

Comparative Study On The Photocatalytic Degradation Of Malachite Green Using Zinc Oxide Under Different Sources Of Radiation

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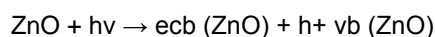
Abstract: Commercial ZnO was used as a catalyst for the degradation of malachite green in aqueous solution. The catalyst was tested under different light sources (dark, visible lamp and solar radiation). The photocatalytic degradation efficiency of the catalyst for the adsorbed malachite green was found to be higher effective (88%) under solar irradiation than visible irradiation (80%) considering both at the same time of irradiation. The photocatalytic degradation efficiency of the catalyst for the adsorbed malachite green in dark was found to be least effective. This implies that ZnO can use for degradation of organic pollutants simply in the presence of sun light.

Keywords: Advanced oxidation processes, irradiation source, Photocatalysis, Zinc Oxide

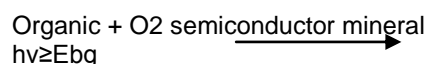
1. INTRODUCTION

Environmental pollution worldwide is proposed to be the greatest problem that chemical scientists will face in the 21st century and an increasing number of scientists are looking for new systems to solve this problem [1]. The chemical industries make products with much beneficial usage; however, they do also have negative impacts on human health and the environment. They release hazardous, calcitrant and toxic chemical substances such as phenol compounds, high molecular weight polymeric surfactants, herbicides and pesticides from industrial wastewater effluent which are well known to be not easily biodegradable [2]. Traditionally, industrial wastewater treatments for these effluents include different techniques such as biological treatment, reverse osmosis and activated carbon adsorption. These techniques often utilize potentially hazardous or polluting materials and even most of them are non-biodegradable. Therefore, the development of an effective treatment technique that can convert pollutants into non-toxic or less harmful materials is highly required. In recent years, there has been the emergence of voluminous literatures on the development of novel effective photocatalytic processes for the treatment of industrial wastewater effluents and municipal wastes that contain toxic and recalcitrant pollutants. Photocatalysis is among the rapidly evolving and efficient technologies for purification of water. With this approach, harmful organic compounds are broken down in the presence of catalyst and ultraviolet (UV) irradiation without generating secondary harmful pollutants [3]. Photocatalysis can be defined as the acceleration of photoreaction in the presence of a catalyst. Photocatalysis in general, heterogeneous Photocatalysis in particular is a rapidly evolving and efficient technology for water and air treatment [6]. Photocatalytic degradation process can be defined broadly as an aqueous phase oxidation process, which is based primarily on the attack of the hydroxyl radical, resulting in the destruction of the target pollutant or contaminant [7]. Photocatalysis reactions are activated by the absorption of photons with sufficient energy (equals or higher than band gap energy) of the catalyst [8]. The absorption of the photon

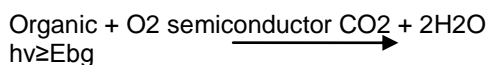
leads to the charge separation due to promotion of an electron (e⁻) from the valance band of the photocatalyst to the conduction band, thus generating a hole (h⁺) in the valance band as in the following reaction (equation i):



In recent years interests has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidize the organic and inorganic substrates [4]. In this context, it is of fundamental importance that semiconductors enable efficient light-induced generation and separations of charges which can subsequently undergo reduction-oxidation reactions with substrates induce a photocurrent. With illumination of semiconductor photocatalysts such as ZnO whose energy is equal to or higher than their band gap energy, absorption of these photons occurs and the bulk of electron-hole pairs generates. These electron-hole pairs dissociate in to free photoelectrons (e⁻) in the conduction band and photo-holes (h⁺) in the valance band. The overall photo mineralization of semiconductor photocatalysis for water and air purification can be summarized by the following equations: Semiconductors such as ZnO, TiO₂, Fe₂O₃, ZnS and WO₃ have been known to possess Photocatalytic character [4]. Among them, zinc oxide has been extensively studied throughout the world and considered as reference photocatalyst in the degradation of organic pollutants, sewage treatment, air purification and disinfection due to its superior photocatalytic performance, non-selective degradation of various organics, deep mineralization rate, and low cost, inert and non-toxic properties [5].



The other thermodynamically favored photo mineralization reaction:



Therefore, the proposed project was aimed at studying the efficiency and impacts of irradiation source on the photocatalytic efficiency of ZnO for photodegradation of malachite green in aqueous solution.

2. MATERIALS AND METHODS

2.1. Experimental Site

The experiments were carried out at Adigrat University research Laboratory.

2.2. Equipment and Apparatus

The equipment and apparatus used in this study were: UV/vis spectrophotometer, glass reactor, and lamp (TORCH 40W) as source light, solar radiation, centrifuge, magnetic stirrer, and analytical balance.

2.3. Chemicals and Reagents

In this study the following chemicals were used: commercial Zinc oxide (ZnO) (scientific park, N.Y, U.S.A.), Malchite green [(C₂₃H₂₅N₂)₂3C₂H₂O₄] (MW. 929 g/mol. 1, BLULUX), and distilled water. All were analytical grade and used with no further purification.

