

Original Research Article

Photocatalytic Decolorization of Brilliant Blue Dye Using Zinc Oxide in the Presence of Sunlight

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ABSTRACT

Zinc oxide is of great technological importance in environmental remediation because of their capability to generate charge carriers when stimulated with required amount of energy. The promising arrangement of electronic structure, light absorption properties and charge transport characteristic has made it possible for its application as Photocatalyst. In this article decolorization of commercial brilliant blue dye was studied using ZnO as catalyst has been discussed. For decolorization of brilliant blue dye, batch experiments were carried out by irradiating aqueous solution of dye, in presence of ZnO under sun light. The effect of operating parameter such as catalyst loading and initial dye concentration has been systematically investigated using UV-Visible spectroscopy to assess their effect on rate of Photocatalytic decolorization. The degradation was found to be effective for catalyst dosage: 0.1g/l, 0.2g/l, 0.3g/l, 0.4g/l and 0.5g/l and concentration range 7ppm, 14ppm, 21ppm, 28ppm and 35ppm. The optimum condition established for degradation was; catalyst dosage 0.2g/l, concentration 14ppm for interval duration of 120 minutes. The experiment results revealed that more than ninety percent of decolorization were achieved for interval duration of 120 minutes for optimized condition of catalyst dosage and concentration variation and the performance of solar Photocatalytic system appears to be suitable for decolorization of brilliant blue dye.

Key words: Photocatalysis, Brilliant blue, Zinc oxide.

INTRODUCTION

Dyes and pigments have been widely used in textile, paper, plastics, leather, food and cosmetics industries to color their products, [1] thus discharging highly colored effluents which can be damaging to the receiving water bodies. The release of colored compounds into water bodies is undesirable not only because of their impact on photosynthesis of aquatic plant but also due their color, biorecalcitrance, potential toxicity, carcinogenicity to animals and human beings. These dyes linger in environment for long periods if let out without adequate

treatment. [2] The conventional technologies currently used to degrade the color of the dye contaminated water include primary (adsorption, flocculation), secondary (biological methods) and chemical processes (chlorination, ozonazation).

However, these techniques are non destructive since they only transfer non biodegradable matter into sludge giving rise to a new type of pollution which needs further treatment. As a result of these problems, advanced oxidation processes (AOPs) have been considered as an effective technology in treating organic chemical dyes in wastewater. AOPs are

group of processes that are based on the generation of hydroxyl radicals and superoxide anion which are highly reactive oxidants. AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade. Heterogeneous catalysis, employed by advanced oxidation processes (AOPs), has emerged as a potential destructive technology leading to total mineralization of most organic pollutants. Photocatalysis systems are the combination of Photocatalyst (semiconductor like TiO_2 , ZnO , Al_2O_3 , RuO_2 , SiO_2 , WO_3 , SnO_2 , ZrO_2 , CdS etc) and UV. [3]

The significant feature of Photocatalyst is that it should possess light absorption capacity, which induces a charge

separation process with the formation of positive holes that are able to oxidize organic. [4-6] In this process, a photocatalyst is activated with UV light, and photoexcited electrons are promoted from the valence band to the conduction band, forming an electron/hole pair (e^-/h^+) (Figure 1). The photogenerated pair (e^-/h^+) is able to reduce and/or oxidize a compound adsorbed on the photocatalyst surface. The photocatalytic activity of Photocatalyst comes from two sources: (i) generation of $\cdot\text{OH}$ radicals by oxidation of OH^- anions, (ii) generation of O_2^- radicals by reduction of O_2 . Both the anions and radical is strong oxidizing agent capable of oxidizing organic compound into CO_2 and water

