Photocatalytic Degradation of Methyl Orange Under UV Using ZnO as Catalyst

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Abstract— Discharge of azo dyes by textile and allied industries to the environment is a growing problem. Research on photocatalytic degradation rate of azo dye such as methyl orange using ZnO in photocatalysis process was the main goal of present study. In this regard, the influence of the main operating parameters such a photocatalyst concentration, dye concentration, and temperature upon dye removal rate under UV irradiation was studied. The composition of catalyst was varied to achieve the best photocatalytic performance. The absorbance of samples was measured by a UV–Vis spectrophotometer. The results reveal that ZnO has high and significant photocatalytic activity and suitable alternative to TiO_2 as photocatalyst. The best reaction dosage of ZnO catalyst was about 0.25gm per 50ml. It was found that about 99.7% removal of the dye could be achieved in 180 mins. The results will be useful for designing the treatment systems of wastewater containing various dyes.

Key words: Photocatalysis, Methyl orange, ZnO, Irradiation, UV-Vis spectrophotometer.

1 Introduction

Environmental problem of toxic wastewater and infected waters is one of the main subjects that researchers work on. Due to this, organic dyes are one of the main industrial wastewater pollutions. More than 50% of textile dyes is azoic dyes such as methyl orange which are recognized by nitrogen π-bound [1-2]. Of the total world production of dyes, up to 20% is lost during industrial processing, causing environmental pollution and contributing to eutrophication that affects aquatic life [3]. Current methods used to treat these effluents are mainly physicochemical, causing a disposal issue for the sludge residue. For example, chemical precipitation and separation of pollutants, electrocoagulation and elimination by adsorption do not destroy the contaminants: they only transfer them to solids which are primarily disposed of into landfills [3]. Applying nanotechnology to dye degradation shows great potential, as nanoparticles can chemically react with the dyes to form non-toxic products that may require no removal [4]. Photocatalysis is a technique utilizing nanotechnology under thorough study now [5-7]. The process of photocatalysis is powered by photons that match or exceed the band gap energy of a given semiconductor. An electron in its valence band (VB) is excited to the conduction band (CB), leaving a positive hole in the VB that forms a hydroxyl radical with the hydroxyl ion in water, which is then available for oxidation. Meanwhile, the excited electron reduces oxygen in the CB, which can also act as an oxidizing agent [8]. However, the photogenerated electrons are unstable in the excited state, thus can easily recombine to their respective holes. This process dissipates the input light energy and results in low-efficiency photocatalysis. Therefore, the development of a more efficient photocatalyst is an important consideration [8-10].

Zinc oxide (ZnO) is a promising candidate as a photocatalytic material since it exhibits higher photocatalytic efficiencies for the degradation of organic contaminants [11–13] compared to other metal oxides including TiO_2 [14–17]. Catalyst surface area is an important factor to enhance photocatalytic activity of metal oxides [18–19]. Larger effective surface area leads to a higher adsorption of organic molecules leading to a better photocatalytic activity. The aim of our work is to synthesize ZnO catalyst with higher photocatalytic activity, and MO was adopted as a compound to evaluate the photocatalytic performance of ZnO catalyst. MO has poor stability and low volatility. The degradation process was monitored by UV-Vis spectrometry.

2 Materials and Methods

2.1 Reagent

All the chemicals were of analytical grade and purchased from Sigma Aldrich. A known dye concentration was prepared in distilled water and used as the stock solution for all studies.

2.2 Research Location

All of the experiments were carried out at laboratories of Applied Chemistry and Chemical Engineering (ACCE) Department of Noakhali Science and Technology University (NSTU).

2.3 Experimental Procedure

The photocatalytic efficiency of the ZnO catalyst was tested by measuring the photocatalyzed discoloration rate of MO in aqueous solution. So the experiment for photodegradation of MO solution under the near-UV light source was first set up. Samples of degraded MO solutions were taken after different time intervals and their absorbance were measured by the UV-Visible Spectrometer at 465 nm, at different times in order to study the degradation of the methyl orange.

2.4 Analytical Method

Stock solution of methyl orange dye (5×10^{-5}M) was prepared in distilled water. It was further diluted as and when required.

