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Improved photocatalytic performance of (ZnO/TiO_2)-β-CD on decolorization of brilliant green dye under UV light irradiation

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The photocatalytic activity of modified semiconductor nanocomposite (ZnO/TiO_2)-β-CD system, for decolorization of brilliant green dye has been studied under UV light (λ_{max}= 365 nm) irradiation and results are compared with the activities of (ZnO/TiO_2), bare ZnO and bare TiO_2. The nanocomposite has been characterized by X-ray diffraction, scanning electron microscopy, UV-vis diffuse reflectance spectroscopy. UV–visible analysis has also been used to confirm the complexation pattern between β-CD and the dye. Various experimental parameters like $ZnO:TiO_2$ ratio, initial concentration of dye, irradiation time and *p*H have been investigated. Kinetic results show that the decolorization reaction follows pseudo-first order kinetics. The mineralization of brilliant green has been confirmed by chemical oxygen demand measurements. A suitable reaction mechanism for decolorization of the dye by (ZnO/TiO_2)-β-CD has also been proposed. The present results show that (ZnO/TiO_2)-β-CD system is an efficient and low cost modified photocatalyst for the treatment of waste water from textile industries.

Keywords: Photocatalysts, Zirconia, Titania, Cyclodextrin, β-Cyclodextrin, Semiconductors, Nanocomposites, Dye decolorization, Brilliant green, UV light

In recent years, environmental pollution is a threat for the survival of human society[1]. Industrial dye stuff, including textile dyes are considered as important environmental issue as they consume considerable amount of water during dyeing and finishing operations[2]. The release of waste water into water sources without treatment is a very serious problem, as most of the dyes are carcinogenic as well as harmful in nature[3]. At present, semiconductor photocatalysis is a promising and efficient method for complete degradation of several organic contaminants. ZnO and TiO_2 are known to be excellent photocatalysts due to their high photocatalytic activity, non-toxic, inexpensive, easy availability, excellent chemical and mechanical stability. They exhibit effective photocatalytic activity under UV light irradiation because both the semiconductors have a similar wide band gap of ~3.2 eV at room temperature[4-6]. When the photocatalyst suspension is irradiated with photons of energy greater than the band gap energy of photocatalyst, the photocatalytic process is initiated and it generates electrons and holes in conduction band (CB) and valence band (VB) respectively. The photogenerated electrons reduce the dissolved oxygen to superoxide radicals and the photogenerated holes oxidize the adsorbed OH^- or H_2O to hydroxyl radicals. These reactions create a powerful oxidative environment and help to destroy the organic pollutants[7]. The major disadvantage of the semiconductor photocatalyst is the recombination of electron-hole pair, which reduces the quantum efficiency resulting in the loss of photocatalytic activity. Considerable efforts to develop highly active photocatalysts by doping, metal deposition, surface sensitization and coupling of semiconductors have been made by reducing recombination of photogenerated charge carriers and improving the photocatalytic efficiency. The coupling of two semiconductors provides a method to achieve a more efficient charge separation, increased lifetime of the charge carriers and enhanced interfacial charge transfer to the adsorbed substrates. As the electron-hole pair recombination is not high in the (ZnO/TiO_2) composite system, it exhibits a better photocatalytic efficiency compared with pure samples of either TiO_2 or ZnO[8, 9].

Cyclodextrins (CDs) are non-reducing cyclic malto-oligosaccarides which are composed of hydrophilic outer surface and hydrophobic inner cavity. They have the ability to form inclusion complexes with various organic and inorganic guest molecules, especially dye molecules. They are also excellent materials for facilitating interfacial electron-hole transfer processes. In the field of environmental research, CDs have been used to promote degradation of hazardous pollutants discharged into aqueous environment and to reduce the environmental impact of the chemical pollutants[10-18]. β-CD, which consists of seven glucose units, plays a significant role in semiconductor photocatalysis by hindering the electron-hole recombination and enhances the photocatalytic performance of semiconductor.

