Study of visible-light photocatalytic degradation of 2,4-dichlorophenoxy acetic acid in batch and circulated-mode photoreactors

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Abstract

Purpose The consumption of pesticides and chemical fertilizers is one of the major environmental and health problems. In this report, 2,4-dichlorophenoxyacetic acid (2,4-D) was chosen to evaluate the impact of photodegradation using LED (Light-emitting diode) (400 and 365 nm) sources in batch and programmable circulated-mode photoreactors respectively.

Methods A β -cyclodextrin (β -CD) grafted titanium dioxide P25 (P25/ β -CD) and complexation of 2,4-D and β -CD were synthesized via photoinduced and spray-drying methods, respectively. The structures were characterized. Moreover, we investigated the effects of the amount of catalyst, the β -CD amount on bed catalyst, irradiation time, kind of photoreactor on the photocatalytic degradation efficiency.

Results Based on the results of experiments in batch reactor, the optimum amount of TiO_2 , β -CD grafted by catalyst were 1 and 0.1 g/L, respectively. In batch-mode the photodegradation efficiency of 2,4-D after 5 h with P25, P25/ β -CD as a photocatalyst and 2,4-D/ β -CD complex with P25 photocatalyst were approximately 81, 85 and 95% respectively. After 8 h of irradiation in circulated-mode reactor, degradation yields with P25, P25/ β -CD and 2,4-D/ β -CD complex along with P25 were 89, 91 and 96% respectively. On the other hand, the circulated-mode photoreactor with high efficiency was appropriate to degradation of the high concentration of 2,4-D solution (200 mg/L). After 5 successive cycles with 25 h of irradiation, P25 and P25/ β -CD maintained as high 2,4-D removal efficiency as 82.6, 84% respectively, with excellent stability and reusability.

Conclusion The photodegradation method can be used as an effective and environmental friendly process in the degradation of organic compound.

Keywords 2,4-Dichlorophenoxyacetic acid (2,4-D) · Light-emitting diode (LED) · 2,4-D/ β -CD complex · Batch-mode photoreactor · Circulated-mode photoreactor

Introduction

2,4-Dichlorophenoxyacetic acid is ordinary herbicide used to control broadleaf weeds existing in grains;

health and environmental associations identify it as high-risk contamination that can instigate cancer-causing mutations on people and animals. As one of phenolic herbicides, due to its biochemical stability, it cannot be decomposed by ordinary

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approaches; therefore, a proficient method to eradicate it is required [1].

The United States environmental protection agency also suggested the acceptable level of 2,4-D, to be 0.1 ppm, for drinkable water [2]. The WHO recognizes 2,4-D as comparatively toxic (Class II) to human beings and animals and endorses 70 µg/L as the maximum allowed concentration in drinking water [3].

The removal of 2,4-D from aqueous mixture has been examined via adsorption, biodegradation, membrane filtration, electrochemical decomposition processes [4], advanced oxidation processes like Fenton [5], photo Fenton [6], UV/H₂O₂ [7], UV/TiO₂ [8] and photochemical process with differ achievement. Photocatalysis, as a method for wastewater treatment, has attracted much attention. This method has been shown to be a nice substitute for breaking down of tenacious compounds [9, 10].

Photocatalytic reactions using semiconductor nanomaterials is a matter of increasing interest [11]. Under light exposure, OH[•] radicals in photocatalysis process as an AOPs method can cause electron transfer from semiconductor to electrolyte interface. In this method, exposure of semiconductor particles to light leads to produce electron-hole pairs. Moreover oxygen in solution plays an important role in accepting electrons from excited catalyst light [12]. Among the available semiconductors, titanium dioxide was an ideal catalyst due to its low cost, non-toxicity, high activity and extreme stability under light exposure [11]. Anatase, rutile and brookite are three crystalline phases of titanium dioxide. [13]. According to the structure and size, the bandgap energy of TiO₂ is from 3.02 eV to 3.4 eV. Common TiO₂ (P25) has a 3.2 eV bandgap, which is identical with the energy of photons with 385 nm wavelength [14]. P25 has a high photoactivity with a combination of 80% anatase and 20% rutile phases, which is due to the delayed recombination of charge carriers (electron-hole) [11].

The latest studies show an amplified photocatalytic efficiency when the surface of TiO₂ particles is adapted with host molecules such as β-cyclodextrin (β-CD) [15]. It is currently used to degrade organic compounds under homogeneous or heterogeneous conditions without any additional oxidizing agents [16]. β-CD not only increases TiO₂ dispersion in water, but also improves the charge transfer from the photo-excited TiO₂ to the electron acceptor guest molecules [17]. Photocatalytic reactions depend on different physical factors such as light source, wavelength and optical radiation power. The LED as a semiconductor device have advantages such as emit light of different wavelength (infrared, visible, or near-ultraviolet), small size, high energy efficiency, mercury-free, cost effective compared to the conventional ultraviolet light sources [18, 19]. There is a report about the reaction was successfully carried out under green and blue LEDs illumination by using ammonium formate as a sacrificial electron donor for CdS nanorod synthesis [20]. Another report based on

highly effect of a semiconductor on photocatalytic reduction of nitroarenes using illumination sources (sunlight or violet LED) was investigated [21].

In the present work, a comparative study was conducted on degradation of 2,4-D with various structures of TiO₂ (P25, anatase, rutile), modified TiO₂ with β-CD and complex of 2,4-D/β-CD in addition to P25. Then batch and circulated-mode photoreactor were investigated to be specified the advantages of each system. On the other hand, the effects of various parameters on photocatalytic degradation of 2,4-D including substrate concentration, types of catalyst, amount of catalyst and irradiation time were studied.

