Journal of Advanced Chemical Sciences 1 (2015) 9–14

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com

Enhanced Photocatalytic Activity of TiO_2 using β-Cyclodextrin on Solar Light Assisted Decoloration of Azocarmine G Dye

S. Pitchaimuthu[1, 2], G. Lakshmi[1], P. Velusamy[1, *]

[1] *Centre for Research and Post-graduate Studies in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi – 626 124, TN, India.*
[2]*Department of Chemistry, Thiagarajar College, Madurai – 625 009, TN, India. (Present Address)*

ARTICLE DETAILS

Article history:
Received 8 December 2014
Accepted 11 December 2014
Available online 12 December 2014

Keywords:
Azocarmine G dye
TiO_2
β-CD
Photocatalytic decoloration

ABSTRACT

The photocatalytic activity of TiO_2 is enhanced by the addition of β-cyclodextrin (β-CD) on decoloration of azocarmine G (AZG) dye under solar light irradiation. The morphologies, phase structures and optical properties of TiO_2 and TiO_2-β-CD catalysts has been investigated by FE-SEM, PXRD and UV–visible DRS respectively. The interaction between AZG dye and β-CD has also been characterized by UV-visible and FT-IR spectral analyses. The TiO_2–β-CD system exists higher photocatalytic activity than pure TiO_2 system. This is attributed to their large surface area, absorption enhancement in solar light region and effective separation of electrons and holes. The percentage removal (~98%) was achieved at acidic pH within 120 minutes. The observed results indicate that decolorization of the AZG dye follows pseudo-first-order kinetics.

1. Introduction

Dyes are one of the most harmful chemical compounds found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [1-3]. They are also esthetically objectionable for drinking and other purposes [4]. Dyes can cause allergy, dermatitis, skin irritation [5] and also provoke cancer [6] and mutation in humans [7].

In recent years, many strategies have been devised to remove the pollutants, including treatment methods such as biological oxidation, chemical and physical processes such as precipitation, adsorption by activated carbon, air stripping, coagulation, reverse osmosis, membrane ultrafiltration, and other chemical and physical methods for the degradation of effluents [8,9]. However, these traditional methods are often costly, non-destructive and may cause secondary pollution, thus greatly limiting their large-scale implementation and hence more efficient and economic methods have to be developed. A number of remarkable progresses have been made in the heterogeneous photocatalytic decoloration of pollutants under different light sources. These techniques have more advantages over the conventional technologies, say decoloration of the dyes into innocuous final products.

TiO_2 has been considered as one of the most promising photocatalysts because of its environment stability, natural abundance, and nontoxicity [10]. However, the light response range of pure TiO_2 is limited in the UV-light region, which restrains its application seriously [11]. Thus a number of efforts have been employed to inhibit the recombination of electron-hole pairs and improve charge transport *via* coupling the wide band gap semiconductor photocatalysts with other materials, such as semiconductor/noble-metal composite, quantum dot-semiconductor composite, C–N doped semiconductor, carbon nanotubes, or fullerene (C_{60})-semiconductor composites [12-17].

Cyclodextrin (CD) modified TiO_2 has attracted renewed interest as Willner and colleagues observed that β-CD could stabilize TiO_2 colloids and facilitate interfacial electron transfer processes [18]. Excellent literatures have been appeared to elucidate the effect of β-CD on TiO_2 photochemical properties. All previous works suggest that β-CD plays electron-donating and hole-capturing roles when linked to TiO_2 colloids, which lead to charge-hole recombination restriction and photocatalytic efficiency enhancement. Some previous papers have also been reported the stimulative effect of CD on the photocatalytic degradation of organic pollutants in TiO_2 suspensions [19-28]. Our previous works have also accounted for the stimulative effect of β-CD on the photocatalytic degradation of dye in TiO_2 and ZnO suspensions under different light radiations [29-31].

In this study, the activity of TiO_2 and the effect of additon of β-CD with TiO_2 on photocatalytic decoloration of AZG dye solution under solar light radiation have been investigated and the results are well documented.

