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OVAT DEGRADATION ANALYSIS OF METHYLENE BLUE USING RICE HUSK ASH (AGRO-WASTE) BASED CATALYST IN SOLAR IRRADIATION

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ABSTRACT

This study investigated the degradation of methylene blue dye with ZnO-CuO/RHA, a synthesised agro waste-based photocatalyst under solar irradiation at ambient temperature. Preliminary screening of the methylene blue degradation facilitated the selection of the best ZnO-CuO/RHA combination. The photocatalytic degradation was done by taking varying weights of catalyst in 100 mL of dissolved 10-30 ppm MB solutions. The sample was magnetically stirred at 500 rpm in darkness before being exposed to sunlight irradiation. The suspension was magnetically stirred continuously and 5 ml was withdrawn intermittently, centrifuged and analysed with UV-Vis spectrophotometer. The effect of catalyst dosage, initial concentration and irradiation time on the photodegradation were studied using the one-variable-at-a-time method. The result showed that the degradation percentages of the catalyst with 1, 2, 3, 4, and 5 wt. % of RHA were 80.31%, 88.23%, 99.94%, 91.06 % and 81.12% respectively after 180 minutes. These results showed that degradation percentage was directly proportional to the irradiation time up to 3 wt. % thereafter, there was a decline in the percentage degradation. Hence, as the irradiation time increases, there was a significant increase in the degradation of methylene blue dye. ZnO-CuO/RHA catalyst was found to possess a higher photocatalytic activity in the presence of sunlight in comparison to bare ZnO-CuO since using RHA as a base for ZnO-CuO increased the surface area resulting in more active sites under visible light irradiation. ZnO-CuO/RHA may serve as an efficient-photocatalyst for industrial applications with excellent prospects.

Keywords: *Photocatalytic degradation, Sunlight irradiation, One-variable-at-a-time*

1. INTRODUCTION

Industrial and domestic wastewater or effluents generally comprises of pollutants in the form of organic and inorganic materials which should be destroyed or removed before disposal into the environment or water bodies. If untreated, these contaminants are retained in the various water bodies i.e. ground and surface waters and causes lasting and irremediable damages to all forms and aspects of the environment (Gajbhiye, 2012). In recent times, heavy and uncontrolled chemical disposal from different industries are major causes of water pollution. The use of dyes and pigments are prevalent in many industries for imparting color to materials such as paper, textiles, plastics, leather, food and cosmetics industries (Mohabansi *et al.*, 2011). A lot of industries utilize dyes for colour impartation on products and the discharge of the generated wastewater containing dye to the ocean, rivers and streams causes severe hazards due to the toxic nature of the pollutants. This makes the treatment of dye wastewater an important issue in solving environmental problems present today (Katheresan *et al.*, 2018).

Methylene blue (MB) dye with molecular formula $C_{16}H_{18}N_3ClS$ is a heterocyclic aromatic chemical compound with a dark green colour that changes to blue when dissolved in water at ambient temperature. MB is commonly used in industries for dyeing cotton, paper stocks, wood, and silk and in the field of medicine and laboratory science (Viswanathan, 2017). Extreme exposure of humans to methylene blue causes the release of aromatic amines such as benzedrine and methylene which has carcinogenic tendencies, and may lead to vomiting, shock, cyanosis and tissue necrosis. The presence of methylene blue is visible and has effect on aquatic life and the biosphere as a whole due to the increase in the biochemical oxygen demand (BOD) level

(Ehrampoush *et al.,* 2011). It is toxic to aquatic microbiota and humans, as a teratogenic substance and inhibits light penetration needed for photosynthesis. (Amini and Ashrafi, 2016).

There are various methods/techniques available for treating dye effluents (Iracà and Romero, 2017). These methods include "biological, chemical, physical and electrochemical methods" as shown in Figure 1.

