ORIGINAL ARTICLE

Modification of the photocatalytic activity of TiO$_2$ by β-Cyclodextrin in decoloration of ethyl violet dye

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ARTICLE INFO

Article history:
Received 14 July 2012
Received in revised form 5 October 2012
Accepted 11 October 2012
Available online 6 December 2012

Keywords:
Ethyl violet dye
β-Cyclodextrin
TiO$_2$
Photocatalytic decoloration
COD

ABSTRACT

The photocatalytic decoloration of an organic dye, ethyl violet (EV), has been studied in the presence of TiO$_2$ and the addition of β-Cyclodextrin (β-CD) with TiO$_2$ (TiO$_2$-β-CD) under UV-A light irradiation. The different operating parameters like initial concentration of dye, illumination time, pH and amount of catalyst used have also been investigated. The photocatalytic decoloration efficiency is more in the TiO$_2$-β-CD/UV-A light system than TiO$_2$/UV-A light system. The mineralization of EV has been confirmed by Chemical Oxygen Demand (COD) measurements. The complexation patterns have been confirmed with UV–Visible and FT-IR spectral data and the interaction between TiO$_2$ and β-CD have been characterized by powder XRD analysis and UV–Visible diffuse reflectance spectroscopy.

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Introduction

Decoloration of organic dyes in wastewater from the industries is some what necessary to have pollution free environment. Because these dyes affect the growth of plants as well as ecosystems by producing aesthetically unpleasant odour and non-biodegradable wastes. It is estimated that from 1% to 15% of the dye is lost during dyeing processes and is released into wastewater [1–3]. There are many processes extensively used to remove the dye molecules from wastewater such as incineration, biological treatment, ozonation, adsorption on solid phases, coagulation, foam flotation, electrochemical oxidation, Fenton or Photofenton oxidation, and membranes, [3–12]. However, the above processes have some kind of limitations, viz. the incineration can produce toxic volatiles; biological treatment methods demand long period of treatment and bad smells; ozonation presents a short half-life. In ozonation the stability of ozone is affected by the presence of salts, pH and temperature, adsorption results in phase transference of contaminant, not degrading the contaminant and producing sludge. Most of these methods are non-destructive, but they generate secondary pollution, because in these techniques the dyes are transferred into another phase and not degrading the pollutants and this phase has to be regenerated. All the
above effects dictate us the necessity to find an alternate method for treatment of wastewater contaminated by organic dyes.

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. Many semiconductor photocatalysts (such as TiO$_2$, ZnO, Fe$_2$O$_3$, CdS, CeO$_2$ and ZnS) have been used to degrade organic pollutants. These semiconductors can act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band [13–19]. Among them TiO$_2$ has been extensively applied as a photocatalyst due to its strong photocatalytic activity, nontoxic, low cost and high stability. However its band gap (3.0–3.2 eV) can capture maximum light energy by the region of ultra violet radiation. To extend the response of TiO$_2$ to UV-A light, the modified TiO$_2$ systems with various methods have also been reported [20–25].

Cyclodextrins (CDs) are non-reducing cyclic maltoligosaccharides produced from starch by cyclodextrin glycosyltransferase and are composed of a hydrophilic outer surface and a hydrophobic inner cavity. CDs can form inclusion complexes with organic pollutants and organic pesticides to reduce the environmental impact of the chemical pollutants [26–28]. In this study, the activity of TiO$_2$ and the effect of addition of β-CD with TiO$_2$ on photocatalytic decoloration of EV dye solution under UV-A light radiation have been studied and the results are well documented.

Experimental

The commercial organic basic dye EV (80% of dye, \(\lambda_{\text{max}} = 595 \text{ nm}\)) received from Loba Chemie was used as such. The semiconductor photocatalyst TiO$_2$ was purchased from SD’s Fine Chemicals. β-Cyclodextrin was received from Himedia chemicals. AnalR grade reagents, HgSO$_4$, Ag$_2$SO$_4$, \(\text{H}_2\text{SO}_4\), \(\text{K}_2\text{Cr}_2\text{O}_7\), HCl, NaOH and Ferroin indicator were received from Merck. Double distilled water was used to prepare the experimental solutions. The physical properties of β-CD and EV dye are shown Table 1.

