

Enhanced Photodecolorisation of Acid Blue 9 Dye by ZnO in Presence of Beta Cyclodextrin in Aqueous Solution under UV Light

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Abstract - A systematic study was made of enhancement of Photodecolorisation efficiency of ZnO with β -Cyclodextrin under UV light. The interaction of the later with ZnO was investigated through XRD, FT-IR, UV-DRS, PL spectra and SEM. In this study, Acid Blue 9 dye was utilized as a model pollutant. The experimental results indicated that β -Cyclodextrin has enabled the adsorption of the dye on to the surface of ZnO which in turn may enhance the photodecolorisation of dyes. The inclusion complex of the dye with β -Cyclodextrin was characterized by UV-visible spectroscopy. The dissociation constant was determined from the modified Benesi-Hilbrande equation. The effects of operational parameters such as initial concentration of dye, dose of ZnO, initial pH of the dye solution and illumination time were investigated. It was observed that Langmuir-Hinshellwood kinetics was followed by the photodecolorisation process in presence and absence of β -Cyclodextrin.

Keywords: β -Cyclodextrin, ZnO, Acid Blue 9, Benesi-Hilbrande equation, Langmuir-Hinshellwood.

I. INTRODUCTION

Zinc Oxide is a n-type and II-VI semiconductor. The wide applications of ZnO such as gas sensor, pharmaceutical, solar cell and photocatalyst [1] have promoted an extensive research in it. Zinc oxide is also a low cost, chemically stable and environmentally friendly semiconducting material [2]. It has a band gap of 3.2 eV comparable with that of TiO₂ and acts as an effective photocatalyst, some times more effective than TiO₂ for the photocatalytic treatment of waste water containing either organic pollutants or heavy metals or both [3]. The presence of organic pollutants such as dyes in waste water is undesirable and has become an important problem in developing countries like India. These dye pollutants have less biodegradability and high chemical stability [4]. The conventional methods applied to remove these dyes such as adsorption, ion-exchange process and flocculation *etc.*, possess certain disadvantages. Hence, an effective, economic and environmentally benign method has become the vital need of today. Among several such available methods, the heterogeneous photocatalysis, an advanced oxidation process is utilized extensively for the remediation of dyes in waste water.

Cyclodextrins are a class of cyclic oligosaccharides consisting of six (α -CD), seven (β -CD) and eight (γ -CD) glucopyranose rings. The D- glucopyranose rings are linked

through α -D-1, 4 glycosidic bonds. They have the doughnut shape with hydrophobic inner cavity and hydrophilic external surface. β -CD is considered to be most useful in the study of host- guest interaction due to its low cost, high solubility and the diameter of the inner cavity (7.14 nm). β -CD can form inclusion complexes with the guest molecules through non-covalent interaction [5].

In recent years, the modification of semiconductors by various metal doping, coupling of semiconductors with oxidants and carbon have been highly explored to enhance the photocatalytic efficiency of semiconductors for the remediation of pollutants [6-8]. Since this kind of enhancement techniques again may lead to a kind of secondary pollution, we aimed to investigate an environmentally friendly method by utilizing β -CD for the enhancement of the photocatalytic activity of ZnO. Acid blue 9 (AB9) dye is an acid dye of triphenyl methane class. It is water soluble anionic dye found in the waste water coming from textile industries on nylon, wool, silk, modified acrylic fibers, food stuffs, tanning and pharmaceuticals industries [9]. It also plays a role as pond dye to control the growth of aquatic algae and weeds in natural and artificial lakes and ponds as algacide and herbicide [10-12]. It is carcinogenic in rats and produce fibrosarcomas after continual injection [13]. Keeping in mind, the hazardous nature of AB9 dye, we considered the removal of this dye from the waste water as one of the significant task.

The present study is aimed at investigating the enhancement of photocatalytic efficiency of ZnO by modification with β -CD for the decolorisation of AB9 dye under UV light illumination. The effects of various operational parameters such as, initial concentration of AB9 dye, dose of ZnO, initial pH of the AB9 dye solution and illumination time for the maximum color removal of the dye have been studied. Moreover, the performance of these operational parameters for the decolorisation of AB9 dye by bare ZnO and ZnO - β -CD systems was compared. The kinetics of photocatalytic decolorisation was studied. The interaction of β -CD with ZnO was analyzed by means of by FT-IR, UV-DRS, XRD, PL spectra and SEM. On the basis of the obtained results, we formulated the mechanism of enhanced photocatalytic decolorisation of AB9 dye by ZnO - β -CD system.

II. MATERIALS AND METHODS

Beta Cyclodextrin and the dye Acid Blue 9 were purchased from Himedia chemicals and used without further purification. The photocatalyst, Zinc Oxide (Merck), Hydrochloric acid (Aldrich) and Sodiumhydroxide (Merck) were all analytical reagent grade. Double distilled (DD) was used throughout the process to prepare the experimental solutions.

1. Photocatalytic Experimental Setup and Evaluation Of Photocatalytic Activity

The photocatalytic experiments were carried out in Heber Mullti Lamp photoreactor (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.