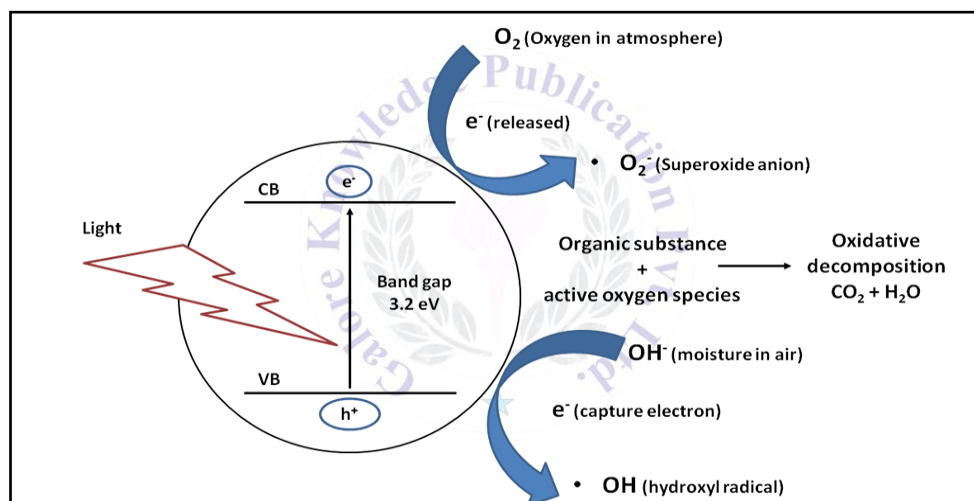


Figure1: Mechanism involved in Photocatalytic degradation of organic compound

To date, many kinds of Photocatalyst have been studied including TiO_2 , ZnO , CdS , WO_3 , and so on, among them ZnO is most extensively used as effective Photocatalyst for high efficiency, photochemical stability, non toxic nature, low cost and the wide spread use ZnO as an effective photocatalyst in practical application which is sensitive to UV light. [7] One main advantage of ZnO is it has high quantum efficiency and absorbs a large fraction of solar spectrum than other semiconductor. [8] Another important characteristic is that ZnO contains various intrinsic defects. Introducing defects into ZnO structure can not only narrow the band

gap to increase the solar light harvesting capability, but also bring many spilt energy gap to set up a possible Photocatalytic system, which sense and shoot environmental contaminants. [9] However the major drawback in heterogeneous photocatalysis is recombination electron hole recombination which leads to lower quantum yield. [10] Hence prevention of electron hole recombination becomes very important. Therefore in the present study an attempt has been made to suppress the electron hole recombination rate by exposing reaction mixture (containing ZnO and dye solution) to natural atmosphere because dissolved oxygen presents an

opposite effect, enhancing Photocatalytic activity, by acting as electron scavenger, resulting in improved parting of electron hole and allowing for more proficient movement of the charge carriers into the photo reaction sites.

The aim of the present study is to investigate efficiency of ZnO as catalyst in degrading brilliant blue dye in presence of sunlight and examine the various operating of parameters for the optimum conditions for the decolorization of dye.

CHEMICAL AND MATERIALS

Food colorant, Brilliant blue (Figure 1) dye having molecular formula $C_{37}H_{34}N_2Na_2O_9S_3$ with color index number 42090 was obtained from kemphasol, $\lambda_{max} = 628$ nm and molecular weight =792.85 g/mol. Zinc oxide is procured form Ranbaxy and used without any further purification. The water used in all the experiment was nano pure water with a resistivity of 18.2 M Ω cm purified by PURELAB Option Q7, ELGA, UK. Percentage transmission was analyzed using UV-Vis spectroscopy.

