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DEGRADATION OF METHYLENE BLUE USING ZNO PHOTOCATALYST FOR WATER PURIFICATION

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ABSTRACT

Current environmental protection concerns the quality of water and air. This strong tendency to want to control the purity of the water leads to the design of sensors. In this work, we study the degradation of methylene blue in the presence of the ZnOphotocatalyst. The photochemical behavior of this molecule depends a lot on the conditions and the nature of the reaction medium; especially the pH of the solution to be degraded and the concentration of the pollutant. We apply the photocatalysis of the dye (at room temperature) under visible light and using a UV lamp. The photocatalytic efficiency was calculated from absorption spectra using UV-visible spectroscopy.

Keywords: ZnO, Photocatalysis, Methylene Blue, Water UV-Visible Spectroscopy.

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1. INTRODUCTION

Water is a vital source for humanity. The population growth and the often uncontrolled management of water resources nevertheless lead to a worrying situation, in terms of quantity and quality. As a result, human activities produce wastewater containing various contaminants (organic matter, nitrogen, phosphorus, micropollutants, minerals and organic ...) inducing a risk for human health and ecosystems [1]. 700 million people across the globe face water scarcity, and it is estimated that this problem will touch 1.8 billion people by 2025 [2].In this situation, the treatment of wastewater for reuse seems to be an encouraging alternative.

The process of photocatalysis [3] is exploited for potential application at water treatment [4]. Photocatalysishas numerous advantages like high efficiency, usage of nontoxic materials and easy environmental friendly working conditions [5].This process is able to destroy the complex chemical bonds of organic or inorganic pollutants to transform them into harmless chemicals using a photocatalyst and light as an irradiation source (Figure 1) [6, 7].

Because the surface of semi-conductor catalyst can be excited under illumination, it can be used to degrade organics, kill bacteria and eliminated peculiar smell [8] by using optical energy in room temperature. Zinc oxide (ZnO)photocatalyst can be applied to eliminate organic pollutant from wastewater [10, 11].ZnO has a wide band gap of 3.17eV. It is capable to generate hydroxyl radicals in sufficient quantity. It is transparent to must of solar spectra. Its form has strong influences on the photocatalytic activity.

In this work, commercial available ZnOis used in the photocatalyticdecolorization and degradation of Methylene Blue (MB); as model water pollutant. The effect of dye concentration and pH of the medium were studied. The photocatalytic performance of ZnO on degradation rate was investigated under both visible light and UV lamp.

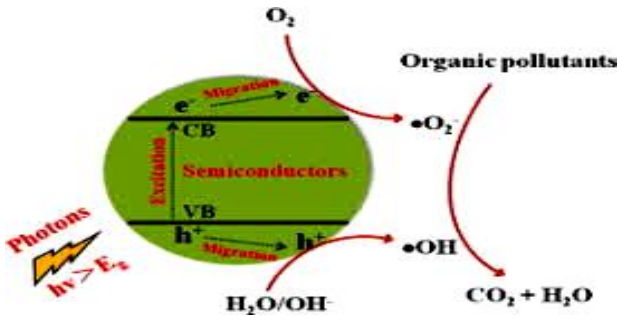

Fig.1. Photocatalysis mechanism[9]

1. EXPERIMENTAL PART

2.1. Materials

2.1.1. Methylene blue (MB)

The molecular formula of MB is $C_{16}H_{18}ClN_3S$.Its IUPAC name is 3,7-bis(Dimethylamino)-phenothiazin5-ium chloride. The structural formula is as shown below in Figure 2. The MB concentration is taken equal to [MB] =5mg/L.