Characterization

X-ray diffraction patterns of powder samples were recorded with a high resolution powder X-ray diffractometer model RICH SIERT & Co with Cu as the X-ray source (\(\lambda = 1.5406 \times 10^{-10} \text{ m}\)). UV–Visible spectra were recorded by a UV–Visible spectrophotometer (Shimadzu UV-1700) and the scan range was from 400 to 700 nm. FT-IR spectra were recorded using “Shimadzu” (model 8400S) in the region 400–4000 cm$^{-1}$ as KBr pellets. UV–Vis diffuse reflectance spectra were recorded on a Shimadzu 2550 UV–Vis spectrophotometer with \(\text{BaSO}_4\) as the background between 200 and 700 nm.

Photocatalytic decoloration experiment

Photocatalytic decoloration experiments under UV-A light irradiation were carried out in an Annular type Photoreactor, with a high pressure mercury vapor lamp (\(\lambda \geq 365 \text{ nm}\), 160 W B22 200–250 V Philips, India). It was used as light energy source in the central axis. EV dye solutions containing the photocatalysts of either TiO$_2$ or TiO$_2$-β-CD were prepared. The pH values of EV 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 [2]. The distance from the light source to the photocell containing EV dye solutions is about 12 cm. Prior to irradiation, TiO$_2$ suspensions were kept in dark for 10 min. to attain adsorption–desorption equilibrium between dye and TiO$_2$ system. During irradiation the reactant solutions were continuously stirred with magnetic stirrer. The tubes were taken out 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 \(\lambda_{\text{max}} = 595 \text{ nm}\)) with visible spectrophotometer (Elico, Model No. SL207). In all the cases, exactly 20 mL of reactant solution was irradiated with required amount of photocatalysts. The pH of the EV dye solutions was adjusted before irradiation process and it was not controlled during the course of the reaction.

By keeping the concentrations of EV 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 EV dye solutions was investigated. The experimental pH of EV dye solution was fixed as 8.3 and the irradiation time was fixed as 120 min.

**Determination of Chemical Oxygen Demand (COD)**

Exactly 50 mL of the sample was taken in a 500 mL round bottom flask with 1 g of mercuric sulfate. Slowly, 5 mL of silver sulfate reagent (prepared from 5.5 g silver sulfate per kg in concentrated sulfuric acid) was added to the solution. Cooling of the mixture is necessary to avoid possible loss of volatile matters if any, while stirring. Exactly 25 mL of 0.041 M potassium dichromate solution was added to the mixture slowly. The flask was attached to the condenser and 70 mL of silver sulfate reagent was added and allowed to reflux for 2 h. After refluxing, the solution was cooled at room temperature. Five drops of Ferroin indicator was added and titrated against a standard solution of Ferrous Ammonium Sulfate (FAS) until the appearance of the first sharp color change from bluish green to reddish brown. The COD values can be calculated in terms of oxygen per liter in milligram (mg O$_2$/L) using the following equation [29].

**COD mg O$_2$/L = (B – A) N 8000 / S**

where \(B\) is the milliliter of FAS consumed by \(\text{K}_2\text{Cr}_2\text{O}_7\), \(A\) is the milliliters of FAS consumed by \(\text{K}_2\text{Cr}_2\text{O}_7\) and EV dye mixture, \(N\) is the normality of FAS and \(S\) the volume of the EV dye.

| Table 1 Physical properties of ethyl violet dye and β-Cyclodextrin. |
|---------------------------------|-----------------|-----------------|
| Name                            | Ethyl violet    | β-Cyclodextrin  |
| Molecular formula               | \(\text{C}_8\text{H}_6\text{N}_2\text{Cl}\) | \(\text{C}_2\text{H}_7\text{O}_3\) |
| Molar weight                    | 492.2           | 1135            |
| Appearance                      | Dark violet powder | White powder   |
| pH                              | 8.3 (Basic dye) | —               |
| \(\lambda_{\text{max}}\)       | 595 nm          | —               |
Results and discussion

X-ray powder diffraction analysis

The X-ray powder diffraction patterns of TiO$_2$, 1:1 physical mixture of TiO$_2$-β-CD and β-CD are presented in Fig. 1a–c respectively. The XRD analysis of TiO$_2$ reveals that sample that exhibits single-phase belongs to anatase-type TiO$_2$ which is identified by comparing the spectra with the JCPDS file # 21-1272. 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$_2$, respectively. The relatively high intensity of the peak for (101) plane is an indicative of anisotropic growth and implies a preferred orientation of the crystallites. Moreover, the addition of β-CD do 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. Addition of β-CD causes no effect on the crystalline feature of TiO$_2$. The same results were also obtained in the previous report [30].

