Enhanced degradation of dye mixtures: physicochemical and electrochemical properties of titania dispersed on clinoptilolite, synergistic influence

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Abstract

Eliminating dye mixtures in the aquatic environment has been of considerable interest due to the future sustainability of the environment, hence it needs to utilize photocatalytic material with synergistic influence aimed at efficient removal of these pollutants. Titania nanoparticles (NPs) dispersed on dealuminated clinoptilolite (TiO_2 -DCP) was synthesized via a sol-gel route. To determine the synergistic influence of as-prepared catalysts on enhanced degradation of dye mixtures (methyl orange—MO and methylene blue—MB), the physicochemical and electrochemical properties were investigated in detail. In comparison to TiO_2 , the prepared TiO_2 -DCP photocatalyst possessed excellent photocatalytic activity on the degradation of dye mixtures (83%—MO and 94%—MB) after 180 min of ultraviolet light irradiation. The partial aggregation reduction of titania NPs, improved absorption edge for more photons generations and efficient photogenerated charge carriers separation by DCP catalyst support are crucial factors for TiO_2 -DCP photocatalyst, synergistic influence on dye mixture removal in this study. The catalytic activity of TiO_2 -DCP could be reused six reaction times for the removal of the dye mixture with a promising potential for environmental remediation.

Keywords TiO_2 -DCP · Sol-gel · Synergistic influence · Dye mixtures · UV-light degradation · Activity · Band structure

1 Introduction

The indiscriminate discharge of industrial wastewater into the water bodies is a major concern to human health, safety and also the ecosystem [1]. However, industrial wastewater from synthetic dyes is a serious pollutant that affects the ecosystem [2, 3]. These synthetic dyes are made up of aromatic structures with different functional groups attached to them, which makes them very difficult to eliminate in wastewater. The removal of synthetic dyes with aromatic bonds is very paramount before being discharged into the ecosystem [4]. Conventional approaches such as adsorption [5], sedimentation [6, 7], biological methods [8], chlorination, ion exchange [9] and membrane

separation [10, 11] have been applied in the elimination of these synthetic dyes discharge. These approaches are limited by their conversion of treated synthetic dye effluents into innocuous substances that requires further purification treatments, while high cost and time consumption also hinder their large scale applications [12, 13]. Heterogeneous photocatalysis under advanced oxidation processes (AOPs) is a promising approach for synthetic dyes removal from water [14], with complete mineralization of pollutants at low cost and ambient temperature conditions [15–19].

Among the semiconductor materials, titanium dioxide (TiO_2) is extensively employed as a photocatalyst for the degradation of toxic and recalcitrant pollutants in

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wastewater due to its chemical stability and nontoxicity [20, 21]. However, the efficiency of pure TiO_2 for degradation of organic pollutants is hindered for practical applications due to its high aggregation tendency, the wide bandgap energy (3.2 eV), the fast recombination rate of photogenerated charge carriers, and post-separation from aqueous solution [22–24]. To enhance the efficiency of pure TiO_2 , many studies have been carried out with the incorporation of TiO_2 with inert support materials, since heterogeneous catalysis is a surface-based process [25–27], that requires adsorption of pollutant by the support material towards the catalyst surface. Support materials utilised for TiO_2 dispersion includes silica [28], clay [29], activated carbon [30] glass [31] and zeolites [32, 33]. Zeolites with three-dimensional (3D) framework structures aid the material transparency to light absorption, ability to participate in the electron transfer process, also their availability in natural form (clinoptilolite) and environmentally friendly makes them good support material for TiO_2 dispersion [34–36]. However, dealumination is an effective approach for improving the physico-chemical properties of natural zeolites [22, 37]. Dealumination contributes largely to removal of amorphous Al-species in the zeolitic framework, thus improving the crystallinity and porosity due to Al elimination [38].

The degradation of dye pollutants employing photocatalyst material is very vital; however, most attention has been focused on a single dye component [39], in comparison to the removal of dye mixtures. As far as we know, the photocatalytic activity of the TiO_2 dispersed on modified natural zeolite (clinoptilolite) on the degradation of dye mixtures [40] component has not been reported in the literature before. The purpose of this study is to investigate how the physicochemical and electrochemical properties of titanium dioxide dispersed on dealuminated clinoptilolite (TiO_2 -DCP) photocatalyst, synergistically influence the degradation of dye mixtures of methylene blue and methyl orange under UV light irradiation. Moreover, the reaction mechanism based on the prepared active photocatalyst properties is also discussed in this study.