Methods and materials

Reagents and apparatus

2,4-D (purity 98%) was procured from Sigma Aldrich. TiO₂-P25 consists of anatase and rutile (80:20) with crystallite size of 30 nm was purchased from Degussa Co, Germany. Ethanol was provided by Merck. β-CD was purchased from Acros Co, Spain. All chemicals were used as received without further purification. Deionized water was used in all experiments. The LED_s (HP Star Co. emitting 400 nm light with an intensity of 100 mW/cm) were used in this study were 365 and 400 nm with 20 W power). The syringe filter (0.2 µm, Millipore) purchased from Satrious-Stedim Co, Germany. Samples of 2,4-D solutions were determined using a Pharmacia Biotech Ultrospec 3100 UV-Vis spectrophotometer at the beginning and the end of the experiments. The oven used at all of the experiments was made by Pars Azma (Iran).

Preparation of P25/β-CD nanoparticles and complex of 2,4-D/β-CD

In the slightly modified P25 nanoparticles with β-CD, a certain amount of P25 (50 mg) and β-CD (5 mg) (P25: β-CD 1:1 mol) suspended solution in 10 mL deionized water was irradiated under ultrasonic bath for 15 min. The resulting solution was stirred during irradiation under a 20 W 400-LED for 8 h.

Preparation of solid complexes of 2,4-D and β-CD was performed according to the spray-drying method reported by Maria J Arias et.al [22]. This method was performed using a Buchi B-290 mini Spray-Dryer. First, the 2,4-D was dissolved in 400 mL ethanol (96% v/v). The appropriate molar ratios of 2,4-D and β-CD were 1:1 [22]. The required amount of β-CD was dissolved in 400 mL deionized water. After that, to form a clear solution, the solutions required 20 min of sonication to mixing, which was spray-dried. The drying conditions were: flow rate: 1000 mL/h, air flow rate: 400 L/h, inlet temperature: 168 °C, outlet temperature: 90 °C.

Characterization

The differential thermal analysis and thermogravimetric analysis measurements were performed by using a STA 409 PC/4/H LXXX NETZSCH (Germany). A linear heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in the range 20–450 $^{\circ}\text{C}$ was applied. The transmission electron microscopy (TEM) image was taken using a Philips CM-120 (The Netherlands) operated at 120 KeV to measure the size of nanoparticles. The specific surface area (BET) was determined by nitrogen (N_2) adsorption-desorption in BELSORP-max (Japan).

FT-IR spectra were recorded using FT-IR spectrometer (Bruker Vector 22) in the region 400–4000 cm^{-1} using KBr pellets.

UV–Vis diffuse reflectance spectroscopy (DRS) were recorded on a Shimadzu 2550 UV–Vis diffuse reflectance spectrophotometer with BaSO_4 as the background between 200 and 800 nm to measure the bandgap of photocatalysts.

The differential scanning calorimetry (DSC) was performed by Mettler machine, with a FP85 furnace, FB80HT temperature control unit and FB89HT software under a static air atmosphere and a heating rate of $10\text{ }^{\circ}\text{C/min}$ at a temperature range of 60 to 440 $^{\circ}\text{C}$. 5 to 10 mg of the sample was placed in aluminum pans, these pans were pierced to exodus the released gases during the heating process.

Photocatalytic degradation

Batch-mode photoreactor

To prepare 2000 mg/L of stock solution, 1 g of 2,4-D powder was dissolved in 500 mL of deionized water applying oil bath at 90 $^{\circ}\text{C}$ for 6 h. Prior to irradiation, the 2,4-D solution was stirred for 1 h in dark to ensure that the adsorption of the 2,4-D onto the surface of photocatalyst reached equilibrium. The LED was utilized 400 nm 20 W power placed under a 100 ml Erlenmeyer flask at 15 mm distance from reaction flask. During all experiments, air was bubbled through 2 mL/min using a specular draft tube. In batch-mode three experiments were carried out separately. Each experiment was performed in triplicates, and all results were expressed as a mean value of the three experiments. In all of these experiments, pH was not monitored.

To investigate the photodegradation of 2,4-D (20 mg/L) in the presence of P25, 1 mL of 2,4-D stock solution (2000 mg/L) was added to 50 mL of deionized water, then 50 mg (1 g/L) of P25 was dispersed in it.

In order to study photodegradation of 2,4-D (20 mg/L) in the presence of P25/ β -CD nanoparticles 1 mL of 2,4-D stock solution (2000 mg/L) was added to 40 mL deionized water and 10 mL of 5.5 mg/L (1.1 g/L) of P25/ β -CD nanoparticles solution (optimum proportion of P25: β -CD 1:1 mol) was added to above solution in a 100 mL volumetric flask.

In the last case to investigate the photodegradation of 2,4-D (20 mg/L) in the presence of 2,4-D/ β -CD complex along with P25 as a photocatalyst, 12 mg of 2,4-D/ β -CD complex powder was dissolved in 50 mL of deionized water applying oil bath at 90 $^{\circ}\text{C}$ for 3 h. Then 1 g/L of P25 was dispersed in this solution in 100 mL volumetric flask.

Circulated-mode photoreactor

The photoreactor consists of five parts: the tank, the exposure chamber, the pump, the transferors (silicone hoses) and the control unit. The solution was conducted from the 500 mL tank to the exposure chamber by a pump at 3000 mL/min flow rate in silicone hoses.

The control unit provides the ability to operator to control the exposure vim and exposure time and the flow rate of the pump. The LEDs employed in this photoreactor altogether were 365 nm in light wavelength and 100 W in power (Fig. 1).

