text{S}_3$

### Variations in pH have the following effects:-

The surface properties of a  $\text{Bi}_2\text{S}_3$  catalyst are very much affected by the pH of the reaction medium. Under a visible light source, the effect of pH on the photocatalytic degradation of Reactive Red 152 with  $\text{Bi}_2\text{S}_3$  was studied in the pH range of 5.0 to 10.0. Up to pH 8, it was seen that as pH goes up, the rate of photocatalytic breakdown of RR 152 goes up. This can be explained by the fact that more  $\text{OH}^-$  ions are available when the pH of a solution goes up. By getting together with the positive holes in the semiconductor, these  $\text{OH}^-$  ions will make more  $\cdot\text{OH}$  radicals. These hydroxyl radicals are what cause dye to break down. Due to the coulombic repulsion between the negatively charged surface of the photocatalyst and the hydroxide anions, the rate of photobleaching of Reactive Red 152 slows down above pH 8. This fact could stop hydroxyl radicals from being made. This slows down the rate at which dye breaks down when exposed to light.

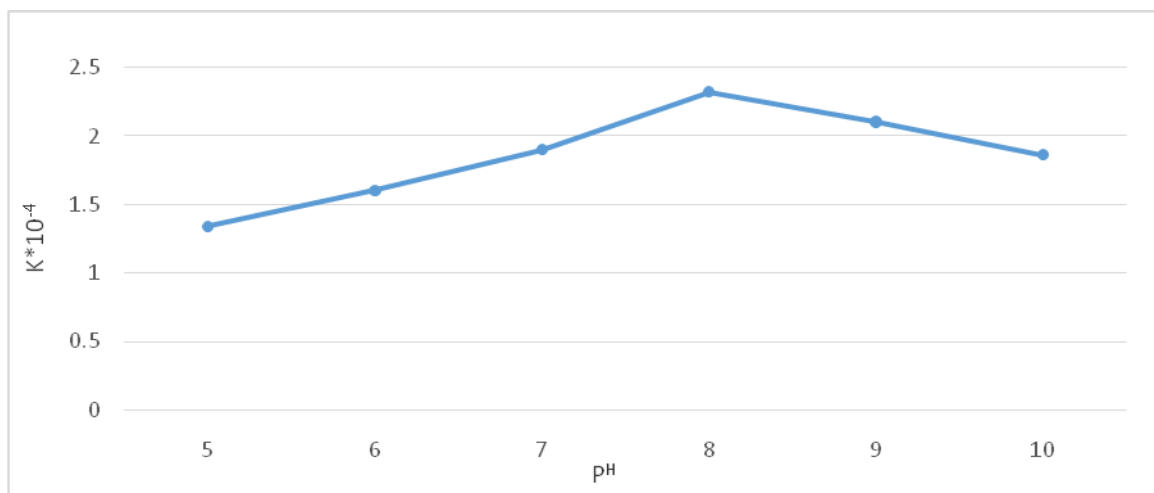


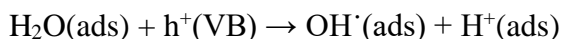
Fig 5: impact of pH variation on the rate of RR 152 degradation

**MECHANISM:-**

1. **Photoexcitation.** When light hits a semiconductor photocatalyst, like  $\text{Bi}_2\text{S}_3$ , it moves a photoelectron from the filled valence band to the empty conduction band. This starts a photocatalytic reaction. The energy of the absorbed photon ( $h\nu$ ) is either the same as or more than the band gap of the semiconductor photocatalyst.

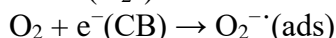


2. **Ionization of water.** After that, the photogenerated holes in the valence band react with water to form the OH radical.

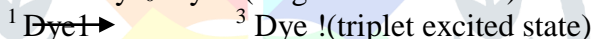
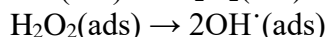
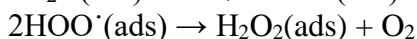
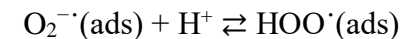


The HO radical that forms on the exposed semiconductor surface is a very potent oxidizer. It non-selectively targets organic molecules that are adsorbed or very near the catalyst surface, causing them to mineralize to varying degrees depending on their structure and stability level.

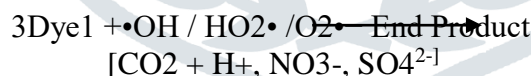
3. **Oxygen ionosorption.** While the photogenerated hole ( $h\nu_{\text{VB}}^+$ ) reacts with surface bound water or  $\text{OH}^-$  to produce the hydroxyl radical, electron in the conduction ( $e_{\text{CB}}^-$ ) is taken up by the oxygen in order to generate anionic superoxide radical ( $\text{O}_2^-$ ).



4. **Protonation of superoxide.** The resulting superoxide ( $\text{O}_2^-$ ) undergoes protonation to make hydroperoxyl radical ( $\text{HO}_2^{\cdot}$ ), followed by  $\text{H}_2\text{O}_2$ , which further dissociates into highly reactive hydroxyl radicals ( $\text{OH}^{\cdot}$ ).



The highly reactive hydroxyl radical ( $\text{OH}^{\cdot}$ ) may oxidise the excited dye to product. The presence of the  $\text{OH}^{\cdot}$  radical as an active oxidising species was confirmed by utilising its scavenger, 2-propanol, where the rate of degradation was greatly reduced.<sup>14</sup>  $\text{OH}^{\cdot}$  radicals first target the dye molecule's azo linkage, abstracting a hydrogen atom or adding themselves to a double bond. After continued irradiation, the dye was completely mineralized and converted into end products. The end products are simple molecules or ions that are less toxic to the environment.



The end products were detected and their presence in the reaction mixture were ascertained either by chemical test or by ion selective electrode method

**CONCLUSION**

In an aqueous solution,  $\text{Bi}_2\text{S}_3$  works well as a photocatalyst to break down the textile dye Reactive Red 152. Degradation is found to depend on many aspects of a reaction, such as pH, dye concentration, and amount of catalyst. At pH 8, 0.25 g  $\text{Bi}_2\text{S}_3$ /100 ml dye solution, and  $3 \times 10^{-5}$  M dye concentration, degradation works best. So, this simple technology of photochemical degradation of colored effluent could help improve the quality of waste water from the textile industry and could also be used in other industries. This process has shown that it is better than other common ways of treating waste water. It makes sure that dangerous contaminants are completely destroyed and that pollutants don't move from one phase to another. Overall, the results show that this photocatalyst should be used to treat textile effluent wastewater.

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