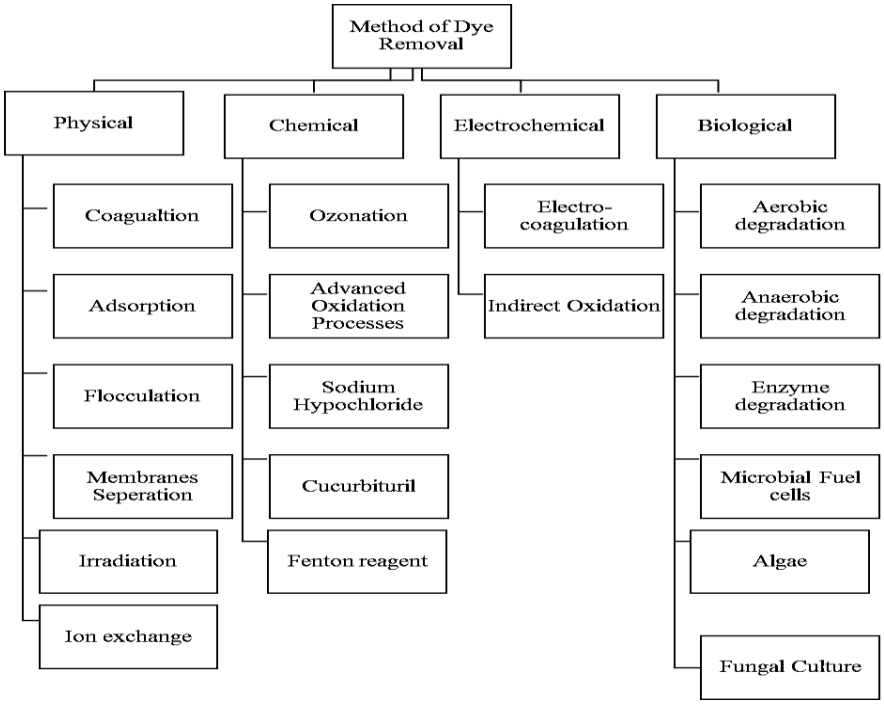

Figure 1: Techniques for waste water treatment (Iracà and Romero, 2017)

Photocatalysis, a technique employed in dye degradation, involves a "catalysis driven light-induced reaction" where the dyes are oxidized or broken down into smaller molecules like water, carbon dioxide, and other mineral byproducts (Mardikar *et. al.,*2018). This reaction takes place under photon or light and thermal condition, where hydroxyl radicals that react with organic material for degradation to occur are generated in the presence of higher oxidation metal ion complexes (Saravanan *et al.*, 2017). The reactions are usually initialized when catalyst absorbs light energy or photons that have a greater energy than the band gap energy from the illumination. The photo-induced electron on the surface of the photocatalyst is transferred from the valence band (VB) to the conduction band (CB), to form hole (h_{VB}^{+}) and electron (e_{CB}^{-}). The general photocatalytic reaction according to Saravanan *et al.*, (2017) is given in Eqn 1 - 10 as;

$$\text{Photocatalyst} + \text{Light Energy} \rightarrow \text{Photocatalyst}\,(e_{CB}^{-} + h_{VB}^{+}) \quad (1)$$

$$\text{Dye} + \text{Photocatalyst}(h_{VB}^{+}) \rightarrow \text{Oxidation process} \quad (2)$$

$$\text{Photocatalyst}\,(h_{VB}^{+}) + H_2O \rightarrow \text{Photocatalyst} + H^{+} + OH^{\bullet} \quad (3)$$

$$\text{Photocatalyst}\,(h_{VB}^{+}) + OH^{-} \rightarrow \text{Photocatalyst} + OH^{\bullet} \quad (4)$$

$$\text{Dye} + \text{Photocatalyst}(e_{CB}^{-}) \rightarrow \text{Reduction process} \quad (5)$$

$$\text{Photocatalyst}\,(e_{CB}^{-}) + O_2 \rightarrow \text{Photocatalyst} + O_2^{\bullet -} \quad (6)$$

$$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet} \quad (7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^{-} + O_2 \quad (9)$$

$$\text{Dye} + OH^{\bullet} \rightarrow \text{Degraded products} \quad (10)$$

Sunlight powered photocatalytic degradation has been studied extensively by various researchers with distinct advantages like sustainability, non-toxicity and cost effectiveness (Foletto *et al.*, 2012; Kant, 2012; Das *et al.*, 2018; Mardikar *et al.*, 2018; Villarrubia *et al.*, 2018). However, the process is one in which the efficiency is highly dependent on properties of the catalyst and the photocatalytic reaction conditions. This implies that great attention has to be placed on the catalyst to enhance the photocatalytic performance as optimal composition of the process conditions and material to obtain high degradation percentage are necessary. Rice