To prepare 20 mg/L of stock solution, 10 mg of 2,4-D powder was dissolved in 500 mL of deionized water applying oil bath at 90 $^{\circ}\text{C}$ for 2 h. In order to study photodegradation of 2,4-D in circulated-mode photoreactor three solution prepared as following:

The 500 mL of prepared stock solution (20 mg/L) with 500 mg (1 g/L) of P25 were placed in a 500 mL Pyrex beaker then irradiated under ultrasonic bath for 15 min until it was dispersed.

100 mL P25/ β -CD nanoparticles solution (optimum proportion of P25: β -CD 1:1 mol) was added to 400 mL of 2,4-D solution (20 mg/L) in a 500 mL Erlenmeyer flask. After that this solution was placed in ultrasonic bath for more dispersed.

The last solution prepared by dissolving of 120 mg of 2,4-D/ β -CD complex powder in 380 mL of deionized water in oil bath at 90 $^{\circ}\text{C}$ for 45 min. Then this solution with 500 mg (1 g/L) of P25 were placed in a 500 mL Pyrex beaker. In all of these experiments, pH was not monitored.

High concentration of 2,4-D solution in circulated-mode photoreactor

100 mL of stock solution (2000 mg/L) was added to 400 mL of deionized water then 500 mg (1 g/L) of P25 was dispersed in it. In other experiment 1200 mg of 2,4-D/ β -CD complex powder was dissolved in 500 mL of deionized water using oil bath at 90 $^{\circ}\text{C}$ for 3 h, then 500 mg of P25 was dispersed in it. In all of these experiments, pH was not monitored.

Analysis

To monitoring of photodegradation efficiency, 5 mL of suspension, every 1 h was taken, filtered with syringe filter

Fig. 1 Setup circulated computerized photoreactor

(0.2 μm , Millipore) and was measured on the 2,4-D absorption band at 284 nm using a UV-Vis spectrophotometer in a 1 cm Pyrex cuvette. The degradation percentage was determined as follows:

$$\text{Photodegradation}\% = \left(1 - \frac{C}{C_0}\right) \times 100$$

Where C_0 and C are absorbance values of the 2,4-D solution before and after irradiation. In order to determine the reproducibility of the results, most of the experiments duplicated for better accuracy. The number of total samples with duplicated repeat were 520. Also, Excel, ChemDraw and Origin were used to draw charts. The experimental error was observed to be within $\pm 4\%$.

The dilution was performed for high concentrations and samples were normalized.

Reusability of catalyst

The reusability of both of P25 and P25/ β -CD nanoparticles were examined by successive five cycles of experiments in batch-mode photoreactor that each cycle was 5 h (maximum duration with high efficiency). The 2,4-D concentration was 50 mL of 2,4-D (20 mg/L) for each cycle. The solution was irradiated under a LED 400 nm 20 W and was bubbled 2 mL/min. After 5 h irradiation of LED, 1 mL of 2,4-D stock solution was added and this cycle was continued 4 times again. At the end of fifth cycle, the suspensions were taken from falcon tubes and centrifuged to remove the bulk solution. Then those catalyst were poured on watch glass and dried at room temperature.

Results and discussion

Characterization of P25/ β -CD nanoparticles and complex of 2,4-D/ β -CD

It is expected that the binding of cyclodextrin to Titania will result from the interaction of its hydroxyl groups with excited Titania at the surface of the photocatalyst by LED radiation. This interaction of hydroxyl groups with Titania will result in the removal of the cyclodextrin hydroxylic proton and increase the solution acidity. The measuring of pH solution was the appropriate confirmation to establish this connection. pH changes in the reaction can be due to β -CD adsorption on the P25 nanoparticles surface and formation of the P25/ β -CD nanoparticles in water under LED irradiation [17]. The β -CD absorption on semiconductors improves the transfer of electrons from the light-stimulated semiconductor to the guest molecule β -CD as an electron receptor [23] and with link to the semiconductors such as TiO_2 it plays as an electron dominating and molecular recognizing [24]. The pH reduction of the model experiment, including titanium and cyclodextrin, was followed by light exposure. The pH was initially about 7 (in the absence of β -CD) and changed over time to 4 (under LED exposure and the presence of β -CD).

After light exposure to TiO_2 nanoparticles, generated negative electrons and positive cavities reduced Ti^{3+} are to Ti^{4+} and produce oxygen anions. Generated oxygen anions become reacted to the oxygen molecule and are released from the TiO_2 nanoparticles. Some of the cavities produce hydroxyl radicals by absorbing water molecules on the surface of TiO_2 nanoparticles [25]. On the other hand, the recombination of electron-hole decreases through covalent bonding between hydroxyl groups of β -CD and TiO_2 and absorption of visible

light increases [26]. It has already been proven that beta-cyclodextrin adsorption on TiO_2 is chemical absorption [17].

The TEM image was used to observe the possible changes in the shape and structures of these nanoparticles before and after addition of cyclodextrin. The results, as shown in the Fig. 2a–d indicate that there were no changes in the lattice structure of P25 after β -CD modification. As shown in Fig. 2c and d, even after application of P25 and P25/ β -CD in 5 consecutive cycles, no change in the structure of these nanoparticles was observed, which indicates the stability of photocatalysts in the system. The results were consistent with that of P25/ β -CD hybrid nanoparticles [27].