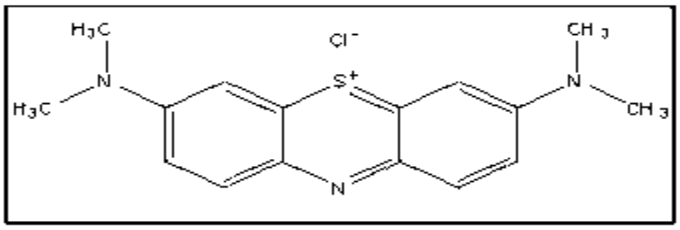

Fig.2. Structure of methylene blue [10]

2.1.2. Photocatytic activity of ZnO

The mechanism of heterogeneous photocatalysis is schematically represented in figure 3. It involves the wide band gap ZnO catalyst.The photogenerated electron moves up to the conduction band while the hole drifts to the bottom of the valence band. Majority of these photogenerated charge carriers undergo wasteful recombination, while escape recombination and initiate redox reactions in molecules adsorbed at the surface of the photocatalyst and thereby degrading them. The photogenerated electrons and holes have been found to degrade almost all types of organic, inorganic, and microbial contaminants [12, 13], owing to their high redox potentials. The fundamental process during photocatalysis is given By Figure 3.

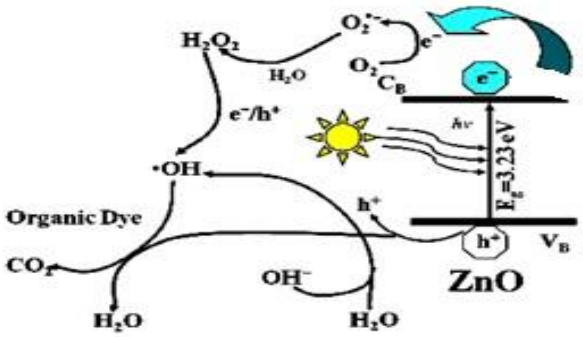

Fig.3. Schematic of ZnOphotocatalytic process

2.2. Apparatus

Studies were conducted using experimental set. It consists of a laboratory photo reactor system, a magnetic stirrer, used to stir the reaction mixture in order to maintain a homogeneous medium, and a UV lamp (wavelength of the source light is 325 nm) put in

closed space (Figure 4). UV light source is use to activates photocatalytic action of Zinc oxide.

Degradation of the dye was studied by measuring the decrease in concentration of dye over a period of time photometrically on UV-VIS parkinelmerspectrophotometer. The spectrophotometer was used to determine the absorbance of MB (maximum wavelength of absorption of MB is λ=664nm).The pH meter equiptronics was used to adjust the pH of the solution.

The following figure shows the reactor for photocatalysis of MB by ZnO.

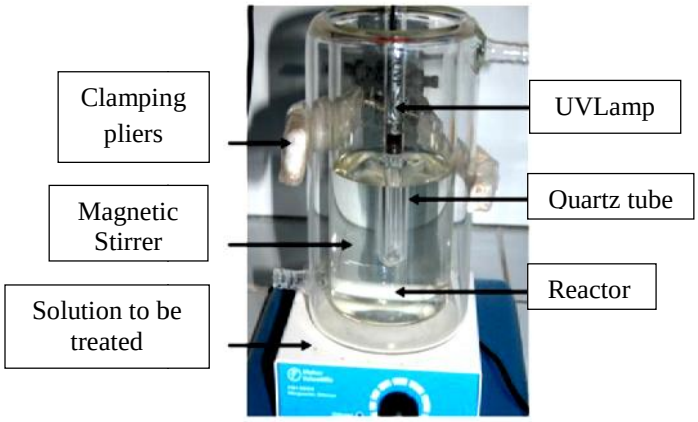

Fig.4.UV/ZnOPhotocatalyst reactor

2.3. Photocatalytic activity tests

The degree of degradation of dyes was evaluated using the following equation:

$$C_t/C_0 = A_t/A_0 \qquad (1)$$

C_t: Concentration of MB in the aqueous solution

C_0: Initial concentration of MB

A_t: Absorbance after time "t" of MB

A_0: Initial absorbance of MB

Thus, the percentage (%) of degradation was calculated from the following equation:

$$\% \text{ Degradation} = (1-A_t/A_0) \times 100 \qquad (2)$$

2. RESULTS AND DISCUSSION

ZnOpowder is efficiently tested as photocatalyst for degradation of MB dye under solar and UV lights. The effect of different parameters such as catalyst loading, dye concentration, solution pH on photodegradation is evaluated.