husk ash is an agricultural waste which contains high silica content of amorphous silica with a large surface area and serves as a suitable support material for the ZnO-CuO metal oxide. CuO based catalysts are prone to rapid deactivation (Poreddy *et al.*, 2015) which can be avoided by providing a support to aid the distribution of the copper oxide particles (Chang *et al.*, 2003). ZnO possesses a smaller pore volume and surface area leading to low adsorption of organic pollutants in on the catalyst system hence it is important to increase or enlarge the specific surface area and adsorption capacity of the catalyst. The use of semiconductor photocatalyst in the removal of pollutants has the advantage of total decomposition & mineralization without waste generation, a feat not feasible with other treatment methods. However, in order to maximize the catalyst and increase the activity, we set out to apply rice husk ash/ZnO-CuO photocatalyst in degrading MB. There is no known report on use of agro-waste in band gap adjustment to facilitate sunlight degradation or as a component in photocatalyst.

2. EXPERIMENTAL

2.1 Materials

The agro based ZnO-CuO/RHA photocatalyst was synthesised using the modified sol-gel method adopted from Widiarti *et al*, (2017) while methylene blue ($C_{16}H_{18}ClN_3S{\cdot}2H_2O$) dissolved in distilled water was the simulated pollutant evaluated to determine the photocatalytic efficiency of the synthesized catalyst. The sunlight irradiation intensity was measured using the Hukseflux pyranometer software during the photocatalysis experiment at a 1-hour interval and a 752S UV- Vis spectrophotometer was used to measure the absorbance for all experiment.

2.2 Methods

2.2.1 Calibration of UV- spectrophotometer

The spectrophotometer was calibrated in order to determine the peak wavelength of methylene blue. 50 mg/l of methylene blue dye served as the stock solution which was diluted into a serial dilution of 30 mg/l, 25 mg/l, 20 mg/l, 15 mg/l, 10 mg/l, and 5 to 1 mg/l. The blank solution used was distilled water and the wavelength was varied from 450 µm to 700 µm to determine the relevant peak and obtain a standard absorbance - concentration curve.

2.2.2 General procedure for the photocatalytic degradation

The photocatalytic activity of ZnO-CuO/RHA for the degradation of methylene blue was conducted under sunlight irradiation at ambient temperature. The experiment was conducted in a beaker with continuous magnetic stirring at 500 rpm for varying reaction time. The reactants (methylene blue and ZnO-CuO/RHA catalyst) were stirred in darkness for 30 minutes to establish equilibrium for adsorption-desorption between the surface of the photocatalyst and the dye under ambient conditions after which it was exposed to sunlight irradiation with intensity of 78.56 kW/m^2 to aid the photocatalytic degradation. During the experiments 5 ml of the sample was withdrawn from the beaker at a 30 minutes interval and centrifuged at 2500 rpm for 20 minutes to be analysed by a UV-Vis spectrophotometer to obtain final concentration. The same procedure was used for every experiment. The percentage of photocatalytic degradation was calculated using equation 11.

$$Degradation = \left(\frac{C_o - C_t}{C_o}\right) * 100 \quad (11)$$

Where C_0 = Initial concentration of methylene blue
C_t = Final concentration of methylene blue after irradiation.

Figure 2 presents a schematic diagram of the experimental setup used to conduct the Photocatalysis in the presence of sunlight.

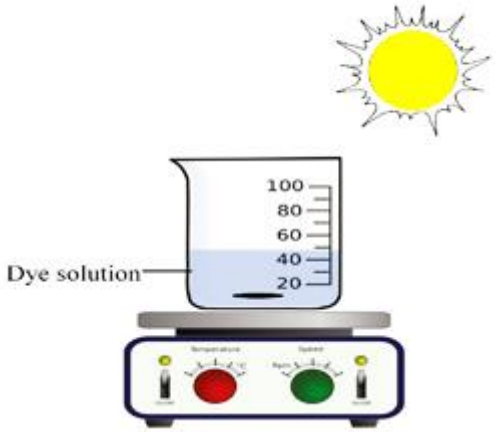

Figure 2: Experimental set up for Photocatalysis

2.2.3 Preliminary screening and Comparative degradation efficiency

The 5 different synthesized ZnO-CuO/RHA catalysts were analyzed under the same conditions of catalyst dosage 0.1 g, in 100 mL of 15 ppm MB concentration for 3 hours (180 minutes) and the catalyst that consistently gave the highest percentage of degradation was selected as the choice catalyst for the process. The photocatalytic degradation was conducted using control catalysts (ZnO, CuO, RHA and a blank sample) to perform a comparative analysis with the selected best catalyst.

