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Enhanced Photodecoloration of Metanil Yellow Dye By ZnO in Presence of Beta Cyclodextrin in Aqueous Solution

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Abstract: Enhancement of photodecoloration of Metanil yellow by ZnO in presence of Beta cyclodextrin (β -CD) was investigated under UV light. The factors influencing the photodecoloration of Metanil yellow such as the initial concentration of the dye, pH of dye solution, amount of catalyst and illumination time were studied. It was observed that the rate of photodecoloration of MY in aqueous solution was enhanced in presence of β -CD. The inclusion of MY in to hydrophobic cavity of β -CD was investigated through UV-Visible spectroscopy. The interaction of β -CD with the surface of ZnO was analyzed by XRD, UV-DRS, FT-IR and PL spectra. The kinetics of photodecoloration by ZnO and ZnO- β -CD was tested with Langmuir-Hinshelwood mechanism.

Key words: Metanil yellow, enhancement, β -CD, photodecoloration.

1. Introduction

Zinc Oxide is used as an effective candidate for the heterogeneous photocatalytic processes. It possesses many advantages like photoactive, inexpensive, non-toxic, photostable, commercially available and chemically inert[1]. Every day large amount of unreacted dyes and dye intermediates are discharged into the aquatic systems from various industries such as paper, textiles, inks, varnishes and paints without processing. These contaminants result in high BOD, COD, toxicity, bad smell and coloration of water effluents[2]. The presence of color and its causative compound are undesirable for domestic or industrial uses as color is visible and can be an indication of pollution[3]. Hence, the decoloration and mineralization of waste water have received an increased attention. Several methods for treating waste water have been developed. The dye effluents can be treated by some traditional methods such as biological methods, flocculation, reverse osmosis, adsorption on activated carbon and ion exchange method[4]. These methods transfer the pollutants from one phase to other phase. Heterogeneous photocatalysis is a promising advanced oxidation technique applied for the degradation and mineralization of pollutants such as organic compounds, dyes and fertilizers that are very difficult to remove by conventional methods[5]. Hence, in recent years, researches on semiconductor photocatalysis for the remediation for the removal of pollutants have grown dramatically.

In general, when the semiconductors are irradiated with the light having energy higher than its band gap, electrons from the valence band are excited to conduction band and an equal number of holes are produced in the valence band. Some of these photogenerated holes and electrons move to the semiconductor surfaces and they undergo redox reactions with suitable substrates. The trapped holes react with chemisorbed water or surface hydroxyl species and produce OH free radicals. The electrons in the conduction band reduce the oxygen

molecules to superoxide ions $O_2^{\cdot -}$ which are in turn converted to OH^{\cdot} free radicals[6]. These free radicals are responsible for the photooxidation of the pollutants adsorbed on the surface of the semiconductors. The energy gap of ZnO is ~ 3.2 eV. Therefore, to trigger the photocatalytic property of ZnO, light having energy in the UV region is required. Another drawback of ZnO is its high rate of recombination of photogenerated electrons and holes. Efforts have been taken to prevent the recombination and enhance the photocatalytic activity through modification with doping[7]. Although doping of metals or non-metals into metal oxide could promote the visible light activity, it can also cause thermal instability, crystal instability and increase in charge carriers trapping which may reduce the photocatalytic efficiency[8]. Therefore, design and synthesis of novel photocatalysts are becoming a quest in the photocatalytic field.

β -Cyclodextrin is a doughnut shaped oligosaccharide composed of seven glucopyranose monomer units with hydrophobic inner cavity and hydrophilic outer ring. Through non-covalent interactions, β -CD can form host-guest inclusion complexes with organic compounds both in solid and liquid phases and thus β -CD can increase their solubility and reduce their toxicity. Also they improve the photocatalytic decomposition through charge transfer from the photoexcited semiconductor surface to electron acceptors (guests) included in the hydrophobic cavity[9,10]. MY is an acidic dye with azo group. It is used in many industries for dyeing silk, paper, leather etc. Generally azo dyes are highly stable and resistant to heat, light and oxidizing agents.[11].