The reaction solutions (50 ml) containing ZnO or ZnO- β -CD and AB9 dye were stirred in dark for 30 minutes before illumination in order to obtain the adsorption – desorption equilibrium and then were illuminated with UV light. The pH of the reaction solutions were not maintained during the course of the processes. At specific intervals of time during the course of the processes, the reaction tubes were withdrawn from the photoreactor one by one and centrifuged. The supernatant solution of the remaining dye was analyzed for the determination of its concentration by UV-Visible spectrophotometer (Schimadzu, 2400 series). For ZnO- β -CD systems, the molar concentrations of the β -CD and dye were kept as 1:1. The photocatalytic efficiency of ZnO and ZnO- β -CD under different experimental conditions were evaluated as Percentage of decolorisation of AB9 = $(C_i - C_t / C_i) \times 100$ ----- Eqn 1
 C_i and C_t is the initial concentration and final concentration of AB9 dye at any time t.

2. Investigation of Interaction of β -CD with ZnO

To investigate the interaction of β -CD with the ZnO, a suspension containing 10 g L^{-1} of β -CD and 1 g L^{-1} of ZnO was taken in the reaction tubes and were illuminated. After illumination for 1 hour, the reaction tubes were taken out and the contents were centrifuged and the precipitated solid materials were filtered off. The precipitates were carefully washed with DD water, dried by slow evaporation of water under room temperature for further characterization. The

above process was continued for 24 hours and the pH of the suspension was noted by pen type pH meter (Make: Hanna).

The XRD patterns were obtained using XPERT diffractogram and compared with that of bare ZnO. The SEM images were recorded on VEGA 3TESCAN at an accelerating voltage of 20.0 Kv. The FT-IR spectra of the solids were recorded on FT-IR IR Affinity-1 (Schimadzu). The UV-Visible diffused reflectance spectra were recorded on the UV-2400 (Schimadzu) series. The RT-Photoluminescence spectra were recorded on Perkin Elmer LS-45 spectrometer.

3. Investigation Of Interaction Of β -CD With AB9 Dye

The solutions containing the fixed concentration of AB9 dye (20 ppm) and increasing concentration of β -CD at the molar ratio of 1:1 to 1:6 for AB9: β -CD was stirred at 500 rpm at room temperature for 24 hours to ensure the equilibrium between free AB9 and β -CD-AB9 inclusion complex. The samples were then analyzed by measuring the absorbance at λ_{\max} of the AB9 using UV-Visible spectrophotometer. The dissociation constant of β -CD/AB9 inclusion complex dye was calculated using modified Bensi-Hilbrande equation.

III. RESULTS AND DISCUSSION

A. Effect of operational parameters

1. Effect of initial concentration of AB9 dye

To investigate the effect of initial concentration of the AB9 dye on the photocatalytic decolorisation efficiency, experiments were carried out on different initial concentrations of AB9 dye varying from 15 ppm to 40 ppm. For all the initial concentrations of AB9 dye, the dose of ZnO (1 g L^{-1}) and UV light intensity are kept fixed so that the same amount of OH° radicals are generated. For ZnO- β -CD systems, the concentrations of β -CD and dye were taken in the 1:1 molar ratio. Fig.1(a) shows the decrease in percentage of decolorisation of AB9 with increase in initial concentration of dye for both ZnO and ZnO- β -CD systems. At the constant amount of OH° radical generation, the chance for the dye molecules to react with the OH° radicals decreases as the concentration of AB9 dye increases. The high concentration of dye molecules also decreases the path length of photons [14]. For the investigating the other operational parameters, the concentration of dye was fixed as 20 ppm. Also, as the concentration of dye increases, more and more dye molecules get adsorbed on to the catalysts surface. Hence, UV light photons could not reach the surface of ZnO. This prevents the formation of excitons and so the production of OH° and $\text{O}_2^{\cdot-}$ radicals.

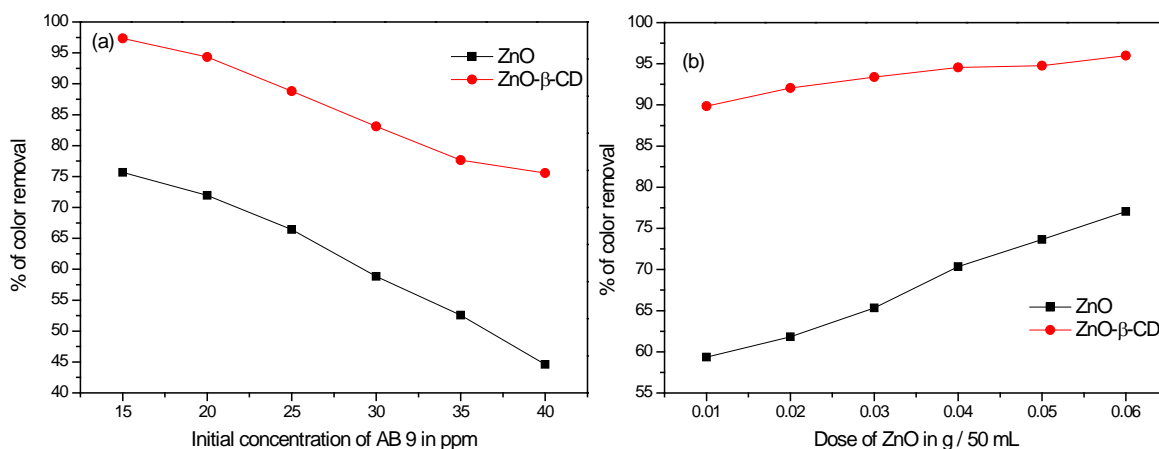


Fig. 1 Percentage of color removal of AB9 dye with (a) various initial concentration and (b) loadings of ZnO for bare ZnO and ZnO - β-CD systems