2.2.4 Photocatalytic Degradation (One-Variable-at-a-Time)

The catalyst dosage of ZnO-CuO/RHA was varied from 0.1 g to 0.3 g in 100 mL of varied concentration of Methylene blue from 10 to 30 ppm at different time intervals.

To investigate the effect of catalyst dosage, different weights of the ZnO-CuO/RHA photocatalyst varying from 0.05 g- 0.20 g were added to 100 ml of methylene blue dye with dye concentration of 5 ppm. The reaction was done in 270 minutes under sunlight irradiation being magnetically stirred (500 rpm).

For the effect of initial concentration, varied concentrations of MB were used with fixed photocatalyst dosage of 0.2 g at different initial concentration of methylene blue ranging from 5 to 30 mg/l (ppm) as prepared from the stock solution. The effect of time was also observed following these experiments.

3. RESULTS AND DISCUSSION

3.1 Calibration of UV-Spectrophotometer

Figure 3 gives the calibration curve of methylene blue with the maximum absorption peaks wavelength of MB at λ_{max} = 664 um. The spectral absorption curve measurement of dyes during the process of photodegradation is a means providing evidence of the structural changes of dyes and determining reaction rates (Jassim, 2017). As absorptivity is an intrinsic property of dyes, the degradation of the dyes is usually accompanied by a color change (wavelength shift) of the solution hence, the color change was monitored by the UV-Vis spectrophotometer to provide more information about the photodegradation. The decrease in the maximum absorbance of MB dye was observed and a linearly dependent relationship was noted between the absorbance and the concentration of methylene blue.

Figure 3 gives the calibration curve which was used to determine the peak wavelength of the methylene blue solution and the standard curve which is a plot of pollutant concentration versus absorbance used for the determination of dye concentration in the prepared solution at different absorbance value. After each measurement at the peak wavelength, the MB concentration was calculated using the model equation given in figure 3b with R^2 = 0.9971 given as:

y = 0.0619x + 0.11; where y = absorbance and x = concentration

3.2 Preliminary Screening

The photodegradation efficiency of ZnO-CuO/RHA on 15 mg/l of methylene blue having varied weights of rice husk ash (RHA) were analyzed. As shown in figure 4, the degradation percentage of the ZCR catalyst with 1, 2, 3, 4, and 5 wt.% of RHA were obtained to be 80.31%, 88.23%, 99.94%, 91.06 % and 81.12% respectively after 180 minutes. Upon increasing the weight of rice husk ash incorporated into the matrix at 4 grams and 5 grams the degradation efficiency decreased to 91.06% and 81.12% respectively, this may be attributed to the accumulation of RHA on the surface of ZnO-CuO that causes a reduction in the light being penetrated unto the active sites of the photocatalyst. With higher RHA weight, activated molecules are deactivated due to the collision with the molecules in the ground state which dominates the reaction, thereby slowing down the reaction rate and increasing time required for degradation. The photocatalytic activity against irradiation time given in figure 5 shows that the catalysts give a linear relationship with increase in time. Hence, the ZnO-CuO with 3 g of RHA was selected as the best catalyst composition for the photodegradation process.