Figure 3 shows the UV-vis DRS spectra of the P25/ β -CD nanoparticles using Degussa P25 as a reference. The Kubelka-Munk formula was used for all semiconductor samples [14]. According to the results shown in Fig. 3, P25/ β -CD displayed a higher absorption than P25 in the visible light. This slight difference is probably due to the interaction of hydroxyl groups of cyclodextrin with the cavities on the titanium surface with visible light. Thus, the cyclodextrin coating, as increases the amount of titanium dispersion in water, will increase the ability to absorb visible light in comparison with

Fig. 3 UV-Vis DRS spectra P25 and P25/ β -CD

the absence of cyclodextrin. This slight increase in the ability to absorb visible light has ultimately led to improvements in the efficiency of commercial titanium in the photodegradation of 2,4-D. Also, according to Table 1, specific surface area (SSA) of the P25 ($70 \text{ m}^2/\text{g}$) and P25 after 5 reaction cycles ($55 \text{ m}^2/\text{g}$) indicating low change in the physical structure of this photocatalyst. On the other hand, based on the Brunauer-Emmett-Teller (BET) method, surface area of P25/ β -CD ($46 \text{ m}^2/\text{g}$) is lower than P25, indicates that cyclodextrin is sited

Fig. 2 TEM images of (a) P25, b P25/ β -CD, c P25 (after 5 cycles) and d P25/ β -CD (after 5 cycles)

Table 1 Physicochemical properties of nanoparticles

Sample	BET (m ² /g)	Mean pore volume (cm ³ /g)	Mean pore diameter (nm)
P25	70	13	37.3
P25 (cycle 5)	55	12.7	32.5
P25/ β -CD	46	10.8	44.3
P25/ β -CD (cycle 5)	49	11.4	38.7

on the P25 under LED irradiation. However, the surface area of the P25/ β -CD was not significantly changed after 5 reaction cycles (49 m²/g), suggesting no significant change in its physical structure.

Thermogravimetric analysis was used to confirm the binding and presence of cyclodextrin on the P25 surface (Fig. 4). In the TGA analysis of the P25/ β -CD nanophotocatalyst a weight loss related to the removal of moisture was observed at a temperature between 25 and 130 °C. Also, TGA study of P25/ β -CD showed cyclodextrin degradation at a temperature of about 220 to 350 °C. The approximate weight loss of cyclodextrin on the P25 surface was calculated to be about 13.3%.

Evidences on the formation of an inclusion complex between 2,4-D and β -CD have been also determined using IR spectroscopy (Fig. 5). The pure 2,4-D FT-IR spectrum in (Fig. 5a) represents the characteristic bands of this compound as follows: carboxylic C=O in 1733 cm⁻¹ and aromatic ring C=C in 1582 and 1481 cm⁻¹, carboxylic O-H in 1392 cm⁻¹, carboxylic C-O two bands at 1437 and 1308 cm⁻¹ and a strong band corresponding to phenolic C-O in 1234 cm⁻¹ and a second band at 1092 cm⁻¹ which is probably due to the CH₂-O- vibration.

In the 2,4-D/ β -CD spectrum (Fig. 5c), certain bands related to 2,4-D are specified, as well as other parts related to the β -

CD, almost all of these bands have been slightly shifted. Carboxylic acids, even if they are in the solid phase, are due to strong hydrogen bonds between the carbonyl group and the hydroxyl group in the form of dimer. 8 cm⁻¹ shift of 1733 cm⁻¹ band to higher frequencies could be due to the weakening of these hydrogen bonds and their substitution with weaker forms. 2,4-D can be imagined as a monomer within the β -CD ring, the intermolecular hydrogen bond between the pesticide and the β -CD is thought to be weaker than the intermolecular hydrogen bond of two 2,4-D molecules between themselves. In 1647 cm⁻¹ and 1334 cm⁻¹ two new bands are observed, which can be assigned to the form of anionic 2,4-D molecules. These two bands correspond respectively to asymmetrical and symmetrical stretching vibrations of carboxylate ions resonance. Also decreasing in intensity of the carboxylic O-H band at 1372 cm⁻¹ probably due to its overlapping with the 1420 cm⁻¹ band of the β -CD, which resulted in a small band at 1414 cm⁻¹. The high frequency of the anti-symmetrical stretching band of the carboxylate group (1647 cm⁻¹) can mean that the group is involved in hydrogen bond formation with the β -CD. The C=C bond of the aromatic ring (1480 cm⁻¹) and the phenolic C=O stretching (1239 cm⁻¹) bands suffers a slight shift due to the overlapping effect of the β -CD band in the same zone as well as the proximity of the β -CD structure that emits the energy of this

Fig. 4 TG/DTG analysis of P25/ β -CD

Fig. 5 FTIR spectra of (a) 2,4-D (b) β -CD (c) complex of 2,4-D/ β -CD

vibration. However, the band at 1239 cm^{-1} , belonging to phenolic C=O stretching, has slightly shifted of 1234 cm^{-1} . The presence of β -cyclodextrin leads to an increase in the solubility of 2,4-D in the solution. According to Gines et al., this increased solubility, on the other hand, creates a new complex of these two substances [22].

Further evidence of the formation of a complex between 2,4-D and β -CD obtained from the DSC thermograms shown in Fig. 4. As shown in (Fig. 6a), the DSC curve for the 2,4-D

has an endothermic fusion peak at 140°C . In contrast, the β -CD for dehydration process shows a wide endothermic peak between 90 and 120°C (Fig. 6b). Also, a solid-to-solid phase transition is observed at 230°C and at the end of the degradation process, which is associated with caramellization occurs at 320°C . As shown in (Fig. 6c), in the case of spray-dried samples, 2,4-D endothermic peak is not seen at 140°C . It can be concluded that the spray-dried samples are factual inclusion complex.