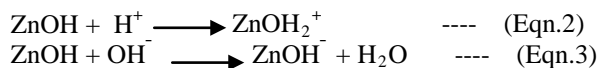
2. Effect of catalyst dose

The percentage of dye removal as a function of dose of the ZnO for bare ZnO and ZnO-β-CD systems are shown in Fig.1 (b). To find out the optimum dose of ZnO, a series of photocatalytic decolorisation experiments were carried out at the natural pH (6.85) of aqueous solution of 20 ppm AB9 dye under UV illumination for 60 minutes. The dose of ZnO was varied between 0.2 g L⁻¹ and 1.2 g L⁻¹. The results show that the decolorisation percentage of dye increases as the dose of ZnO increases due to increase in available surface area and number of active sites for the adsorption of AB9 dye molecules. The increased surface area may increase the penetration and absorption of light photons. These processes occurred simultaneously and enhanced the production OH[•] radicals and superoxide radicals. This had obviously resulted in increase in efficiency of ZnO for decolorisation of AB9 dye [15].

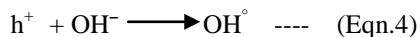
3. Effect of pH

The initial pHs of the dispersions play significant roles in photocatalytic decolorisation of dyes. But, it is very difficult to construe precisely the role of pH as it influences the acid-base properties of the amphoteric semiconductor photocatalysts (ZnO). The zero point charge (Pzc) of ZnO is ~ 9.0. At pH < Pzc, the surface of ZnO as positively charged and could absorb more anionic species while the reverse is

true at pH > Pzc. At pH > Pzc, The change in surface charge of ZnO is explained as follows.



The adsorption of AB9 is favored at acidic pHs. The role of pH on the photocatalytic decolorisation of AB9 was investigated in the range 3-12 with 50 ml of 20 mg L⁻¹ AB9 and 1 g L⁻¹ of catalyst loading (Fig.2 (a)). The results show that the maximum percentage of removal was obtained at pH 3. The percentage of decolorisation increases with decrease in pH from 6 to 3 and then increases at pHs 9 and 10. It is reasoned on the basis of more efficient generation of OH[•] radicals by ZnO with increasing concentration of OH⁻ at higher pHs. The formation of OH[•] radicals in alkaline solutions is due to the reaction between the holes and OH⁻ ions of the alkaline solution [16].



The results are consistent with the previous literature that relates the Pzc, pH and photocatalytic activity [17]. As the OH⁻ ions concentration was extremely high at pH 12, they compete with the dye molecules to get adsorbed on ZnO and may change the ZnO surface as more negatively charged. The electrostatic repulsion between the dye anion and the negatively charged ZnO surface resulted in reduced photocatalytic activity [18].

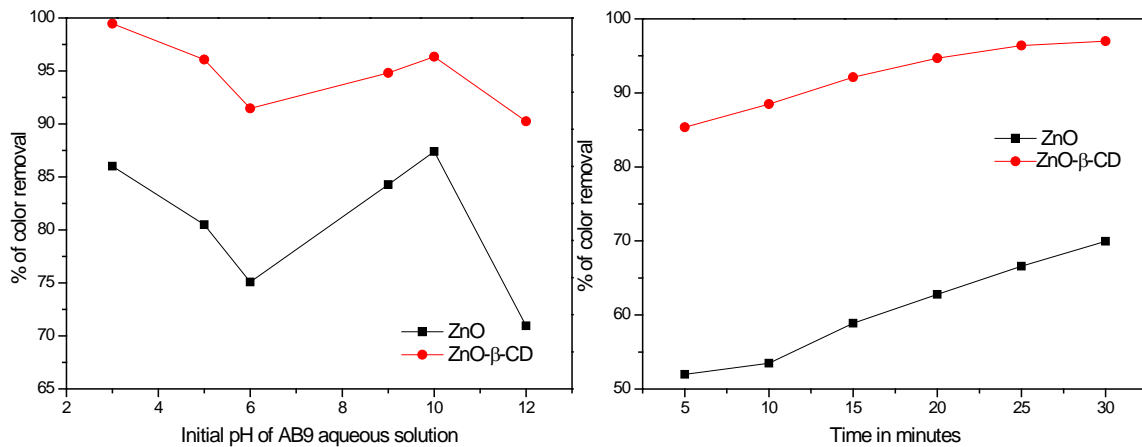
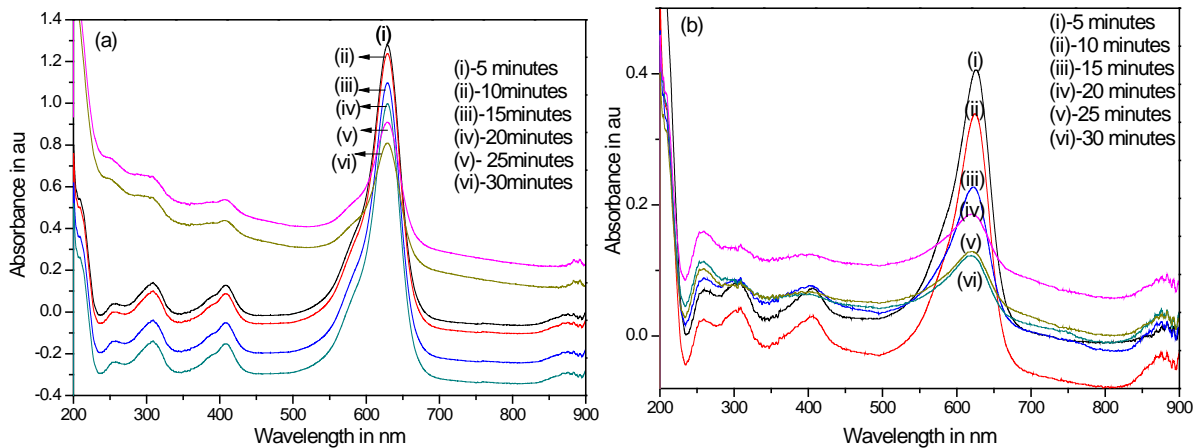


