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PHOTO CATALYTIC DYE DEGRADATION USING SOLAR CONCENTRATOR

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Abstract:

During dyeing process, industries consume large quantity of water and subsequently produce large volume of wastewater. This wastewater is rich in color and contains different dyes. Methylene Blue dye is one of them. In this paper, Copper (Cu) impregnated to TiO_2 (Cu/TiO_2) is used as catalyst which is used to enhance the photo catalytic degradation of Methylene Blue dye. Photo degradation percentage was calculated spectrophotometrically by the measurements of absorbance at λ_{max} = 664 nm. Different Concentration of catalyst was synthesized (5%, 7%, 10% and 12%) and the effect of different concentrations of Cu/TiO_2 photo catalyst for the degradation of Methylene blue has been investigated in terms of percentage degradation of dye. Experiments were conducted in both UV Multi lamp Reactor as well as immersion Type Visible lamp reactor. This paper investigates a new method of dye degradation with the help of a solar concentrator. The use of this method of dye degradation helps to reduce energy consumption; and also has less environment impact when compared to conventional method which uses chemicals to degrade dye. XRD analysis, High Resolution Transmission electron microscopic analysis was used for catalyst characterization.

Key Words: Solar Concentrator, Methylene Blue, Absorbance & Catalyst

1. Introduction:

Bright and fabulous, attractive outlook and ever changing fashion have revolutionized the textile industry which has been whole heartedly catering the new generation. The textile waste water is characterized by high content of dye stuff. In contrast to the production of beautiful fabrics, the backside discharge of waste water containing high concentration of dyes has raised a serious environmental concern. [1] The effluent from textile processing is often discharged to municipal sewage treatment plants or directly to waterways. 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, ozonization). [2] However these techniques are non-destructive since they only transfer the non biodegradable matter into sludge, giving rise to a new type of pollution which needs further treatment. Use of conventional dye waste water treatment methods are becoming increasingly challenging for existing plants. The US department of commerce has projected a 3.5 fold increase in textile production between 2010 and 2020. The stability and non-degradability of dyes causes major problems in its treatment and thus demands a sustainable and eco-friendly method. In past few years there has been a considerable research focused on the development of various techniques to treat dye waste water. Textile dyes are a considerable source of eutrophication as well as non-aesthetic pollution that can produce dangerous byproducts by further oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Apart from the toxic effects of dyes in wastewater streams, presence of dyes can cause reduced light penetration resulting in reduced photosynthetic activity thus making oxygen unavailable for biodegradation of microorganism in the water. Among the various methods Photo catalytic conversion is an effective method to convert the dye present in waste water to harmless compound water. Methylene Blue (MB) is an inexpensive and common dye used in textile industry. Methylene blue is a cationic dye. It is most commonly used for coloring paper, temporary hair colorant, dyeing cotton wools and so on. MB, has very harmful effects on the living things. After inhale symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans. The molecular formula of MB is $C_{16}H_{18}N_3SCl$.Its IUPAC name is 3, 7-bis (Dimethylamino) phenothiazin- 5-ium chloride. The structure of methylene blue is shown in Fig 1. It has a characteristic deep blue colour in the oxidized state. Maximum absorbance of MB is found at 664nm. Amongst a variety of catalysts, semiconductor photo catalyst containing titanium dioxide (TiO_2) is widely used. Titanium dioxide (TiO_2) has been shown to be a promising semiconductor photo catalyst. TiO_2 is considered to be promising photo degradation catalysis because it posses five basic characteristics: 1) photoactive, 2) able to utilize visible and/or near UV light, 3) biologically and chemically inert, 4) photo-stable, and 5) inexpensive. It is a semiconducting material that may be chemically activated by light. It has an energy band gap of 3.0-3.2 eV, which is equivalent to the energy of near UV radiation (<400nm). The photo catalytic properties of titanium dioxide were discovered by Akira Fujishima in 1967 and published in 1972 as discussed earlier. The process on the surface of the titanium dioxide was called the Honda-Fujishima effect.