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The photocatalytic degradation of MO dye was studied after addition of catalyst (0.05gm, 0.1gm, 0.25gm of ZnO) in 50 mL dye solution (0.05m M). Irradiation was carried out in wooden photo reactor. Cooling water bath was used to minimize thermal effect. The whole setup was kept in dark and allowed ZnO to suspend in the MO solution for 30 min for physical adsorption. Initial concentration of MO, in term of light absorbance, was measured by UV-Visible spectrometer at 465 nm. The whole solution was exposed to UV light by using 4 X 20 W UV lamp under constant stirring. After a given irradiation time, about 2 mL of the mixture was withdrawn and the catalysts were separated from the suspensions by centrifugation (at 13000 rpm). This degraded solution was taken for absorbance measurement. Before the measurement, a calibration curve was obtained using the standard MO solution with a series of known concentrations.

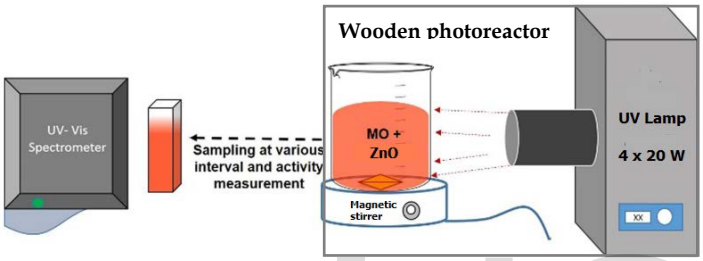


Fig. 1 Experimental set-up. A scheme showing ZnO mixed with methyl orange (MO) dye. The solution was exposed to visible light (source: UV lamp, 4 X 20 W).

The decolorization and photocatalytic degradation efficiency have been calculated as:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where, C_0 and C_t correspond to the initial and final concentration of dye before and after photo-irradiation.

In order to study the degradation kinetics, a pseudo first order kinetic model was used. The general rate equation is given as:

$$-dC/dt = k.C.C_{OH^*}$$

Where, C represents the methyl orange concentration and C_{OH^*} represent the hydroxyl radical concentration.

By the pseudo-stationary hypothesis (i.e. the C_{OH^*} can be considered to be constant because of the continuous hydroxyl ion generation by photocatalysis and the rate depends only on methyl orange concentration), hence the rate expression can be written as:

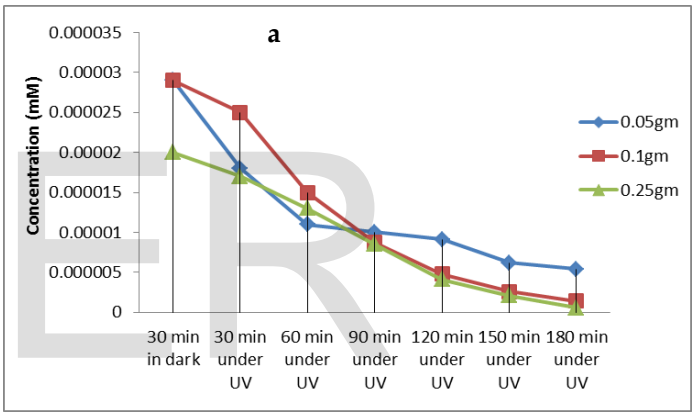
$$-\ln(C/C_0) = kt$$

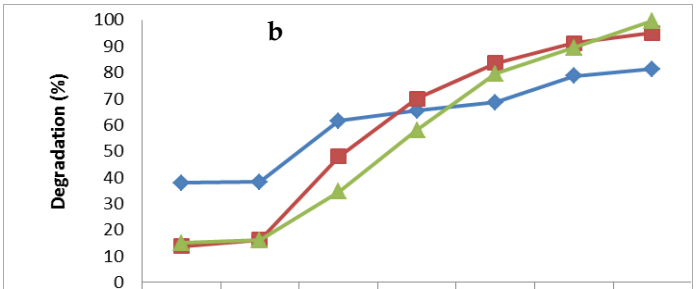
3 Results and Discussion

The photocatalytic treatment using ZnO catalyst was employed for the effective degradation of Methyl Orange dye solution in photo reactor at 298 K. The photocatalytic experimental effects are discussed below-