A. Effect of light radiation

Solar radiation has the advantage of being an inexhaustible energy emitted by the sun, a free source without any toxic effects on our environment. In addition, the two photocatalysts absorb a small percentage of the total sunlight intensity. It would be interesting to investigate the photocatalytic degradation of an aerated MB solution in the presence of ZnO.

When a semiconductor is irradiated with light having energy (E=hv) equal to or more than band gap energy a heterogenousphotocatalytic reaction occurs at the solid solution contact surface. The semi conductor forms a pair valance band (VB) hole and conduction band (CB) electron.The hole generated is capable of oxidizing the substrate and the electron of CB. Figure 5 gives the mechanism.

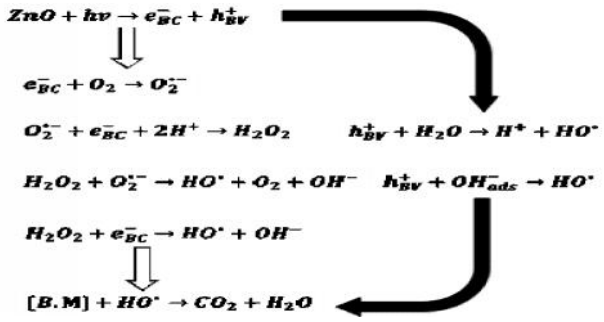

Fig.5. Mechanism of photocatalytic activity of ZnO

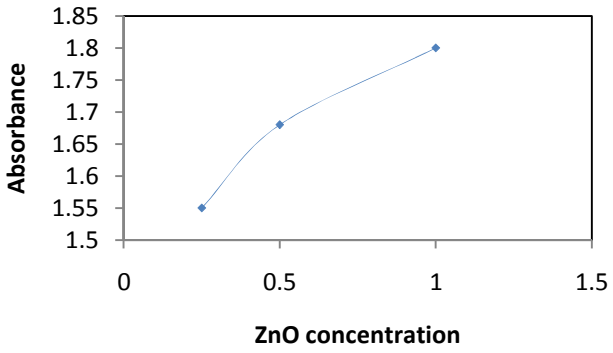

Fig.6. Visible/ZnOdegradation of MB

Degradation of dyes in presence of light (Figure 6) shows degradation kinetics of MB by ZnO under solar irradiation.

The percentage of degradation under intense visible light was 85% and under UV light, it was 98%within 6hour and 15minutes respectively. The effect of light (visible and UV) with respect to % degradation could be observed at higher concentrations of the dyes (not shown here).

The results revealed that the photocatalytic activity increases with increase of the illumination time and reaches to 98% after 15 min illumination time. Such data reveals the relative high activity of the prepared catalysts which enables the complete degradation of the methylene blue in such short illumination time, and the catalyst has active sites for carrying out the reaction [12].

3.1. Effect of pH

pH is an important parameter in the photocatalytic oxidation processes. The effect of the pH on the degradation rate is due to the modification of the electrical double layer of the solid electrolyte interface, which affects the adsorption-desorption processes and the separation of the photogenerated electron-hole pairs in the surface of the catalyst particles [14]. The surfaces of photocatalysts are positively charged in acidic solutions and negatively charged in alkaline solutions [15].To show the effect of pH on MB photodegradation,experiments in solutions at three different pHs were done (to evaluate the effect of ZnO catalyst in acidic and alkaline solutions). The initial pH of dye solution was varied from pH 3-11.From the graph, the pH of dye solution changes from acidic to alkaline; the percentage degradation increases with pH owing to the electrostatic interactions between the negative photocatalyst's surface and the MB cations. This implies that alkaline condition is more favorable for photocatalytic degradation of the dye. It may be due to easy formation of the reactive intermediates that is hydroxyl radicals, which further help in enhancing the photo degradation rate (reaction rate).