Keeping in view the above, a new approach of employing a modified semiconductor system, viz., (ZnO/TiO_2)-β-CD, for the decolorization of BG dye as a model pollutant under UV light irradiation has been attempted. To the best of our knowledge this is the first report of its kind. In order to ascertain its photocatalytic activity, various parameters have been studied and a suitable reaction mechanism has been proposed. From the results, the reasons for the greater photocatalytic ability of (ZnO/TiO_2)-β-CD have been reported.

Materials and Methods

Brilliant green (BG) a basic dye ($C_{27}H_{34}N_2O_4S$, λ_{max} = 625 nm, toxic in nature) obtained from Loba Chemie (India) was used as such. The catalysts, i.e., ZnO and TiO_2 were received from Merck Chemicals, India. β-CD was purchased from Hi Media Chemicals (P) Ltd. All other chemicals and reagents were purified whenever required. Doubly distilled water was used throughout the study.

The morphology of the various samples was examined by scanning electron microscopy (FEG Quanta-250). The X-ray diffraction patterns of the powdered samples were recorded using 'X'PERT PRO diffractometer with Cu-Kα radiation. UV-vis diffuse reflectance spectra (UV-DRS) of the samples were recorded on a Shimadzu 2550 UV-vis spectrophotometer between the range of 200 and 700 nm with $BaSO_4$ as the background. UV-visible spectra were recorded using UV-visible spectrophotometer (Shimadzu UV-1700) and the scan range was set as 400 to 700 nm. The absorbance of the dye solutions, before and after irradiations was measured using visible spectrophotometer (Elico-207).

Preparation of modified catalyst, (ZnO/TiO_2)-β-CD

The physical mixture of the nanocomposite mixture (ZnO/TiO_2) was prepared by thorough physical mixing of ZnO and TiO_2 in the ratio of 8:2 using agate mortar. The modified form of the catalytic mixture with β-CD was prepared by mixing a suspension containing 2.0 g L^{-1} of the physical mixture of (ZnO/TiO_2) with 10.0 g L^{-1} of β-CD and magnetically stirred for 24 h and centrifuged. The solid phase was then carefully washed with deionised water, filtered and dried[4].

For the determination of dissociation constant (K_D) for the host-guest complex the following procedure has been adopted. BG dye (2.07×10^{-4} *M*) was prepared in deionised water and various concentrations of β-CD like 2.07, 4.14, 6.21, 8.28, 10.35×10^{-4} *M* were prepared in a 25 mL standard measuring flask. The solutions were magnetically stirred for 24 h and the inclusion patterns were confirmed by the UV-visible spectral analysis.

Photocatalytic studies

Photocatalytic experiments were carried out under UV light irradiation, using a Heber multilamp photoreactor (HML MB 88) with eight lamps as the UV light source. The lamps emit UV radiations mainly at 365 nm with a power output of 30 W. The distance between the UV source and the sample holder was 5 cm. Glass tubes with 60 mL capacity (37 cm height and 15 mm diameter) were used as sample holders. In all the cases, exactly 50 mL of the reactant solution was irradiated with required amount of photocatalyst. The *p*H values of the BG dye solutions were monitored with a digital pen *p*H meter (Hanna Instruments, Portugal) before the irradiation process, and adjusted to the desired value with HCl and NaOH solutions; it was not controlled during the course of the reaction. Prior to irradiation, the reaction mixture was stirred well in the dark for 15 min. to achieve adsorption-desorption equilibrium between the dye and catalytic system. During irradiation, the reactant solutions were stirred continuously with a magnetic stirrer. The reaction tubes were taken out at different intervals of time and the solutions were centrifuged well. The supernatant liquid from each sample holder was collected and labeled for determination of concentration of the dye remaining in solution by measuring the absorbance at λ_{max} = 625 nm. The chemical oxygen demand (COD) of the dye solutions before and after photocatalytic reactions was determined by the potassium dichromate reflux method, where unreacted oxidant was estimated by titrating with ferrous ammonium sulphate using Ferroin indicator[17, 18].