UV–Visible diffuse reflectance spectra

The diffuse reflectance spectra of TiO$_2$ and TiO$_2$-β-CD catalysts are provided in Fig. 2, respectively. As shown in Fig. 2b, TiO$_2$-β-CD has slightly higher absorption intensity in the visible region compared to the bare TiO$_2$ Fig. 2a which is due to the ligand to metal charge transfer (LMCT) from β-CD to Ti$^{IV}$ located in an octahedral coordination environment [31].

UV–Visible and FT-IR spectral analyze

The molecular structure of β-CD allows to form host/guest inclusion complexes with various guest molecules of suitable dimensions. In this study, the inclusion complex between EV dye and β-CD was characterized with UV–Visible and FT-IR spectral data as given in Figs. 3 and 4. UV–Visible spectral analysis was carried out to the solutions containing different amount of β-CD and a constant amount of EV dye (4.062 × 10$^{-5}$ M). The concentration of β-CD was varied 1–7 times as that of EV dye. The solutions were magnetically stirred and their absorption spectra were recorded in the range of 400–700 nm. From the UV–Visible spectra it is clearly observed that the absorbance of inclusion complex increases with increasing the concentration of β-CD [27]. In this work, the optimum molar ratio between β-CD and EV dye is fixed as 1:1.

Fig. 1 X-ray powder diffraction patterns of: (a) TiO$_2$, (b) 1:1 physical mixture of TiO$_2$-β-CD and (c) β-CD.

Fig. 2 Diffuse reflectance spectra of: (a) TiO$_2$ and (b) TiO$_2$-β-CD.

Fig. 3 UV–Visible spectral analysis for the complexation pattern between β-CD and EV dye. (a) β-CD (b) EV dye (c) 1:1 EV/β-CD (d) 1:2 EV/β-CD (e) 1:3 EV/β-CD (f) 1:4 EV/β-CD (g) 1:5 EV/β-CD and (h) 1:6 EV/β-CD.
Though IR measurements are not employed for detecting inclusion compounds (due to the superposition of host and guest bands), in some cases where the substrate has characteristic absorbance in the regions where β-CD does not absorb, IR spectrum is useful [32]. From the FT-IR spectra Fig. 4a–d, it is observed that the peaks corresponding to –CH (3101 cm⁻¹), –CH₃ (2970 & 2873 cm⁻¹), aromatic system (3315 & 3197 cm⁻¹) for the EV dye molecule (Fig. 4b) are present in the 1:1 physical mixture of β-CD-EV dye complex (Fig. 4c), where as hidden in the β-CD-EV dye 1:1 complex (Fig. 4d). Moreover, it contains all the absorption peaks related to β-CD (2²-OH (3382 cm⁻¹), –CH (2927 cm⁻¹) and –OH (1080 cm⁻¹). It is interesting to note that the spectrum of a physical mixture of β-CD and EV dye resembles more of the EV dye peaks than that of their complex spectrum. In addition, decrease in intensities of many bands are observed in β-CD-EV dye complex spectrum. The complexation between the EV dye molecule and β-CD has been authentically proved by the FT-IR spectral data.

**Effect of initial concentration of EV dye solution**

The effect of initial concentration of EV dye solution was investigated with TiO₂ and TiO₂-β-CD by varying the initial concentration of EV dye from 1.02 × 10⁻⁵ M to 6.1 × 10⁻³ M. It is observed that the percentage removal of EV dye molecules decreases with an increase in the initial concentration of EV. From the above results it has been found out that the photocatalytic decoloration efficiency is high for TiO₂-β-CD/UV-A light system compared to that of TiO₂/UV-A light system. The presumed reason is that, when the initial concentration of dye is increased, generation of OH⁺ radicals on the surface of TiO₂ is reduced since the active sites were covered by dye molecules. Another explanation for this is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases due to the impermeability of the dye solution. It also causes the dye molecules to adsorb light and the photons never reach the photocatalyst surface, thus the percentage removal of EV dye decreases [33,34]. The optimum concentration of EV dye was fixed as 4.062 × 10⁻³ M for further studies.