2 Experimental

2.1 Materials

Methylene blue (MB, 99%) and methyl orange (MO, 98%) dyes (Fig. 1) were obtained from Sigma Aldrich. Hydrochloric acid (HCl, 36–38%), sodium hydroxide (NaOH), barium sulphate (BaSO_4 , 99%), Dimethylformamide (DMF, 98%) and sodium sulphate (Na_2SO_4) were from Merck Company, then used without further purification. Titanium-n-butoxide, ethanol, all solution was prepared using deionized

Fig. 1 Chemical structure of **a** methyl orange and **b** methylene blue

water. The pH of the solution was adjusted with HCl or NaOH solution.

2.2 Synthesis and characterization of catalysts

The synthesis of dealuminated clinoptilolite (DCP) and titanium dioxide on dealuminated clinoptilolite (TiO_2 -DCP) has been described elsewhere in our previous studies [41]. Dealuminated clinoptilolite (DCP) was prepared via the ion exchange method, while TiO_2 -DCP was prepared via a sol-gel method. Natural Clinoptilolite (CP) obtained from the Pratley Perlite mining company (South Africa) was crushed in an agate mortar and sieved to less than 100 μm particle size. The micro sieved CP particle was subjected to dealumination, by adding 20 g into 1 M NH_4Cl stirred solution at 90 °C for 24 h to achieve the desired ion-exchange process. The resultant mixture was filtered, washed several times with distilled water until the supernatant pH was neutral. The treated CP sample was dried at 150 °C overnight, then calcined in the muffle oven at 550 °C for 8 h required for activation of the dealuminated Clinoptilolite (DCP). For TiO_2 -DCP synthesis, 1 g of the prepared DCP powder was dispersed in 20 mL aqueous solution of ethanol. A mixture of 10 mL of titanium-n-butoxide in 50 mL ethanol and water solution (1:1) was added drop wise to the stirred solution of DCP mixture, which was further stirred for 3 h at 25 °C. The product was separated, thoroughly rinsed with distilled water, dried at 120 °C overnight and calcined at 550 °C for 4 h.

The powder X-ray diffraction pattern of the TiO_2 -DCP and TiO_2 was examined using Bruker X-ray diffractometer with Cuka source in a 2θ range of 10 to 80°. The morphology and composition of the TiO_2 -DCP were analyzed using scanning electron microscopy equipped with EDAX

system for Energy Dispersive Spectroscopic analysis. The bond vibrations of TiO_2 -DCP and DCP samples were analyzed on Fourier transform infrared (FTIR) spectrophotometer machine (Perkin Elmer spectrum 400) at the wavelength range of $600\text{--}4000\text{ cm}^{-1}$. Thermogravimetric analysis (TGA) was carried out using Perkin Elmer STA 6000 thermal simultaneous analyzer at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from 30 to $900\text{ }^\circ\text{C}$ within 19.8 ml/mins under nitrogen purge stream. The diffuse reflectance spectra of TiO_2 -DCP and TiO_2 -samples were recorded using a UV-visible spectrophotometer (PerkinElmer, Lambda 950, USA) in the wavelength range of $200\text{--}900\text{ nm}$. The photocurrent measurements were conducted using Biologic SP 240 potentiostat workstation using a standard three-electrode cell, comprising of a platinum wire as a counter electrode, Ag/AgCl (saturated KCl) as a reference electrode and a (WE). The working electrode was prepared by dispersing the prepared material (5 mg) in a 0.2 mL DMF solution, then 20 μL was drop cast on the WE and 0.2 M Na_2SO_4 used as the electrolyte solution. First, cyclic voltammetry (CV) was recorded from -0.80 V to 0.20 V in 0.2 M Na_2SO_4 at a scan rate of 50 mV s^{-1} to estimate the electrochemical behavior of the prepared photocatalysts. Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potential and recorded over a frequency range of 100 kHz to 40 mHz with an ac amplitude of 5 mV.