By keeping the concentrations of BG dye and β-CD as constant at the molar ratio of 1:1, the effect of all other experimental parameters on the rate of photocatalytic decoloration of BG dye solutions were investigated. The optimum amount of catalysts and irradiation time were fixed as 2.0 g/L and 120 min. respectively. The *p*H of BG dye solution was 4.2.

Results and Discussion

Characterization

To study the role of β-CD, SEM image of β-CD was compared with that of (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD (Fig.1a-c). β-CD shows amorphous surface (Fig. 1a). While Fig. 1(b), suggests that (ZnO/TiO_2) has irregular particles and a flake-like structure. The results indicate that ZnO and TiO_2 are thoroughly mixed with each other. The modified semiconductor catalyst, i.e., (ZnO/TiO_2)-β-CD exhibits morphology similar to that of (ZnO/TiO_2), as evidenced in Fig. 1(c). From the SEM analysis it is concluded that addition of β-CD to (ZnO/TiO_2) has no effect on the morphology of the latter. This indicates that the β-CD molecules are simply adsorbed on the surface of the (ZnO/TiO_2). It is also observed that the surface of (ZnO/TiO_2)-β-CD is very loosely packed. This kind of surface can provide a better adsorption environment and more active sites for the photocatalytic decolorization reactions[17, 18].

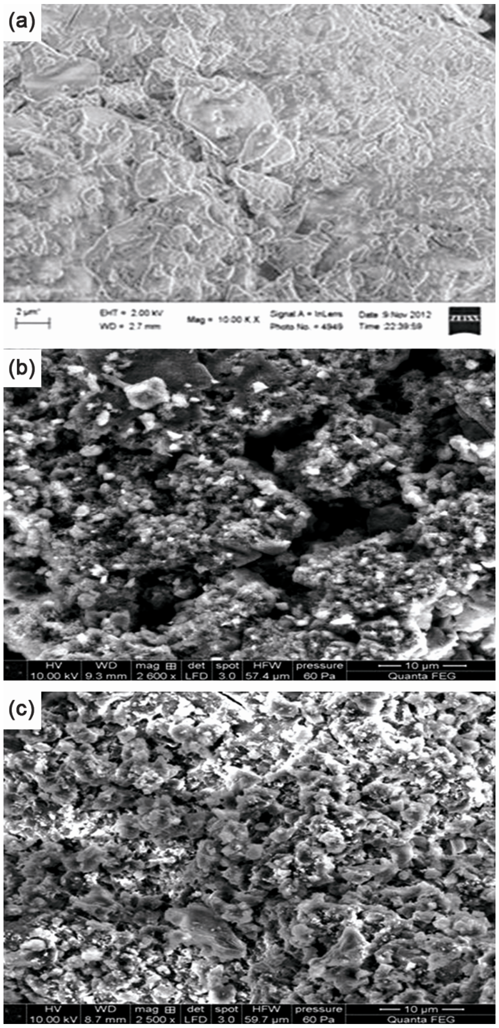

Fig. 1—SEM images of ZnO/TiO_2/β-CD. [(a) β-CD; (b) (ZnO/TiO_2); (c) (ZnO/TiO_2)-β-CD].

X-ray diffraction pattern of the powdered forms of β-CD, TiO_2, ZnO, (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD are provided in Fig. 2 (1-5). The characteristic peaks at 31.73°, 34.45°, 36.28°, 47.51° and 56.68° correspond to (100), (002), (101), (102) and (110) diffraction peaks of wurtzite ZnO, indicating that ZnO possesses a hexagonal crystal structure. The high intensity peaks of (101) show an anisotropic growth and imply the preferred orientation of the crystallites. Diffraction peak at 25.38°, 37.9°, 48.07°, 53.94° and 55.18° correspond to (101), (004), (200) (105) and (211) planes of TiO_2 indicate that TiO_2 exhibits single phase anatase type. These results are comparable with JCPDS (36-1451) and JCPDS (21-1272) for bare ZnO and bare TiO_2 respectively[19]. This is further confirmed by the XRD pattern of (ZnO/TiO_2)-β-CD system which is similar to that of (ZnO/TiO_2). Thus, it may be concluded that addition of β-CD on the surface of the catalytic mixture (ZnO/TiO_2) leads to no change in the crystal structure of (ZnO/TiO_2). Moreover, the addition of β-CD does not cause any shift in peak positions of (ZnO/TiO_2) phase.

