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Investigation of Photocatalytic Activity of (ZnO/TiO_2) Modified by β-Cyclodextrin in Photodecoloration of Rhodamine B under Visible Light Irradiation

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ABSTRACT

This paper explains an enhanced photocatalytic activity of (ZnO/TiO_2) modified by β-cyclodextrin (β-CD) through photodecoloration of Rhodamine B (RhB) dye in aqueous solution under visible light irradiation (60 W mercury lamp). The phase structures and the optical property of (ZnO/TiO_2) and (ZnO/TiO_2-β-CD) were characterized by XRD and UV-DRS analyses. The effects of various operational parameters like concentration of RhB dye, amount of catalysts, irradiation time, initial pH and ratio of (ZnO/TiO_2) have been studied. The maximum removal was obtained at basic pH (pH=12). The kinetic data follows first order reaction. The photocatalytic efficiency of (ZnO/TiO_2-β-CD) is compared with (ZnO/TiO_2), bare ZnO and bare TiO_2. A suitable catalytic as well as inclusion reaction mechanism for (ZnO/TiO_2-β-CD) has been established.

1. Introduction

Dyes are one of the toxic compounds and they create serious environmental problems. Because it is very difficult to degrade completely by conventional methods due to their high chemical stability [1]. Semiconductor photocatalysis is an alternative and effective method for solving the above problems. Among various semiconductor photocatalysts, TiO_2 is a promising photocatalyst to degrade various kinds of organic pollutants. It is due to the physical and chemical stability, low cost, easy availability, nontoxic and unique electronic and optical properties. However the main drawback is low quantum yield and lack of visible light absorption hinder its practical application [2-4].

In semiconductor photocatalytic processes, under light irradiation, an electron excited from the valence band to conduction band and forms holes in valence band which interact with H_2O or OH^- adsorbed on the surface of catalyst to generate hydroxyl radical ($OH^{\bullet}$), or the electron in the conduction band interact with adsorbed O_2 to yield $O_2^{\bullet-}$ [5]. These radicals are responsible for degradation of dye molecules. In general, the photocatalytic efficiency of metal oxide is minimized by recombination electron-hole pairs in the bulk of the material. Numerous efforts have been made to enhance the visible light utilization of TiO_2 include sensitization, doping, coupling with other semiconductors, *etc*. The (ZnO/TiO_2) system increases the separation of charge carriers and exhibit better photocatalytic activity than single photocatalyst [6]. ZnO is an alternative photocatalyst for TiO_2 which has similar band gap and better photocatalytic performance when compared to TiO_2 in the degradation of several organic contaminants [7].

Cyclodextrins (CDs) are one of an excellent material for facilitating interfacial electron-hole transfer processes. CDs are able to form inclusion complexes due to their internal cavity which is hydrophobic in nature and external surface is hydrophilic one. All previous works suggest that β-CD plays electron-donating and hole-capturing role when linked to TiO_2 colloids, which lead to charge-hole recombination inhibition and photocatalytic efficiency enhancement [8-15]. Our previous works have explained an enhanced photocatalytic activity by β-CD on the photocatalytic degradation of various dyes in TiO_2 and ZnO under different light radiations [16-18].

In the present work, photocatalytic activity of (ZnO/TiO_2-β-CD) and decoloration of RhB dye under visible light irradiation have been investigated and photocatalytic efficiency are compared with bare semiconductors. The results are well documented.

2. Experimental Methods

2.1 Materials

RhB dye (molecular formula = $C_{28}H_{31}ClN_2O_3$, λ_{max} = 544 nm) obtained from Loba Chemie (India) was used as such. The catalysts *viz.*, ZnO and TiO_2 were received from Merck chemicals, India. β-CD was purchased from Hi Media Chemicals (P) Ltd. All the other chemicals and reagents were used as received. DD water was used throughout the experiment.

2.2 Preparation of (ZnO/TiO_2)

The (ZnO/TiO_2) composite was prepared by mixing 80 mg of ZnO and 20 mg of TiO_2 as a powder mixture (in the ratio of ZnO/TiO_2 80:20) using Agate Mortar.

