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HETEROGENEOUS PHOTOCATALYTIC DEGRADATION OF TEXTILE DYES: MAKING WATER CLEAN BY TUNGSTEN CONTANING MATERIALS

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***Abstract*:** The heterogeneous photocatalytic water cleaning process has gained attention due to its efficiency in degrading and mineralizing the recalcitrant organic compounds. This process is based on the light-enhanced generation of highly reactive hydroxyl radicals, which oxidizes the organic matter and convert it into water, CO_2, inorganic compounds etc. The present work consists of photocatalytic degradation of dyes which are released by textile industries in water, using tungsten containing photocatalysts (WO_3, $BaWO_4$, $Ba_3Y_2WO_9$). It is observed that the degradation of the dyes (Azure B and P-Rosaniline hydrochloride) depends on several parameters such as pH, dye concentration, photocatalyst, concentration, intensity of light and reaction temperature. Kinetic studies reveal that the photocatalytic process follows pseudo-first order kinetics.

Index terms: Heterogeneous, Photocatalyst, Degradation, Hydroxyl radical etc.

I. INTRODUCTION

The reuse and recycling of wastewater effluent is becoming a necessity for water utilities in rural as well as in urban areas to augment our limited fresh water supply, which is currently under pressure due to rapid population growth (Mitchell et al.2002). Enhanced concerns over public health and associated environmental hazards due to the presence of toxic organic compounds in wastewater have been reported. Dyes are well known for their bio-recalcitrant and acute toxicity and are being continuously introduced into the aquatic environment through various anthropogenic activities. Up to 20 % of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Chen et al.2001; Gracia et al.2006, 2008). The presence of toxic organic compounds in wastewater effluent is still a major hindrance in water recycling (Mahmoodi et al.2007; Tayade et al. 2007; Jun et al.2018; Abhilash et al. 2019; Guo et al.2019). Synthetic dyes are produced and consumed at a large scale and can cause considerable environmental pollution and serious health-risk due to their stability and toxicity. A wide range of methods has been developed for the removal of synthetic dyes from wastewater to decrease their impact on the environment. Because of incomplete removal during primary and secondary treatment processes, they are ubiquitous in secondary wastewater effluents at low concentration.

Heterogeneous photocatalytic oxidation process employing catalyst and sunlight has demonstrated promising results for the degradation of persistent organic pollutants producing more biologically degradable and less toxic substances (Guettay et al.2005; Hincapie et al.2006, Maldonando et al.2007; Malato et al.2002; Daneshwar et al.2007; Kansal et al.2007; Kaur et al. 2016; Wang et al. 2016; Dnyaneshwar et al.2017; Li et al.2019; Birben et al.2017). This process is largely dependent on the in-situ generation of hydroxyl radicals under ambient conditions which are capable of converting a wide spectrum of toxic organic compounds including the non-biodegradable one into relatively innocuous end products such as CO_2, H_2O etc.(Zhang et al.2006; Li et al.2013; Kuriakose et al.2014; Roushani et al. 2015; Pu et al.2017; Eshaghi et al.2018). In the process, destruction of recalcitrant organics is governed by combined action of sun light as energy source and photocatalyst as an energetic radiation source and an oxidizing agent. Heterogenous photocatalytic process includes following reaction:

$$\text{Photocatalyst} \xrightarrow{h\nu} e^- + h^+ \qquad (1)$$

In this reaction, h^+(hole) and e^-(electron) generated at photocatalyst surface are powerful oxidizing and reducing agents, respectively. The generated hole is responsible for bringing up oxidation whereas the generated electrons bring around reduction of these pollutants, mineralizing them. Present work consists of mineralization of such synthetic dyes by tungsten containing photocatalysts and a comparison of degradation is done for binary, ternary and quaternary catalysts.

II. RESEARCH METHODOLOGY

A comparative study of degradation of dyes (Azure B and P-Rosaniline hydrochloride)by solar light and tungsten based photocatalysts (Tungsten oxide WO_3, Barium tungsten oxide $BaWO_4$, Barium yttrium tungsten oxide $Ba_3Y_2WO_9$) is carried out. Stock solutions of dyes (P-Rosaniline hydrochloride 0.0809g/250 ml=$1x10^{-3}$M and AzureB 0.3058g/250ml=$1x10^{-3}$M) were prepared indoubly distilled water and diluted as required. Dye solutions were taken in a beaker and pH was adjusted by the addition of prestandardized HCl and NaOH solutions. The pH of the solution was measured by a digital pH meter (Henna imported pen type). Photocatalyst was added to these solutions and were exposed to light. The light intensity was measured by solarimeter (CEL 201). Decrease in Optical density of each of the solution was recorded by spectrophotometer (systronics106) and a water filter was used to avoid the heat reaction.