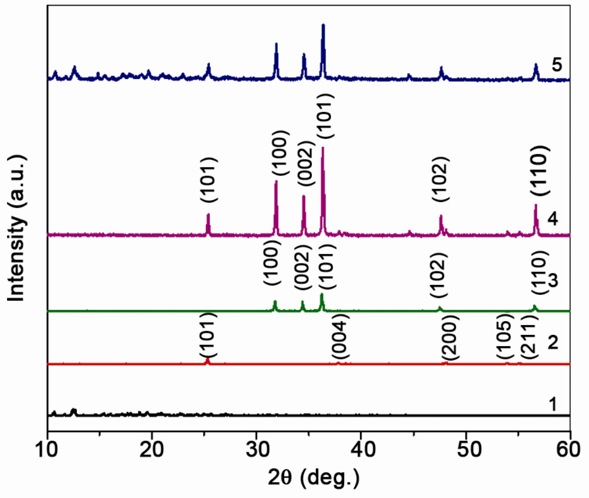

Fig. 2—XRD patterns of ZnO/TiO_2/β-CD. [β-CD (1); TiO_2 (2); ZnO (3); (ZnO/TiO_2) (4); (ZnO/TiO_2)-β-CD (5)].

UV-visible diffuse reflectance spectra

The optical properties of ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD have been studied with UV-vis DRS and the spectra are shown in Fig. 3. The DR spectra reveal that all the samples exhibit an optical absorption maximum at near visible region. Binding of β-CD on (ZnO/TiO_2) significantly affects the absorptive properties of (ZnO/TiO_2). However, (ZnO/TiO_2) shows only a slight variation of absorption as compared to that of ZnO and TiO_2. The (ZnO/TiO_2)-β-CD system has higher absorption than (ZnO/TiO_2), ZnO and TiO_2. The optical band gap of all the samples have been calculated by extrapolating the straight linear portion of the plot between $(\alpha h\nu)^2$ and hν to the energy axis. The estimated band gap energy values are respectively 3.20 eV, 3.27 eV, 3.18 eV and 3.16 eV for ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD system.

FT-IR spectra of β-CD, (ZnO/TiO_2) composite and (ZnO/TiO_2)-β-CD systems are presented in the Supplementary Data, Fig. S1. FT-IR spectrum of β-CD shows sharp bands at 942 $cm^{-1}$and 757 cm^{-1} due to the vibration of α-1-4 linkage and ring breathing vibrations. The peaks appeared at 707 cm^{-1} and 579 cm^{-1} are assigned to the pyranose ring vibrations and the broad band at 3380 cm^{-1} represents the hydroxyl groups of β-CD. The above mentioned peaks corresponding to β-CD are not observed in the FT-IR spectrum of (ZnO/TiO_2)-β-CD system. This shows a strong adsorption of β-CD molecules onto the (ZnO/TiO_2) surfaces. There is no significant peaks noted in the FT-IR spectrum of (ZnO/TiO_2) nanocomposite.