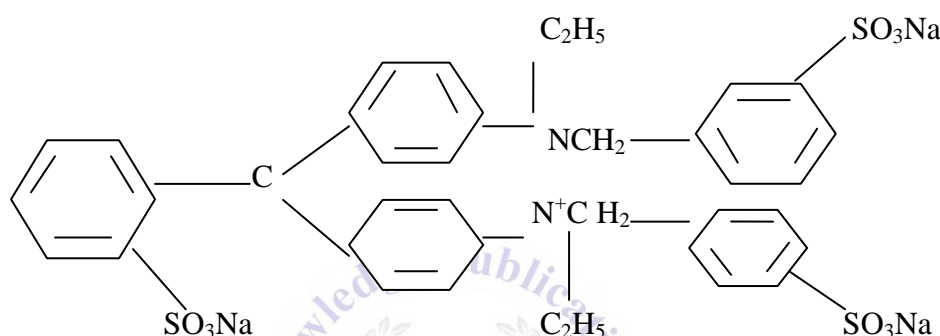


Figure 2: Molecular structure Brilliant Blue Dye

3. Experiment

Brilliant blue dye was used as a model to investigate photocatalytic degradation using ZnO as catalyst. Brilliant blue dye solution of concentration 14ppm was prepared using nano pure water for which batch experiment of photocatalytic degradation of brilliant blue dye was carried out by varying amount of catalyst (i.e. 0.1g, 0.2g, 0.3g 0.4g and 0.5g) and by varying dye concentration i.e. (7ppm, 14ppm, 21ppm,28ppm and 35ppm) for optimized amount of catalyst dosage i.e. 0.2g. The reaction mixture containing dye and catalyst were irradiated to sun light to initiate decolorization process for time duration of 120 minutes. In order to monitor the effect of catalyst dosage and initial dye concentration in degrading brilliant blue dye, aliquot of about 2-3ml was withdrawn from the reaction mixture for every 10 minutes which was centrifuged for 10 minutes at 1000rpm and then analyzed using UV-Visible spectroscopy to determine the percentage decolorization of brilliant blue

dye in reaction mixture by measuring percentage transmission of model dye i.e. brilliant blue at $\lambda_{max} = 628$ nm.

4. RESULT AND DISCUSSION

4.1 Effect of Catalyst variation

To study the effect of catalyst concentration in the removal of color, catalyst at various concentrations were employed i.e. 0.1g, 0.2g 0.3g, 0.4g and 0.5g keeping dye concentration constant at 14ppm. Decolorization was monitored by measuring the percentage transmission at 628nm and the results are shown in figure 3, 4, 5, 6, and 7. The results revealed that percentage transmission increased with increasing catalyst dosage up to 0.2g/l and then showed slightly decrease in photocatalytic activity. This could be the due increased in active site on catalyst surface up to optimum level then gradually decreases because of light scattering effect at higher catalyst loading which could lead to decrease in photon intensity, so strong absorption of light through first successive

layer of solution and prevent light from passing through all the layers in the reaction vessel. However, it increases significantly due to higher production of hydroxyl radical and superoxide anions upon the interaction of semiconductor (ZnO) with sunlight. But above optimum level of catalyst dosage i.e. 0.2g/l percentage transmission slightly reduce due decrease in the formation of super oxide anion and hydroxyl radical. It should be noted that catalyst loading affects both the number of active sites on

photocatalyst and penetration of sunlight through suspension because the increase in catalytic loading number of active sites increases but penetration of sunlight is decreased due to shielding. [11] It should also be noted that optimum value of catalyst loading is strongly dependent on the type and initial concentration of pollutant. [12] The optimum concentration of catalyst for effective color removal for the dye of concentration 14 ppm was found to be 0.2g/l. [Figure 4].