In this paper, we report an enhanced UV light driven photocatalytic removal of MY in aqueous solution by ZnO in presence of β -CD. We have confirmed the interaction of β -CD with ZnO and MY through XRD, UV-DRS, PL spectra and UV-Visible spectra. The effects of initial concentration of the dye, initial pH of MY solution, the amount of ZnO and illumination time were investigated.

2. Experimental

2.1 Materials

The commercial organic dye Metanil Yellow (MY) was received from Loba. ZnO was purchased from Merck chemicals. β -CD was received from Himedia chemicals. All other chemical were used without further purification. Millipore water was used throughout the study to prepare all experimental solutions.

2.2 Experimental set up for degradation of MY under UV light

The photocatalytic experiments were carried out by employing Heber Mullti Lamp photoreactors (HM MP 88). The photoreactor consists of 8 numbers of 8 W Mercury lamps (Sankyo, Denki, Japan) as UV light source ($\lambda_{max} = 365$ nm) and highly polished anodized aluminum reactor. Four numbers of cooling fans are mounted at the bottom of the reactor to dissipate the heat generated during the experiment. The reaction vessels are borosilicate glass tube of 12 mm diameter and 30 cm length.

2.3 Photocatalytic experiment

The stock solution of the dye was prepared with a concentration of 1 g / 1000 ml and was diluted to desired concentration. The reaction solution containing dye and ZnO with and without β -CD were stirred for 30 minutes in dark to ensure the adsorption-desorption equilibrium. The reaction solutions were adjusted to desired pH value with HCl or NaOH. The reaction solutions are not supplied with air and are magnetically stirred during illumination. The batch type photocatalytic reactions were carried out. At different time intervals the reaction solutions were withdrawn and centrifuged. The absorbance of the supernatant solutions was measured for the determination of concentration of remaining dye using UV-visible spectrophotometer. The concentration of the dye in the sample was calculated from standard calibration curve. The percentage of removal was estimated using the equation,

$$\text{Percentage of Removal of dye} = (C_i - C_f) \times 100 / C_i$$

where, C_i and C_f are respectively, the initial and final concentration of MY dye at different time intervals respectively.

2.3 Investigation of interaction of β -CD

To understand the interaction of β -CD with ZnO the suspension containing ZnO and β -CD were stirred for 30 minutes and centrifuged to separate the solid. The solid was dried by slow evaporation at room temperature

and were characterized by XRD, SEM and UV-DR spectra. The host-guest interaction of β -CD with MY dye molecules was studied by UV-Visible spectrometer (Model: Schimadzu, 2400 series).

3. Results and discussion

3.1 Characterization of ZnO - β -CD

X-ray powder diffraction patterns of ZnO and ZnO - β -CD are presented in fig 1. All the diffraction peaks of ZnO showed that the ZnO conserves its crystalline features. But the full wave half width maximum of ZnO - β -CD was slightly increased (from $2\Theta = 0.131$ to 0.139) and therefore the average particle size also gets decreased. This decrease in particle size increases the surface area. The UV-visible Diffused Reflectance spectra of ZnO and ZnO - β -CD are recorded with Schimadzu UV2400 pc series. The percentage of reflection was converted to absorbance by Kubelka-Munk formula[12]. The band gap value of ZnO - β -CD (3.28 eV) was reduced than bare ZnO (3.30 eV). This is attributed to the ligand to metal charge transfer (LMCT) between β -CD and Zn^{II} [13].

The SEM images of ZnO and ZnO - β -CD are shown in fig.2. It was observed that the particle morphology of ZnO - β -CD has markedly varied from ZnO.