Fig.2 Percentage of color removal of AB9 dye (a) under different pHs by bare ZnO and ZnO - β-CD systems (b) at different time intervals

4. Effect of illumination time and kinetic analysis

The percentage of decolorisation increase with increase in time and is shown in Fig.2 (b). Fig.3 (a) and (b) exhibit the time dependent change in UV -Visible absorption spectra of AB9 dye during photocatalytic processes utilizing bare ZnO and ZnO- β-CD as photocatalysts respectively. As seen, the characteristic absorption intensity of AB9 dye at 629 nm decreased with increase in illumination time and finally disappeared. The continuous decrease in intensity of the UV bands proves the gradual degradation of the dye. Moreover, no new bands are appeared in either UV or visible regions apart from the regular bands. A slight

hypsochromic shift was observed. These results confirmed that AB9 undergoes photocatalytic degradation under UV light illumination. Fig.3(c) shows the L-H kinetics of decolorisation of AB9 dye with ZnO and ZnO- β-CD at its natural pH with the initial concentration of 20 ppm and optimized dose 1 g L^{-1} . The slope of the linear regression gives the apparent rate constant k . The value R^2 of the linear fitting for both the systems is more than 98 % indicates that the photocatalytic decolorisation followed pseudo- first order kinetics. From the rate constant values (Table 1), it can be seen that the photocatalytic decolorisation efficiency of ZnO - β-CD system was 3.44 times greater than bare ZnO.



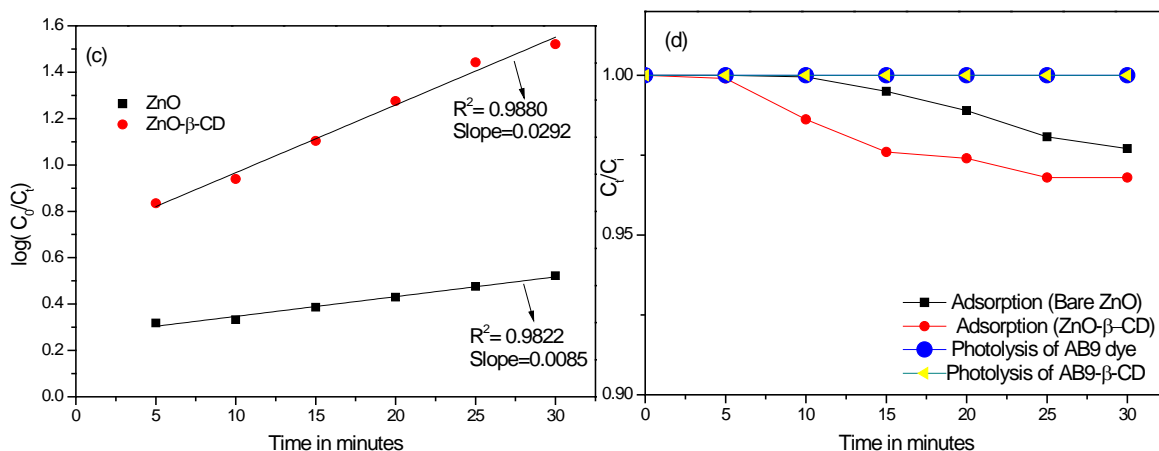


Fig.3 Absorbance spectra of AB9 dye under different illumination time for (a) bare ZnO (b) ZnO- β -CD;

(c) Langmuir-Hinshelwood kinetics for decolorisation of AB9 dye; (d) Extent of color removal of AB9 dye under different experimental conditions

B. Adsorption and photostability of AB9 dye

Fig.3 (d) shows the extent of color removal upon adsorption by bare ZnO and ZnO - β -CD, photolysis of AB9 in presence and absence of β -CD. In fact, the maximum percentage of dye removal obtained by adsorption with bare ZnO was 2.3 % and that of ZnO - β -CD was 3.2 %. This may be due to the inclusion property of β -CD to hold AB9 in its cavity and its bonding to Zn atoms. The β -CD adsorbed on to the surface of ZnO acts as a bridge between ZnO and AB9 dye included into its hydrophobic cavity and increased the adsorption capacity. Similar results were explained for the enhancement of redox ability of TiO₂ by P. Lu et al. [19].