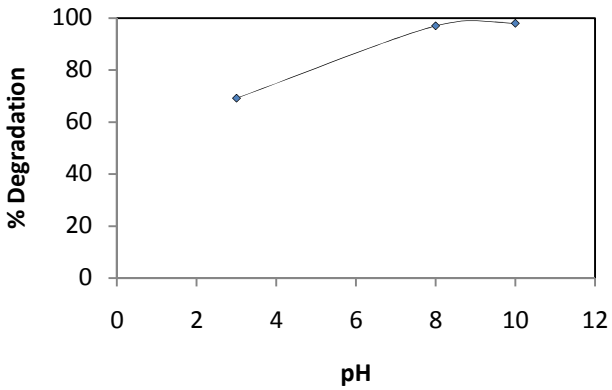

Fig.7. Effect ofpH on MB degradation

3.2. Effect of concentration

The decrease in the concentration was followed by measuring the absorbance of methylene blue at definite periods of time during the photocalysis. The experiment were conducted by

varying catalyst concentration from 1g/L, 0.5g/L and 0.25g/L for the dye solution at pH = 8 (neutral medium) under UV light at ambient temperaturesince this was the material with the best photocatalytic activity.

As shown in figure 8, it can be seen that UV/ZnOphotocatalysis effectively degrades methylene blue. It was found that the dye concentration is decreasing with ZnO concentration. As seen, increasing the initial dye concentration from1 to 0.25g/L decreases the photodegradation efficiency of methylene blue. The photodegradation efficiency is related to the formation of hydroxyl radicals, which is the critical species in the degradation process.Increasing catalyst concentration both the number of dye molecules adsorbed and the number of photons absorbed were increased which promotes the degradation rate. I.e.: more the concentration is higher more the adsorbed organic substances on the surface of the catalyst is higher and the solution became more intensely colored. Therefore, there are only fewer active sites for adsorption of HO^- so the generation of HO• will be reduced [16-18]. Since the most effective decomposition of methylene blue was observed with [ZnO] =0.5g/L it wasfaster than the other concentrations. The efficiency was 98% in 15 mn.

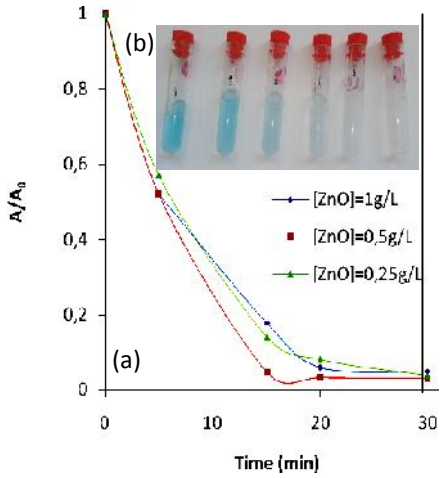

Fig.8. Comparative removal of MB over time

(a) : Photodegradation of MB dye solution under UV light radiation with respect to time

(b) : Color changes effect vs time

3. CONCLUSION

The photocatalytic activity of the metal oxides depends on various factors including composition, phase structures, surface hydroxyl groups, and adsorbents.

ZnOmaterial is an attractive candidate for photocatalyticwater treatment. Under the solar light, photocatalysis demonstrates to be technically feasible but slow. As far as UV lighting is concerned, ZnO has a better photocatalytic activity. The most efficient decomposition of methylene blue is observed for the concentration [ZnO] =0.5 g/L; it is faster than the other concentrations. The MB efficiency is 98% in 15mm. degradation is also, most effective at neutral pH.

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