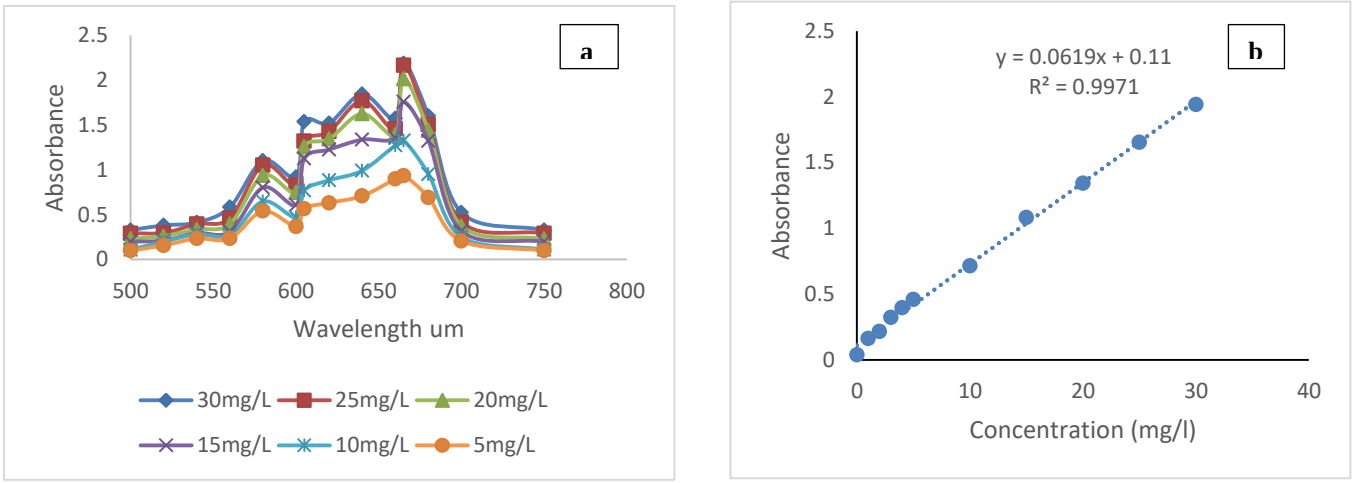

Figure 3: (a) Calibration Curve (b): The Spectrophotometer calibration curve of Methylene Blue dye at λ= 664 um

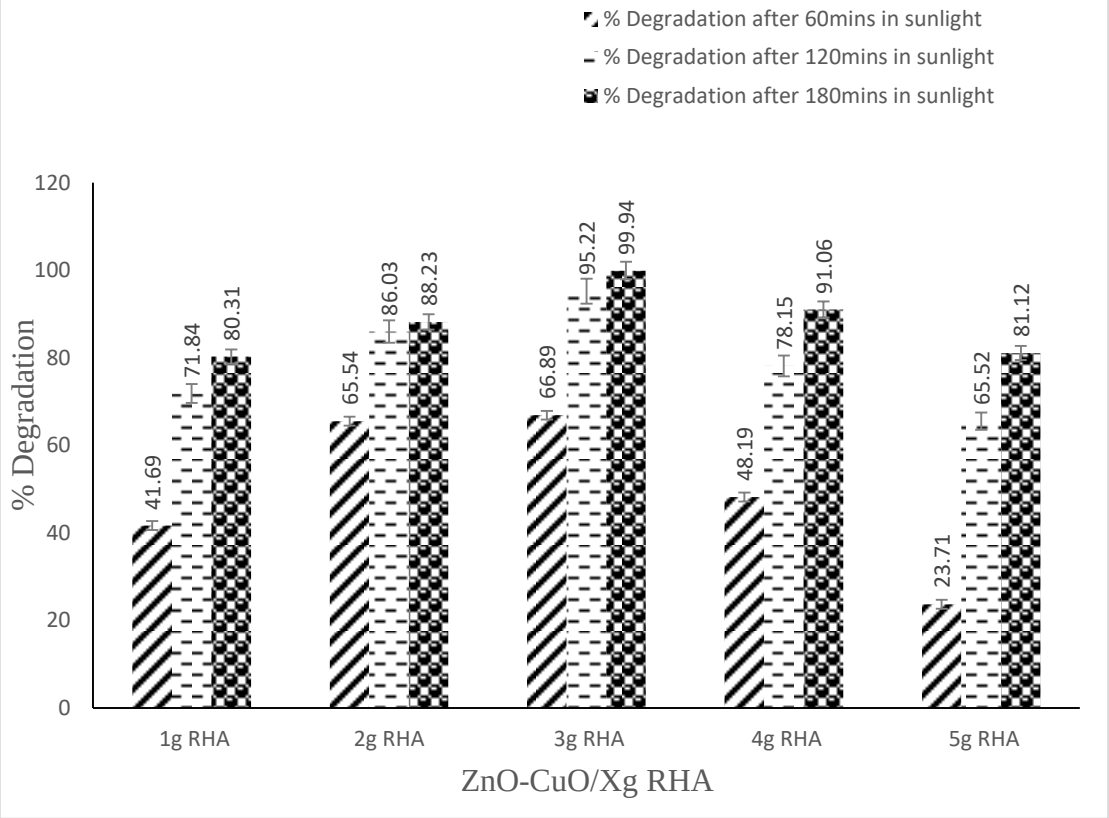

Figure 4: Catalytic activity of different RHA wt. % (ZnO-CuO/RHA) on the photodegradation of MB

3.3 Comparative degradation efficiency

ZnO, CuO, and RHA were tested as a form of control for the process of photocatalytic gradation of MB.