2.3 Photocatalytic degradation procedure

The photocatalytic activities of the TiO_2 -DCP, TiO_2 , and DCP were conducted in an ACE photochemical reactor (Sigma-Aldrich, Z567523) of 1.0 L capacity, 10 cm diameter, 15 cm height, and the light source was a mercury arc lamp (450 W), placed in a 5 cm diameter quartz tube. The wavelength range of the mercury arc lamp through the quartz tube is within the range of $300\text{--}600\text{ nm}$. A fixed volume of 500 mL dye mixtures of MO and MB solution of 40 ppm was used as initial concentration. The dye mixtures solution with the prepared photocatalysts (0.1 g) were magnetically stirred for 60 min in the dark to achieve adsorption-desorption equilibrium, then the light is switch on. The degradation of the dye mixtures was carried out for 180 min under the ultraviolet (UV) light irradiation. 4 mL of the solution was withdrawn from the reactor after designated minutes of irradiation time, centrifuge, filter and the concentration decrease of dye mixtures (MO and MB) was determined using UV-Vis spectrophotometer (Perkin Elmer Lambda 25) at 465 and 665 nm respectively. All analysis were done in triplicates, and the mean values with standard errors were reported. The degradation efficiency (%R) of the photocatalyst on dye mixtures removal was determined with the expression below:

$$\%R = 1 - \frac{C_t}{C_o} \times 100\% \quad (1)$$

where C_o is dye mixtures initial concentration at the beginning of light illumination and C_t concentration at certain reaction time t .

3 Results and discussion

3.1 Characterization

In the XRD pattern, the diffraction planes of DCP in the TiO_2 -DCP photocatalyst in Fig. 2 are crystalline exhibiting reflections at 2θ values at 13.3° , 17.3° , 23.1° , 30.2° , 32.0° corresponds to diffraction card peak (JCPDS Card No. 025-1349). The diffraction card (JCPDS Card No. 021-1272) of TiO_2 anatase peak at $2\theta = 25.6^\circ$, 38.1° , 48.1° , 53.9° , 55.1° , 62.9° and 75.2° , while the card data (JCPDS Card No. 021-1276) of TiO_2 rutile peaks [42] is at $2\theta = 27.4^\circ$ and 44.1° for TiO_2 -DCP and TiO_2 samples in Fig. 2. The average crystallite sizes for the TiO_2 and TiO_2 -DCP were calculated according to the Scherrer equation [43] on the peak at 25.6° of anatase TiO_2 . According to the equation, TiO_2 and TiO_2 -DCP photocatalyst has a crystallite size of 11.6 and 22.6 nm respectively. The heterojunction between TiO_2 and DCP affirm more adhesion and aggregation of TiO_2 nanoparticles.

The EDAX spectra (Fig. 3a, b) obtained for the TiO_2 -DCP catalyst indicates that TiO_2 nanoparticles are distributed on the HCP surface, with the partial aggregation of spherical titania nanoparticles. The observed Ti and O peaks were consistent with the formation of TiO_2 nanoparticles on the DCP, while peaks of Al and Si represent the DCP. The EDAX

Fig. 2 XRD patterns of TiO_2 -DCP and TiO_2

Fig. 3 EDX spectra of TiO₂-DCP

spectra confirm the dispersion of titania within the DCP matrix, which restrained agglomeration of TiO₂ partially and will contribute to the catalyst higher activity on dye mixtures removal.

The FTIR spectra of TiO₂-DCP and DCP are shown in Fig. 4a, the zeolitic water stretching vibration at 3400 cm⁻¹ was broader with the TiO₂-DCP sample as a result of dispersion of titania on the DCP surface [44]. The distorted OH bending of CP is pronounced with TiO₂-DCP at 1620–1640 cm⁻¹ which indicated the co-existence and assemblage of TiO₂ within the DCP matrix. The sharp absorption peak at 1070 cm⁻¹ is attributed to an asymmetrical stretching vibration band of Si(Al)-O in tetrahedral Si(Al)O₄ in DCP [45]. The stretching vibrations of Ti-O-Si and Ti-O-Al appeared at 750 cm⁻¹ were evident for both samples. The slight peak change at 3400 and 1620 cm⁻¹ with TiO₂-DCP photocatalyst (due to more surface hydroxyl groups) evidence a firm interaction between the TiO₂ and DCP [45–47].

The thermogravimetric analysis (TGA) pattern of TiO₂-DCP is shown in Fig. 4b. The TGA result is coherent with the literature [48] and weight loss occurs at 3 different temperatures, which are attributed to exchangeable cations present in the zeolite and also the presence

of volatile organic species. The first major weight loss occurred at 30–200 °C is due to desorption of physisorbed water and hydroxyl species from the HCP cavities [49, 50]. At this weight loss for TiO₂-DCP, the decomposition of titanium hydroxide to form TiO₂ could be another factor. The weight loss at 200–500 °C is ascribed to exchangeable cations within the HCP and third weight loss at 500–800 °C is ascribed to water present in the silanol nest and the phase transformation of the photocatalyst.