2.3 Preparation of (ZnO/TiO_2-β-CD)

In order to study the interaction of β-CD on (ZnO/TiO_2) surface, a suspension containing 2.0 gL^{-1} of physical mixture of (ZnO/TiO_2) and 10.0 gL^{-1} of β-CD was magnetically stirred for 24 h, centrifuged and then the solid phase was collected. After being centrifuged, the solid phase of the suspension was carefully washed with deionised water. Eventually, (ZnO/TiO_2-β-CD) system was dried at 50 °C. The samples in this way was used for XRD and UV-DRS analyses.

2.4 Characterization

X-ray diffraction patterns of powder samples were recorded with a high resolution powder X-ray diffractometer model RICH SIERT & Co with CuKα radiation as the X-ray source (k = 1.5406 x 10^{-10} m). UV–visible diffuse reflectance spectra were recorded on a Shimadzu 2550 UV–visible spectrophotometer with $BaSO_4$ as the background between 200 and 800 nm.

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2.5 Photocatalytic Experiments

Photocatalytic experiments were carried out under visible light irradiation. Annular type visible (Hg vapour lamp λ=534 nm) photo reactor is used as the light source in the central axis. Exactly 50 mL of RhB dye solution with required amount of catalysts and at definite concentration was irradiated under visible light. Prior to irradiation, the reaction mixture was stirred in the dark for 10 minutes to achieve adsorption saturation. At regular intervals, 5 mL of the sample was taken out and centrifuged to remove the catalysts. Absorbance at 544 nm was measured to determine the concentration of RhB after the photocatalytic decoloration process with the help of visible spectrophotometer (ELICO, Model No. SL207). The molar ratio concentrations of RhB dye and β-CD were kept constant at 1:1. The natural pH of RhB dye solution was 3.6, irradiation time was 120 minutes and the ratio of ZnO and TiO_2 was fixed as 80:20. The pH values of RhB dye solution were adjusted using a digital pen pH meter (Hanna instruments, Portugal) depending on desired values with HCl and NaOH solution.

3. Results and Discussion

3.1 X-ray Diffraction Studies

X-ray diffraction patterns of β-CD, ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2-β-CD) are given in Fig. 1. 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 type of ZnO which indicate that ZnO possesses a hexagonal crystal structure. The high intensity peaks of (101) indicate the anisotropic growth and imply preferred orientation of the crystallites. Diffraction peaks at 25.38°, 37.9°, 48.07°, 53.94° and 55.18° correspond to (101), (004), (200) (105) and (211) planes of TiO_2 which indicate that TiO_2 exhibits single phase anatase type. The results are compared with JCPDS (21-1272) and JCPDS (36-1451) for TiO_2 and ZnO respectively [19]. From the results it is confirmed that the XRD patterns of (ZnO/TiO_2-β-CD) is similar to that of (ZnO/TiO_2). This indicates that addition of β-CD on (ZnO/TiO_2) suggested that the crystal structure of (ZnO/TiO_2) has not been changed even by to the addition of β-CD. Moreover, the addition of β-CD do not cause any shift in peak position of that of (ZnO/TiO_2) phase.

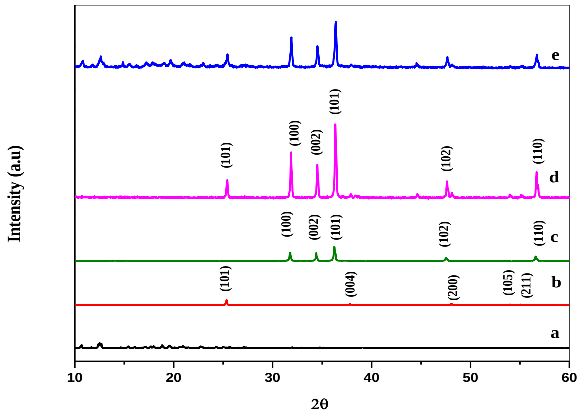

Fig. 1 XRD patterns of a) β-CD; b) TiO_2; c) ZnO; d) (ZnO/TiO_2); e) (ZnO/TiO_2)-β-CD.