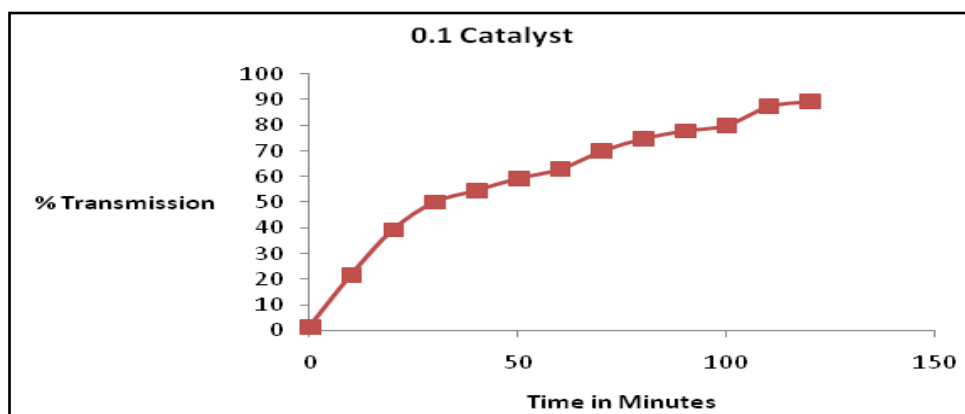


Figure 3: Effect of catalytic (0.1) loading rate in decolorization of brilliant blue dye

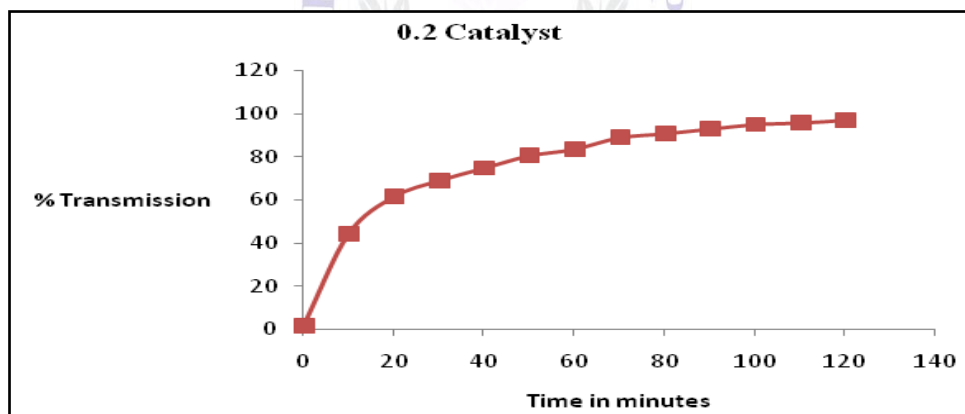


Figure 4: Effect of catalytic (0.2) loading rate in decolorization of brilliant blue dye

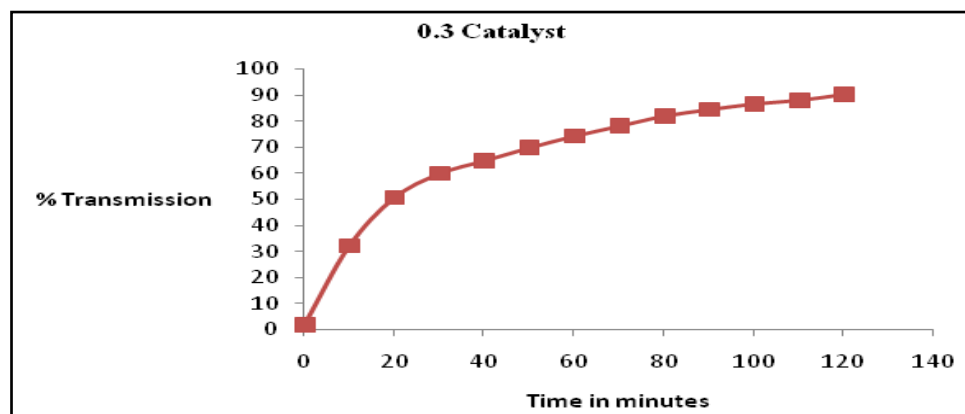


Figure 5: Effect of catalytic (0.3) loading rate in decolorization of brilliant blue dye