The optical properties of TiO₂, and TiO₂-DCP shown in Fig. 5a. The TiO₂ catalyst has its absorption edge less than 410 nm in the UV-DRS spectra, while the TiO₂-DCP sample has an absorption edge at about 420 nm. The incorporation of DCP in the TiO₂-DCP show improved light-harvesting ability in the optical spectrum, which is due to their 3D framework structure. The estimated bandgap energy (E_{bg}) of TiO₂ and TiO₂-DCP is calculated from the following equation below:

$$E_{bg} = \frac{1240}{\lambda} \quad (2)$$

where E_{bg} is the bandgap energy in eV and λ is the wavelength in nanometres. The bandgap (E_{bg}) values of TiO₂ and TiO₂-DCP are 3.08 eV, and 2.94 eV respectively. The

Fig. 4 **a** FTIR spectra plot of TiO₂-DCP and DCP; **b** thermal analysis of TiO₂-DCP

Fig. 5 **a** UV–Vis absorption spectra as-prepared samples and **b** plot of $(\alpha h\nu)^{0.5}$ versus $h\nu$ (photon energy) for TiO_2 -DCP and TiO_2

shift to the lower energy for TiO_2 -DCP photocatalyst is very advantageous for more absorption of photons in enhanced degradation of the dye mixtures.

PL analysis confirms the charge carrier separation for TiO_2 and TiO_2 -DCP sample catalysts (Fig. 5b). The emission intensity of TiO_2 -DCP was lower than that of the TiO_2 catalyst, indicating that the addition of DCP effectively restrained the recombination rate of photo-induced charge carriers in the TiO_2 -DCP catalyst. This results in more free reactive species formation for enhanced activity.

The CV of the TiO_2 showed the lowest redox current intensity in Fig. 6a. When TiO_2 NPs were immobilized on the DCP (TiO_2 -DCP), the redox current intensity was more enhanced as compared to the TiO_2 , which means higher catalytic activity and better stability for the TiO_2 -DCP catalyst. Overall, DCP presence in the composite (TiO_2 -DCP) facilitates efficient photogenerated charge carriers transfer from the TiO_2 conduction band (CB), which invariably accelerates the formation of reactive oxidative species for enhanced photocatalytic activity on dye mixtures removal. The EIS Nyquist plot for TiO_2 and TiO_2 -DCP sample are shown in Fig. 6b. The TiO_2 -DCP sample has a small arc radius as compared to TiO_2 in the EIS plot (Fig. 6b), highlighting a small resistance charge for electron transfer and prevents recombination with holes at the composite interface.

Fig. 6 **a** Cyclic voltammetry and **b** electrochemical impedance spectroscopy of the as-prepared samples (TiO_2 -DCP and TiO_2)

3.2 Photocatalytic degradation of the dye mixtures

The photocatalytic activities of TiO_2 -DCP, TiO_2 , and DCP were evaluated on the degradation of dye mixtures solution under UV light irradiation. The degradation of the dye mixtures with no photocatalyst showed poor efficiency between 27 and 30% after 180 min UV irradiation, highlighting the significant presence of a catalyst required for enhanced degradation. However, TiO_2 -DCP showed enhanced degradation efficiency on the dye mixtures up to 83% (MO) and 94% (MB) than TiO_2 , DCP and photolysis alone. The high degradation efficiency of TiO_2 -DCP is attributed to abundance of surface hydroxy groups in reducing charge carrier separation [51] (From Fig. 4a analysis), DCP support in reducing the bandgap of TiO_2 , thus enhancing absorption properties for more generation of reactive oxidative species. The DCP catalyst support (Fig. 6a), also restrain the recombination rate of photo-induced charge carriers, which in turn produces reactive oxidative species for enhanced degradation of the dye mixtures removal.