Titanium dioxide exhibits three major crystalline phases: rutile, anatase and brookite. Rutile is the most stable phase for small crystals (< 11nm), anatase for large crystals (> 35nm) and brookite in between Rutile and anatase are the most studied of the phases, particularly in the field of surface science. Rutile is the most thermodynamically stable phase at high temperature whereas Anatase can be obtained by calcining the samples at temperatures around 400 °C while at temperatures between 550 and 600 °C, rutile start forming and becomes the predominant phase at higher temperature. Upon heating, anatase and brookite are observed to form rutile. Only rutile and anatase are commonly used in photo catalysis since brookite phase is not stable above 150ºC. The anatase form has the free electrons in its crystal lattice, thus it is an n-type semiconductor. In fact, anatase has been reported to give the best combination of photo activity and photo stability.

The present work is designated to investigate the photo catalytic degradation of Methylene Blue dye over Cu doped with TiO_2, (Cu/TiO_2) containing different Cu contents (Cu = 5,7,10 and 12 wt %).

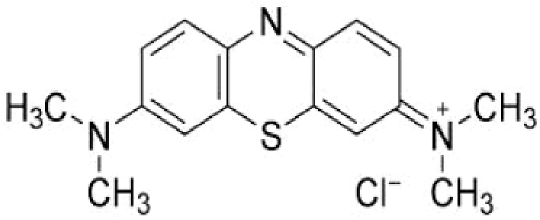

Figure 1: Structure of Methylene Blue

2. Experimental Methods:

Materials:

Methylene blue (Merck), Titanium dioxide and Copper Nitrate solution was used. All the chemicals used are of Analytical Grade. All the solutions are prepared in distilled water.

Preparation of Catalyst:

Cu/TiO_2 catalyst were prepared using Copper nitrate solution and Titanium Dioxide. figure 2 shows the preparation procedure. The amount of Copper loaded onto Titanium dioxide was 5,7,10 and 12 w/w% by using Copper Nitrate as the Cu precursor. The addition of Cu to the support was done by using the impregnation method: appropriate amount of copper nitrate solution was diluted in small amount of water. Then the titanium dioxide was added to the solution and this solution is stirred along with heating at 80ºC with the help of Magnetic stirrer with heater. The solution is then heated at 150ºC for 2 hours in order to remove excess amount of water. Catalyst is then calcined at 500ºC for 3 hours and then allowed to cool down to room temperature to form Cu/TiO_2 catalyst.

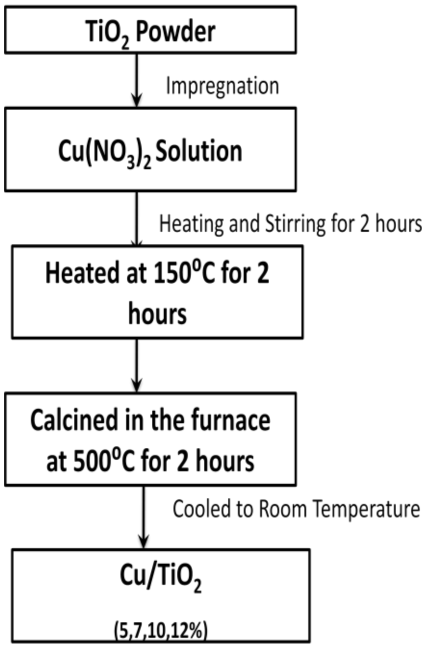

Figure 2: The procedure of catalysts preparation

Characterization:

The crystalline phase of Cu/TiO_2 catalyst was studied by X-ray diffractometer with Cu Kα radiation. A 2θ range of 10º to 90º was scanned with a step of 0.0130. The XRD patterns shows the major peaks at 2Θ = 27.5° which shows the presence of TiO_2 whereas reflections at 36.16º confirms the presence of Cu in oxide phase with the JCPDS data (48-1548). The Fig 2 below shows the XRD analysis results of Cu/TiO_2 catalyst.