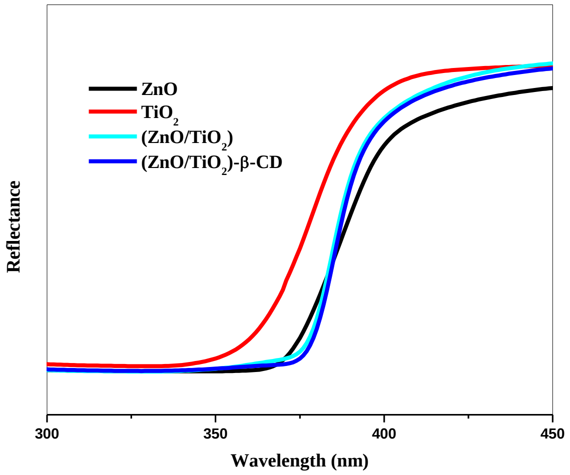

Fig. 2 UV-Visible diffuse reflectance spectra

3.2 UV-Visible Diffuse Reflectance Spectra

UV–Vis DRS are utilized to determine the optical properties of ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2-β-CD) as shown in Fig. 2. All the samples exhibit an optical absorption below 400 nm. Binding of β-CD on (ZnO/TiO_2) system significantly affect the absorptive properties of (ZnO/TiO_2) system. (ZnO/TiO_2) shows only slight variation of band gap energy as compared to that of ZnO and TiO_2. It is due to that incorporation of TiO_2 into ZnO. (ZnO/TiO_2-β-CD) has higher absorption than (ZnO/TiO_2), ZnO and TiO_2. From UV-DRS spectra, the band gap energy of (ZnO/TiO_2-β-CD) (3.30 eV) is lower than ZnO (3.38 eV), TiO_2 (3.42 eV) and (ZnO/TiO_2) (3.35 eV). It indicates that (ZnO/TiO_2-β-CD) has higher the photocatalytic activity than (ZnO/TiO_2), ZnO and TiO_2.

3.3 Dissociation Constant Measurement

The dissociation constant (K_D) value for the complexation between β-CD and dye can be calculated using the Benesi–Hildebrand equation.

$$([C]\,[S]/\Delta OD) = ([C] + [S]/\,\Delta\varepsilon) + (K_D/\Delta\varepsilon) \qquad (1)$$

where [C] and [S] represent the concentrations of the β-CD and RhB dye molecules respectively, at equilibrium. ΔOD represents the increase in absorption upon addition of β-CD. Δε = difference in molar extinction coefficients between the bound and the free RhB dye molecule. K_D is the dissociation constant. The K_D can be obtained from the ratio of the intercept ($K_D/\Delta\varepsilon$) and the slope ($1/\Delta\varepsilon$) from the linear plot of [C] [S]/ΔOD vs {[C] + [S]} (Fig. 3). In this study, the determined K_D value is 0.378×10^{-5} M which confirms the formation of strong inclusion complex between β-CD and RhB dye [20-22].

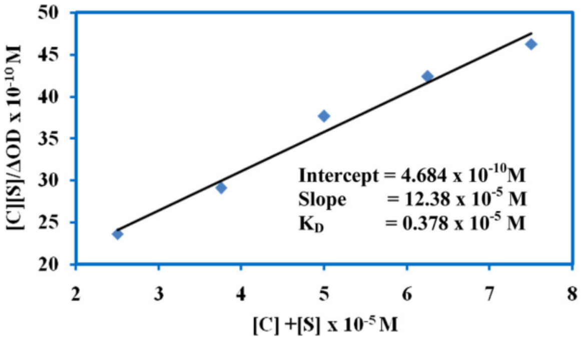

Fig. 3 Plot of [C] [S]/ ΔOD vs. {[C] +[S]} for RhB/β-CD complex

3.4 Photocatalytic Activity Measurement under Visible Light

3.4.1 Effect of Initial Concentration of Dye

The effect of initial concentration of RhB dye on various catalysts like ZnO, TiO_2, (ZnO/TiO_2) and (ZnO/TiO_2-β-CD) with fixed amount of catalysts 2 g/L and irradiation time 120 min are given in Fig. 4.