Figure 7b shows the UV absorption spectra of the dye mixtures solution at different UV light irradiation times with the TiO_2 -DCP photocatalyst. As depicted in Fig. 7b, the characteristic absorption peak of MO and MB in the dye mixtures significantly stand out at 465 and 665 nm

respectively. The MB dye in this study degrades faster than MO with TiO_2 -DCP under UV light radiation (Fig. 7b), which is similar to other works degrading the dye mixtures at lower concentrations [52, 53]. The absorbance peak height for individual dye in the solution mixture reduced gradually for the UV irradiation time, highlighting the significant breakdown of the aromatic structure of the dye mixtures that occurred during the degradation process. Also, Table 1 highlights the comparison of the performance of TiO_2 -DCP with various photocatalysts [40, 52, 54–56]

developed in recent years for the removal of dye mixtures of MO and MB. The catalytic performance of TiO_2 -DCP is much higher than that of $\text{Bi}_6\text{O}_6(\text{OH})_3$ and ZnO photocatalysts as presented in Table 1, while comparable or improved in performance with other photocatalyst as well.

The plot of $-\ln(C_t/C_0)$ versus the irradiation time for the degradation of dye mixtures in the presence of prepared samples is shown in Fig. 8a. The first-order kinetic model as derived from the Langmuir–Hinshelwood kinetic equation was applied in this study to quantify

Fig. 7 **a** Photodegradation efficiency of prepared samples on dye mixtures solution; **b** absorption spectra decrease of the dye mixtures solution with degradation time in the presence of TiO_2 -DCP. Error bars represent standard deviations of triplicate tests

Table 1 Comparison of degradation efficiency of MO and MB

Sample	Degradation time (min)	% Degradation efficiency (MO and MB)	Reaction conditions for MO and MB	References
TiO_2 -Ag	600	86, 86	0.01 g catalyst, 10 mL, 10 mg/L	[40]
TiO_2 -Sn		94, 96		
TiO_2 -Zn		99, 99		
Au@TiO_2	12	95, 84	0.02 g catalyst, 20 mL, 13 mg/L	[52]
PANI/ZnO	180	98, 99	0.1 g catalyst, 100 mL, Con. n.m	[54]
ZnO	120	80, 97	0.5 g catalyst, 500 mL, 10 mg/L	[56]
$\text{Bi}_6\text{O}_6(\text{OH})_3$	60	64, 76	0.1 g catalyst, 200 mL, 12.5 mg/L	[55]
TiO_2 -DCP	180	83, 94	0.1 g catalyst, 500 mL, 40 mg/L	This work

Con. n.m concentration not mentioned

Fig. 8 **a** Kinetic fit; **b** rate constant and half-life values of the prepared samples on the degradation of dye mixtures solution

the degradation efficiency of the samples using the expression below:

$$\ln \frac{C_t}{C_0} = -kt \quad (3)$$

The rate constant (k) was obtained from the regression analysis of the linear curve (Fig. 8a) in the plot and Fig. 8b shows the calculated values. The calculated rate constant of TiO_2 -DCP was 0.0093 and 0.0148 min^{-1} for MO and MB, which was 4.21 and 2.68, 4.31 and 3.40, 7.40 and 4.97 times higher than TiO_2 , HCP and photolysis alone respectively. The fast reaction rate of TiO_2 -DCP photocatalyst highlights its excellent removal of the dye mixtures.

Aside from the excellent photocatalytic efficiency of TiO_2 -DCP, the reusability of the photocatalyst was also studied for other potential applications in the removal of pollutants. The reusability of TiO_2 -DCP on the degradation of the dye mixtures was carried out for six consecutive cycles. After each cycle, the solution containing the dye mixtures and catalyst were recovered by centrifugation process and then washed with deionized water 3 times. The washed catalyst is then dried at 110 °C overnight and applied for the next cycle. Figure 9a shows the degradation efficiency of the TiO_2 -DCP catalyst on the dye mixtures after six cycles under UV light irradiation after 180 min. TiO_2 -DCP catalyst demonstrates a slight reduction in the degradation efficiency on the dye mixtures with an increase in the number of cycles, and at the end of the sixth cycle, 80 and 90% removal was obtained for MO and MB in the dye mixtures. The recycled TiO_2 -DCP (after six reaction cycles) was analyzed via FTIR spectroscopy to elucidate the effect of recycling hampered the structure of the catalyst. The FTIR spectrum of the recycled TiO_2 -DCP (Fig. 9b) was very similar to that of the fresh one, highlighting that TiO_2 -DCP was stable after a repetitive cycle.