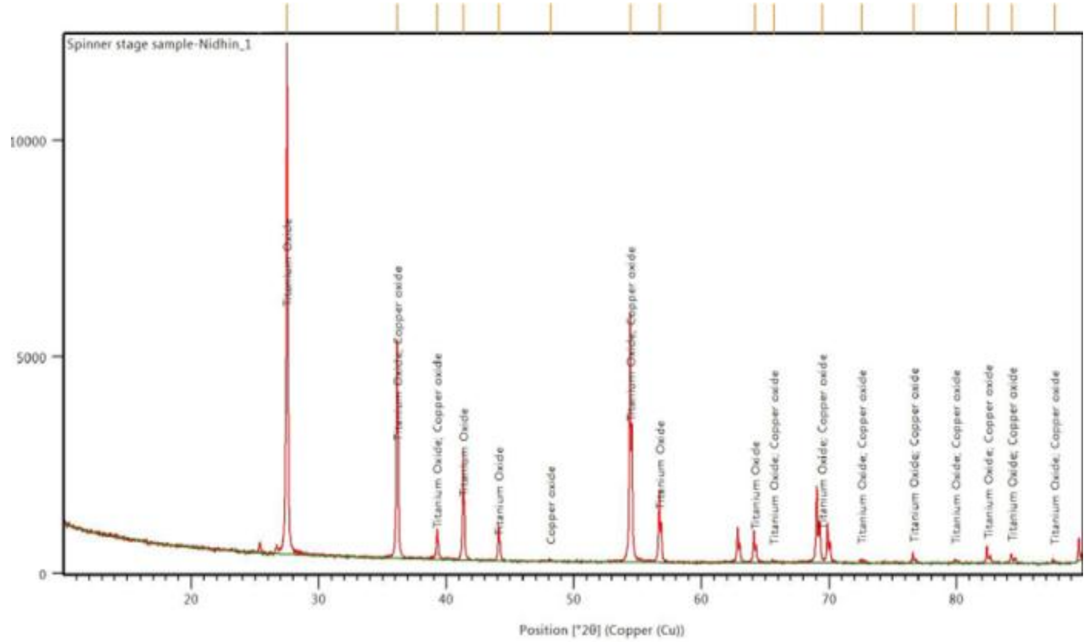

Figure 3: XRD Analysis

HR TEM:

High Resolution Transmission electron microscopy (HRTEM) can give a real space image on the distribution of particles, their surface and shape. With a finely focused electron probe, not only imaging of materials is possible, but also a single particle can be identified. Besides, electron microscopy shows the shape and state of particles. Samples were placed onto a carbon-coated copper grid (400 holes) by physically interacting the grid and powders, and analyzed to see the particles that remained adhered to the grids. Detailed surface images of photo catalyst were obtained by transmission electron microscope (TEM). HRTEM of powder catalyst was performed at 100 kV. It was observed that the mean particle size was 0.24 ± 0.01μm (Figure 4)