Fig. 6 DSC thermograms of (a) pure 2,4-D (b) pure β -CD and (c) complex of 2,4-D/ β -CD

One of the characteristics of cyclodextrin as host molecule for organic species is the change in the absorption rate of these species as a result of the formation of a complex with cyclodextrin hydrophobic cavities [28]. Thus, by increasing the absorbance of the 2,4-D herbicide, it can be concluded to the formation of the 2,4-D complex with the cyclodextrin. For this purpose, an aqueous solution of 2,4-D with a specific concentration was used. The UV-Vis spectrum of this solution was evaluated and a specific amount of cyclodextrin solution was added step by step. As shown in Fig. 7, the intensity of the spectrum of this compound is increased with increasing cyclodextrin concentration. Therefore, the above process represents the formation of a complex between cyclodextrin hydrophobic cavities and 2,4-D. It has also been reported that UV-visible properties are affected by the formation of host-guest complexes between β -CD and organic complexes in solution medium [28].

Effect of operational parameters

The effect of the amount of catalyst on the photocatalytic degradation of 2,4-D

The effect of the amount of catalyst on the degradation efficiency was investigated over P25. According to the results, when the amount of P25 increased to 50 from 25 mg/50 mL, yield of degradation approximately quadruplicated. In the other hand at the high amount of P25, photocatalytic degradation yield was decreased. Based on this result, an optimum amount of P25 was determined 50 mg/50 mL = 1 g/L (Table 2, Entry 2). Achari et al. (2013) was reported that with increased amount of P25, the light available is utilized efficiently and light becomes the limiting factor. Also, increasing concentration of catalyst causes decrease in the degradation of 2,4-D due to light scattering and reflection by the suspended particles [18].

Fig. 7 UV-Vis spectral analysis for the complexation pattern between β -CD and 2,4-D

Table 2 The effect of the amount of materials on the photocatalytic degradation of 2,4-D (2,4-D concentration = 20 mg/L, time = 1 h, LED = 400 nm 20 W, batch-mode reactor)

Entry	P25 (g/L)	β -CD (g/L)	Photodegradation (%)
1	0.5	—	8
2	1	—	34
3	2	—	31
4	3	—	21
5	4	—	17
6	1	0.05	15
7	1	0.1	57
8	1	0.2	55
9	1	0.3	53
10	1	0.4	49

Significant Bold in Entry:

2: Optimum amount of P25 concentration

7: Optimum amount of β -CD concentration

Catalyst selection

To select the best bed of catalyst, several experiments were performed on 1 g/L P25, rutile and anatase aqueous solution. The results didn't show any degradation efficiency was happened using rutile and anatase as photocatalyst in batch-mode by using LED (400 nm, 20 W) during an hour degradation time. Even β CD-modified anatase didn't improve the degradation efficiency. But synthesized rutile/ β -CD was indicated 20% degradation of 2,4-D which was less than P25 or P25/ β -CD under the above conditions (Table 3).

Effect of β -CD amount on bed catalyst

The effect of the β -CD concentration from 0.05 to 0.4 g/L on 1 g/L of P25 (optimum value) was investigated for photodegradation of 2,4-D. The observed results show that the photodegradation efficiency increases by increasing the amount of β -CD to 0.1 from 0.05 g/L by about four times. However, with increasing β -CD concentration, the photocatalytic

Table 3 Effect of catalyst selection on the photocatalytic degradation of 2,4-D (2,4-D concentration = 20 mg/L, time = 1 h, LED = 400 nm 20 W, batch-mode reactor)

Entry	Nanoparticle	Concentration (g/L)	Photodegradation (%)
1	P25	1	34
2	rutile	1	N.R
3	anatase	1	N.R
4	rutile/ β -CD	1	20
5	anatase/ β -CD	1	N.R

Significant Bold in Entry:

1: The degradation efficiency of P25 under the mentioned conditions

degradation function decreases. Based on this result, an optimum amount of β -CD was determined 0.1 g/L (Table 2, Entry 7). Velusamy et al. (2013) was confirmed the optimum molar ratio between β -CD and pollutant (AY99 dye) fixed as 1:1 [29].

Promotion effects of β -CD on the photodegradation of 2,4-D

The results showed that the effect of cyclodextrin/P25 on the photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D) compared to P25 is relatively higher. According to the results, after one hour of irradiation, degradation efficiency of 2,4-D was increased to 57% compared P25 at the same time (34%). Due to the production of P25/ β -CD, progress was achieved in degradation efficiency, but this improvement was not significant at 2,4-D degradation compared to P25. However, according to other reports, the presence of β -cyclodextrin on P25 can significantly increase the degradation or reduction processes [24].

Absorption of β -CD on TiO_2 in the form of monolayer with Langmuir adsorption isotherm [30] is obtained through coordinate bond between OH group of β -CD and oxygen of TiO_2 and enhances catalytic activity of TiO_2 [24].

Modifying TiO_2 with cyclodextrin through interactions between the hydroxyl groups of β -CD and TiO_2 keeps the organic molecules near the photocatalyst surface to improve TiO_2 photocatalyst redox capability by increasing interaction [31].