III. RESULT AND DISSCUSSION

Solution of the dye was taken in a beaker; pH of the solution was adjusted and to it the photocatalyst was added. This solution was then exposed to light and a water filter was used to cut off thermal side reaction. The optical density (O.D.) of the solution was recorded at different time intervals and graph was plotted between time and (1+logO.D.). The data are summarized as typical run in figure-1 for P-Rosaniline hydrochloride and figure-2 for Azure-B. These were found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant was determined by

$$K=2.303 \times \text{slope}$$

Use of scavenger suggested the participation of $OH^{\cdot}$ free radical in the reaction which is found to be strong enough to break different bonds of dyes. Controlled experiments proved the reaction neither to be photodegradation nor to be catalytic degradation rather it was a photocatalytic degradation process.

3.1 Effect of pH

pH is the major factor affecting the degradation of dye. It was varied in range 5.3 to 8.9, for both dyes and for all the three photocatalysts, with keeping all other factors constant. The maximum rate of degradation for P-Rosaniline hydrochloride is observed at 8.6, 8.6, 7.3 (Table-1, Fig.3) and for Azure B is observed at 7.8, 7.3, 7.3(Table-1, Fig.7) with the three semiconductors (WO_3, $BaWO_4$, $Ba_3Y_2WO_9$) respectively. On augment of pH value concentration of OH^- ions rises which may support increase in number of $OH^{\cdot}$ free radicals. Beyond a particular pH for both the dyes, if pH is increased further, the rate decreases due to repulsion between excessive OH^- ions on photocatalyst surface and electron rich dye surface.

3.2 Effect of dyes concentration

The rate of dye degradation was studied for both the dyes with all the three photocatalysts. All other factors were kept constant. It was observed that the rate of degradation increases up to a certain concentration of dyes for P-Rosaniline hydrochloride (Table-1, Fig.4) and for Azure B(Table-1, Fig.8). It is because of availability of more surface area of dyes for $OH^{\cdot}$ free radical to abstract an electron, and so rate of degradation increases. After a certain value, the increase in concentration of dye imparts a darker color to the solution which does not allow larger number of photons to reach the surface of photocatalyst. As a result, a smaller number of $OH^{\cdot}$ free radicals are produce reducing the rate of photo degradation.

3.3 Effect of weight of photocatalysts

The weight of photocatalyst is found to affect the rate of degradation. The weight of all the three photocatalysts was varied with keeping all other factors constant and the data are given for P-Rosaniline hydrochloride (Table-1 and Fig.5) and Azure B (Table-1 and Fig.9). It was observed that photocatalytic degradation rate increases up to certain limit with all the three photocatalysts because of increase in exposed surface area of photocatalyst to generate $OH^{\cdot}$ free radicals increases and so the rate of reaction increases rate. Further increases in the weight of photocatalysts after a particular value (WO_3 0.12g, $BaWO_4$ 0.18g, $Ba_3Y_2WO_9$ 0.12g) production of greater number of OH free radicals cause crowding and thus they are forced to recombine resulting in decrease in the rate of degradation.

3.4 Effect of intensity of light

Intensity of light is a major factor affecting the degradation of dyes. It was varied with keeping all other factors. The three photocatalysts (WO_3, $BaWO_4$, $Ba_3Y_2WO_9$) shows maximum rate of degradation at 37mW/cm^2 light intensity for P-Rosaniline hydrochloride(Table-1, Fig.6) and Azure B(Table-1, Fig.10). It is due to fact that with increase in intensity of light, the number of photons striking per unit area of the photo catalyst increases which generates a greater number of hole-electron pairs. This increases the number of $OH^{\cdot}$ free radicals as the hole abstracts an electron from OH^- ions, causing breakdown of weaker bond of dyes. Higher intensities were not studied as increase in intensity may cause thermal reaction instead of photocatalytic one.