2. Experimental

2.1 Materials

The commercial organic dye azocarmine G (AZG) (Molecular Formula = $C_{28}H_{18}N_3NaO_6S_2$, C.I. NO. 50085, λ_{max} = 516 nm) (Fig. 1) obtained from Loba Chemie was used as such. The semiconductor photocatalyst TiO_2 was purchased from Merck Chemicals. β-cyclodextrin was received from Himedia chemicals. All other chemicals were of the analytical grade, received from Merck and used without further purification. Double distilled water was used throughout this study for the preparation of all the experimental solutions.

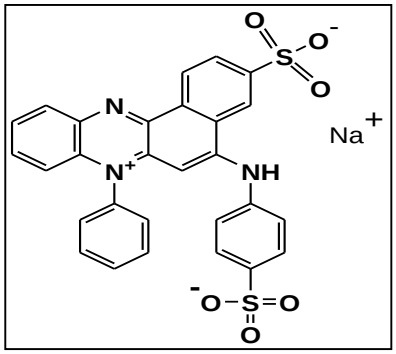

Fig. 1 Structure of AZG dye

*Corresponding Author.
Ph.: Tel.: +91 9443572149; *Fax*: +91 04562 254970
Email Address : velusamyanjac@rediffmail.com (P. Velusamy)

2.2 Characterization

FE-SEM was used to investigate the morphology of the samples β-CD, TiO_2 and TiO_2-β-CD. FE-SEM images were obtained on a Carl ZEISS (ΣIGMA Series, Germany) microscope recorded at an accelerated voltage of 2 kV. X-ray diffraction patterns of powder samples were recorded with a high resolution X-ray powder diffractometer model RICH SIERT & Co with CuK_α radiation as the X-ray source (λ = 1.5406 x 10^{-10} m). UV–vis diffuse reflectance spectra were recorded on a Shimadzu 2550 UV-vis spectrophotometer with $BaSO_4$ as the background between 200 nm and 700 nm. UV-visible spectra were recorded by UV-visible spectrophotometer (Shimadzu UV-1700) and the scan range was from 200 nm to 700 nm. FT-IR spectra were recorded using Shimadzu (model 8400S) in the region 4000 cm^{-1} – 400 cm^{-1} as KBr pellets.

2.3 Photocatalytic decoloration experiment

Photocatalytic decoloration experiments were carried out under solar light irradiation by using sun light as the source in the central axis. AZG dye solutions containing the photocatalysts of either TiO_2 or TiO_2-β-CD were prepared. The pH values of AZG dye solutions were adjusted using digital pen pH meter (Hanna instruments, Portugal). Depending on desired values with HCl and NaOH solution, as their effect on the adsorption surface properties of TiO_2 is negligible [32]. Prior to irradiation, TiO_2 suspensions were kept in dark for 10 min. to attain adsorption-desorption equilibrium between dye and TiO_2. The tubes were taken out from the light radiation at different intervals of time and the solutions were centrifuged well. The supernatant liquid was collected and labeled for the determination of concentrations for the remained dye by measuring its absorbance (at λ_{max} = 516 nm) with visible spectrophotometer (Elico, Model No. SL207). In all the cases, exactly 50 mL of reactant solution was irradiated with required amount of photocatalysts. The pH of the AZG dye solutions was adjusted before irradiation process and it was not controlled during the course of the reaction. After the photocatalytic procedure, the irradiated samples were collected and COD values were determined using open reflux method [29-31].

By keeping the concentrations of AZG dye-β-CD as constant with the molar ratio of 1:1, the effect of all other experimental parameters on the rate of photocatalytic decoloration of AZG dye solutions was investigated. The experimental pH of AZG dye solution and the irradiation time were fixed as 7.1 and 120 min.

2.4 Preparation and characterisation of TiO_2-β-CD system

In order to study the interaction of β-CD on TiO_2 surfaces, a suspension containing 2.0 g/L TiO_2 and 10.0 g/L 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 double distilled water. Eventually, the TiO_2-β-CD system was dried at 50 °C. The sample prepared in this method was used for FE-SEM, XRD, and UV-DRS analyses.

For studying the inclusion complex between β-CD and AZG dye to the saturated solution of β-CD in distilled water, equimolar amount of AZG dye was added and stirred continuously for 24 h. The formed complex powder was filtered, washed with diethyl ether to remove uncomplexed AZG dye, and dried in an air oven at 50 °C. The resultant complex obtained was used for FT-IR spectral analysis.