**Effect of initial pH of EV dye solution**

The pH value is one of the important factors influencing the rate of decoloration of organic compounds in the photocatalytic processes. It is also an important operational variable in actual wastewater treatment. The EV dye decoloration is highly pH dependent. The photocatalytic decoloration of EV dye at different pH values varying from 1 to 11, clearly shows that the photocatalytic decoloration efficiency is higher in basic medium.

The zero point charge value for TiO₂ is zero at pH 6.8, positive at pH below 6.8 and negative at pH above 6.8 [20,35]. It is well documented that TiO₂ is negatively charged in basic medium, and so it attracts cations in basic medium and repels anions. As EV dye is a basic one, at basic pH, the photocatalytic removal of EV dye is higher than at acidic pH. Further, at basic pH more hydroxide ions (OH⁻) in the solution induced the generation of hydroxyl free radicals (HO·), which came from the photooxidation of OH⁻ by holes forming on the titanium dioxide surface [36]. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photocatalytic decay of EV dye may be accelerated in an alkaline medium.

Another reason for the decrease in the activity of TiO₂ in acidic media is due to the effect of chloride ions present in the EV dye molecule. The effect of chloride ions on the decolorisation rates of the pollutants is discussed in detail in the literature, and is believed to be quite negative. There are three different issues addressed [37].

- At low pH levels (<5), the catalyst exists primarily as TiOH⁺ and TiOH. Under these conditions, the negatively charged chloride ions are attracted to the catalyst surface therefore competing with pollutant species for active sites, resulting in low degradation [38].
- The chloride ions in the suspension could act as electron scavengers competing, in this case, with molecular oxygen. This will inhibit the formation of the superoxide radicals that are essential for the formation of the actual oxidation agent, the hydroxyl radicals. The efficiency of the photocatalyst would once again be decreased [39,40].
- Another possible reaction of the chloride ions could be with the free radicals in the suspension, leading to the consumption of the radicals that are desired in high concentration in order to react with organic pollutant [41].

**Effect of TiO₂ concentration**

Optimizing the amount of TiO₂ is needed for getting highest decoloration rate. Hence in this study the quantity of the catalyst was varied from 1.25 g L⁻¹ to 7.5 g L⁻¹. It is noticed that, the photocatalytic decoloration efficiency increases with an increase in the amount of TiO₂. This is due to the fact that increase in the number of EV dye molecules adsorbed on TiO₂ surface leads to increase in rate of decoloration [42]. As TiO₂ concentration increases, the availability of TiO₂ surface for the adsorption of EV dye increased.
**Effect of illumination time**

Illumination time plays an important role in the decoloration process of the pollutants from wastewater. The illumination time was varied from 30 min to 180 min. It is interesting to note here that the remaining EV dye concentration is decreased with an increase in illumination time. It is observed that nearly 96.5% decoloration of EV dye solution is achieved within 180 min.

**Decoloration kinetics**

The photocatalytic decoloration process of EV dye tends to follow pseudo-first order kinetics in the presence of catalysts used in this study. The regression curve of natural logarithm of EV concentration vs. reaction time (Fig. 5) gives straight line in both the cases, using the formula,

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

where \( C_0 \) and \( C_t \) represent the initial concentration of the EV dye in solution and that of illumination time of \( t \), respectively, and \( k \) represents the apparent rate constant (min\(^{-1}\)) [43,44].

Fig. 6 and Table 2 show the maximum percentage removal of EV with various operational parameters. It is observed that TiO\(_2\)-β-CD/UV-A light system exhibits better photocatalytic decoloration efficiency than that of TiO\(_2\)/UV-A light system.

**Mineralization**

β-CD is photochemically stable. It does not undergo degradation under illumination. Hence, the COD corresponds to EV dye molecules alone. The mineralization experiments were carried out at different pH from 1 to 11. With the EV dye solution TiO\(_2\) 5 g L\(^{-1}\) and aqueous β-CD solution were added. The concentration ratio between β-CD and EV 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 are indicating that the COD decreases with increasing the initial pH of EV dye solution (Table 3).