IV. CONCLUSION

Maximum degradation conditions were extracted for both dyes, by all the three photocatalysts and maximum rate was determined by various calculations. Rate of degradation of Azure-B with WO_3 was 9.2×10^{-5} (s^{-1}) at pH 7.8, dye concentration 5×10^{-6} M, photocatalyst weight 0.12 g and light intensity 37mW/cm^2. Similarly, with $BaWO_4$, the rate of degradation is found 4.9×10^{-5} (s^{-1}) at pH 7.3, dye concentration 4×10^{-6} M, weight of photocatalyst 0.18g and light intensity 37mW/cm^2 for Azure-B. In case of Barium yttrium tungsten oxide ($Ba_3Y_2WO_9$) the rate of degradation of dye Azure-B was 8.44×10^{-4} (s^{-1}) at pH 7.3, dye concentration 5×10^{-6} M, weight of photocatalyst 0.12 g and light intensity 37mW/cm^2. The rate of degradation for P-Rosaniline hydrochloride dye with WO_3 was 4.46×10^{-4}(s^{-1}) at pH 8.6, dye concentration 1×10^{-5}M, photocatalyst weight 0.12g and light intensity 37mW/cm^2. Similarly, with $BaWO_4$, the rate of degradation is found 7.19×10^{-4}(s^{-1}) at pH 8.6, dye concentration 1×10^{-5}M, weight of photocatalyst 0.16g and light intensity 37mW/cm^2. And in case of Barium yttrium tungsten oxide ($Ba_3Y_2WO_9$) the rate of degradation of dye P-Rosaniline hydrochloride was 2.0×10^{-3}(s^{-1}) at pH 7.3, dye concentration 1×10^{-5}M, weight of photocatalyst 0.14 g and light intensity 37mW/cm^2. A comparative study for degradation of both the dyes by all the three photocatalysts shows that degradation rate as well as degradation conditions are excellent with quaternary photocatalyst $Ba_3Y_2WO_9$ and better results are obtained with Azure B. It is concluded here by that an eco-friendly and environmental protecting process is proposed which compares the photocatalytic activity of all three photocatalysts. The processes utilize solar energy and may be used to make the planet clean and pollution free.

V. ACKNOWLEDGEMENT

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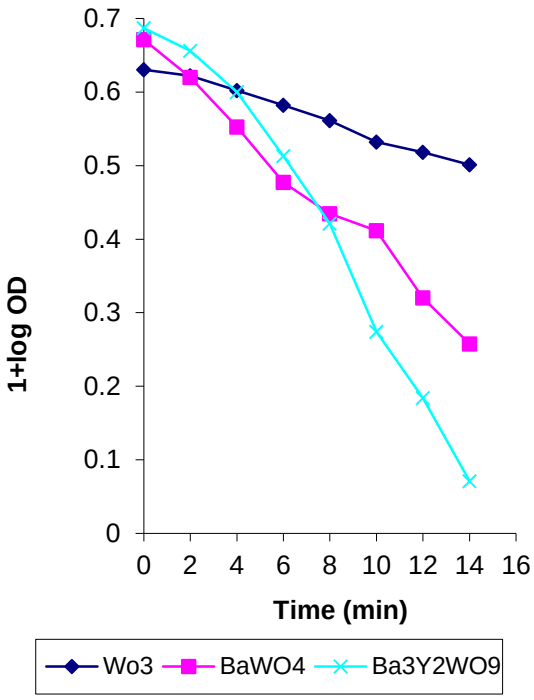
Table-1 Comparative study for Azure B and P-Rosaniline hydrochloride

Factors	WO_3		$BaWO_4$		$Ba_3Y_2WO_9$	
	Azure B	P-Rosaniline hydro-chloride	Azure B	P-Rosaniline hydro-chloride	Azure B	P-Rosaniline hydro-chloride
Rate Constant (s^{-1})	0.92×10^{-4}	0.441×10^{-3}	0.49×10^{-4}	0.719×10^{-3}	8.44×10^{-4}	2.0×10^{-3}
pH	7.8	8.6	7.3	8.6	7.3	7.3
Concentration of dye (moles/litre)	5×10^{-6}	1×10^{-5}	4×10^{-6}	1×10^{-5}	5×10^{-6}	1×10^{-5}
Photocatalyst concentration (gm)	0.12	0.18	0.18	0.16	0.12	0.14
Intensity of light (mW/cm^2)	37	37	37	37	37	37