3. Results and Discussion

3.1 Field Emission Scanning Electron Microscopy (FE-SEM)

Fig. 2 (a, b and c) depicts FE-SEM micrograph of the bare β-CD, bare TiO_2 and TiO_2-β-CD respectively. Bare CD shows amorphous surface. The surfaces of bare TiO_2 and TiO_2-β-CD exhibit similar morphology which indicates that there is no change in the lattice structure of TiO_2. However, the outer boundary of the TiO_2-β-CD was distinctly different from TiO_2. This may due to the aggregation of TiO_2 and β-CD particles as the surfaces of the particles are very loose. This kind of surface structure can provide a better adsorption environment and more active sites for the photocatalytic reaction [30, 31].

3.2 Powder X-ray diffraction patterns (PXRD)

The X-ray powder diffraction patterns of bare TiO_2, bare β-CD and TiO_2-β-CD are presented in Fig. 3 (a-c). The PXRD analysis of TiO_2 reveals that the sample exhibits single-phase which belongs to anatase-type TiO_2 and it is identified by comparing the above spectra with the JCPDS file #21-1272. Diffraction peaks at 25.38º, 37.9º, 48.07º, 53.94º and 55.18º correspond to (101), (004), (200), (105) and (211) planes of TiO_2 respectively. The relatively high intensity of the peak for (101) plane is an indicative of anisotropic growth which implies a preferred orientation of the crystallites. Addition of β-CD does not cause any shift in peak position to that of TiO_2 phase. The results also demonstrated that the anatase TiO_2 conserved their anatase crystal features. Addition of β-CD causes no effect on the crystalline feature of TiO_2. The same results are also reported by Zhang *et al.* [24].