The photolytic experiments with AB9 dye were carried out in the absence of ZnO and indicated that AB9 dye was highly photostable and the results are depicted in Fig.3 (d). Thus the decrease in absorbance intensities during photocatalytic process was exclusively due to the photocatalytic degradation of AB9 dye by ZnO.

C. Photostability of β -CD and photocatalytic degradability of β -CD

The photostability and photocatalytic degradability of β -CD was investigated by illuminating β -CD only and the suspension containing ZnO and β -CD with UV light for 60 minutes respectively. The concentration of β -CD before and after was determined from phenolphthalein colorimetry [20]. But it was found that no β -CD was degraded during the process.

D. Investigation of interaction of β -CD with ZnO

X-ray powder diffraction patterns of bare ZnO and ZnO - β -CD are presented in Fig. 4 (a) and (b). All the sharp and intense diffraction peaks of ZnO - β -CD showed that the ZnO conserves its crystalline features as bare ZnO. The diffraction patterns are matched well with the standard JCPDS data card no: 36-1451. It could be seen that the peaks at 2θ corresponding to bare ZnO are slightly shifted to higher angles in ZnO - β -CD. These peak shifts may be due to the lattice strain between ZnO and ZnO - β -CD. This has clearly indicated that β -CD was adsorbed on to the bare ZnO through the interaction of secondary hydroxyl groups with the Zn⁺² in the semiconductor. Similar results were reported by J.W. Kim et al. They have explained the bonding of β -CD on the surface of TiO₂ through the interaction of secondary hydroxyl groups with the Ti⁺⁴ [21].

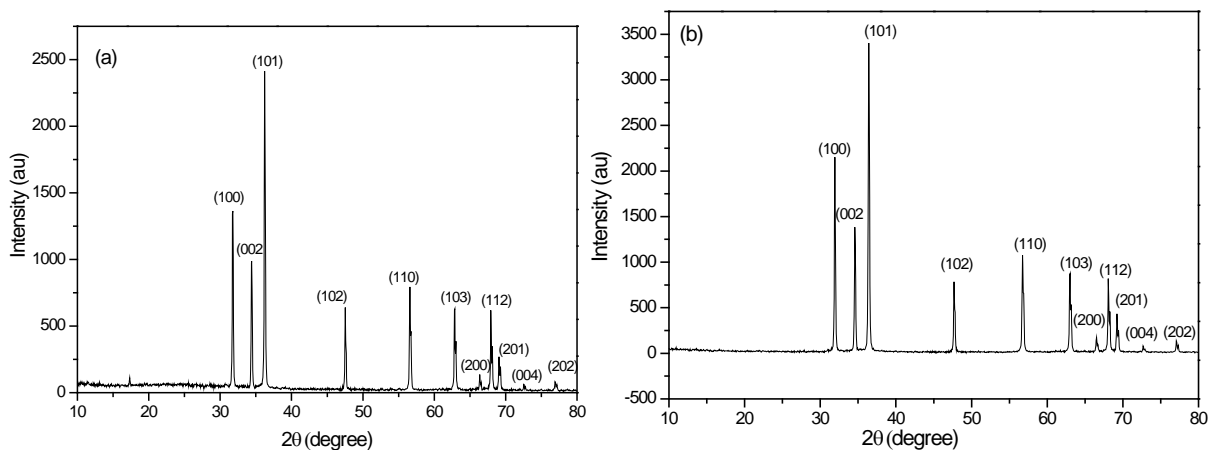


Fig. 4 X-ray powder diffraction patterns of (a) bare ZnO and (b) ZnO - β -CD

Figs.5 (a) and Fig.5 (b) shows the UV-Visible Diffused Reflectance spectra of bare ZnO and ZnO- β -CD respectively. The band gap value of bare ZnO (3.28 eV) was

slightly increased to 3.29 eV after interaction with β -CD. This is attributed to the ligand to metal charge transfer (LMCT) between β -CD and Zn^{II} [22].