2.4. Experimental Methods

2.4.1. Photocatalytic degradation experiment

Photocatalytic degradation of Zinc Oxide was carried out in a reactor tube made of glass with an effective volume of 500 ml and having an internal diameter of 8 cm with provision for air purging during photocatalysis and an outlet for the collection of samples from the reactor. A known amount of commercial photocatalyst (0.5 gram) and 150 ml of malachite green (50 ppm) was taken in a reactor tube with a capacity of 500 ml and the suspension was stirred in dark for one hour in each experiment to obtain adsorption equilibrium before illumination of the reactor. Prior to illumination of the sample by visible or by solar radiation air (oxygen) was purged using hand purge into the solution in order to have homogeneous composition. During the reaction, the solution was maintained at room temperature and the distance of the lamp from the solution was kept to 9 cm. 10ml of the sample was withdrawn each time at 20 minutes time interval for over the irradiation time of 2 hours. The suspension was centrifuged at 3500 rpm in order to settle down the catalyst particles at the bottom of the test tube before analysis. The absorbance of the clear solution was measured at a λ max of 450 nm for quantitative analysis using certain amounts of catalysts. To check whether the malachite green is easily degradable or not, blank experiment (without addition of any catalyst) has also been done. Photocatalytic degradation experiment was conducted using the commercial zinc oxide (ZnO) Different source of radiation may have different efficiency as they have different intensity and wave length. The percentage degradation of the catalyst was measured and the percent absorption was calculated for each case using the following equation

$$\text{Adsorption (\%)} = \left[\frac{A_0 - A_t}{A_0} \right] \times 100$$

Where, A_0 is the initial absorbance of the degraded solution and A_t is the absorbance of the solution after degradation

3. RESULTS AND DISCUSSION

Commercial ZnO was used as a catalyst for the degradation of malachite green in aqueous solution. The catalyst was tested under different light sources (dark, visible lamp and solar radiation).

3.1. Blank Experiment

Since there are various dyes which are degraded when exposed to direct visible light or solar radiation in a short period of time even without the presence of catalyst, initial investigation ("blank" experiment without addition of any photocatalyst on to the solution of malachite green) was done in order to determine whether the MG solution is resistant to degradation under Visible and solar irradiation or not. However, insignificant changes were observed for the duration of 120 minutes (< 10%) both under solar and visible light sources. This showed that the organic compound in the solution was very stable and do not have self-destruct mechanism even if it was irradiated under the light sources for 2 hours [18]. The result obtained is given in the following Table1.

Table 1: degradation of MG without catalyst under visible irradiation

Irradiation time in minute	% of degradation
20	2.3
40	3.4
60	7.4
80	8
100	8.5
120	9.2

3.2. Degradation of MG under Dark

Dark experiment has also been done to know the degree of photodegradation of adsorption of MG over the studied photocatalyst under non-irradiation. From the result given in table2 it is possible to understand that the dye can be absorbed by the catalyst and the adsorption efficiency can also be reached up to 30%. But this is not degradation because there was no irradiation.

Table2. Degradation of MG in the presence of catalyst under dark condition

Irradiation time in minute	% of degradation
20	18
40	23.3
60	24.69
80	26.6
100	28.3
120	30

3.3. Degradation of MG under the Visible Light Irradiation

0.5 gram of commercial ZnO photocatalyst and 150 ml of malachite green (50 ppm) was taken in a reactor tube with a capacity of 500 ml and the suspension was stirred in dark first. Then it was subjected to visible light source lamp and the photocatalysis reaction (degradation) was continued for 2 hrs and the following results were recorded.

Table 3. Degradation efficiency of ZnO for removal of MG under the visible light irradiation

Irradiation time in minute	% of degradation
20	41.13
40	49.9
60	59.4
80	73.3
100	75
120	80

This phenomenon can be explained by the light scattering caused by the light proof catalysts, indeed with increasing time the light penetration through the solution and hence the photoactivated volume of the suspension shrinks (Epling and Lin, 2002) and degradation efficiency increase.

3.4. Degradation of MG Under the solar Irradiation

0.5 gram of commercial ZnO photocatalyst and 150 ml of malachite green (50 ppm) was taken in a reactor tube with a capacity of 500 ml and the suspension was stirred in dark first. Then it was subjected to solar radiation source and the photocatalysis reaction (degradation) was continued for 2 hrs and the following results were recorded.

Table 4: Degradation efficiency of ZnO for removal of MG under solar irradiation

Time (min)	%DE orA%
20	40.6
40	55.8
60	69
80	86.9
100	87
120	88

This phenomenon can be explained by the light scattering caused by the light proof catalysts, indeed with increasing time the light penetration through the solution and hence the photoactivated volume of the suspension shrinks [12] and degradation efficiency increase. But the relative degradation efficiency is highest than the other irradiations. This may be due to highest energetic radiation the solar source [9].

CONCLUSION

In this project paper, commercial ZnO has been used as a photocatalyst for the photo-degradation of malachite green. The efficiency of the catalyst was compared under three conditions of irradiations i.e. under dark, visible lamp source and solar radiation. The relative degradation efficiency of the catalyst was found to be highest under solar radiation (.....) than under the other sources. Therefore, knowing the best irradiation source is of paramount importance from the design and time conservation and economical points of view as these could affect the degree of degradation efficiency of catalysts.

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