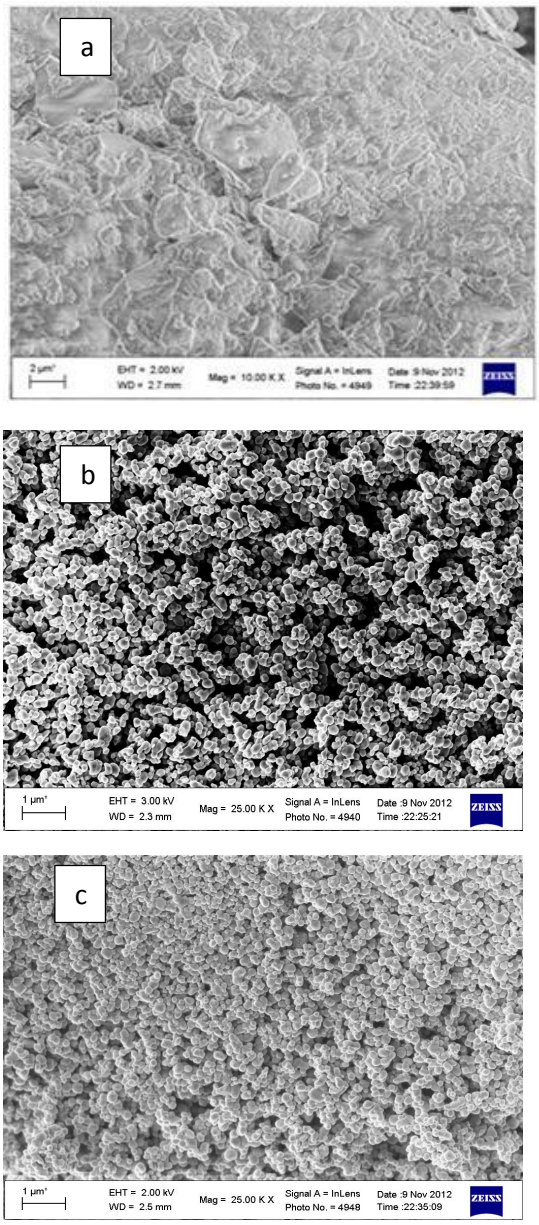

Fig. 2 FE-SEM micrograph of (a) bare β-CD (b) bare TiO_2 (c) TiO_2-β-CD

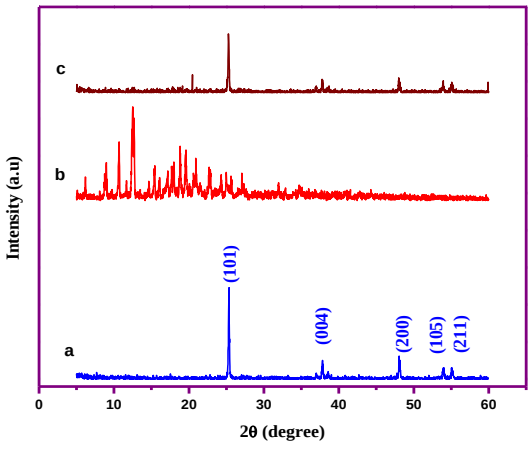

Fig. 3 X-ray powder diffraction patterns of (a)bare TiO_2 (b)bare β-CD (c)TiO_2- β-CD

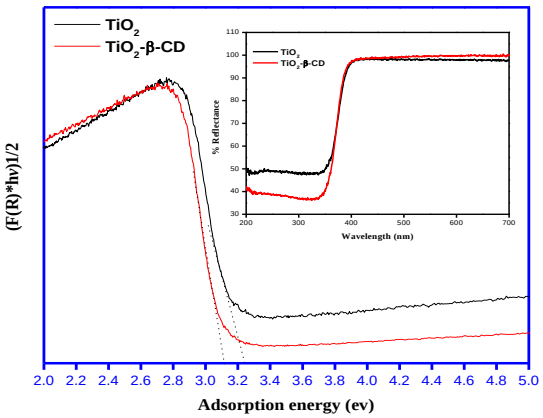

Fig. 4 UV-Visible DRS spectra of Bare TiO_2 and TiO_2-β-CD (Inset: Reflectance *vs* Wavelength (nm))

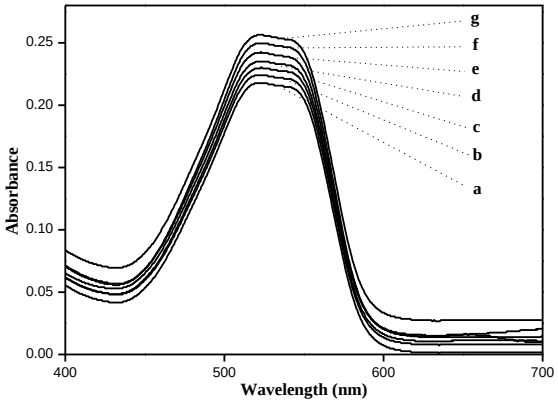

Fig. 5 UV-Visible spectral analysis for the complexation pattern between β-CD and AZG dye (a) AZG dye (b) 1:1 β-CD/ AZG (c) 2:1 β-CD/ AZG (d) 3:1 β-CD/ AZG (e) 4:1 β-CD/ AZG (f) 5:1 β-CD/ AZG (g) 6:1 β-CD/ AZG