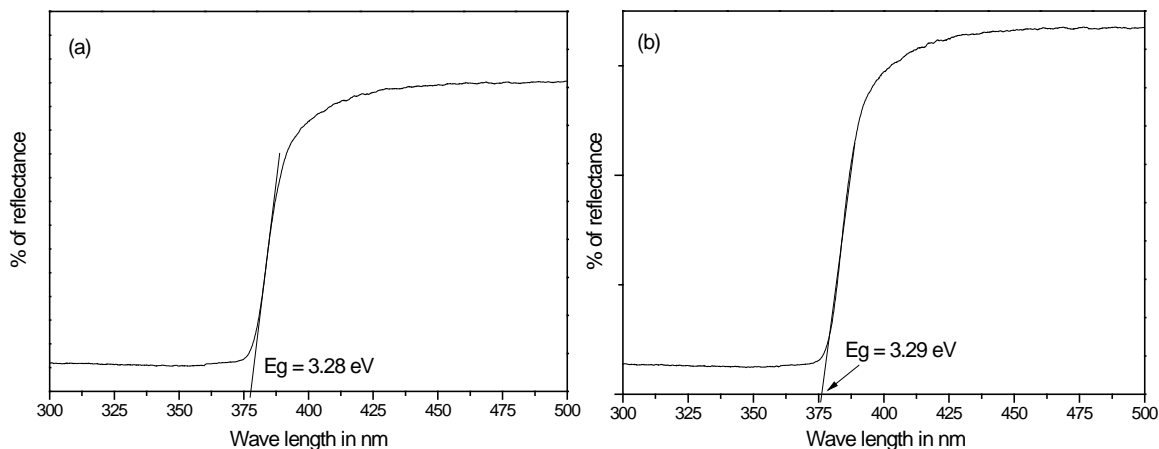


Fig.5 UV- Visible Diffused Reflectance Spectra of bare ZnO and ZnO- β -CD

The FT-IR spectra of bare ZnO and ZnO - β -CD are shown in Fig.6 (a) and (b). It was found that the intensities of bands of free β -CD at 941 cm^{-1} , 756 cm^{-1} due to vibration of α -1-4 linkage and ring breathing vibration, 705 cm^{-1} and 579 cm^{-1} assigned to pyranose ring vibration were greatly

reduced or disappeared and the band at 3400 cm^{-1} was suppressed to a great extent in ZnO - β -CD indicating that the β -CD has bound to ZnO through the rim hydroxyl groups. Thus β -CD should be chemisorbed on ZnO during the course of the photocatalytic reaction [23].

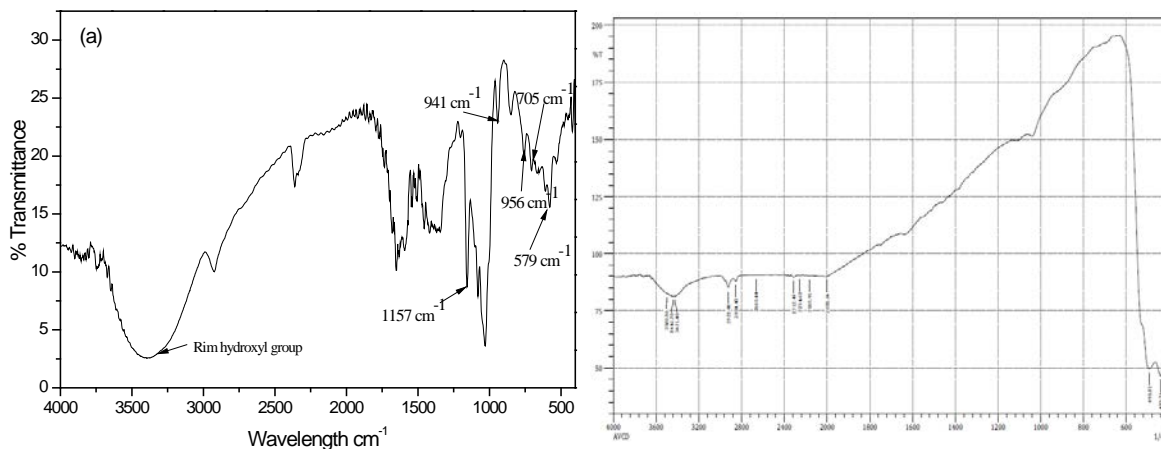
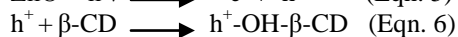
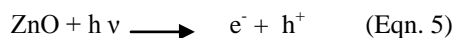


Fig.6 FT-IR Spectra of (a) β -CD and (b) ZnO- β -CD

SEM images are shown in Fig.7. The images of the bare ZnO were composed of nearly rod like structures. Few chunk particles (shown within the circles) were clearly seen in the SEM images of ZnO - β -CD along with rods. The appearance of chunk particles indicates that the β -CD was adsorbed on the surface of ZnO rods.

The room temperature Photoluminescence spectra of bare ZnO and ZnO - β -CD were presented in Fig.8. The PL spectra of the photocatalysts exhibited near band edge emission (NBE) at 387.6 nm and two types of visible

luminescence at 520 nm and 789.2 nm . It was observed that the PL intensity (NBE) of the ZnO - β -CD was decreased compared to the bare ZnO. This indicated that the electrons - holes (e^-/h^+) recombination was very much reduced in the ZnO - β -CD. This lowering of PL intensity suggested more photocatalytic activity for ZnO - β -CD system [24]. The reaction of β -CD with ZnO surface is shown below:



