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S-scheme heterojunction $g-C_3N_4/TiO_2$ with enhanced photocatalytic activity for degradation of a binary mixture of cationic dyes using solar parabolic trough reactor



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ARTICLE INFO

Article history: Received 4 May 2021 Received in revised form 23 July 2021 Accepted 13 August 2021 Available online 16 August 2021

Keywords: Solar parabolic trough g-C₃N₄/TiO₂ Continuous flow loop photoreactor Mixture dyes Simultaneous degradation

ABSTRACT

Developing photocatalytic systems by larger design to achieve degradation of dye pollutants by using solar light is highly desirable. Present work is devoted to the synthesis of step-scheme (S-scheme) $g-C_3N_4/TiO_2$ heterojunction which subsequently employed for simultaneous degradation of a binary mixture of Methylene blue (MB) and Rhodamine B (RhB) solution in parabolic trough collectors (PTC) as continuous flow loop photoreactor. The as-prepared $g-C_3N_4/TiO_2$ was analyzed by various techniques such as FE-SEM, EDS, XRD, FT-IR, BET, elements mapping and DRS. The composite central design (CCD) was applied to express mathematical relationships among variables such as process time, catalyst mass and initial concentrations of MB and RhB in the degradation process. The photocatalytic activity of the as-prepared composite is higher than pure TiO_2 and $g-C_3N_4$ that is attributed to the positive synergetic effect of S-scheme between $g-C_3N_4$ and TiO_2 nanostructure. Under solar irradiation in PTC, $g-C_3N_4/TiO_2$ was able to degrade about 94.92 and 93.07% of binary mixture MB and RhB, respectively.

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1. Introduction

Wastewater purification has a high priority for a sustainable society and water storages due to overpopulation (Zhang et al., 2017; Durgalakshmi et al., 2020; Mehdi Sabzehmeidani et al., 2020), since the consumption of unclean water is one of the major destructions of human death (Wang et al., 2017). Hence, many attempts were devoted to construct and design new protocols for the purification of wastewater before being discharge into environments. These approaches are composed of adsorption, photo-degradation, photoelectron-Fenton, sono-photodegradation, electro-Fenton process, and biodegradation (Singh et al., 2018; Gao and Wen, 2016; Moradi et al., 2020). Amongst mentioned processes, photocatalytic degradation has high efficiency for conversion of pollutants into environmentally friendly and comparatively non-toxic compounds. Huge amounts of harmful substances in effluents of factories that are entered into water resource media encourage researchers to synthesize applicable photocatalyst to remove or eliminate these hazardous compounds (Sabzehmeidani et al., 2021; Siegrist et al., 2014; Tian et al., 2021).

Advanced oxidation processes (AOPs) generally supply high efficiency to degrade residual effluent organic matter by light irradiation especially in the presence of heterogeneous photocatalysts for the oxidation of pollutants materials and improve groundwater quality (Mousavi-Kamazani et al., 2015; Wang and Zhuan, 2020). Titanium diox-

https://doi.org/10.1016/j.cherd.2021.08.015

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ide (TiO₂) as an intrinsically n-type semiconductor materials with wide band gap energy extensively suggested for diverse applications such as photocatalysts, batteries, supercapacitors, solar cells, optical devices and sensors, while it's generally known as good candidates for efficient degradation of organic pollutants (Fan et al., 2012; Li et al., 2018; Asl et al., 2021). But TiO₂ has a serious disadvantage and cannot absorb visible light owing to its large band gap of 3.2 eV. The decrease of band gap composite nanomaterials content of TiO₂ can yield high responsiveness under visible light for photocatalytic degradation (Song et al., 2016; Montazerozohori et al., 2015).