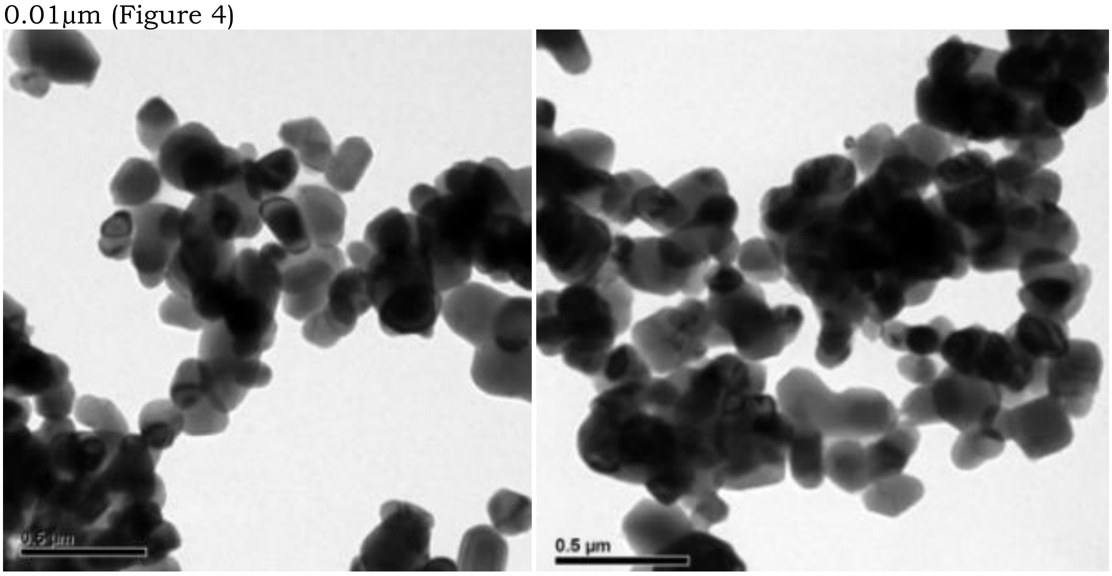

Figure 4: HRTEM images of Cu/TiO_2 Powder

3. Experimental Setup:

Studies were conducted using a Multi Lamp Reactor (UV illumination) which consists of 4 mercury lamps each of 8 W (predominantly wavelength 365 nm). 4 Reactor tubes can be placed in a reactor at the same time for the study. Immersion type photo reactor was used for the study in the visible light which consists of a tungsten lamp of 500W. The spectra were taken with double beam UV-VIS spectrophotometer (AU-2701). Then the same study was conducted on a solar concentrator.

Solar Concentrator Specifications:

Parameter	**Value**
Inner Diameter	38.10 mm
Outer Diameter	41.40 mm
Focal Length	120 mm
Length	300 mm
Aperture Width	200 mm

Table 1: Specifications of Solar Concentrator

4. Procedure and Analysis:

Reactor:

For the degradation experiments, dye solution was prepared as follows: 1000 ml of distilled water was added to 10 mg of dye resulting in formation 10 ppm of dye solution. Now 100ml of this dye solution is transferred into different reactor tubes and to this 250mg catalyst (Cu/TiO_2) of different concentration (5, 7, 10 and 12%) was dispersed. This reactor tubes are the connected with the air heater in order to provide proper mixing. In these experiments 4 reactor tubes are placed at a time. The dye solution of different concentration in the reactor tubes is then placed in the reactor and was then subjected to irradiation under UV lamps. This same procedure is followed for visible lamp reactor. 5ml of the dye solution was taken out at an equal interval of 60 minutes with the help of pipette. The degraded solution was taken for spectra measurement. The absorption spectra were recorded and the rate of degradation was observed in terms of change in absorbance values at λ_{max}=664 nm. The Percentage of degradation was calculated from the following

$$\text{Percentage Degradation} = (A_0-A_t)/A_0 * 100 \qquad (1)$$

Where A_0 the absorbance at time t=0 min

A_t the absorbance after time t minutes

Solar Concentrator:

For the degradation experiments same dye solution is transferred into the copper tube of the solar concentrator then both the inlet and outlet valves of the concentrator is closed. The setup is adjusted in such a way that maximum amount of solar concentration can be achieved. 5ml of the dye solution was taken out from the concentrator after each time interval of 60 minutes. The solution is then taken for spectra measurement, absorption were recorded and the rate of degradation was observed in terms of change in intensity at λ_{max}=664 nm. The percentage of degradation was calculated using the same formula-equation (1).

Figure 5: Solar Concentrator

5**. Results and Discussions:**

Absorption Spectra of MB Degradation. Fig.5 displayed maximum UV-vis absorption at wavelength of 664 nm. The maximum absorption kept the same during the photo degradation progress. This indicated that it was a sign of MB concentration level after degradation. So it was possible to measure the absorbance at 664nm each time, and the resulting data of degradation ratio were valid. The absorption peak of the spectra rapidly decreased with increased time and almost disappeared for 180 min light irradiation. The maximum absorption value and percentage degradation were calculated for both dye solution of both UV reactor as well as visible reactors.