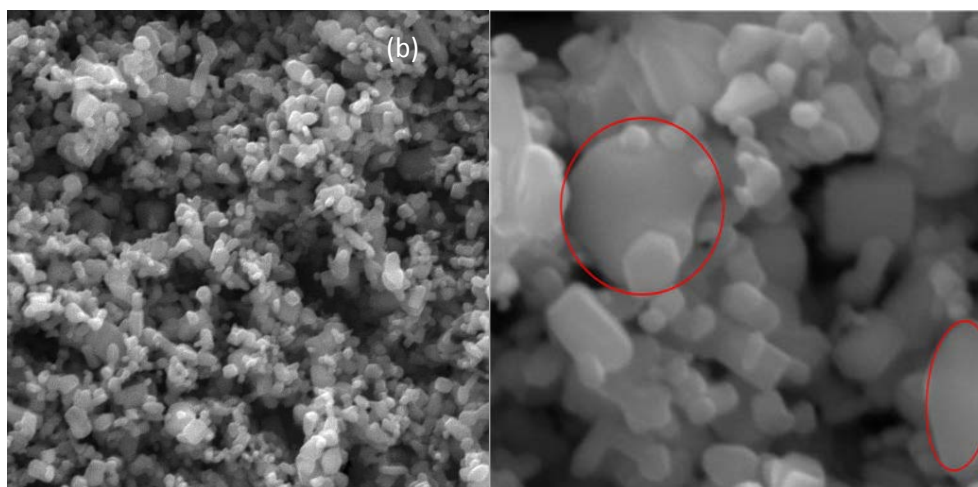


Fig.7 SEM images of bare (a) ZnO and (b) ZnO -β-CD

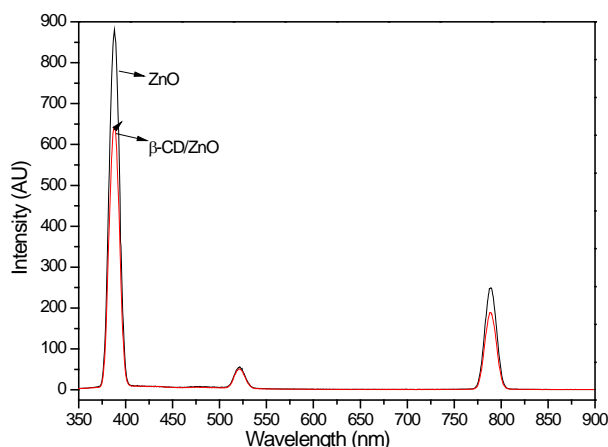


Fig.8 Photoluminescence Spectrum of bare ZnO and ZnO -β-CD showing the NBE and visible luminescence Peaks with their PL intensity

β -CD act as the hole scavenger that are produced upon the illumination of ZnO with UV light. Hence it helps in reducing the e^-/h^+ recombination and may enhance the photocatalytic activity of ZnO. The results were consistent with report of X. Zhang et al who explained about the photodegradation of dyes using light-induced self assembly TiO_2/β -cyclodextrin hybrid nanoparticles under visible light irradiation [25].

As the β -CD binds (chemisorptions) to the surface of ZnO through the formation of bonds utilizing the rim hydroxyl groups, there would be definitely the elimination of protons. This was confirmed by the decrease in pH from 6.7 to 6.

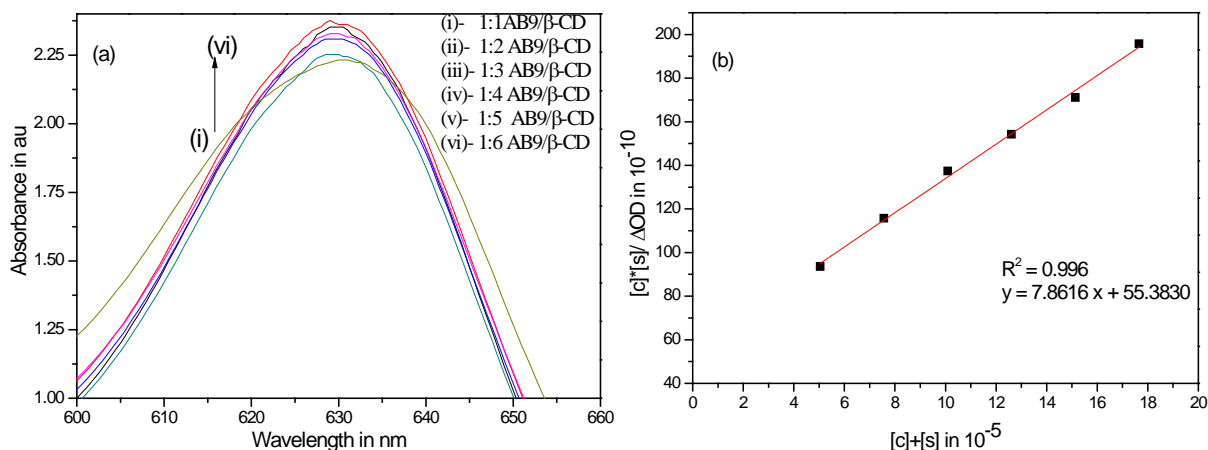
E. Determination of formation constant for β -CD-AB9 inclusion complex

The host-guest inclusion complex of β -CD with AB9 was characterized by UV-Visible spectra. Fig.9 (a) shows the UV-Visible spectral change in the absorption spectra of AB9 dye upon inclusion with β -CD. It was observed that intensity of absorbance increases with increase in

concentration of β -CD with no shift in the maximum wavelength (λ_{max}). This suggests the existence of supra molecular interaction between β -CD and AB9 dye. As the AB9 dye molecule included into the hydrophobic cavity of β -CD, its freedom of rotation was decreased and resulted in increased absorbance [26]. The dissociation constant was determined from the modified Benesi-Hildebrand equation.

$$\{[\beta\text{-CD}][\text{AB9}]/\Delta\text{OD}\} = \{[\beta\text{-CD}] + [\text{AB9}]/\Delta\epsilon\} + \{K_d/\Delta\epsilon\} \quad (\text{Eqn. 7})$$