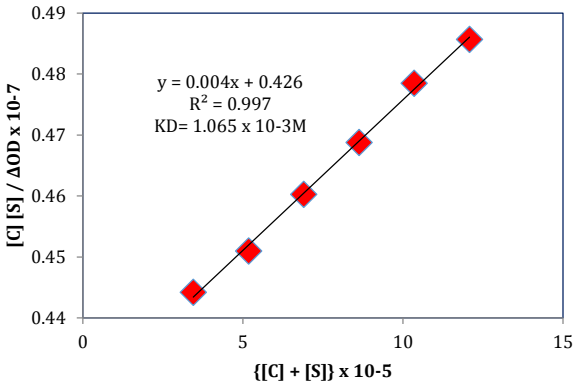

Fig. 6 {[C] [S]/ Δ OD)} x 10^{-7} vs {[C] + [S]} x 10^{-5}

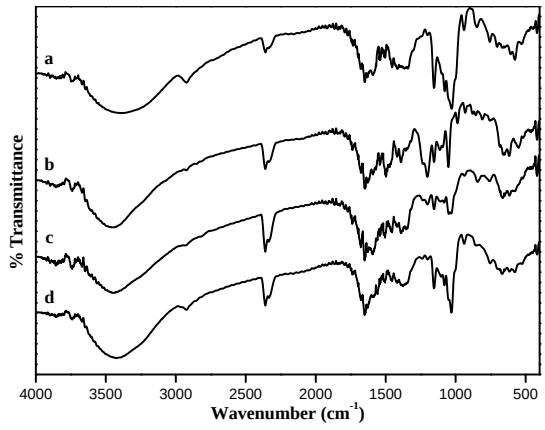

Fig. 7 FT-IR spectral analysis: (a) β-CD (b) AZG dye (c) β-CD/AZG dye physical mixture (d) β-CD/AZG 1:1 complex

3.3 UV-Visible diffuse reflectance *spectra*

The UV-visible diffuse reflectance spectra of bare TiO_2 and TiO_2-β-CD are shown in Fig. 4. β-CD modification leads to a significant effect on the optical characteristics of TiO_2. The TiO_2-β-CD has slightly higher absorption intensity in the visible region compared to the bare TiO_2 system Fig. 4 (Inset). This is attributed to the charge transfer from β-CD to Ti (IV) (*ie.* ligand to metal charge transfer (LMCT)) located in an octahedral co-ordination environment [26, 29, 30].

3.4 UV-Visible spectral analysis

The molecular structure of β-CD allows various guest molecules with suitable dimensions to form host/guest inclusion complexes. In this study, the inclusion complex between β-CD and AZG dye was characterized with UV-Visible spectrum as given in Fig. 5. It depicts that the absorbance of inclusion complex increases with increasing the concentration of β-CD [23]. The optimum molar ratio between β-CD and AZG dye was fixed as 1:1.

3.5 Dissociation constant measurements

The dissociation constant (K_D) value for the complexation between β-CD and AZG dye can be calculated using the following Benesi-Hildebrand equation [33, 34].

$$\frac{[C]\,[S]}{\Delta OD} = \frac{[C] + [S]}{\Delta \varepsilon} + \frac{K_D}{\Delta \varepsilon}$$

where, [C], [S] represent the concentrations of the host, guest molecules respectively at equilibrium.

ΔOD = the increase in absorption upon addition of β-cyclodextrin

$\Delta \varepsilon$ = the difference in molar extinction coefficients between the bound and the free guest.

K_D = dissociation constant

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 x 10^{-7} M *vs* {[C] + [S]} x 10^{-5} M (Fig. 6). The determined K_D value is 1.065 x 10^{-3} M.

3.6 FT-IR spectral analysis

Though IR measurements are not employed for detecting inclusion compounds (due to the superposition of bands), in some cases where the substrate has characterstic absorbance in regions where β-CD does not absorb, IR spectrum is useful [33].

From the FT-IR spectra given in Fig. 7, it is observed that the peaks corresponding to monosubstituted benzene (1615 cm^{-1}, 1596 cm^{-1} and 1496 cm^{-1}) for the AZG dye molecule (Fig. 7b) are appearing in the β-CD-AZG dye 1:1 physical mixture (Fig. 7c), whereas hidden in the β-CD/AZG dye 1 :1 complex (Fig. 7d). Moreover, it contains all the absorption peaks related to β-CD (Fig. 7a). It is interesting to note here that the spectrum of a physical mixture of β-CD and AZG dye resembles more of the AZG dye peaks than that of a complex spectrum. In addition, decreases in intensities of many bands are observed in β-CD-AZG dye complex spectrum. It clearly confirms that there is a strong inclusion of the AZG dye molecule inside the β-CD cavity.

3.7 Effect of initial dye concentration

The photocatalytic decoloration of AZG dye was carried out at different initial concentrations ranging from 1.7253 x 10^{-5} M to 10.3523 x 10^{-5} M for both TiO_2/solar light system and TiO_2-β-CD/solar light systems. The percentage removal of AZG dye was decreased with increasing the concentration of dye (Fig. 8a). An explanation for this behaviour is that as initial concentration increases, more and more dye molecules are adsorbed on the surface of TiO_2. There are only a fewer active sites for the adsorption of hydroxyl ions, thus diminishes the generation of hydroxyl radicals.