Therefore, β -CD can promote the charge transfer rate from the photo-excited TiO_2 to the electron acceptor guest molecule [17]. Because β -CD plays electron-donating and hole-capturing roles when binding to TiO_2 colloids, which lead to photocatalytic efficiency enhancement and charge-hole recombination restriction [29, 32, 33]. Furthermore, when the unreacted guests are placed inside the cyclodextrins cavity, their excited states durability will be extended. Therefore, cyclodextrin exacerbates the electron injection from the excited pollutants to the TiO_2 conduction band and thereby increases photodegradation [24]. By Xu Zhang, it has been shown that modification with cyclodextrin has a significant effect on anatase TiO_2 characteristics, and the TiO_2 / β -CD visible absorption intensity is greater than that of TiO_2 [34]. According to the survey results of Xu Zhang, all the hybrid materials synthesized by photo induced method, after modification with β -CD compared to the bare TiO_2 , had higher absorption intensity in the visible light region. Thus, the degradation of rhodamine B was intensely enhanced [35]. Deng was studied enhancement

of TiO_2 photocatalytic by β -CD for decolorization of dye solutions and increasing the dyes decolorization rate in the presence of β -CD was proved. β -CD by binding on the TiO_2 surface and forming a complex, cause interaction of the dyes anions with TiO_2 surface and the active species produced by TiO_2 under irradiation [36].

Effect of 2,4-D/ β -CD complex on photodegradation of 2,4-D

One of the ways in which the effect of cyclodextrin on the degradation reaction of pollutant can be studied is to create a complex of cyclodextrin and 2,4-D. The Stability and spatial arrangement of this complex reported by Cleber P.A. Anconi et.al was successfully developed to enhance the phenoxy solubility [37]. Solubility may be effective in increasing degradation efficiency. The complex was tested and the results were significant. The 2,4-D/ β -CD complex was used to study of its effect on 2,4-D photodegradation compared to P25 and P25/ β -CD. In this work, the photocatalytic degradation of pollutant under an hour irradiation with LED (400 nm 20 W) in presence of 2,4-D/ β -CD complex by P25 as a photocatalyst was improved 43% and 20% compared to P25/ β -CD and P25, respectively (Table 4, Entry 3).

Effect of irradiation time in batch-mode photoreactor

Irradiation time plays a vital role in the degradation process of the pollutants because irradiation time was increased to complete destruction of the contaminants with the nanoparticles. According to Fig. 8. the degradation efficiency of P25, P25/ β -CD as photocatalysts and 2,4-D/ β -CD complex with P25 after during 5 h were approximately 81, 85 and 95% respectively. This efficiency did not increase dramatically with increasing time.

Effect of photoreactor kind on photodegradation of 2,4-D

In the present study, the effect of the circulated-mode photoreactor on the removal of 2,4-D contaminants was surveyed. In order to investigate the effect of batch and circulated-mode photoreactors in the photodegradation of 2,4-D, three experiments including P25, P25/ β -CD and complex of 2,4-D/ β -CD with P25 were carried out. According to Fig. 9. the degradation yield of every case after 1 h of irradiation were 63, 75.5 and 78% respectively in circulated-mode photoreactor.

Table 4 Comparison with P25, P25/ β -CD and 2,4-D/ β -CD complex on the photocatalytic degradation of 2,4-D (2,4-D concentration = 20 mg/L, time = 1 h, LED = 400 nm 20 W, batch-mode reactor)

Entry	Materials	Concentration of photocatalyst (g/L)	Photodegradation (%)
1	P25	1	34
2	P25/ β -CD	1	57
3	2,4-D/ β -CD*	0.24	77.8

*with P25 as a photocatalyst

Fig. 8 Photocatalytic degradation of 2,4-D (20 mg/L) with P25 (50 mg) for all experiments in batch-mode reactor (LED = 400 nm, 20 W, 100 mW/cm, adsorption-desorption time = 1 h in dark)

Compared to the batch-mode photoreactor (Fig. 8), the 2,4-D photodegradation rate was significantly increased in the circulated-mode photoreactor during an hour with P25 and P25/β-CD photocatalyst. The results obtained from the effect of the circulated-mode photoreactor for the removal of contaminants is consistent with other papers [38, 39]. The degradation efficiency of the 2,4-D/β-CD complex with the P25 photocatalyst was almost identical in both of the photoreactors during one hour. Also, the amount of 2,4-D degradation yield for P25, P25/β-CD and complex of 2,4-D/β-CD with P25 in 8 h of irradiation in circulated-mode photoreactors were 88.8, 90.4 and 96%, respectively.

The impact of circulated-mode photoreactor on the photodegradation of high concentration 2,4-D

The effect of the photoreactor on photodegradation of 200 mg/L (10 fold of initial concentration) with P25 photocatalyst and 2,4-D/β-CD complex along with P25 were investigated over a 12 h period of time.

Fig. 9 Photocatalytic degradation of 2,4-D (20 mg/L) with P25 (500 mg) for all experiments in circulated-mode reactor (overall 365 nm 100 W, adsorption-desorption time = 1 h in dark, at room temperature)

According to Fig. 10, the 2,4-D photodegradation rate with P25 and 2,4-D/β-CD complex with P25 has a high efficiency, indicating a good effectiveness of the photoreactor in both reaction conditions. In fact, a high concentration of 2,4-D was used to prove the high efficiency of circulated-mode photoreactor. These results show that the photoreactor can also destroy the high concentrations of pollutants; this experiment was carried out in a batch-mode photoreactor and did not succeed.

It is important to consider this issue from an environmental point of view, that with uncontrolled use of this herbicide, its presence in the environment and ecosystems causes soil, surface and groundwater contamination [37] and consequently it can enter the food chain, hence, using of the photoreactor can reduce the pollution significantly.