The requirement of lower energy consumption and easy and low-cost wastewater treatment processes, encourage researchers to synthesize photocatalysts that are green and have band gap applicable for activation under solar irradiation. Graphitic carbon nitride (g-C₃N₄) attains great interest as catalyst for exhibiting high activity in electrocatalytic reactions (Che et al., 2018). Recently, as a metal-free semiconductor, many focuses have been conducted on the graphite carbon nitride (g-C₃N₄), with a range band gap from 2.4 to 2.8 eV, in the field of photocatalysis water treatment (Hassankiadeh et al., 2015; Heidarpour et al., 2020; Seyed Dorraji et al., 2017). Due to the high significant recombination rate of carriers and low photocatalytic activity of g-C₃N₄, researchers have used various strategies to improve the photocatalytic activity of the g-C₃N₄ composite such as semiconductor compositing (Li et al., 2013), metal deposition (Huang et al., 2020), non-metal deposition (Chang et al., 2018) and noble metal deposition (Samanta et al., 2014). Thus $g-C_3N_4$ in the presence of light irradiation is prominent material as a photocatalyst in the photocatalytic degradation process, which usually such modification improves the photocatalytic performance (Li et al., 2020). Thus, various strategies have been proposed to progress the photocatalytic performance. The heterojunction structure effectively improves the transmission and separation of photoinduced electrons by hybridizing semiconductors with suitable band alignments. The step scheme (S-scheme) heterojunction can better explain the dilemma of remaining high charge separation efficiency and reserving strong redox ability at same time (Xu et al., 2019; Wang et al., 2020).

Solar radiation has both economic and natural resources compared to the processes using artificial light (UV and visible). However, the development of a practical photocatalytic system also helps reduce the cost-effective photocatalytic degradation process (Spasiano et al., 2015; Sundar and Kanmani, 2020). Generally, two types of solar reactors have been designed and developed for photocatalytic degradation that includes non-concentrate and concentrated solar irradiation in point (concave) or line (parabolic) (Razavi et al., 2021; Tanveer and Tezcanli Guyer, 2013; Oyama et al., 2010). Therefore, solar parabolic trough collector is a promising candidate as an applicable photocatalytic system for the degradation of organic pollutants (McLoughlin et al., 2004). The parabolic trough collectors (PTC) system contains a form that supports a reflective concentrating parabolic surface in the focal line as shown in Fig. 1. Aperture planes reflect and concentrate all the solar radiation on the geometric focus of the parabola in a glass tube. Also, PTCs could simultaneously receive thermal energy from collectors and volatile organic compound flows do not evaporate. The various solar photocatalytic reactors with concentrating collectors, have advantages of simple design and cheap and in addition PTCs have been well investigated and used for solar electric and heat generation systems and degradation of industrial wastewaters. By PTCs, both solar heat and UV light with high intensity are supplied to the photocatalyst for degradation reaction (Sano et al., 2004; Pucar Milidrag et al., 2018; Tagle-Salazar et al., 2020). Overall, based on the advantages and disadvantages of both concentrating and non-concentrating collectors, further research is needed to decide which system is applicable.

Therefore, the present study describes a photocatalyst namely g- G_3N_4/TiO_2 with a low band gap was used for photocatalytic degradation of a binary mixture of MB and RhB in a solar parabolic trough reactor and under blue LED light in a batch reactor. Finally, The CCD method was used for modeling and optimization of the photo-degradation process in various main variables (mixture MB and RhB dyes concentration, (LED and solar) irradiation time, photocatalyst mass, and pH. Langmuir–Hinshelwood (L–H) kinetics model was used for the kinetics



Fig. 1 – The experimental setup based on a PTC plant: schematic (a); photo (b).

study of the photocatalytic degradation process. Moreover, the originality of the present study is encompassed in the degradation of dyes pollutants for approaching to engineering scale photo-reactor by PTC. Preparation of $g-C_3N_4/TiO_2$ composite as promising photocatalyst by coupling of $g-C_3N_4$ with synthesized TiO_2 in order to use PTC as a continuous flow loop photoreactor is the novelty of this report. The synthesized $g-C_3N_4/TiO_2$ composite has potential applications in the treatment of dye from industrial wastewater.

2. Experimental

2.1. Chemicals and apparatus

Chemicals used were prepared from Merck and Sigma-Aldrich Company (Germany) including 1,3,5-Triazine-2,4,6-triamine (Melamine), titanium butoxide (Ti(OBu)4), Methylene blue (MB) and Rhodamine B (RhB) and ethanol. The sample was characterized by scanning electron microscopy (FESEM, TESCAN MIRA3), XRD patterns (Bruker AXS (D8, Advance) instrument employing the reflection Bragg-Brentano geometry using Cu Ka (1.54 Å)). Fourier transform infrared (FTIR) spectroscopy of g-C₃N₄/TiO₂ was characterized using a Perkin Elmer RX-IFTIR Spectrometer over a range of 500–4000 cm⁻¹. Dye concentrations were analyzed by measuring the absorbance using a UV absorption spectroscopy (model V-530, Jasco, Japan).