Another possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of photons entering the solution decreases. In low concentration of dye the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [35, 36]. Further, as the concentration of dye molecules increases, the photons get intercepted before they can reach the surface of the catalyst. Hence, the absorption of photons by the catalyst decreases, and consequently the decoloration rate is reduced [37, 38]. The same effect was observed by Matthews [39] during the photocatalytic degradation of methylene blue dye with TiO_2 catalyst. The optimum concentration of AZG dye was fixed as 3.4507 x 10^{-5} M for further studies.

Cite this Article as: S. Pitchaimuthu, G. Lakshmi, P. Velusamy, Enhanced photocatalytic activity of TiO_2 using β-cyclodextrin on solar light assisted decoloration of azocarmine G dye, J. Adv. Chem. Sci. 1 (1) (2015) 9–14.

3.8 Effect of pH

The wastewater from textile industries usually has a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH [36, 37]. Hence, attempts have been made to study the influence of pH in the degradation of dyes in the solar light irradiation. As AZG dye is an anionic dye, photodegradation of AZG dye at different pH from 1 to 11, clearly shows that acceptable results are obtained in acidic medium. The effect of pH on the degradation is shown in Fig. 8b. As the zero point charge of TiO_2 is 6.8, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. Thus a negative surface charge does not favor the adsorption of dye anions due to their electrostatic force of repulsion. Due to the electrostatic attraction of the positively charged catalyst with the ionized sulfonic group of this acidic dye, leads to a higher decoloration rate. At these pH values there is also the formation of more number of $OH^{\bullet}$ radicals which react with dye molecules and increase the decoloration level [38-40]. The uptake of dye anion is much higher in acidic solutions than those in neutral as well as in alkaline conditions. Hence, at high pH values the hydroxyl radicals are as rapidly scavenged as they do not have the opportunity to react with dye molecules [41].

The interpretation of effects of pH on the efficiency of the photodegradation process is a very difficult task, because three possible reaction mechanisms can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conduction band. The importance of each one depends on the nature of the substrate and pH of the medium [42]. In the present case, it can be presumed that the main reaction is presented by the hydroxyl radical attack, which can be favoured by the high concentration of the hydroxyl radicals at around acidic pH. An additional explanation for the pH effects can be related with changes in the specification of the dye. That is, protonation or deprotonation of the dye can change its adsorption characteristics and redox ability.

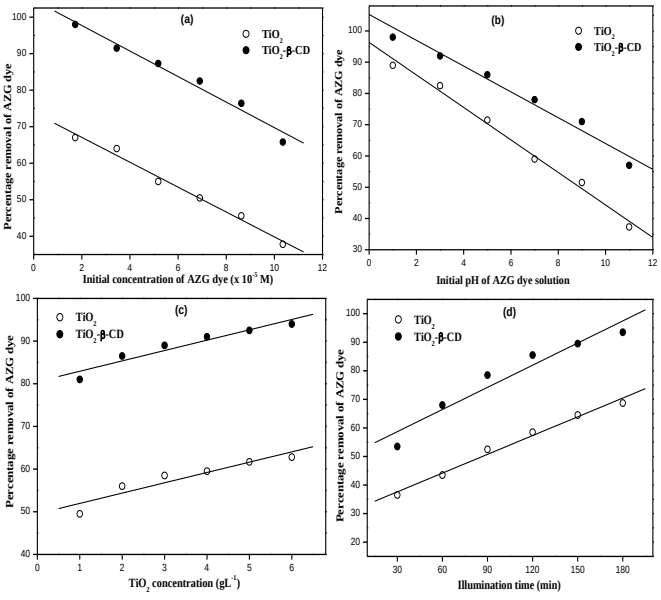

Fig. 8 Effect of operational parameters (a) Effect of initial concentration of AZG dye (b) Effect of initial pH of AZG dye (c) Effect of TiO_2 concentration (d) Effect of llumination time