**Measurement of dissociation constant**

The dissociation constant (\( K_D \)) value for the complexation between β-CD and EV dye can be calculated using the Benesi–Hildebrand equation [32]. \( K_D \) can be obtained from the ratio of the intercept (\( K_D/\Delta e \)) and the slope (1/\( \Delta e \)) from the linear plot of [C] [S] /\( \Delta OD \) vs. [C] + [S] (Fig. 7). The determined \( K_D \) value is 7.1579 × 10\(^{-3}\) M.

\[
\frac{[C][S]}{\Delta OD} = \frac{[C] + [S]}{\Delta e} + K_D
\]

where [C] and [S] represent the concentrations of the host and guest molecules respectively at equilibrium, \( \Delta OD \) is the increase in absorption upon addition of β-CD. \( \Delta e \) is the difference in molar extinction coefficients between the bound and the free guest, \( K_D \) is dissociation constant.

**Mechanism of the effect of β-CD on photodecoloration**

The following reactions a, b, c, d, e, f, g, h, i), (j, k explain the induced photodecolorisation of EV dye by three systems viz. TiO\(_2\), EV dye – β-CD inclusion complex and TiO\(_2\)-β-CD.

1. EV dye + TiO\(_2\) → H\(_2\)O + CO\(_2\) + Mineralization products
2. β-CD + TiO\(_2\) → TiO\(_2\)-β-CD
3. EV dye + β-CD → β-CD-EV dye
4. EV Dye + TiO\(_2\)-β-CD → TiO\(_2\)-β-CD-EV Dye
5. TiO\(_2\)-β-CD-EV Dye + hν → TiO\(_2\)-β-CD\(^{+}\)EV Dye\(^{+}\)
6. TiO\(_2\)-β-CD-EV Dye\(^{+}\) + O\(_2\) → TiO\(_2\)-β-CD-EV Dye + O\(_2\)
7. TiO\(_2\)-β-CD-EV Dye\(^{+}\) + O\(_2\) → TiO\(_2\)-β-CD-EV Dye + O\(_2\)
8. EV Dye\(^{+}\) → Products
9. EV Dye + O\(_2\) → Products
10. EV Dye + O\(_2\) → Products

As β-CD shows higher affinity on TiO\(_2\) surface than dye molecules, they can adsorb on TiO\(_2\) surface, engage the active sites and would capture holes on active TiO\(_2\) surface resulting in the formation of stable TiO\(_2\)-β-CD complex (b). The reaction (c) is the inclusion complex reaction of β-CD with EV dye molecules and it should be the key step in photocatalytic
decoloration in TiO$_2$ suspension containing β-CD [30]. EV dye molecules form inclusion complex, resulting in the indirect photodecoloration is to be the main reaction channel. EV dye molecules enter into the cavity of β-CD, which is linked to the TiO$_2$ surface in the equilibrium stage (d) and they absorb light radiation followed by excitation (e). An electron is rapidly injected from the excited dye to the conduction band of TiO$_2$ (f) and (g). Another important radical in illumination of TiO$_2$-β-CD is the superoxide anion radical (°C$_5$O$_2$) (h). The dye and dye cation radical then undergo degradation (i, j, k).

In general, the lifetimes for the excited states of unreacted guests is prolonged when incorporated inside the cavity of cyclodextrins. Therefore, cyclodextrin facilitates the electron injection from the excited dyes to the TiO$_2$ conduction band and thereby enhances the degradation [31].

**Conclusion**

Comparing the results obtained from all the operational parameters discussed above, it is observed that TiO$_2$-β-CD/UV-A light system exhibits better photocatalytic decoloration efficiency than that of TiO$_2$/UV-A light system. Effect of addition of β-CD on EV dye photodecoloration in TiO$_2$ suspension that would probably lead to a high efficiency and selectivity photodecoloration of EV dye using TiO$_2$ as catalyst.

Photocatalytic decoloration of EV 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.

**Conflict of interest**

The authors have declared no conflict of interest.

**Acknowledgements**

The authors thank the Management and the Principal of Ayya Nadar Janaki Ammal College, Sivakasi, 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, Ayya Nadar Janaki Ammal College, Sivakasi and Department of Earth science, Pondicherry University, Pondicherry are highly appreciated for recording the UV–Visible, FT-IR spectra and Powder XRD patterns respectively.

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