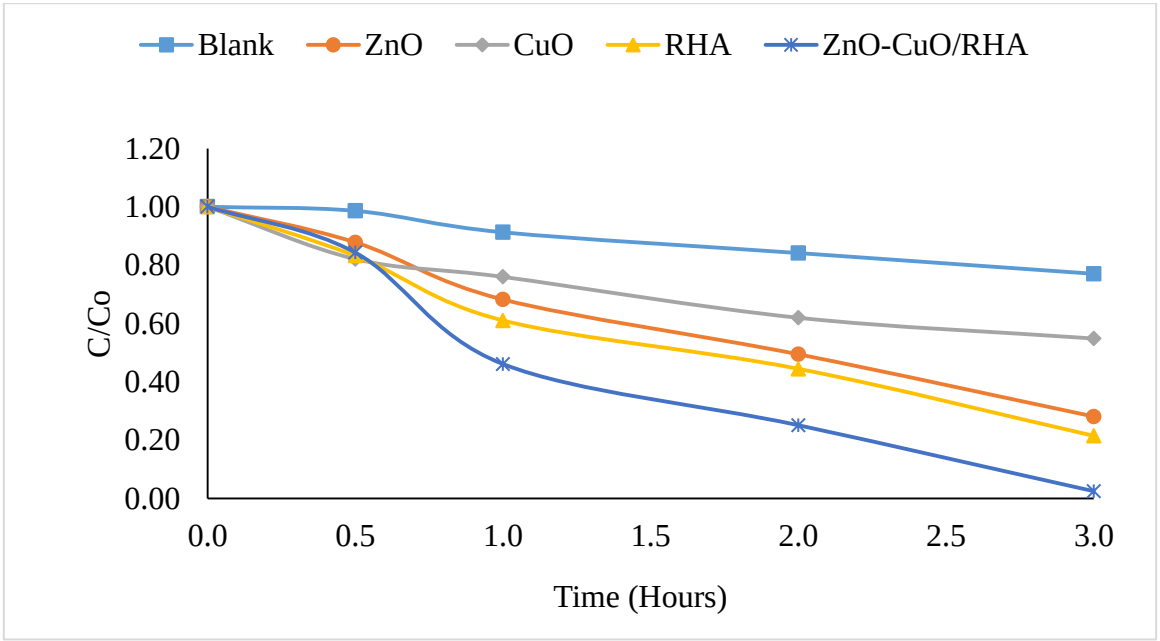

Figure 5a: Plot of concentration ratio versus time using the different catalyst

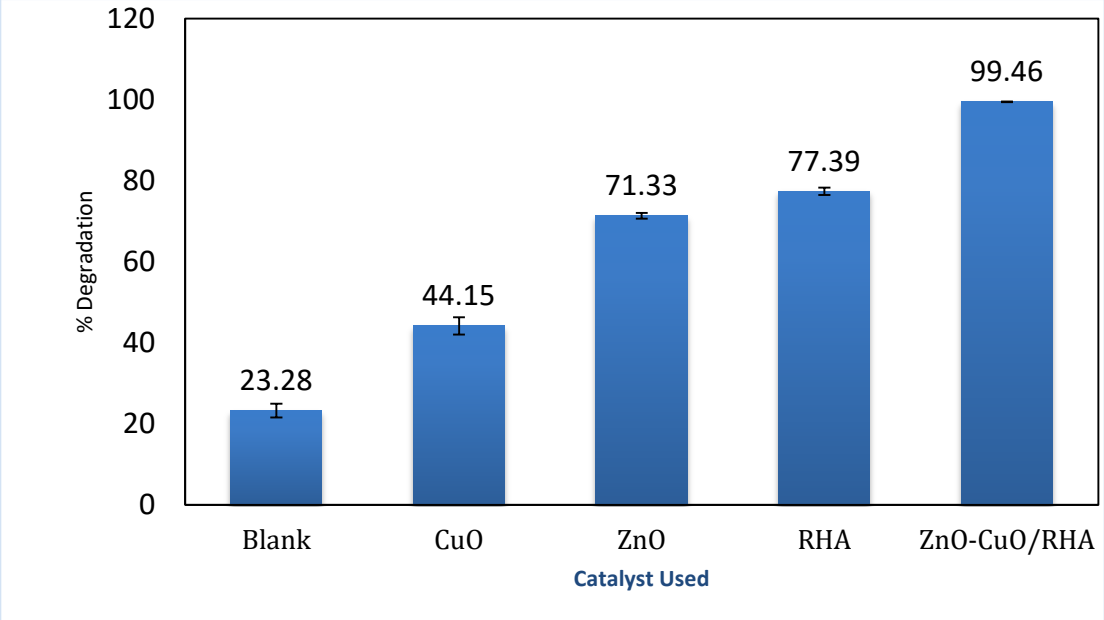

Figure 5b: Photocatalytic Activity of MB using Control Catalyst

The degradation of MB with a blank solution (no catalyst), with ZnO, CuO, RHA and the ZnO-CuO/RHA catalyst was conducted using the same conditions as the preliminary screen and the result is shown in figure 5b to be 23.28%, 44.15%, 71.33%, 77.39% and 99.46 % respectively after 3 hours. From figure 5a, the concentration ratio against time was given and it was observed that there is no remarkable degradation with the blank samples, this is due to the absence of a catalyst. The plot in 5a shows a notable increase in the photocatalytic activity of the synthesized catalyst, this implies that the catalyst synthesized has higher degradation activity for the degradation of methylene blue when compared with the singular control catalyst.

Probable reasons for this is the resultant increase in the surface area of the synthesized catalyst after coupling with rice husk ash an agricultural waste with high surface area Shu-Ting *et al.* (2014) which enables the ZnO-CuO/RHA catalyst to have a more active site leading to faster and higher degradation of the dye. According to Zaman *et al.