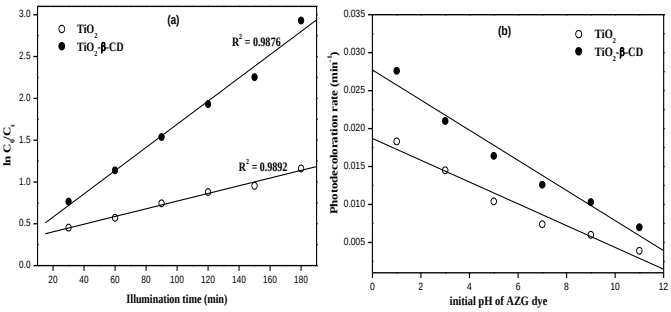

Fig. 9 Kinetics of AZG dye decoloration (a) ln C0/Ct vs Illumination time (b) Photodecoloration rate vs initial pH of AZG dye

3.9 Effect of dose of TiO_2 variation

The influence of TiO_2 concentration from 1.0 to 6.0 gL^{-1} for AZG dye on the photodecoloration efficiency was investigated. The observed results revealed that the photodecoloration efficiency increases with increase in TiO_2 concentration (Fig. 8c). This can be explained in terms of availability of active sites on the catalyst surface, which increases the number of dye molecules adsorbed followed by the increase in the density of particles in the area of illumination [43]. The optimum amount of catalyst for photocatalytic decoloration of AZG dye was found to be 4.0gL^{-1}. All the above, process parameters were performed with this concentration of TiO_2. The minimum percentage removal of AZG dye at lower TiO_2 dose can be attributed to the fact that more light is transmitted through the reactor and the transmitted light is not utilised in the photocatalytic reaction [44].

3.10 Effect of illumination time

Illumination time plays a vital role in the decoloration process of the pollutants. The illumination time was varied from 30 min. to 180 min. The remaining concentration of AZG dye is decreased with an increase the illumination time (Fig. 8d). It is observed that nearly 93.5 % decoloration of AZG dye solution for TiO_2-β-CD is achieved with in 180 min.

3.11 Pseudo-first order kinetics

The experimental results indicate that the degradation rates of the photocatalytic decoloration process of AZG dye over illuminated TiO_2 fitted with the pseudo-first order kinetic model AZG [45, 46]. The regression curve of natural logarithm of AZG dye concentration *vs* illumination time gives straight line in both the cases (*ie.*, TiO_2/solar light system and TiO_2-β-CD/solar light system) (Fig. 9a). The linearity of plot suggests that the photodecoloration reaction approximately follows pseudo-first order using the formula,

$$\ln (C_0/C_t) = k_t$$

where C_0 and C_t represent the initial concentration of the corresponding AZG dye in solution and that of illumination time of t respectively and k_t represents the apparent rate constant (min^{-1}) at time t.

3.12 Promotion effects of β-CD on the photodecoloration rate

The β-CD molecules promote the photodecoloration rate of AZG dye in the TiO_2-β-CD/solar light system compared to that of TiO_2/solar light system (Fig. 9b). Further, the effects of β-CD observed in this study are not due to a simple extension of the photodecoloration mechanism of AZG dye in the absence of β-CD, but due to the introduction of another mechanism, possibly sustained by the high inclusion abilities of β-CD with AZG dye molecules and also the trapping of radicals generated by the TiO_2 [47].This is the reason for having better decoloration of AZG dye molecules in TiO_2-β-CD/solar light system than that of TiO_2 /solar light system.

3.13 Mineralization

β-CD is photochemically stable. It does not undergo degradation under illumination. Hence, the COD corresponds to the degradation of AZG dye molecules alone. The mineralization experiments were carried out at different pH from 1 to 11. To the solution of AZG dye solution TiO_2 2 gL^{-1} and aqueous β-CD solution were added. The concentration ratio between β-CD and AZG dye was made as 1:1 ratio. The photocatalytic procedure was followed, the irradiated samples were collected and COD values were determined. The obtained results indicate that the percentage reduction of COD decreases with increasing the initial pH of AZG dye solution (Fig. 10).