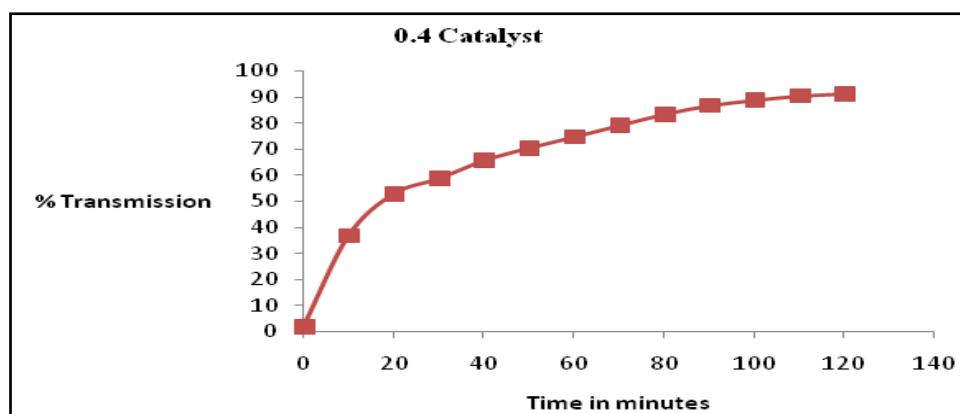


Figure 6: Effect of catalytic (0.4) loading rate in decolorization of brilliant blue dye

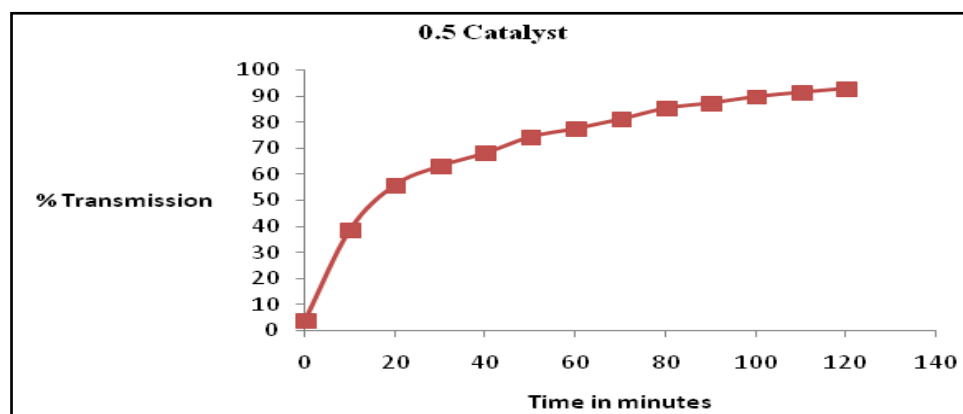


Figure 7: Effect of catalytic (0.5) loading rate in decolorization of brilliant blue dye

4.2 Effect of Concentration Variation

To study effect of concentration in the removal of color, dye amount at various concentrations were employed i.e. 7ppm, 14ppm, 21ppm, 28ppm and 35ppm keeping catalyst concentration constant at 0.2g/l. Decolorization was monitored by measuring the percentage transmission at 628nm and the results are shown in figure 8, 9, 10, 11 and 12. The results revealed that Photocatalytic degradation increased up to 14ppm beyond which it decreases. The increase in degradation may be due to the fact that as the concentration of brilliant blue was increased, more dye molecules were available for excitation and energy transfer and hence an increase in rate was observed. [13] However it decreases beyond 14ppm because as the initial concentration increased more dye molecules were adsorbed on the surface of the catalyst, consequently the generation of hydroxyl radical was reduced since active sites were occupied by dyes. An increase in initial dye concentration results in increase amount of

dye adsorbed on the catalyst surface, affecting the catalytic activity of the Photocatalyst. Moreover the reduction of the light path length as the concentration and deepness of the color of the solution rises also cannot be neglected. [14] At higher dye concentration a significant amount may be absorbed by dye molecules rather than the catalyst and this may also reduce the catalyst efficiency. [15] As the initial concentration of dye increases, the color of the solution becomes deeper which result in the reduction of penetration of light to the surface of the catalyst, decreasing excitation of catalyst. Due to increase of initial concentration of dye more and more organic compound i.e. dye is adsorbed on the surface of ZnO. Therefore, generation of hydroxyl radicals is reduced, since there are only fewer active sites in the system causing little adsorption of hydroxyl ions, which in turn leads to the decrease in generation of hydroxyl radical. Thus, the rate of hydroxyl generation on catalyst surface accordingly will decrease.