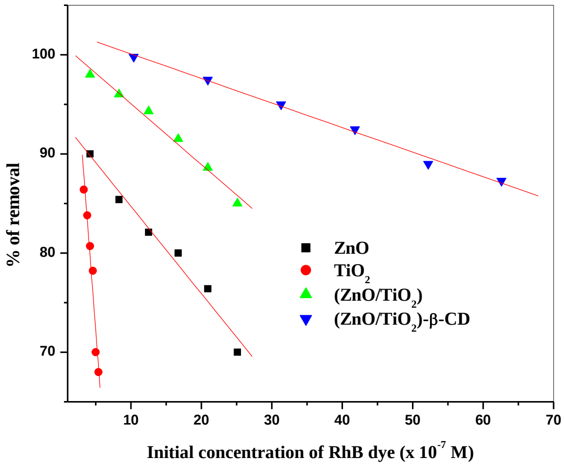

Fig. 4 Effect of initial concentration of RhB dye

The concentrations of dye solutions are varying from 4.2-25.1 x 10^{-7} M for ZnO and (ZnO/TiO_2), 3.3-5.4 x 10^{-7} M for TiO_2 and 10.4-62.6 x 10^{-7} M for (ZnO/TiO_2-β-CD) at pH 3.6. The results show that the increase in the concentration of RhB dye decreases the percentage removal of dye from 90.2-70% for ZnO, 86.4-68% for TiO_2, 98-85% for (ZnO/TiO_2) and 99.8-87.3% for (ZnO/TiO_2-β-CD). At lower concentration of RhB dye, the

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percentage removal is found to be higher. At the same time, the reverse effect is obtained when higher concentration of RhB dye. The reason for decreasing removal efficiency is due to that more RhB dye molecules adsorbed on the catalysts surface increases the light absorbed by dye molecules rather than by the catalyst. Further the path length of photons entering the dye solution is decreased and fewer photons are reached on the catalyst surface. Hence the generation of $OH^{\bullet}$ and $O_2^{\bullet -}$ radicals and decoloration rate is decreases [23, 24]. The optimum concentration of RhB dye was fixed as 12.5 x 10^{-7} M for ZnO, 4.6 x 10^{-7} M TiO_2, 20.9 x 10^{-7} M for (ZnO/TiO_2) and 41.8 x 10^{-7} M for (ZnO/TiO_2-β-CD) for further studies.

3.4.2 Effect of Amount of Catalysts

The effect of catalyst dose on the photodegradation of RhB dye under visible light irradiation was investigated by changing the dose of the catalysts from 0.6-3.6 g/L for ZnO, TiO_2 and 1-6 g/L for (ZnO/TiO_2) and (ZnO/TiO_2-β-CD). The results are presented in Fig. 5. The results show that increase of the catalyst dose increases the efficiency of degradation rate. It is due to increasing the total surface area and number of active sites which help to increase the generation of more number of photons, more number of dye molecules adsorbed on the catalytic surface and density of particles in the area of illumination also increased. Hence an excess amount of catalysts are not involved in catalytic activity and aggregation of particles which causes decreasing the number of active sites and also decreases the penetration of light and light scattering which leads to lower generation of $OH^{\bullet}$ and $O_2^{\bullet -}$ radicals and thus rate is low [25, 26]. The optimum catalyst dose was fixed 2 g/L.