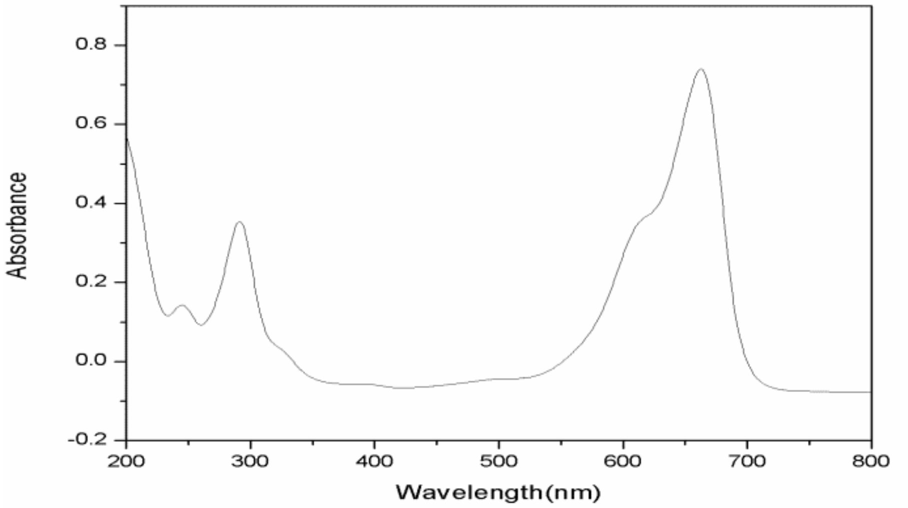

Figure 5: UV-Visible Spectrum of Methylene Blue Dye Solution

Effect of Percentage of Degradation on Different Loading of Catalyst:

UV lamp Reactor: Experiments were carried out in 4 different loading of the catalyst as discussed above. Results for the percentage degradability on multi lamp UV reactor is given in figure 6

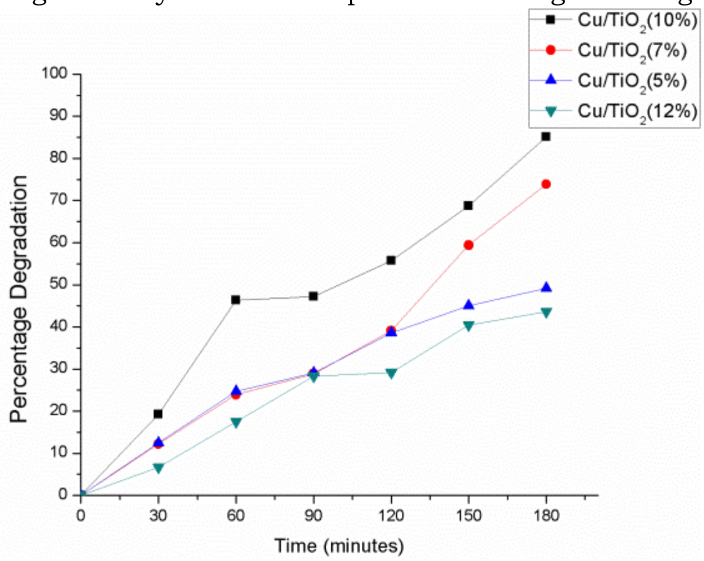

Figure 6: Percentage Degradation in UV Multi Lamp Reactor

The maximum Degradation of 85.14% was achieved for Cu/TiO_2 (10%) catalyst

Visible Lamp Reactor:

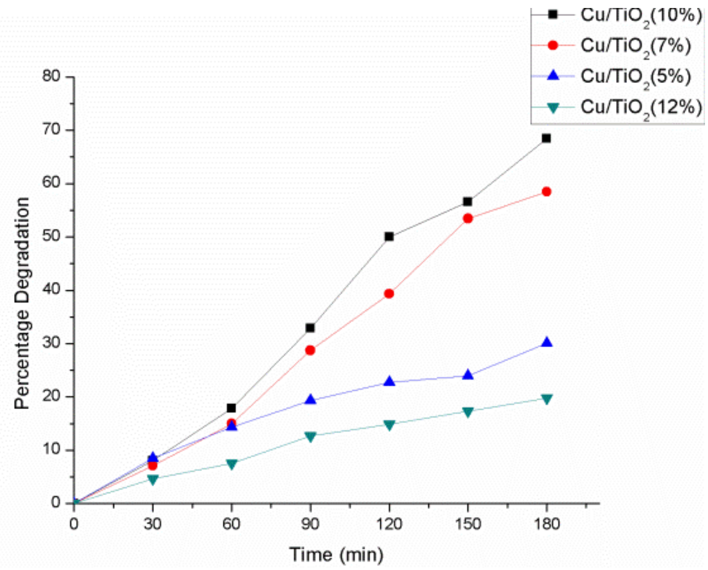

Figure 7: Percentage Degradation in Visible Tungsten Lamp Reactor

Figure 7 shows the percentage degradability of different catalyst in a Visible Tungsten Lamp Reactor. Maximum degradation is achieved for Cu/TiO_2 catalyst and the degradation percentage is 58.50%