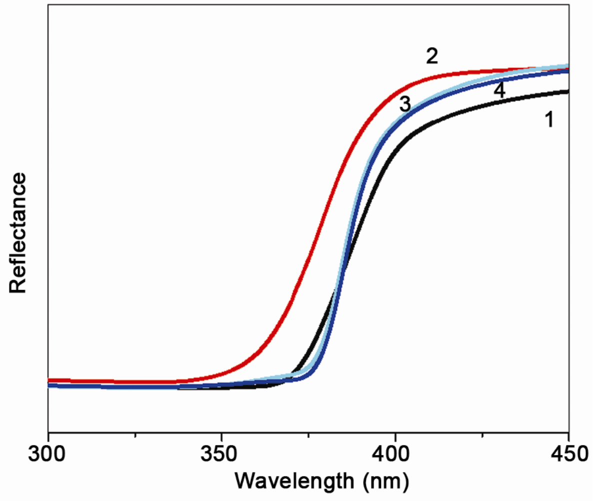

Fig. 3—UV-DRS of ZnO/TiO_2/β-CD. [ZnO (1); TiO_2 (2); (ZnO/TiO_2) (3); (ZnO/TiO_2)-β-CD (4)].

UV-visible spectral analysis

The UV-visible spectral analysis was carried out to confirm the complexation pattern between β-CD and BG dye (Supplementary Data, Fig. S2). From this figure, it is evidenced that, the absorbance of the inclusion complex increases with increasing concentration of β-CD. The dissociation constant, K_D, for this host-guest complexation determined using Benesi-Hildebrand equation is found to be 2.01×10^{-4} *M*, which confirms the formation of a strong inclusion complex between β-CD and BG dye[20]. The optimum molar ratio between β-CD and BG dye was fixed as 1:1.

Photocatalytic activity

The photocatalytic activity depends on the content of TiO_2 in (ZnO/TiO_2) catalytic mixture and in (ZnO/TiO_2)-β-CD system. To account for this, the effect of $ZnO:TiO_2$ ratio on BG decolorization was studied (Supplementary Data, Fig. S3). The experiments were carried out by varying the ratio between ZnO and TiO_2 as 9:1, 8:2, 7:3, 6:4, 5:5 and 4:6. Higher the content of TiO_2, lower was the photocatalytic activity of (ZnO/TiO_2) as well as (ZnO/TiO_2)-β-CD system. This is due to the fact that excess amount of TiO_2, promotes the recombination of electron-hole pairs in TiO_2 and decreases the light penetration instead of providing an electronic pathway, and thus reduces the reaction rate. Hence, an optimum ratio between ZnO and TiO_2 is needed to prevent the reduction of the activity of the catalyst in the photocatalytic process[21, 22]. In this study, the optimum ratio of $ZnO:TiO_2$ was fixed as 8:2.

The effect of initial concentration of BG was investigated by varying its concentration from $(2.07\text{-}10.35)\times10^{-5}M$ for ZnO and TiO_2 and from $(5.17\text{-}25.9)\times10^{-5}M$ for (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD system (Supplementary Data, Fig. S4). The results show that increase in the concentration of BG dye decreases the percentage removal of dye from 93.0% to 79.0% with ZnO, 90.5% to 75.3% with TiO_2, 95.0% to 81.0% with (ZnO/TiO_2) and 99.2% to 85.0% with $(ZnO/TiO_2$-β-CD) system. As the initial concentration of dye increases, the percentage of decolorization decreases. This is attributed to the following reasons: (i) At higher concentrations of the dye solution, larger number of dye molecules are adsorbed on the surface of catalysts. At the same time, the adsorbed dye molecules are not immediately degraded because the light intensity, dose of the catalyst and illumination time are constant and hence the light penetration is less; (ii) The solution becomes more intensely coloured and hence path length of the photons entering into the solution is less; (iii) Another possible reason is that as the concentration of dye increases, a significant amount of UV light could be absorbed by the dye molecules rather than by the catalytic system; (iv) At higher concentrations, availability of dye molecules is high and there will be more competition between the dye molecules for attachment to the active sites of the catalytic system. Therefore, the formation of $OH^{\bullet}$ and $O_2^{-\bullet}$ radicals is reduced and hence the decolorization efficiency is decreased[23-27]. The optimum concentration of BG dye was fixed as 8.2×10^{-5} *M* for ZnO, 6.21×10^{-5} *M* for TiO_2, 15.5×10^{-5} *M* for (ZnO/TiO_2) and 25.9×10^{-5} *M* for (ZnO/TiO_2)-β-CD system to carry out further studies.