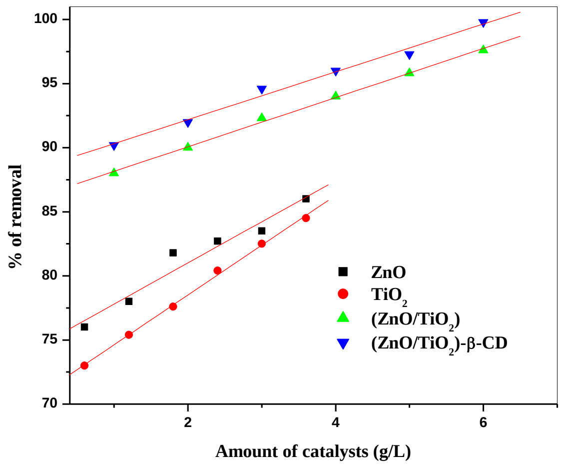

Fig. 5 Effect of amount of catalysts

3.4.3 Effect of Irradiation Time

The effect of irradiation time for decoloration of RhB dye is studied by varying from 30 min to 180 min. The decoloration efficiency increases with increase of irradiation time as shown in Fig. 6. It is attributed to the fact that there is enough time to produce more number of hydroxyl and superoxide radicals. At 180 min. the percentage decoloration is 99.2% for (ZnO/TiO_2-β-CD).

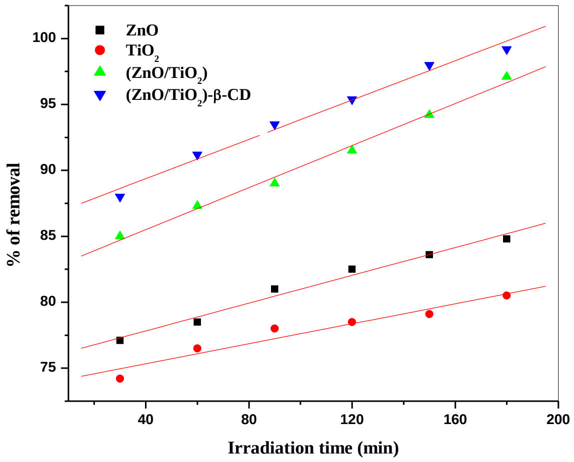

Fig. 6 Effect of irradiation time

3.4.5 Kinetics

The degradation rates of the photocatalytic decoloration process of RhB dye over photocatalysts fitted with pseudo-first order kinetic model for RhB. The linearity of the plot in Fig. 7 suggests that the disappearance of dye approximately follows the pseudo-first order using the formula,

$$\ln (C_0 / C_t) = kt \qquad (2)$$

where C_0 and C_t represent the initial concentration of RhB dye and that of irradiation time (t), respectively. k represents apparent rate constant [27]. The rate constant values were calculated as 6.45 x 10^{-3} min^{-1} for ZnO, 4.99 x 10^{-3} min^{-1} for TiO_2, 2.505 x 10^{-2} min^{-1} for (ZnO/TiO_2) and 3.178 x 10^{-2} min^{-1} for (ZnO/TiO_2-β-CD).

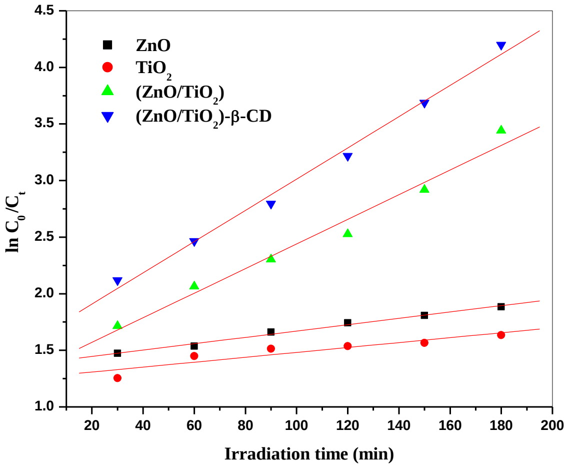

Fig. 7 Decoloration kinetics

3.4.6 Effect of pH

pH plays an important role in the photocatalytic processes. It depends on the surface charge property of the photocatalysts. The experiments were examined in the range 2-12. Fig. 8 indicates that the percentage decoloration of dye increased with an increase in the pH of the solution. The pH effect is related to the point of zero charge (pzc) of TiO_2 at pH 6.2 and ZnO at pH 9.0. [28]. In acidic media, (pH < pzc), the surface is positively charged and in alkaline media (pH > pzc) the surface is negatively charged. The electrostatic attraction between positively charged dye cation and negatively charged catalyst surface is favorable in alkaline medium and consequently adsorption property increased at basic medium. Hence the decoloration higher at basic pH. At acidic media, there is columbic repulsion between dye cation and positively charged catalyst surface observed and hence the percentage removal of dye is less in acidic pH [29, 22].