2.2. Synthesis of $g-C_3N_4/TiO_2$

Melamine powder (1.0 g) was put into the furnace and annealed at 500 °C with a heating rate of 10 °C min⁻¹ in a muffle furnace and kept for 4 h. The cooling to ambient temperature leads to the formation of light yellow solid bulk g-C₃N₄ and subsequently converted to g-C₃N₄/TiO₂ (2:1) composite as follows: 0.5 g of the g-C₃N₄ was mixed with 1.5 mL deionized water and 5 mL ethanol following and stirred for 2 h. Then 1 mL of titanium butoxide was added to this g-C₃N₄ solution and again was stirred for 2 h and dried at 60 °C. The collected products were calcined at 500 °C for 2 h.

2.3. Solar parabolic trough collector and analytical procedures

The parabolic trough collectors (PTCs) plant comprises a solar reactor consisting of a continuously stirred tank, centrifugal



Fig. 2 – FE-SEM images of $g-C_3N_4/TiO_2$ (a and b), EDS spectrum of $g-C_3N_4/TiO_2$ nanocomposites and EDS mapping of C, N, O and Ti elements (c and d).

recirculation pump and parabolic solar collector unit with a reasonable area of (50 cm \times 140 cm). This unit was located on a medium-density fibreboard connecting the glass tubing valves and mounted on fixed south facing tilted 30° in our laboratory (latitude of Yasouj, Iran) with respect to the horizontal plane (Fig. 1). Solar trials were made for 360 min as maximum time in clear days during the months of September-December (2017). Solar irradiation concentrates in the outer glass absorber tubes in the focal line and the total illuminated volume inside the 6 glass absorber tubes (diameter = 2 cm, length = 50 cm) was around 942 mL with connecting tubing in an aluminum frame on a fiberboard tilted of 30° for better collection of the direct solar rays. The photocatalytic degradation experiments were carried out in glass absorber tubes for certain airflow rate inside tubes. According to CCD experimental design, a fixed and selected amount of photocatalyst was dispersed in an aqueous solution containing dyes with a certain concentration, which was stored in a stirred tank with a 7-L capacity. The solution pH was adjusted at 10 by Metrohm model-780, using dilute NaOH. The parabolic trough solar photocatalytic reactors operate for 30 min in the darkness to ensure complete equilibration of adsorption/desorption of dyes onto the photocatalyst. The photo-degradation of dyes was carried out in batch mode under LED (blue) irradiation according to their previously reported in the literature procedures. The schematic

of the batch reactor setup includes a strip blue LED lamp with wavelength 460 nm (SMD 5050 Flexible Strips, 14.4 W/m, Ltd. China). The sample was brought out from a stirred tank at a specific time and centrifuged at 3000 rpm for 4 min to separate the photocatalyst particles and then analyzed using UV–vis spectrophotometer. The degradation efficiency equation for photo-degradation of mixture dyes was: $P_{dye} = \frac{(C_0 - C_t)}{C_0} \times 100$. Where P_{dye} is the degradation efficiency percentage (%), C_0 (mg/L¹) and C_t (mg/L¹) are the concentration of such dyes in the mixture at the initial time and after degradation, respectively.

2.4. Experimental design

In the present study, three-level CCD (low, central and high) with four factors was used for modeling the dyes photodegradation in the presence of $g-C_3N_4/TiO_2$ under parabolic trough solar collector in continuous mode and LED in batch mode. The contribution of main and interaction factors like MB and RhB concentration (X₁ and X₂), catalyst mass (X₃) and irradiation (Solar or LED) time (X₄) on simultaneous photocatalytic degradation of RhB and MB with at least number of experiments (Table 1) were examined. In the present research, 18 individual experimental runs based on small CCD experiments were examined to correlate their mathematical relationship with response quadratic polynomial equation.