The effect of irradiation time for the decolorization of BG dye was studied by varying the irradiation period from 30–180 min. The decolorization efficiency increases with increase of irradiation time. The reason is that there is enough time to produce a larger number of hydroxyl and superoxide radicals. The decolorization rates of the photocatalytic decolorization process of BG dye over photocatalysts was fitted with pseudo-first order kinetic model. $\ln (C_0/C_t) = kt$, where C_0 and C_t represent the initial concentration of BG dye and that of irradiation time of *t* respectively and *k* represents rate constant. The linearity of the plot (Supplementary Data, Fig. S5) suggests that the decolorization of dye follows pseudo-first order kinetics.

The study of effect of *p*H, one of the very important parameters in the photocatalytic oxidation processes, provides a clear idea about the surface charge properties of a photocatalyst, charge of dye molecules, adsorption ability of dye on a photocatalytic surface and the concentration of hydroxyl radicals available during the course of the reaction process[28]. In this study, the effect of *p*H on the reaction solution was carried out between *p*H 2 and 12 (Supplementary Data, Fig. S6). It was observed that the percentage decolorization of dye increases with an increase in the *p*H of the solution. This can be explained on the basis of following reasons: The *p*H effect is related to the point of zero charge (pzc)[29] of TiO_2 at *p*H 6.2 and of ZnO at *p*H 9.0. In acidic media, (*p*H < pzc), the surface is positively charged and in alkaline media (*p*H > pzc), the surface is negatively charged. The electrostatic attraction between positively charged dye cation and negatively charged catalytic surface are favorable in alkaline medium and consequently adsorption property increased at basic medium. Hence, the decolorization is efficient in basic *p*H. In acidic media, columbic repulsions between dye cation and positively charged catalytic surface are observed and hence the percentage removal of dye is less in acidic *p*H[30]. At basic *p*H, catalytic surfaces are negatively charged due to the adsorbed OH^- ions. The presence of a large number of OH^- ions on the catalytic surface as well as in the reaction medium favors the production of $OH^{\bullet}$ radical[31].

To confirm the mineralization of BG dye, the photocatalytic degradation was investigated by COD analysis. COD allows measurements of waste in terms of the total quantity of oxygen required for the degradation of organic pollutants into CO_2 and inorganic ions[26,27]. In this study, the COD values of BG dye solution are reduced after the photocatalytic decolorization process under UV light irradiation (Fig. 4). The COD values of BG dye solution (at *p*H 4.2), in the presence of different photocatalysts, viz., ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD, before irradiation are 644, 635, 724 and 845 mg O_2/L respectively. However, the COD values of BG dye solution (at *p*H 2-12) in the presence of different photocatalysts, viz., ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2)-β-CD, after irradiation are 522–200, 597–266, 509–166 and 494–62 mg O_2/L respectively. These results indicate that the BG is mineralized at higher *p*H values. The decrease in COD is highest with (ZnO/TiO_2)-β-CD system as compared to other catalytic systems studied herein.