(P-Rosaniline hydrochloride)

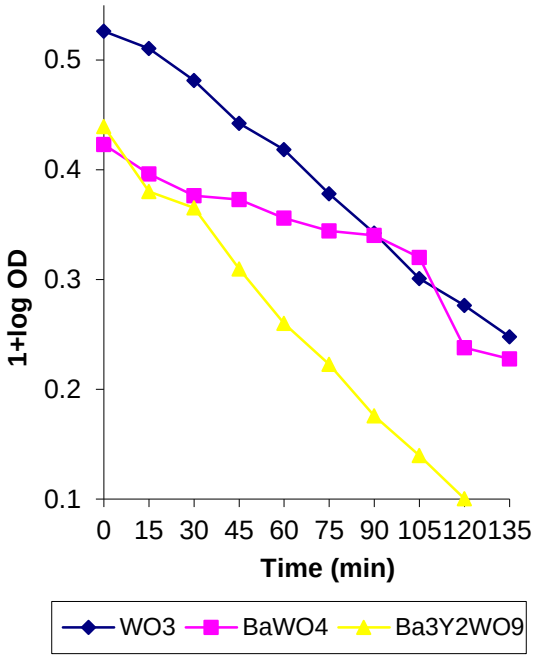


Figure-2 Typical Run (Azure B)

Figure-1 Typical Run

Graphical representation for P-Rosaniline hydrochloride

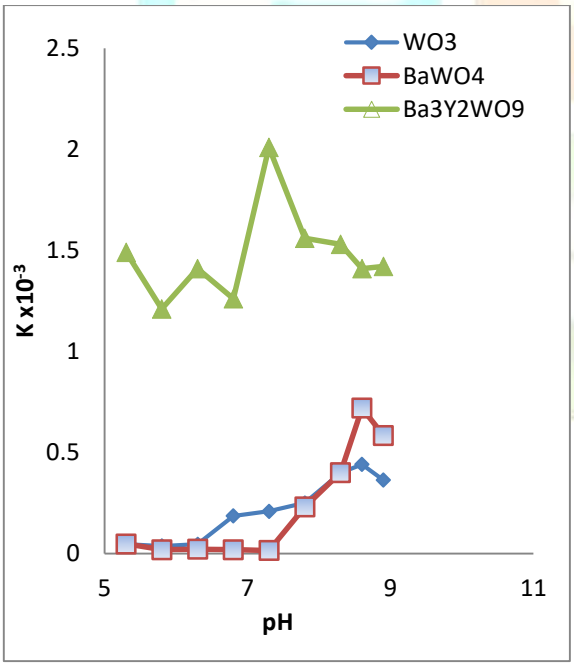


Figure-3 Effect of pH

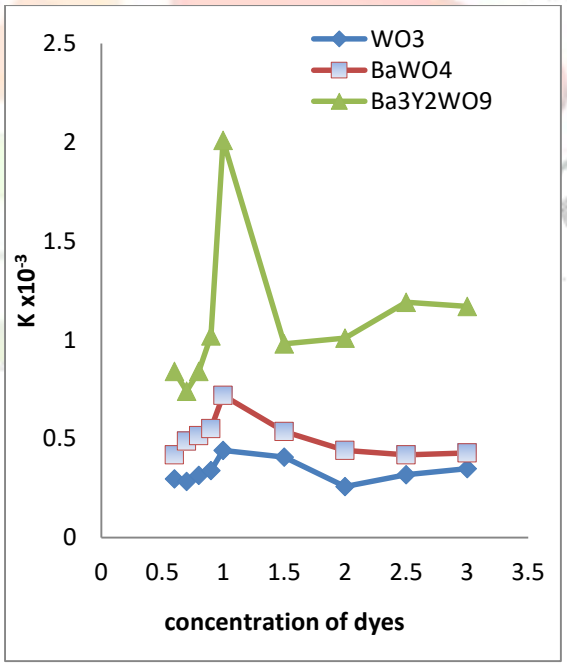


Figure-4 Effect of dye concentration (in moles/litre)