Solar Concentrator:

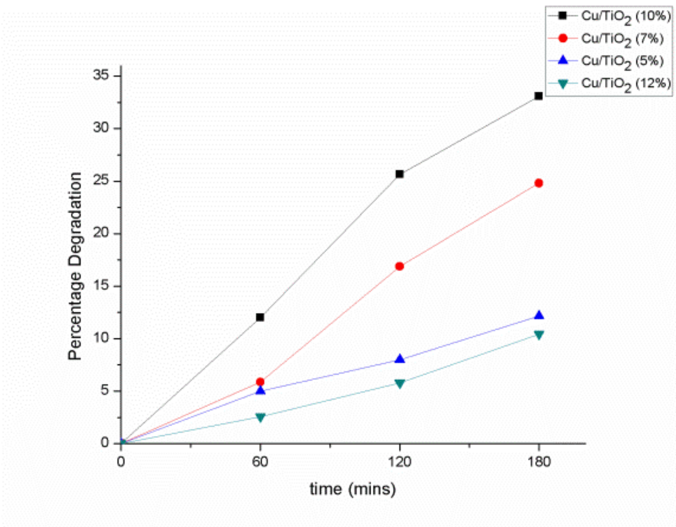

Figure 8: Percentage Degradation in a Solar Concentrator

Figure 8 shows the percentage degradability of different catalyst in Solar Concentrator. Maximum degradation is achieved for Cu/TiO_2 catalyst and the degradation percentage is 33.08%

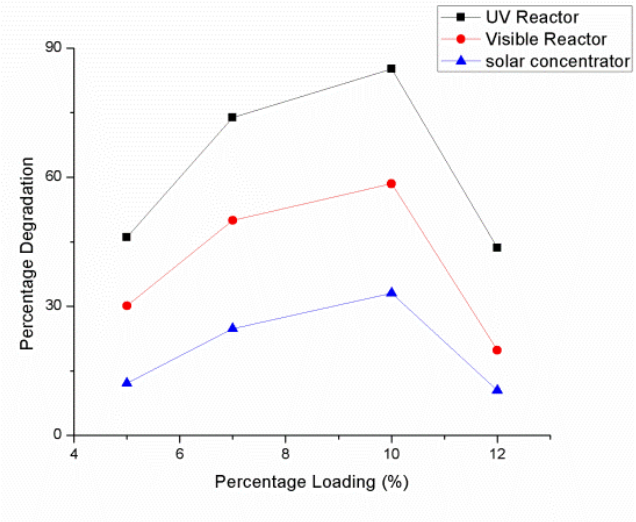

Figure 9: Comparison of Degradability at different catalyst loadings

The graph shows (Fig. 9.) shows the comparison of the percentage degradability on different Catalyst loadings. The results shows the maximum degradability was achieved for Cu/TiO_2 (10%) in all the three cases studied. However maximum degradation was achieved for UV Reactor followed by the Visible Reactor and Solar Concentrator.

6. Electrical Energy Consumption:

The electrical energy consumption of both the Reactors and solar concentrator was calculated and is shown in Table.2.

Reactor	Energy Consumed* (kWh/litre)	Percentage Degradation (%)
UV	704	85.14
Visible	3200	58.50
Solar Concentrator	153.6#	33.08

Table 2: Electrical Energy Consumption

* Assuming Energy consumed for 1 year (320 days, 8hrs/day)

#Energy Received

Conclusion:

Photo catalytic degradation appears to be a promising technology that has many applications in environmental cleanup systems. The photo catalytic degradation of Methylene Blue was examined using Cu/TiO_2 catalyst in UV reactor, visible reactor and also under the solar concentrator. The influences on parameters such as loading of catalyst vs percentage of degradation were studied. The Photo catalytic dye degradation using Cu/TiO_2 catalyst in solar concentrator was proved out be a cost effective method to degrade dye from textile industry into non toxic compounds.

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