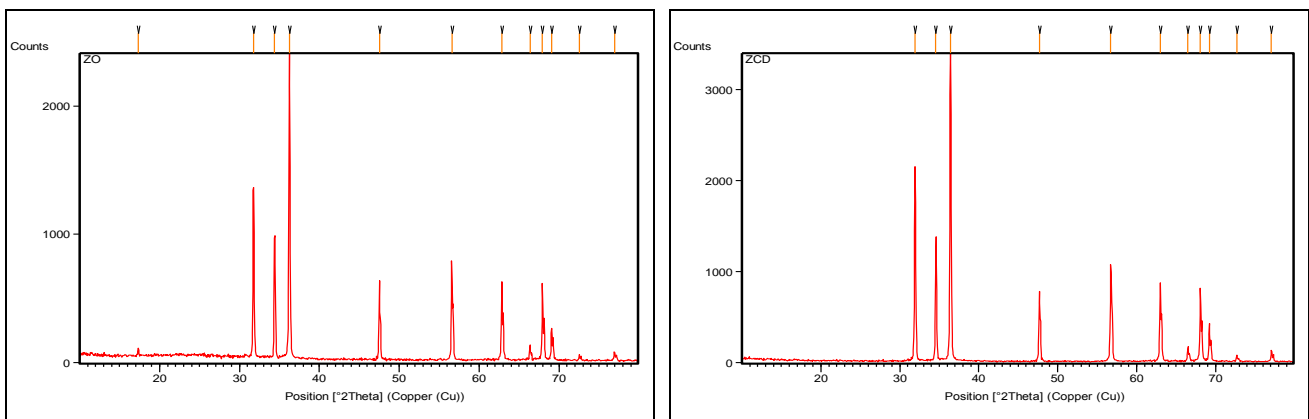


Fig1: XRD of bare ZnO(left) and ZnO - β -CD (right)

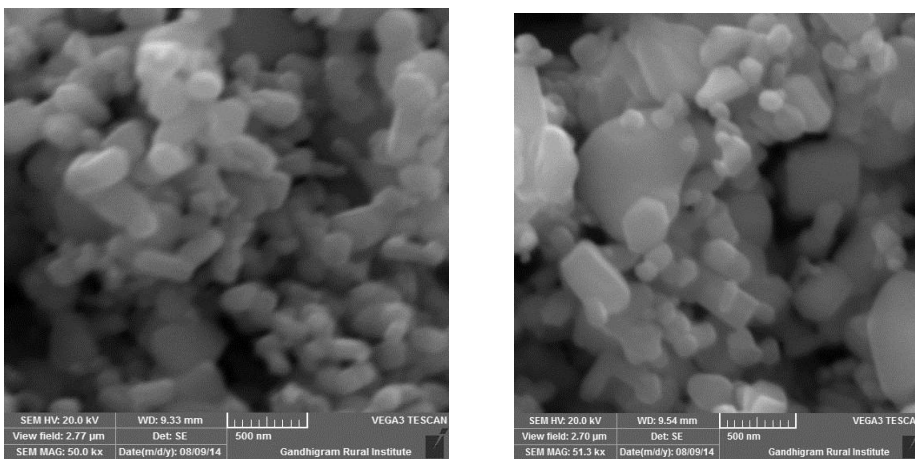
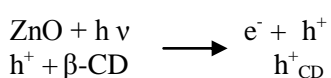


Fig 2: SEM images of bare ZnO(left) and ZnO - β -CD (right)

Fig.3 displays the PL spectra of ZnO and ZnO - β -CD respectively. It was found that the PL intensities of the ZnO - β -CD were decreased compared to the bare ZnO. This indicated that electrons – holes (e^-/h^+) recombination was very much reduced in the ZnO - β -CD which favors more photocatalytic behavior. The reaction of β -CD with ZnO surface is shown below:



Thus β -CD is highly reactive in scavenging the holes formed on ZnO. Hence it helps in reducing the e^-/h^+ recombination[14].