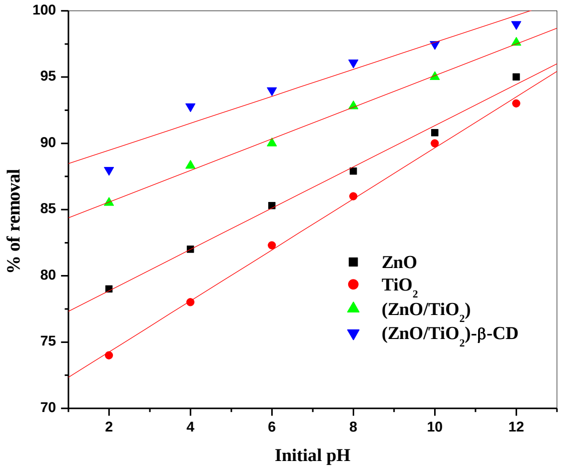

Fig. 8 Effect of initial pH

3.4.7 Effect of (ZnO/TiO_2) Ratio

The effect of (ZnO/TiO_2) ratio on RhB decoloration are shown in Fig. 9. The experiments were carried out by varying ratio of ZnO and TiO_2 from 90:10, 80:20, 70:30, 60:40, 50:50 and 40:60. The decoloration efficiency decreases with increases the amount of TiO_2. Higher the content of TiO_2 reduces the photocatalytic activity of (ZnO/TiO_2) and (ZnO/TiO_2-β-CD). It

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can be explained that aggregation of TiO_2 around the active centers of the surface area of ZnO reduces photocatalytic activity of both the catalysts [30,31]. The optimum ratio of (ZnO/TiO_2) was fixed as 80:20.

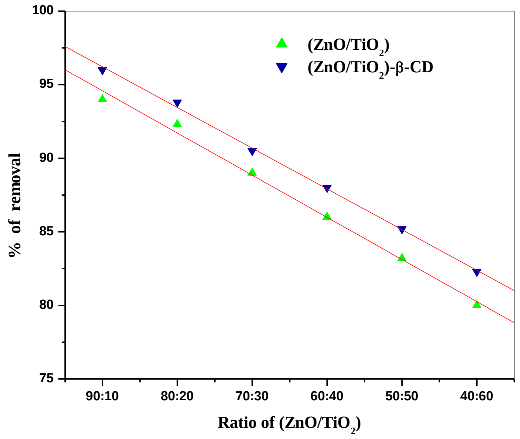

Fig. 9 Effect of (ZnO/TiO_2) ratio

3.4.8 Mechanism for Photocatalytic Behavior of (ZnO/TiO_2-β-CD)

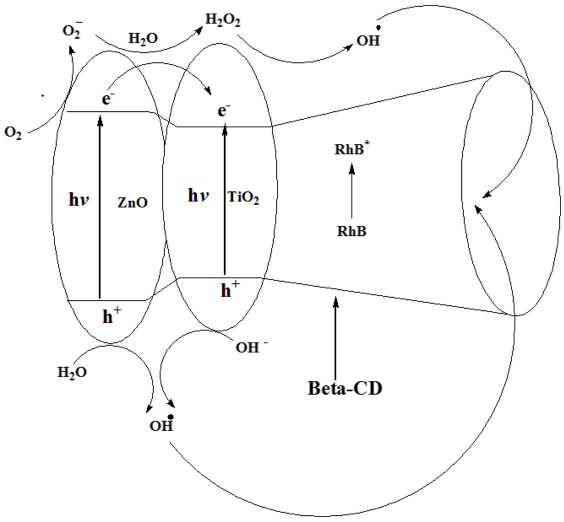

Fig. 10 Mechanism for the enhanced photocatalytic activity of (ZnO/TiO_2-β-CD) in decoloration of RhB dye