2,4-D absorption rate on P25

In order to prove the photodegradation process of 2,4-D in the presence of P25 nano photocatalyst, the optimal amount of this nanoparticle (50 mg) stirred with 50 ml

Fig. 10 Photocatalytic degradation of 2,4-D (200 mg/L) with P25 (500 mg) for all experiments in circulated-mode reactor (overall 365 nm 100 W)

of 20 mg/L 2,4-D solution in dark for 12 h. After this time, the heterogeneous mixture was straightened with a nozzle filter for separating solid particles of nanoparticles and identified by a UV-Vis spectrophotometer at a maximum absorption wavelength of 284 nm compared to prime sample. According to the obtained data, the absorption rate was about 8%, indicating that no reduction is observed in the amount of 2,4-D in the absence of LEDs.

Reusability of catalyst

Based on main philosophies of green chemistry, the most important factors in photocatalytic processes are the catalytic recovery and the stability of the nanoparticles to reduce organic pollutants in aqueous solution at the end of the irradiation time. To study this matter, the photocatalytic performance of P25 (Fig. 11a) and P25/ β -CD (Fig. 11b) were investigated after five cycles. After 25 h (5 cycles) of irradiation, P25 and

P25/ β -CD maintained as high 2,4-D removal efficiency as 82.6, 84% respectively. A trace decrease in the photocatalytic efficiency has seen due to the partial loss of photocatalyst in the course of the photodegradation process. These results are consistent with the retention of good photocatalytic activities of those nanoparticles after five cycles.

Conclusion

In this study, LEDs were shown to be a promising light source in batch and circulated-mode photoreactors for photocatalytic degradation of 2,4-D. The interaction of the 2,4-D with β -CD created a new inclusion complex in solution and in the solid state. The application of differential scanning calorimeter (DSC), Infrared spectroscopy (FTIR) and UV-Visible have allowed to investigate the inclusion process. P25/ β -CD hybrid nanoparticles were synthesized by a photoinduced self-assembly process that

Fig. 11 Reusability and photocatalytic efficiency of (a) the P25 and b the P25/ β -CD aqueous solution for degradation of 2,4-D under LED irradiation after 5 h

was better than P25 to photodegradation process in both of the photoreactors.

However, compared to P25 and P25/ β -CD photocatalysts, the 2,4-D/ β -CD complex with P25 is a more efficient system for degradation of 2,4-D. The use of circulated-mode photoreactor for photodegradation of the high concentration of 2,4-D solution (200 mg/L) with P25 and 2,4-D/ β -CD complex with P25 had remarkable results. Performing tests on the reusability of P25 and P25/ β -CD nanoparticles in five cycles showed that both nanoparticles had good efficiencies over a period of 25 h and insignificant reduction in degradation efficiency is due to a slight reduction in the amount of photocatalysts used during the photodegradation process.

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Compliance with ethical standards

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References

- López-Granada G, Barceinas-Sanchez JDO, López R, Gómez R. High temperature stability of anatase in titania–alumina semiconductors with enhanced photodegradation of 2, 4-dichlorophenoxyacetic acid. *J Hazard Mater*. 2013;263:84–92.
- Kundu S, Pal A, Dikshit AK. UV induced degradation of herbicide 2,4-D: kinetics, mechanism and effect of various conditions on the degradation. *Sep Purif Technol*. 2005;44(2):121–9.
- Ova D, Ovez B. 2, 4-Dichlorophenoxyacetic acid removal from aqueous solutions via adsorption in the presence of biological contamination. *J Environ Chem Eng*. 2013;1(4):813–21.
- Ji R, Bian X, Chen J. Degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D) by novel photocatalytic material of tourmaline-coated TiO_2 nanoparticles&58; kinetic study and model. *Materials*. 2013;6(4):1530–42.
- Pignatello JJ. Dark and photoassisted iron (3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ Sci Technol*. 1992;26(5):944–51.
- Schenone AV, Conte LO, Botta MA, Alfano OM. Modeling and optimization of photo-Fenton degradation of 2,4-D using ferrioxalate complex and response surface methodology (RSM). *J Environ Manag*. 2015;155:177–83.
- Murcia M, Verzhinin N, Briantceva N, Gomez M, Gomez E, Cascales E, et al. Development of a kinetic model for the UV/ H_2O_2 photodegradation of 2,4-dichlorophenoxyacetic acid. *Chem Eng J*. 2015;266:356–67.
- Rivera-Utrilla J, Sánchez-Polo M, Ocampo-Pérez R. Role of activated carbon in the photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid by the UV/ TiO_2 /activated carbon system. *Appl Catal B Environ*. 2012;126:100–7.
- Kanakaraju D, Glass BD, Oelgemöller M. Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. *Environ Chem Lett*. 2014;12(1):27–47.
- Liang N, Zai J, Xu M, Zhu Q, Wei X, Qian X. Novel $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterojunction photocatalysts with enhanced visible light responsive activity and wastewater treatment. *J Mater Chem A*. 2014;2(12):4208–16.
- Zand Z, Kazemi F, Hosseini S. Development of chemoselective photoreduction of nitro compounds under solar light and blue LED irradiation. *Tetrahedron Lett*. 2014;55(2):338–41.
- Wang H, Zhang L, Chen Z, Hu J, Li S, Wang Z, et al. Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. *Chem Soc Rev*. 2014;43(15):5234–44.
- Li R, Weng Y, Zhou X, Wang X, Mi Y, Chong R, et al. Achieving overall water splitting using titanium dioxide-based photocatalysts of different phases. *Energy Environ Sci*. 2015;8(8):2377–82.
- López R, Gómez R. Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO_2 : a comparative study. *J Sol-Gel Sci Technol*. 2012;61(1):1–7.
- Chalasanani R, Vasudevan S. Cyclodextrin-functionalized $\text{Fe}_3\text{O}_4/\text{TiO}_2$: reusable, magnetic nanoparticles for photocatalytic degradation of endocrine-disrupting chemicals in water supplies. *ACS Nano*. 2013;7(5):4093–104.
- Landy D, Mallard I, Ponchel A, Monflier E, Fourmentin S. Remediation technologies using cyclodextrins: an overview. *Environ Chem Lett*. 2012;10(3):225–37.
- Kakroudi MA, Kazemi F, Kaboudin B. β -Cyclodextrin– TiO_2 : green Nest for reduction of nitroaromatic compounds. *RSC Adv*. 2014;4(95):52762–9.
- Yu L, Achari G, Langford CH. LED-based photocatalytic treatment of pesticides and chlorophenols. *J Environ Eng*. 2013;139(9):1146–51.
- Jo W-K, Tayade RJ. New generation energy-efficient light source for photocatalysis: LEDs for environmental applications. *Ind Eng Chem Res*. 2014;53(6):2073–84.
- Ramdar M, Kazemi F, Kaboudin B, Taran Z, Partovi A. Visible light active CdS nanorods: one-pot synthesis of aldonitrone. *New J Chem*. 2016;40(11):9257–62.
- Ramdar M, Kazemi F, Kaboudin B. A photocatalytic green system for chemoselective reduction of nitroarenes. *Chem Pap*. 2017;71(6):1155–63.
- Ginés JM, Pérez-Martínez JJ, Arias MJ, Moyano J, Morillo E, Ruiz-Conde A, et al. Inclusion of the herbicide 2, 4-dichlorophenoxyacetic acid (2,4-D) with β -cyclodextrin by different processing methods. *Chemosphere*. 1996;33(2):321–34.
- Sasikala R, Shirole A, Sudarsan V, Sudakar C, Naik R, Rao R, et al. Enhanced photocatalytic activity of indium and nitrogen co-doped TiO_2 –Pd nanocomposites for hydrogen generation. *Appl Catal A Gen*. 2010;377(1–2):47–54.
- Velusamy P, Pitchaimuthu S, Rajalakshmi S, Kannan N. Modification of the photocatalytic activity of TiO_2 by β -Cyclodextrin in decoloration of ethyl violet dye. *J Adv Res*. 2014;5(1):19–25.
- Montazer M, Pakdel E. Functionality of nano titanium dioxide on textiles with future aspects: focus on wool. *J Photochem Photobiol C: Photochem Rev*. 2011;12(4):293–303.
- Pitchaimuthu S, Lakshmi G, Velusamy P. Enhanced photocatalytic activity of TiO_2 using β -Cyclodextrin on solar light assisted decoloration of azocarmine G dye. *J adv Chem Sci*. 2014;9–14.