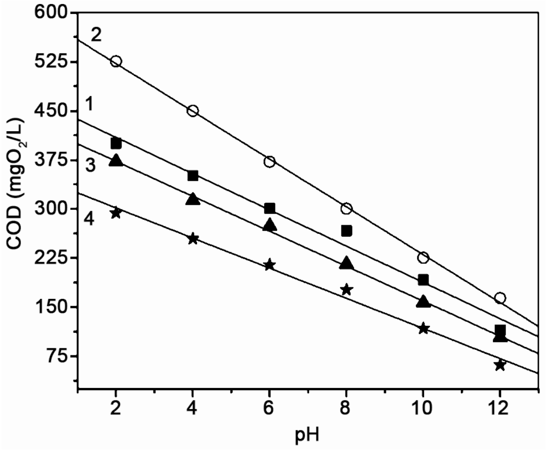

Fig. 4—Determination of chemical oxygen demand. {[BG] = 8.2×10^{-5} *M* for ZnO, 6.21×10^{-5} *M* for TiO_2, 15.5×10^{-5} *M* for (ZnO/TiO_2) and 25.9×10^{-5} *M* for (ZnO/TiO_2)-β-CD; dose = 2 g/ L; irradiation time =120 min. ZnO (1); TiO_2 (2); (ZnO/TiO_2) (3); (ZnO/TiO_2)-β-CD (4).

Mechanism for photocatalytic performance of (ZnO/TiO_2)-β-CD system

A suitable reaction mechanism has been proposed for explaining the photocatalytic decolorization of BG dye in the presence of (ZnO/TiO_2)-β-CD and given as Scheme 1 (steps 1 to 16) and Fig. 5. It is well reported that β-CD molecules have a higher affinity for (ZnO/TiO_2) surface than BG dye molecules and so they would be adsorbed on the (ZnO/TiO_2) surface and occupy the reaction sites effectively[16-18]. Further, β-CD molecules capture the holes available on the active surface of the catalytic mixture (ZnO/TiO_2), resulting in the formation of a stable β-CD-(ZnO/TiO_2)-β-CD system (step 5). The BG dye molecules enter into the cavity of β-CD molecules which are adsorbed on the (ZnO/TiO_2) surface at the equilibrium stage. The steps 6 and 7 explain the inclusion complex pattern of β-CD with BG dye molecules and are the key step in photocatalytic decolorization process in the

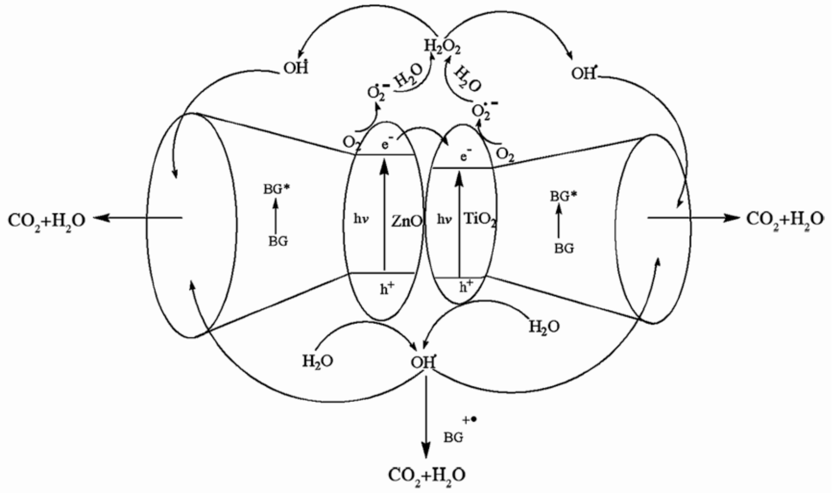

Fig. 5—Photocatalytic performance of (ZnO/TiO_2)-β-CD on decolorization of BG dye.

$$\text{BG dye} + \text{ZnO} \longrightarrow CO_2+H_2O+\text{Mineralized products} \tag{1}$$

$$\text{BG dye} + TiO_2 \longrightarrow CO_2+H_2O+\text{Mineralized products} \tag{2}$$

$$\text{BG dye} + (\text{ZnO}/TiO_2) \longrightarrow CO_2+H_2O+\text{Mineralized products} \tag{3}$$

$$(\text{ZnO}/TiO_2)+\beta\text{–CD} \longrightarrow (\text{ZnO}/TiO_2)\text{-}\beta\text{–CD} \tag{4}$$

$$\beta\text{–CD}+(\text{ZnO}/TiO_2)\text{-}\beta\text{–CD} \longrightarrow \beta\text{–CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{–CD} \tag{5}$$