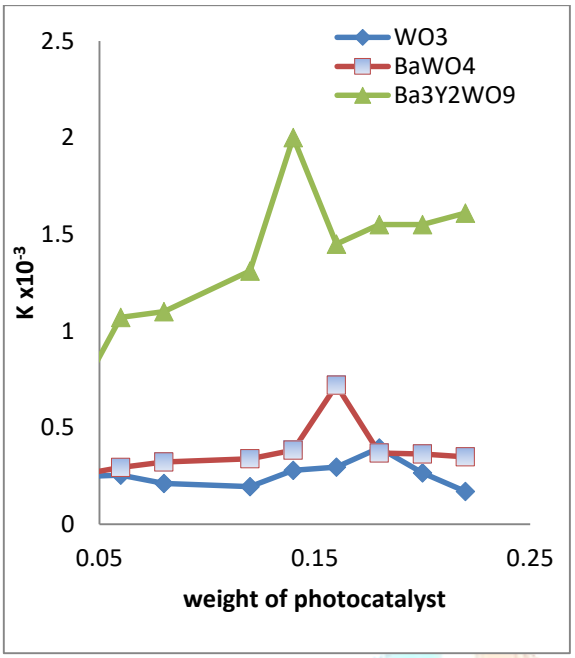


Figure-5 Photocatalyst concentration (in g)

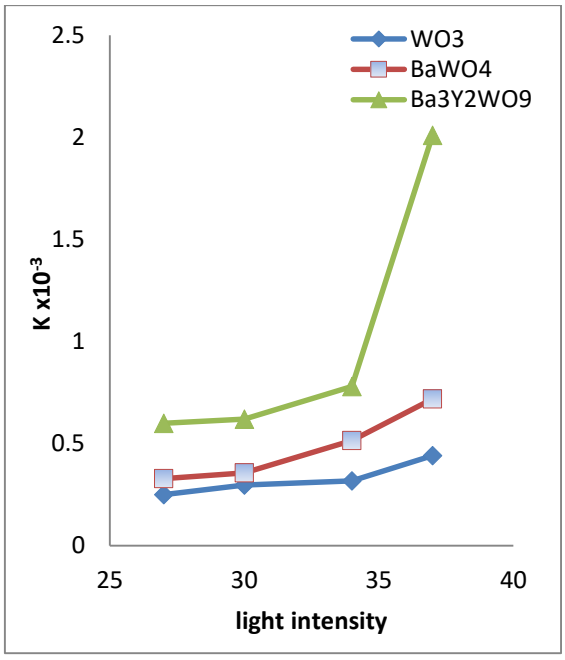


Figure-6 Effect of intensity of light (in mW/cm^2)