27. Zhang X, Wu F, Deng N. Efficient photodegradation of dyes using light-induced self assembly TiO_2/β -cyclodextrin hybrid nanoparticles under visible light irradiation. *J Hazard Mater.* 2011;185(1): 117–23.
28. Hu Q-D, Tang G-P, Chu PK. Cyclodextrin-based host–guest supramolecular nanoparticles for delivery: from design to applications. *Acc Chem Res.* 2014;47(7):2017–25.
29. Pitchaimuthu S, Rajalakshmi S, Kannan N, Velusamy P. Enhanced photocatalytic activity of titanium dioxide by β -cyclodextrin in decoloration of acid yellow 99 dye. *Desalin Water Treat.* 2014;52(16–18):3392–402.
30. Zhang X, Wu F, Wang Z, Guo Y, Deng N. Photocatalytic degradation of 4, 4'-biphenol in TiO_2 suspension in the presence of cyclodextrins: a trinity integrated mechanism. *J Mol Catal A Chem.* 2009;301(1–2):134–9.
31. Yang Z, Zhang X, Cui J. Self-assembly of bioinspired catecholic cyclodextrin TiO_2 heterosupramolecule with high adsorption capacity and efficient visible-light photoactivity. *Appl Catal B Environ.* 2014;148:243–9.
32. Sakthivel P, Velusamy P. Modification of the photocatalytic performance of various metal oxides by the addition of β -cyclodextrin under visible light irradiation. *Journal of water process engineering.* 2017;16:329–37.
33. Lu S, Sun N, Wang T. Research on photocatalytic degradation of methyl orange by a β -Cyclodextrin/Titanium dioxide composite. *General Chemistry.* 2017;3(3):164–9.
34. Attarchi N, Montazer M, Toliyat T. Ag/ TiO_2/β -CD nano composite: preparation and photo catalytic properties for methylene blue degradation. *Appl Catal A Gen.* 2013;467:107–16.
35. Zhang X, Li X, Deng N. Enhanced and selective degradation of pollutants over cyclodextrin/ TiO_2 under visible light irradiation. *Ind Eng Chem Res.* 2011;51(2):704–9.
36. Lu P, Wu F, Deng N. Enhancement of TiO_2 photocatalytic redox ability by β -cyclodextrin in suspended solutions. *Appl Catal B Environ.* 2004;53(2):87–93.
37. Pereira R, Anconi C, Nascimento C, De Almeida W, Dos Santos H. Stability and spatial arrangement of the 2, 4-dichlorophenoxyacetic acid and beta-cyclodextrin inclusion compound: a theoretical study. *Chem Phys Lett.* 2015;633:158–62.
38. Behnajady M, Modirshahla N, Daneshvar N, Rabbani M. Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO_2 on glass plates. *Chem Eng J.* 2007;127(1–3):167–76.
39. García-Martínez M, Canoira L, Blázquez G, Da Riva I, Alcántara R, Llamas J. Continuous photodegradation of naphthalene in water catalyzed by TiO_2 supported on glass Raschig rings. *Chem Eng J.* 2005;110(1–3):123–8.

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