Where, $[\beta\text{-CD}]$ is the concentration of β -CD, $[\text{AB9}]$ is the concentration of AB9 dye, ΔOD is the increase in absorption of AB9 dye upon inclusion with β -CD, $\Delta\epsilon$ is the difference in molar extinction coefficient between the bound and free AB9 dye and K_d is the dissociation constant. Fig.9 (b) shows the plot of $\{[\beta\text{-CD}][\text{AB9}]/\Delta\text{OD}\}$ vs. $\{[\beta\text{-CD}] + [\text{AB9}]\}$. The linearity of the plot reflects the formation of 1:1 complex [33]. The K_d value of β -CD- AB9 dye was calculated from the ratio of intercept and slope of the linear plot of $\{[\beta\text{-CD}][\text{AB9}]/\Delta\text{OD}\}$ vs. $\{[\beta\text{-CD}] + [\text{AB9}]\}$. The determined K_d is 7.04×10^{-5} M.

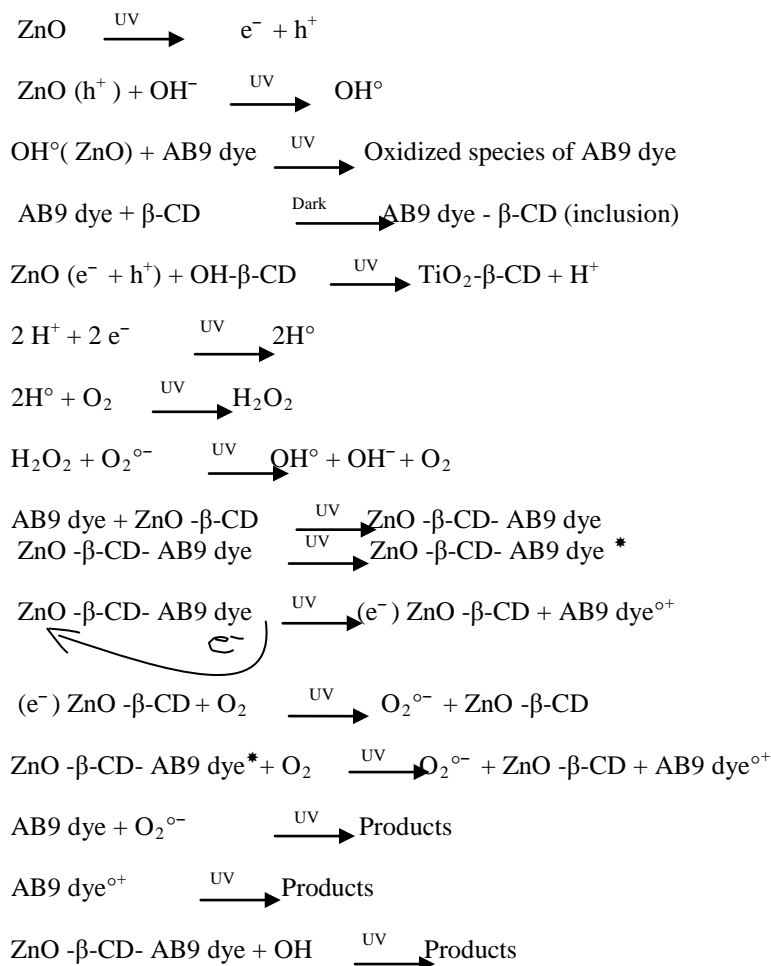


F. Mechanism of enhanced photodecolorisation of AB9 dye

On the basis of the results obtained, we propose the plausible mechanism of enhancement of photodecolorisation of AB9 dye by β-CD as follows.



Upon illumination of ZnO with UV light of energy greater than the band gap energy of ZnO, the following reactions could occur in the photocatalytic system.



G. Comparison of photocatalytic efficiency of ZnO and ZnO-β-CD

TABLE. I COMPARISON OF PERCENTAGE OF DECOLORISATION, R² AND RATE CONSTANT

S.No	Photocatalyst	Optimum Dose of photocatalyst	Percentage of decolorisation	R ²	Rate constant
1	ZnO	1g L ⁻¹	69.94	0.9822	0.0085
2	ZnO - β-CD	1g L ⁻¹	96.99	0.9880	0.0292

The maximum percentage of decolorisation achieved with 1g l⁻¹ of bare ZnO for 20 ppm AB 9 dye solution under 90 minutes of illumination was 69.94. With the same experimental conditions, ZnO -β-CD system produced 96.99 % percentage of decolorisation. On comparing the rate constants for the photocatalytic decolorisation of AB9 dye by ZnO and ZnO-β-CD systems, it was proved that β-CD could more effectively enhance the photocatalytic efficiencies of bare ZnO for decolorisation of AB9 dye via the formation of inclusion complex with dye and increased adsorption of dye on to the surface of ZnO.

IV. CONCLUSION

In summary, we have demonstrated the development of new strategy for the photocatalytic degradation of dye pollutants in presence of molecular containers with AB9 dye and β-CD as the model pollutant and molecular container respectively. It was observed that major role played by β-CD in the decolorisation process were formation of inclusion complex with dye and adsorption of β-CD on ZnO. The effects of initial concentration of dye, dose of ZnO and initial pH of the aqueous dye solution were studied for both ZnO and ZnO- β-CD systems. The decolorisation process of the model pollutant AB9 dye by ZnO and ZnO- β-CD obeyed pseudo-first order kinetics.

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