Graphical representation for Azure B

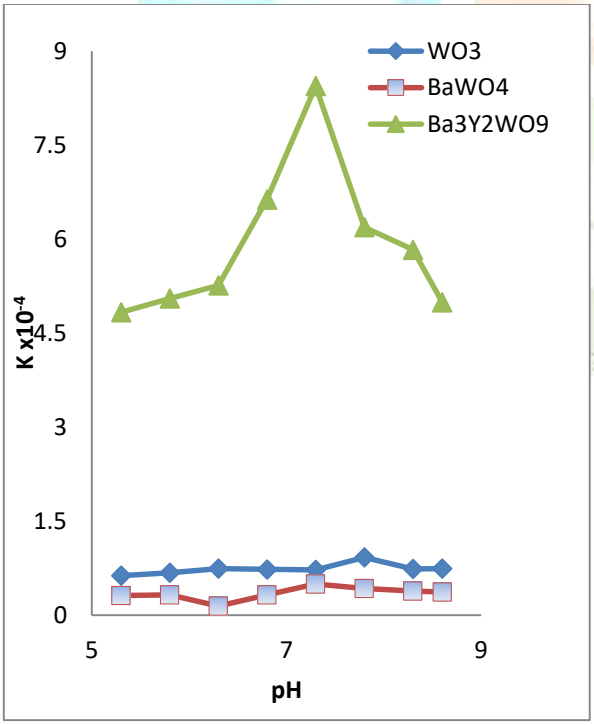


Figure-7 Effect of pH

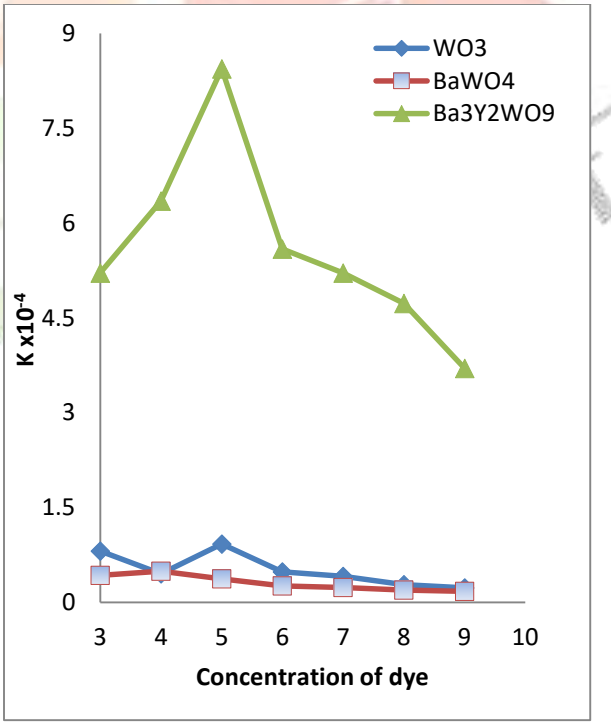


Figure-8 Effect of dye concentration (in moles/liter)

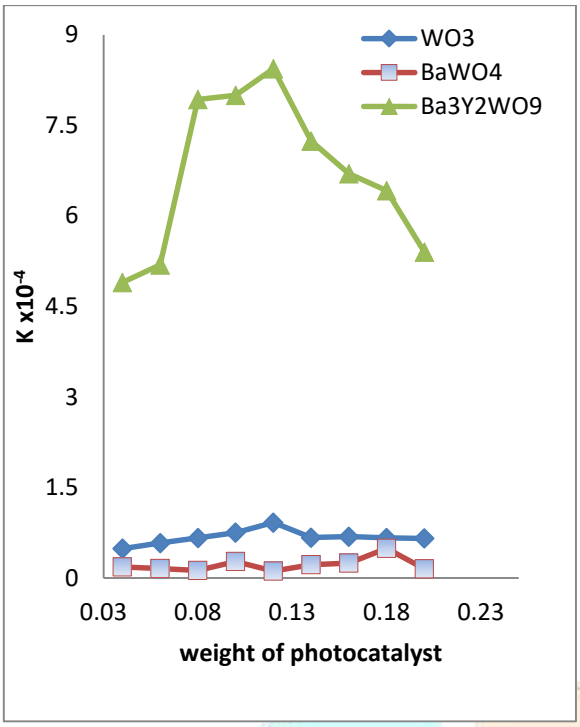


Figure-9 Effect of photocatalyst concentration (in gm)

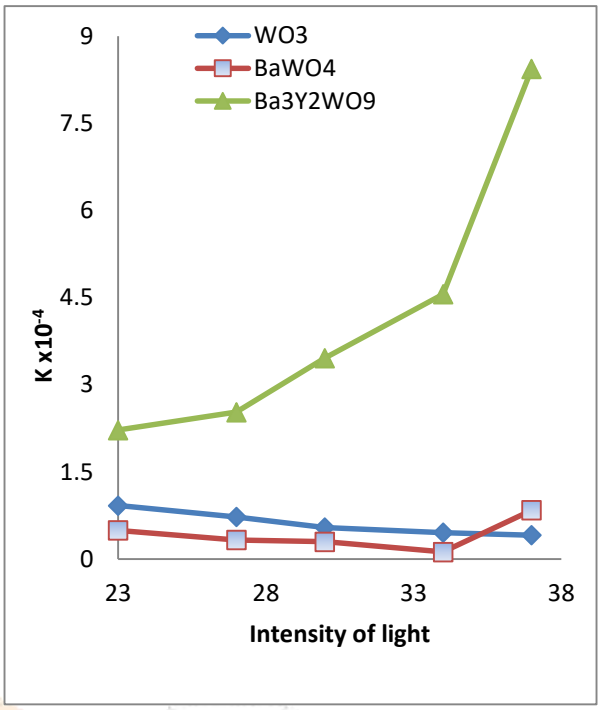


Figure-10 Effect of intensity of light (mW/cm^2)