3.1 Effect of Photocatalyst Concentration

In photocatalyst process, one of the main parameter of discoloration of dye solution is photocatalyst concentration. To study the effect of catalyst loading on the photodegradation of MO, experiments were carried out by varying the amount of ZnO. The changes in the concentration of MO aqueous solution under visible light irradiation in the presence of ZnO are illustrated in Fig. 2 (a). It has been found that concentration lowers with time passed, which indicates that the catalyzed dye present in solution is removed subsequently under action of UV light. The observation also indicates that dark condition is also required for an effective degradation of dye. Fig. 2 (b) showed that by increasing ZnO concentration, degradation of dye was increased. It was observed that percentage of MO degraded after 180 min increased from 81.4 to 99.7% with increase in catalyst loading from 0.05–0.25 g/L. This occurs for two reasons, first of all there is more radiation intensity and the second one is lower wavelength that resulted in electron exiting of materials.





	30 min in dark	30 min under UV	60 min under UV	90 min under UV	120 min under UV	150 min under UV	180 min under UV
0.05gm	37.9	38.4	61.5	65.4	68.6	78.7	81.4
0.1gm	13.8	16.3	48.1	70.1	83.6	91.1	95.1
0.25gm	15	16.2	34.7	58	79.5	89.5	99.7

Fig. 2 Photodegradation of MO with ZnO (at different load) as a function of time (a) concentration, mM; (b) degradation, %.

3.2 Effect of Catalyst Loading on Reaction Rate

The change of rate constant with change in catalyst loading is shown in Fig. 3. It can be seen that the rate constant increased with the increase of catalyst load and then decreased. The increase in rate constant with the increase in amount of ZnO is

due to an increase in number of active sites on photocatalyst surface. The reduction in the rate constant when the catalyst amount is increased above 0.25g is due to light scattering and reduction in light penetration through the solution. With higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates the reaction, thus reducing the rate of reaction.

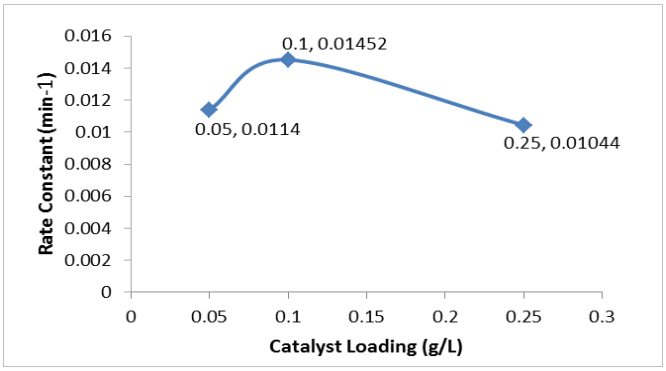


Fig. 3 Variation of rate constant with catalyst loading.

There is very slight fluctuation in case of lower catalyst amount. In this case the reaction kinetics can easily be predicted. The calculated value was based on first order kinetics rate equation. Maintaining regularity on k values ensure that kinetics is of first order type.

4 Conclusions

Heterogeneous photocatalysis process is eco-friendly way to reduce the pollution load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatment, in the presence of biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoids transfer of pollutants from one phase to another. Methyl orange dye has been successfully degraded in the presence of ZnO photocatalyst. The results obtained in the present study show the efficiency of AOP's in removing dyes, this process has proved its superiority to other conventional methods of wastewater treatment, in the presence of biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoids transfer of pollutants from one phase to another. It was observed that catalyst dosages significantly affect the photo catalytic degradation of MO. The Results of the study indicate that ZnO is very effective & suitable alternative to TiO_2. The best reaction dosage of ZnO catalyst is about 0.25gm/50ml. The maximum degradation efficiency of dye was achieved with the combination of UV in the presence of ZnO. Hence, it can be concluded from the observations that photocatalysis under UV can be suitably and cost effectively employed for the degradation of dyes effluent with little more retention time.

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Competing Interests

The authors declare that they have no competing interests.

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