3.3 Possible degradation mechanism of TiO_2 -DCP

The photocatalytic mechanism of the TiO_2 -DCP catalyst on the dye mixtures degradation can also be deduced from the band structure is presented in Fig. 10. The valence band edge of TiO_2 -DCP was calculated in line with the concepts of electronegativity [57]. Therefore the band potentials of a semiconductor can be calculated by the following empirical equation below [58]:

$$E_{VB} = X - E_e + 0.5E_g \quad (4)$$

$$E_{CB} = E_{VB} - E_g \quad (5)$$

In the equation above, E_{VB} is valence band (VB) edge potential, E_{CB} is a conduction band (CB) edge potential, E_g is the bandgap energy of the semiconductor, X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, and E_e is the energy of free electrons on the hydrogen scale (about 4.5 eV). The X value of TiO_2 is ca. 5.79 eV and the bandgap energy calculated from Taucs plots for TiO_2 -DCP is 2.94 eV, while the E_{VB} and E_{CB} of TiO_2 -DCP are estimated to be 2.71 eV and -0.23 eV respectively. Based on the estimated values of E_{VB} and E_{CB} for TiO_2 -DCP, the reaction mechanism is proposed and also described by Eqs. (5) to (10). The dye mixtures solution is first adsorbed onto the surface of the TiO_2 -DCP catalyst. Then upon illumination with the UV light, TiO_2 absorbs sufficient light photon with energy ($h\nu$) equal to its bandgap, which invariably results in the creation of electron-hole pairs. The excited electrons move from the valence band (VB) into the conduction band (CB), while the holes are left behind in the VB as shown in Fig. 10. The generation of superoxide radical (O_2^-) is not allowed because the potential of the electrons at the CB of TiO_2 is not negative enough than the redox potential of O_2/O_2^- (-0.33 eV). The excited electrons are also immediately transferred to DCP, here DCP in this

Fig. 9 **a** Reusability of TiO_2 -DCP photocatalyst on the degradation of dye mixtures solution under UV light irradiation for 180 min and **b** FTIR spectra of recycled and fresh catalyst

Fig. 10 The proposed photocatalytic mechanism of TiO₂-DCP on the degradation of the dye mixtures

system acts as an electron transporter, due to its high electron mobility of zeolites framework [59]. The transfer of the photogenerated electrons to the DCP framework occurs in femtoseconds, where a continuous transfer of electrons from the metal-semiconductor to the support material keeps the electrons away from TiO₂ to avoid recombination with the hole. This excited electrons on HCP molecular surface are been trapped by O₂ molecules in the aqueous solution to produce O₂^{•-} radicals which attacks the dye mixtures. Furthermore, considering the potential of holes at the VB of TiO₂ (2.79 eV) is more positive than the redox potential of OH⁻/OH (2.38 eV), the holes can easily oxidize H₂O/OH⁻ into hydroxyl (•OH) radicals, which is another key radical species in oxidizing the dye mixtures (Fig. 10). Invariably, both O₂^{•-} and OH[•] radicals generated from TiO₂-DCP degrade the dye mixtures into CO₂, H₂O, and other products.

Overall, the abundance of active sites, reduced band-gap of TiO₂ upon introduction of DCP as the catalyst support, also its ability (DCP) to transport and separate photoexcited charge carriers from TiO₂ are all crucial physicochemical and electrochemical properties of TiO₂-DCP with synergistic influence on enhanced degradation of dye mixtures in this present study.

4 Conclusions

Sol-gel route was employed for the synthesis of TiO₂-DCP photocatalyst, its synergistic influence on catalytic applications based on physicochemical and electrochemical properties was evaluated. For this purpose, the degradation of dye mixtures (MO and MB) under UV light irradiation was investigated. Results from this study establish the synergistic influence of partial aggregation, increased crystallite size, extended absorption edge and higher separation efficiency of photogenerated charge carriers for the formation of reactive oxidative species, evidenced the enhanced catalytic activity of TiO₂-DCP in comparison to TiO₂ and HCP on the degradation of dye mixtures (83%—MO and 94%—MB). The kinetics study of dye mixtures photodegradation follows the pseudo-first-order reaction model. The TiO₂-DCP photocatalyst had good reusability and stability for practical applications after six reaction cycles (as evidenced by FTIR spectra). The reaction mechanism for the TiO₂-DCP photocatalyst with excellent photocatalytic activity was proposed via band structure analysis and elucidated in this study. The excellent activity of TiO₂-DCP nanocomposite reveals a promising photocatalyst for various pollutants removal from wastewater.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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