* (2012) , the reactants that aid degradation of organic dyes includes free radicals like the hydroxyl radicals and super oxide anions generated when hydrogen peroxide (H_2O_2) is broken down. It was observed from figure 5b that the ZnO-CuO/RHA catalysts has higher degradation in the presence of sunlight when compared with zinc oxide, copper (II) oxide and rice husk ash individually, likely due to reduction in bandgap energy levels by tuning the valence bands of ZnO with CuO and the higher surface area of the catalyst.

3.4 Effect of Catalyst Dosage

During the process of photocatalytic degradation, the catalyst dosage or loading is an important factor to determine the cost of the photocatalyst. Figure 6 shows the plot of the percentage degradation with respect to the catalyst dosage to observe the effect of catalyst dosage over time.

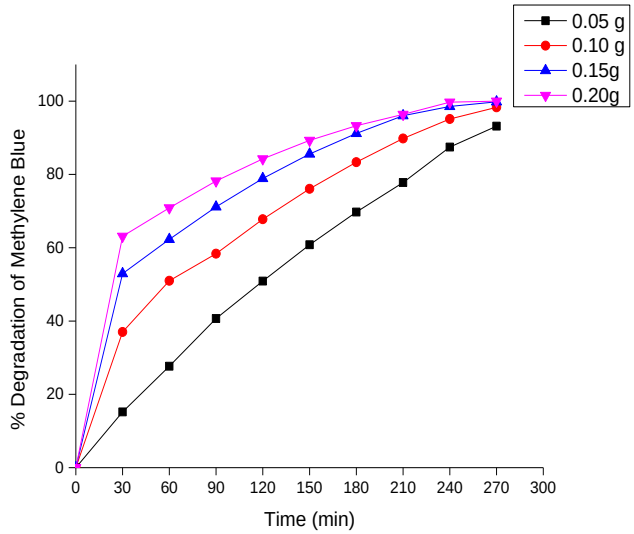

Figure 6: Plot showing the effect of catalyst dosage

A plot of percentage degradation of methylene blue dye for various catalyst dosage against time is given in figure 6. It was observed that an increase in the photocatalyst dosage resulted in an increase in the percentage (%) degradation and rate of reaction as degradation occurred faster as catalyst dosage increases.

As catalyst dosage increased the number of active sites available on the surface of the catalyst also increased. However, it was observed for 0.15 and 0.2 grams that after 240 min there is no significant increase in the degradation. This implies that using a higher catalyst dosage reduces the time required but if it is too high it can lead to ineffective degradation and wasting of resources.