$$\text{BGdye} +\beta\text{–CD} \longrightarrow \text{BG dye-}\beta\text{–CD} \tag{6}$$

$$\text{BG dye} +\beta\text{–CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{–CD} \longrightarrow \text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD} \tag{7}$$

$$\text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD+BG dye} \longrightarrow \text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye} \tag{8}$$

$$\begin{aligned}\text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye}+h\nu \longrightarrow\ & \text{BG dye*-}(\beta\text{-CD-}(\text{ZnO}/TiO_2)^{\bullet 1}\text{-}\beta\text{-CD})\text{-BG dye*} + \\ & \text{BG dye*-}(\beta\text{-CD-}(\text{ZnO}/TiO_2)^{\bullet 3}\text{-}\beta\text{-CD})\text{-BG dye*}\end{aligned} \tag{9}$$

$$(\text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye})^* \longrightarrow \text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)(e^-)\text{-}\beta\text{-CD-BG dye} \tag{10}$$

$$(\text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye})^* \longrightarrow \text{BG dye}^{\bullet+}\text{-}\beta\text{-CD-}(e^-)(\text{ZnO}/TiO_2)(e^-)\text{-}\beta\text{-CD-BG dye}^{\bullet+} \tag{11}$$

$$\text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye*} +O_2 \longrightarrow \text{BG dye-}\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD-BG dye} +{}^1O_2 \tag{12}$$

$$(e^-)\beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD}+O_2 \longrightarrow \beta\text{-CD-}(\text{ZnO}/TiO_2)\text{-}\beta\text{-CD}+O_2^{\bullet-} \tag{13}$$

$$\text{BG dye}+O_2^{\bullet-} \longrightarrow \text{Mineralized products} \tag{14}$$

$$\text{BG dye} +{}^1O_2 \longrightarrow \text{Mineralized products} \tag{15}$$

$$\text{BG dye}^{\bullet+} \longrightarrow \text{Mineralized products} \tag{16}$$

Scheme 1

suspension containing β-CD resulting in the formation of BG dye-β-CD-(ZnO/TiO_2)-β-CD-BG dye (step 8). During photolysis, the dye molecules absorbed light energy followed by excitation (step 9). During excitation, the electrons are transferred from the conduction band of ZnO to the conduction band of TiO_2 (step 10). At the interface of the two catalysts, a regular electron flow takes place from the higher Fermi level to the lower the Fermi level. The energy levels of ZnO and TiO_2 follow the order: ZnO (CB) > TiO_2 (CB)[21] and the electrons are rapidly injected from the excited BG dye molecules to CB of ZnO and CB of TiO_2 (steps 11 and 12). Superoxide anion radicals are also formed in the presence of oxygen (step 13). The dye and dye cation radicals then undergo degradation processes and yield the mineralized products (steps 14, 15 and 16).

Conclusions

In this work, the photocatalytic ability of (ZnO/TiO_2)-β-CD system under UV light irradiation for the decolorization of BG dye was investigated. The catalysts were characterized by their SEM, XRD and UV-DRS spectral data. UV-visible study confirms the formation of inclusion complex between β-CD and BG dye. The photodecolorization efficiency is high at basic *p*H. The kinetics of photocatalytic decolorization of BG dyes follow pseudo-first order reaction kinetics. COD results show that BG dye is mineralized to a greater extent at basic *p*H. The modified photocatalyst (ZnO/TiO_2)-β-CD system was found to have superior photocatalytic activity than (ZnO/TiO_2), ZnO and TiO_2. This is due to the synergistic effect of ZnO and TiO_2 and the formation of strong inclusion complexes between β-CD and BG dye molecules. Thus, (ZnO/TiO_2)-β-CD system can be considered as an excellent photocatalyst for detoxification of organic pollutants in waste water treatment.

Acknowledgement

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Supplementary Data

Supplementary data associated with this articles, viz., Figs. S1-S6 are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(01) 43-49_SupplData. pdf.

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