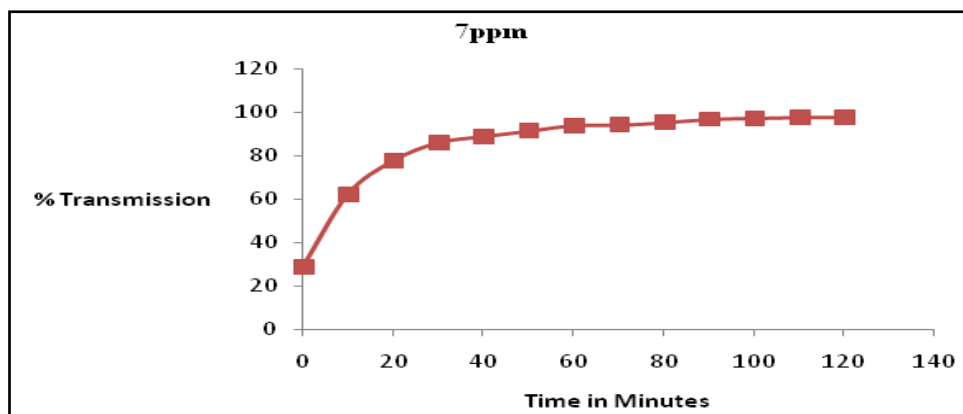


Figure 8: Effect of concentration (7) variation in decolorization of brilliant blue dye

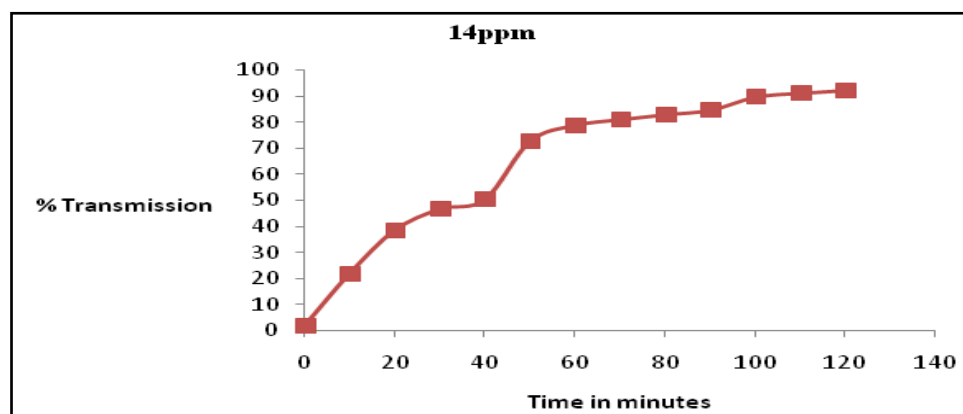


Figure 9: Effect of concentration (14) variation in decolorization of brilliant blue dye

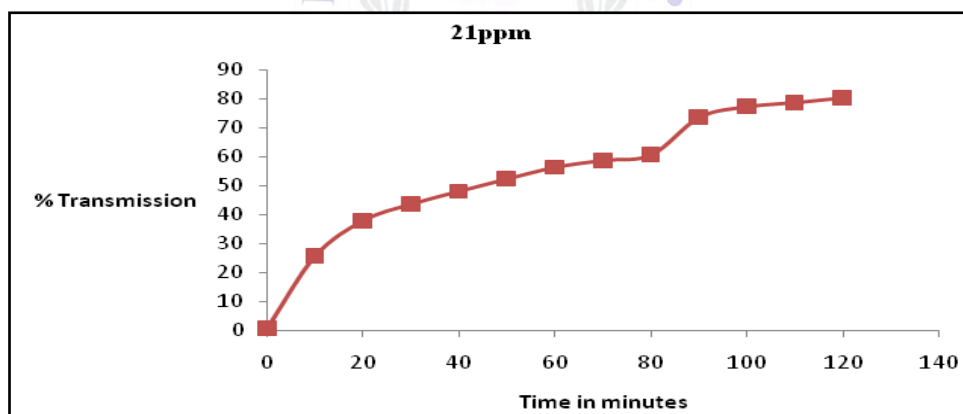


Figure 10: Effect of concentration (21) variation in decolorization of brilliant blue dye