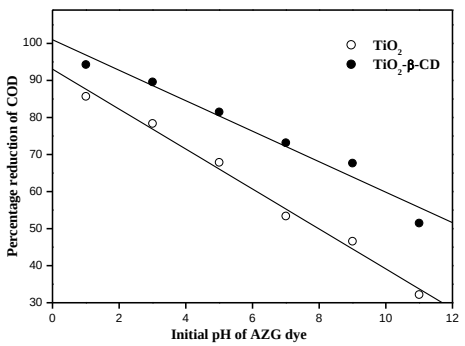

Fig. 10 Mineralization of AZG dye

3.14 Mechanism of the effect of β-CD on photodecoloration

The proposed mechanism for the photocatalytic decoloration of AZG dye by the excitation of TiO_2-β-CD system is shown in Fig. 11. As β-CD has higher affinity on metal oxide surface than dye molecules, they can be adsorbed on TiO_2 surface and engage the active sites. β-CD would capture the holes on active TiO_2 surface resulting in the formation of stable TiO_2-β-CD complex. Thus the formation of inclusion complex between β-CD and AZG dye molecules is being the key step as well as the main reaction channel in photocatalytic decoloration in TiO_2 suspension containing β-CD [24]. Thus the AZG dye molecules in TiO_2-β-CD system absorb light radiation in the equilibrium stage followed by excitation. An electron is rapidly injected from the excited dye to the conduction band of TiO_2 [24, 29, 30]. Further, the formed superoxide anion radical ($\bullet O^{2-}$) is also responsible for the photodecolation of the dye and dye cation upon illuminated in TiO_2-β-CD system.

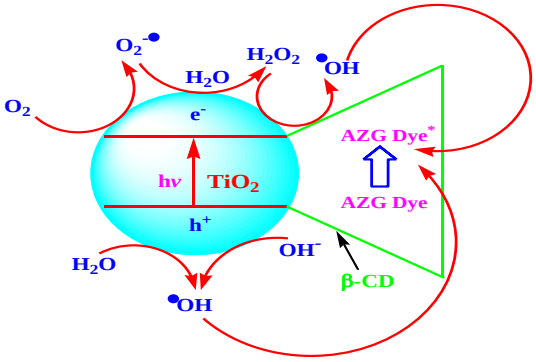

Fig. 11 Proposed Mechanism of the effect of β-CD on photodecoloration of AZG dye

4. Conclusion

In this work, we carried out a detailed study of the effect of β-CD on the photodegradation of AZG dye in TiO_2 suspension. XRD analysis reveals that TiO_2 conserved their anatase crystal features during the irradiation. Addition of β-CD does not cause any shift in peak position of that of TiO_2 phase. The results also demonstrated that the anatase TiO_2 conserved their anatase crystal features. UV-Visible diffuse reflectance spectra demonstrated that β-CD addition leads to a significant effect on the optical characteristics of TiO_2. TiO_2-β-CD system has slightly higher absorption intensity in the visible region compared to the bare TiO_2 system.

Comparing the results obtained from all the operational parameters discussed above, it is observed that TiO_2-β-CD systems exhibits better photocatalytic decoloration efficiency than that of TiO_2 systems. Effect of addition of β-CD on dye photodecoloration in TiO_2 suspension would probably lead to a high efficiency and selectivity than that of photodecoloration of dyes using TiO_2 as catalyst. This work provides basic information on the promotion effects of β-CD on the photodegradability of TiO_2 on dye in aqueous solution. Photocatalytic decoloration of dye is highly pH dependent. The COD analysis reveals that complete mineralization of dye could be achieved. The photocatalytic decoloration process follows pseudo first order kinetics.

Acknowledgment

The authors thank the Management and the Principal of Ayya Nadar Janaki Ammal College, Sivakasi, TamilNadu, India for providing necessary facilities. Authors also thank the University Grants Commission, New Delhi, for the financial support through UGC-Major Research Project Ref. [UGC - Ref. No.F. No. 38-22/2009 (SR) Dated: 19.12.2009]. The Instrumentation Centre of Ayya Nadar Janaki Ammal College, Sivakasi, the Centre for Nanoscience and Nanotechnology of Bharathidasan University, Tiruchirappalli, and the Department of Earthscience of Pondicherry University, Pondicherry are highly appreciated for recording the UV–Visible, FT-IR spectra, FESEM and Powder XRD patterns respectively

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Cite this Article as: S. Pitchaimuthu, G. Lakshmi, P. Velusamy, Enhanced photocatalytic activity of TiO_2 using β-cyclodextrin on solar light assisted decoloration of azocarmine G dye, J. Adv. Chem. Sci. 1 (1) (2015) 9–14.