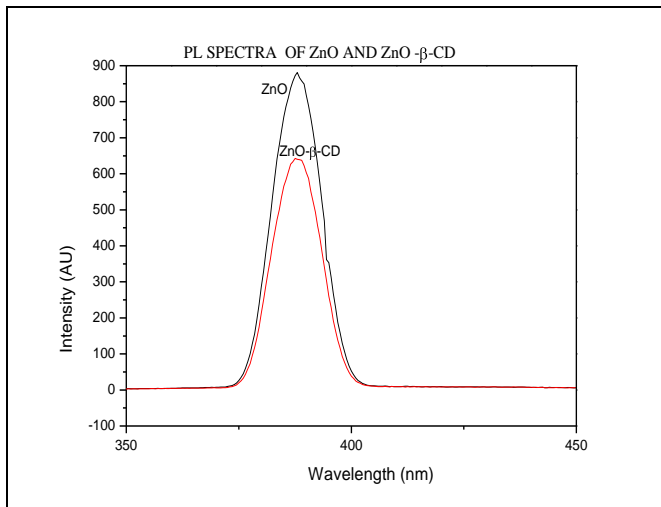


Fig 3: PL spectra of bare ZnO and ZnO - β -CD

3.2 Determination of formation constant for β -CD-MY inclusion complex

β -CD can form host-guest complex with MY dye. The host-guest inclusion complex was characterized by UV-Visible spectra. Fig.5 shows the UV-Visible spectra of β -CD-MY inclusion complexes. It was observed that maximum absorbance value increases with increase in concentration of β -CD. As the MY dye molecule included into the hydrophobic cavity of β -CD, its freedom of rotation was decreased and resulted in increased absorbance[15]. The formation constant was determined from the modified Benesi-Hildebrand equation[16]. It was found that the MY formed 1:1 Complex with β -CD.

3.3. Factors influencing the photodecoloration

3.3.1 Effect of initial concentration of MY

The effect of initial concentration of MY on the photodecoloration was studied with different concentrations ranging from 10 ppm to 20 ppm for ZnO and ZnO - β -CD systems. The percentage of decoloration was decreased with increase in initial concentration of MY (Fig.5). As the concentration of the dye increases, more number of MY molecules get adsorbed on the surface of the photocatalyst and therefore the light photons could not react with the catalyst surface. Also, at higher concentration, the light photons travel upto a smaller distance only due to scattering by dye molecules[16].

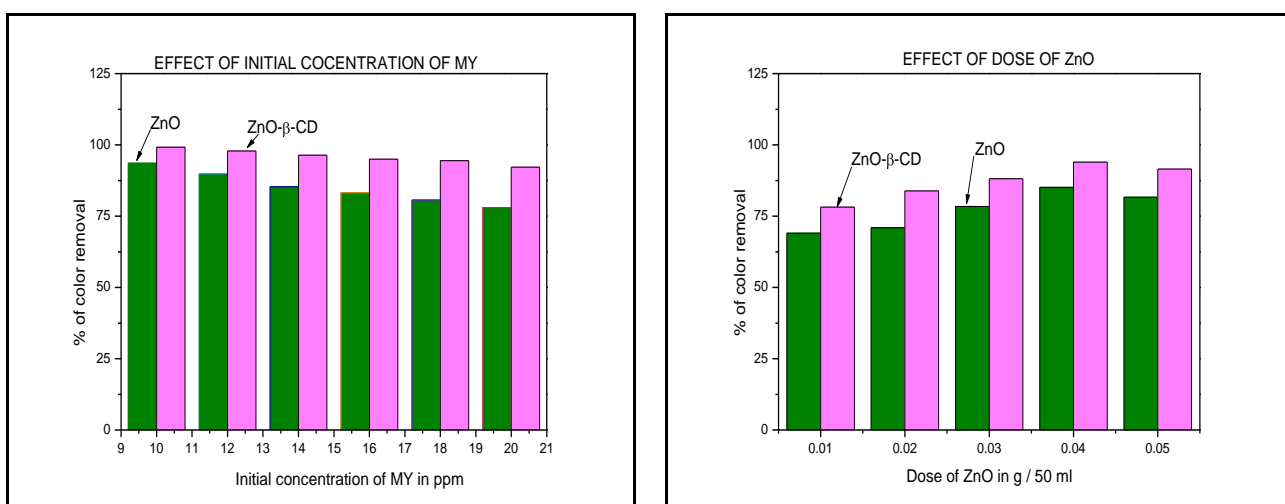


Fig 5: Effect of initial concentration of MY (left) and effect of dose on MY decoloration (right)

3.3.2 Effect of catalyst dose

The dye solution was irradiated for 60 minutes with ZnO dose ranging from 0.01g/50 ml to 0.05 g / 50 ml. Fig 6b shows the plot of percentage of decoloration vs the dose of the catalysts. The observed results revealed that the percentage of decoloration increases with increase in dose of the catalysts upto 0.04 g / 50 ml and then decreases. With increase in the amount of photocatalyst, the number of active sites available on the surface of the photocatalysts for the adsorption of MY molecules increases and this led to the high percentage of decoloration. Further increase in the amount of photocatalysts cause opaqueness and scatters the light photons and thus decreased the percentage of removal[17].