RhB dye + ZnO → $CO_2 + H_2O$ + mineralization products (a)
RhB dye + TiO_2 → $CO_2 + H_2O$ + mineralization products (b)
RhB dye + (ZnO/TiO_2) → $CO_2 + H_2O$ + mineralization products (c)
(ZnO/TiO_2)+ β-CD → (ZnO/TiO_2-β-CD) (d)
RhB dye + β-CD → β-CD–RhB dye (e)
RhB dye + (ZnO/TiO_2-β-CD) → (ZnO/TiO_2-β-CD)-RhB dye (f)
(ZnO/TiO_2-β-CD)-RhB dye + hν → (ZnO/TiO_2 -β-CD)$^{\bullet 1}$-RhB dye* +
(ZnO/TiO_2-β-CD)$^{\bullet 3}$-RhB dye* (g)
(ZnO/TiO_2-β-CD)-RhB dye* → (ZnO/TiO_2(e^-)-β-CD)-RhB dye (h)
(ZnO/TiO_2-β-CD)-RhB dye* → (e^-) (ZnO/TiO_2-β-CD) + RhB dye$^{\bullet +}$ (i)
(ZnO/TiO_2-β-CD)-RhB dye* + O_2 → (ZnO/TiO_2-β-CD)-RhB dye + $^1O_2$ (j)
(e^-)(ZnO/TiO_2-β-CD) + O_2 → (ZnO/TiO_2-β-CD) + $O_2^{\bullet -}$ (k)
RhB dye$^{\bullet +}$ → Products (l)
RhB dye + $^1O_2$ → Products (m)
RhB dye + $O_2^{\bullet -}$ → Products (n)

The photocatalytic decoloration of RhB dye in the presence of (ZnO/TiO_2-β-CD) is explained in the mechanism as shown in Fig. 10 [equations a to n]. The RhB dye molecules are entered in the cavity of β-CD which is linked to the (ZnO/TiO_2) surface at the equilibrium stage. β-CD molecules could be adsorbed on (ZnO/TiO_2) surface and occupy the reaction sites. Because it has higher affinity with (ZnO/TiO_2) surface than RhB dye molecules. β-CD could capture the holes available on the active (ZnO/TiO_2) surface resulting in the formation of stable (ZnO/TiO_2-β-CD) (d). The reaction (e) explains the inclusion complex reaction of β-CD with RhB dye molecules and it should be the key step in photocatalytic decoloration in suspension containing β-CD. The complex (ZnO/TiO_2-β-CD)-RhB dye is formed (f). Then, the dye molecules were absorbing radiation followed by excitation (g). At the time of excitation, the electrons are transfer from the conduction band of ZnO to the conduction band of TiO_2 (h). Because at the interface of two materials, the electron flow is taking place from higher Fermi level to lower Fermi level. The conduction Bands of ZnO and TiO_2 are -4.05 eV and -4.2 eV respectively. The energy level of ZnO and TiO_2 follow the order: ZnO (CB) > TiO_2 (CB) [32] and an electron is rapidly injected from the excited dye to either CB of ZnO or CB of TiO_2 (i) and (j). Superoxide anion radical was formed in the presence of oxygen (k). The dye and dye cation radical then undergo degradation (l, m, and n).

4. Conclusion

In this work, the photocatalytic ability of (ZnO/TiO_2-β-CD) under visible light irradiation for the decoloration of RhB dye was investigated. The obtained results are compared with bare ZnO, TiO_2 and modified semiconductor (ZnO/TiO_2) surfaces. The catalysts were characterized by XRD and UV-DRS analyses. The experimental results indicate that the percentage of removal increased with increasing amount of catalysts, irradiation time, pH and decreased with increasing initial concentration of dye and ratio of (ZnO/TiO_2). The photodecoloration efficiency is high in basic pH. (ZnO/TiO_2-β-CD) system exhibits a better photocatalytic efficiency than (ZnO/TiO_2), ZnO and TiO_2. It is due to the formation of inclusion complex between RhB dye and β-CD and synergistic effect of ZnO and TiO_2. This method is very effective for retarding recombination of electron-hole recombination and increases the photocatalytic efficiency of ZnO and TiO_2.

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