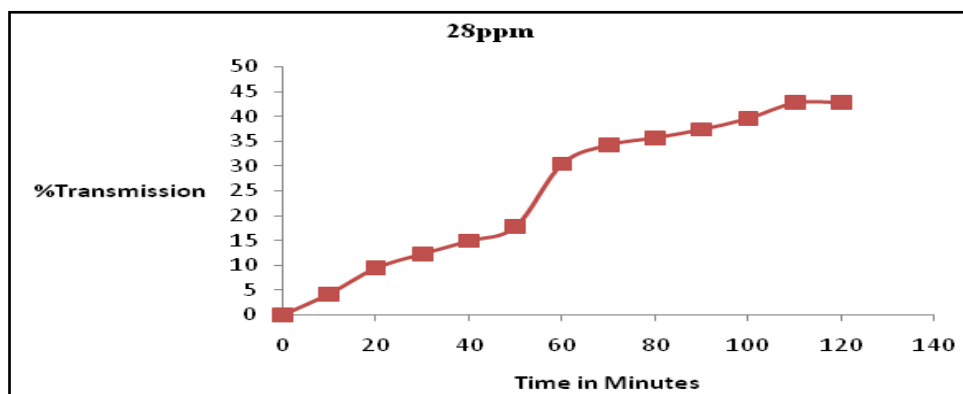


Figure 11: Effect of concentration (28) variation in decolorization of brilliant blue dye

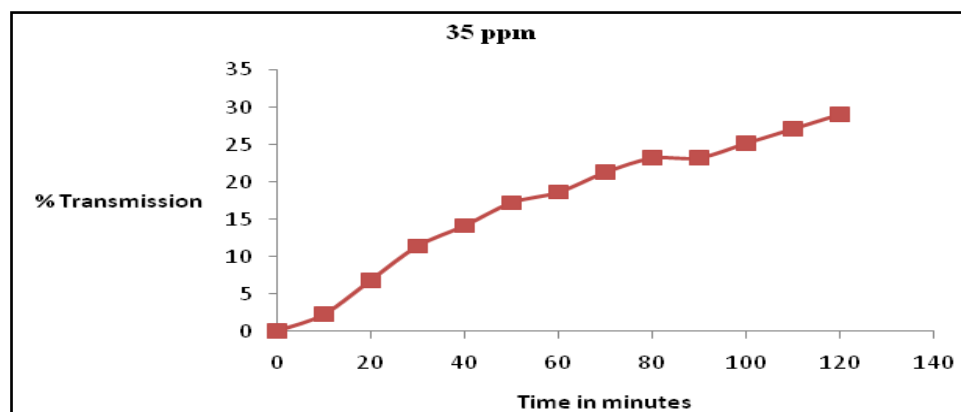


Figure 12: Effect of concentration (35) variation in decolorization of brilliant blue dye

5. CONCLUSION

ZnO is a good photocatalyst capable of mineralizing the dye brilliant blue in the presence of sunlight. The results showed that dye degradation was affected by dye concentration and amount of catalyst. It was found that brilliant blue dye removal percent decreased when the catalyst dosage and concentration increased because of the reduction in generation of hydroxide radical and superoxide anion due to less interaction of catalyst (ZnO) with sunlight therefore there is optimum condition for catalyst loading rate and concentration of dye solution. The reduction in percentage transmission indicated decolorization of dye in aqueous solution. Therefore it can be concluded that brilliant blue dye can be comfortably degraded using ZnO under sunlight.

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