3.3.2 Effect of illumination time

The effect of illumination time was investigated with the aqueous solution containing 20 mg / l of MY. As the time of contact between the catalyst and the dye is increased, the percentage of removal gets increased. The kinetics of photodecoloration of MY by ZnO and ZnO - β -CD systems was evaluated through Langmuir-Hinshelwood model.

$$R = \frac{dc}{dt} = \frac{k K C}{1 + KC}$$

where 'R' is the rate of decoloration of MY, 'C' is the concentration of MY, 't' is the illumination time, 'k' is the rate constant and K is the adsorption coefficient of the reactant (MY). When KC value is so small compared to unity in the denominator, it could be neglected and the equation can be written in the form of natural logarithmic equation as ,

$$\ln(C_0 / C_t) = k t$$

where C_0 is the initial concentration of MY and C_t is the concentration of MY dye at any time 't' and k is the pseudo first order rate constant. Fig.6. shows the linear plot of $\ln(C_0 / C_t)$ vs the irradiation time. The slope of the linear regression gives the apparent rate constant 'k'. The value R^2 of the linear fitting for all the samples are more than 95 % . It can be noticed that all the ZnO - β -CD system showed remarkable photocatalytic activity for the decoloration of MY. From the rate constant value, it can be seen that the photocatalytic decoloration efficiency of ZnO - β -CD system was four times greater than bare ZnO.

3.3.3 Effect of pH

The textile effluents that are discharged into the water stream are having different pHs and so the study of effect of pH is inevitable. The effect of pH on the photodecoloration of MY dye was examined in the pH ranging from 4 to 9. MY is an anionic azo dye. The surface of the photocatalysts is positively charged below its point of zero charge. The point of zero charge for ZnO is ~ 9.1 . Below this pH the ZnO surface is positively charged and so it attracts more MY dye onto its surface electrostatically. Thus there is a decrease in percentage of decoloration with increase in pH [17].

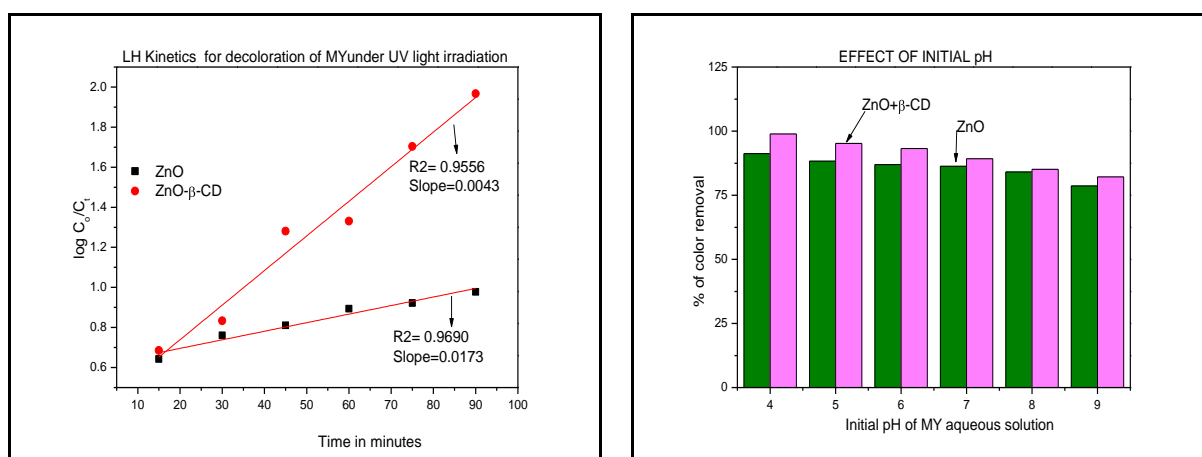


Fig 6: Effect of illumination time (left) and effect of initial pH on MY decoloration (right)

4.0 Conclusion

The results show that the betacyclodextrin could be successfully utilized for the enhancement of the photocatalytic decoloration of the Metanil yellow by ZnO. These studies indicate that ZnO - β -CD system possesses good photodecoloration ability which may be due to the formation of inclusion complex between MY dye and β -CD.

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