3.5 Effect of Initial Concentration

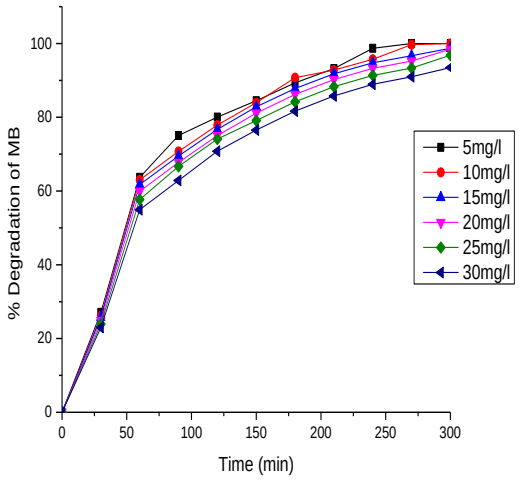

Figure 7: Plot showing the effect of initial concentration

The Photocatalytic degradation of MB solution with an initial concentration of 5 to 30 mg/L resulted in a degradation rate that exceeded 97% at 3 hours, as shown in Figure 7 with the plot of the percentage degradation versus time for different initial concentrations. From this plot a sharp inclination is observed in the first 30 minutes this is because during the process of achieving adsorption-desorption equilibrium in the absence of sunlight, part of the dye was absorbed on the surface of the photocatalyst and as the reaction proceeds, the percentage degradation decreased as initial concentration of the dye increased. As the initial concentration increased, the quantity of reactants and the reaction intermediates adsorbed on the photocatalyst surface increased forming a layer over the surface that leads to reduction in hydroxyl radicals' formation because active sites available for formation of hydroxyl ion reduces as light penetration needed to activate the photocatalyst is reduced (Zhao *et al.*, 2017). The highest % degradation obtained was at 5 mg/l initial concentration of methylene blue because it had the lowest dye concentration. As the initial concentration increased, the photocatalytic efficiency decreased and this is attributed to decrease in solution transmittance which affects photon absorption in the system. The high concentration of methylene blue causes an excessive absorption of dye molecules on the surface of the catalysts.

3.6 Effect of Time

To observe and investigate the effect of time on the photocatalytic degradation process, different concentrations of MB and catalyst dosages were tested and is shown in figure 8.

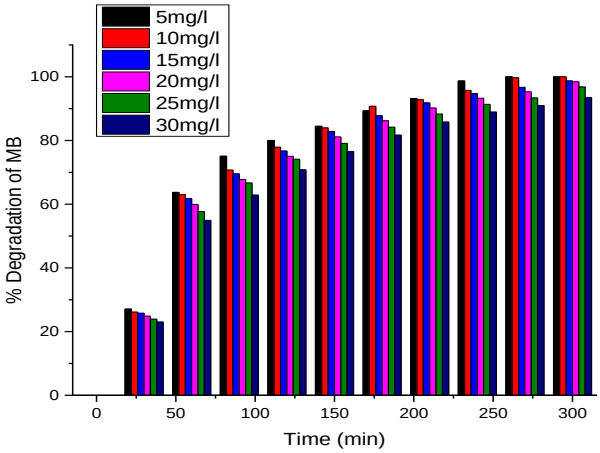

Figure 8: Plot showing the effect of initial concentration

The effect of time on the degradation of different concentration of methylene is given in figure 8 and it was observed that as the reaction time increased, the degradation percentage also increased. For each experiment remarkable increase in degradation percentage was observed as time of reaction increases. This tallies with what was reported by (Bharati *et al.*, 2017; Mardikar *et al.*, 2018) in the photocatalytic degradation of MB and certifies that the time of reaction or exposure to sunlight is directly proportional to the degradation of methylene blue.

4. CONCLUSIONS

The photocatalytic degradation of methylene blue with ZnO-CuO/RHA catalyst was conducted. ZnO-CuO/RHA was found to possess a higher photocatalytic activity when compared with ZnO-CuO. This was premised by the increased surface area that RHA base provided to ZnO-CuO/RHA. This resulted in more active sites under visible light irradiation for high photocatalytic efficiency. The effect of process parameters, dye concentration, catalyst dosage and irradiation time were explored studying one variable at a time. As catalyst dosage increased the number of active

sites available on the surface of the catalyst also increased and a higher catalyst dosage reduces the time required but if it is too high may lead to ineffective degradation and wasting of resources. As concentration increases, the active sites available for formation of hydroxyl ion reduces as light penetration needed to activate the photocatalyst is reduced. The highest % degradation obtained was at 5 mg/l initial concentration of methylene blue because it had the lowest dye concentration. This provided the advantage of determining the percentage linear removal of dye MB as it increases with increasing irradiation time. ZnO-CuO/RHA may be used as an efficient photocatalyst in the treatment of industrial wastewater.

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