Table 1	l – Expe	rimental	factors an	d CCD mat	rix for deg	radation of	f mixture	dyes in P	ГC.			
Variable	2		—α LED	-1	0	+1	+α	—α Solar	-1	0	+1	+α
X ₁ : conc. of MB (mg/L)			5	10	15	20	25	5	10	15	20	25
X ₂ : conc. of RhB (mg/L)			5	10	15	20	25	5	10	15	20	25
X3: catalyst mass (g)			0.005	0.01	0.015	0.02	0.25	0.005	0.01	0.015	0.02	0.25
X ₄ : irradiation time (min)		30	60	90	120	150	20	40	60	80	100	
LED										Solar		
Run	X1	X ₂	X ₃	X4	P% _{MB}	P% _{RhB}	X ₁	X ₂	X ₃	X4	P% _{MB}	P% _{RhB}
1	15	15	0.015	90	80.63	84.26	5	15	0.015	60	71.50	98.61
2	20	20	0.010	60	81.51	60.62	20	10	0.02	80	87.25	98.47
3	15	25	0.015	90	55.00	88.31	15	15	0.015	60	93.00	84.23
4	20	20	0.020	60	78.32	93.41	10	10	0.010	40	58.47	90.00
5	25	15	0.015	90	72.15	87.04	15	15	0.015	60	92.48	84.00
6	10	10	0.020	60	76.00	97.68	25	15	0.015	60	47.34	91.00
7	15	15	0.015	150	74.15	95.63	15	5	0.015	60	83.75	95.00
8	5	15	0.015	90	68.32	99.12	15	15	0.015	20	63.00	88.00
9	15	15	0.025	90	86.00	94.32	15	15	0.015	100	77.64	98.11
10	15	5	0.015	90	80.85	92.14	20	20	0.020	40	81.30	96.4
11	15	15	0.005	90	55.83	63.58	20	10	0.010	80	63.76	88.28
12	15	15	0.015	30	59.61	85.79	20	20	0.010	40	84.10	64.29
13	15	15	0.015	90	81.23	83.67	10	20	0.020	80	74.20	97.98
14	10	20	0.020	120	71.21	95.00	10	20	0.010	80	55.30	93.00
15	10	10	0.010	60	55.00	87.00	15	15	0.005	60	57.86	66.7
16	10	20	0.010	120	52.31	90.64	10	10	0.020	40	79.31	98.54
17	20	10	0.010	120	59.47	85.014	15	15	0.025	60	89.00	96.00
18	20	10	0.020	120	83.51	97.63	15	25	0.015	60	94.10	85.00

Analysis of variance (ANOVA) is a credible way to evaluate the accuracy of the fitted model. The p-value and F-value determine the significance of the model which was designed by ANOVA (Sabzehmeidani et al., 2020).

3. Results and discussion

3.1. Characterization of photocatalyst

FESEM image of g- C_3N_4/TiO_2 nanocomposites (Fig. 2a and b) reveals partial agglomeration of TiO_2 nanoparticles onto the g- C_3N_4 sheet-like structure, while also, confirm and denote suitable porosity of composite which indirectly is proportional with the mass transfer of species to the surface and pores of photocatalyst and favorable their subsequent photo-degradation. Energy-dispersive X-ray (EDS) spectrums of g- C_3N_4/TiO_2 nanocomposites sample containing 2.3% wt. of Ti confirms the presence of N, C, Ti and O elements (Fig. 2c and d). The distribution maps of elements show that N, C, Ti and O cover uniformly all the surface area, indicating that Ti as a source of TiO₂ has formed uniform in g- C_3N_4 .

The crystal structures of as-prepared g-C₃N₄, TiO₂ and g-C₃N₄/TiO₂ materials were investigated by XRD analysis (Fig. 3) which confirm and assign to support TiO₂ and g-C₃N₄ according to the standard PDF card, while all the peaks of TiO₂ can be ascribed to either both anatase and rutile TiO₂. As shown in the XRD pattern in this figure, a peak is found at 27.5, which can be assigned to (002) diffraction planes of g-C₃N₄ phase and (110) diffraction peaks of rutile TiO₂. For anatase TiO₂, eight typical diffraction peaks appear at 25.43°, 38.00°, 44.51°, 54.39°, 55.21°, 64.14°, 69.96°, 75.37°, which can be attributed to (101), (004), (122), (105), (211), (204), (116) and (215) crystal planes of rutile TiO₂ (JCPDS NO. 01-073-1764), respectively. Rutile TiO₂ has eight typical diffraction peaks that appear at 27.32°, 36.12°, 39.23°, 41.12°, 54.39°, 56.83°, 62.80°, 69.30°



Fig. 3 – XRD patterns of TiO_2 , g- C_3N_4 and $TiO_2/g-C_3N_4$ composites.

which can be assigned to (110), (101), (200), (111), (211), (220), (002) and (112) crystal planes of rutile TiO₂ (JCPDS NO. 00-004-0551), respectively. The average crystallite size of $-C_3N_4/TiO_2$ was calculated as about 47.74 nm based on the Debye–Scherrer formula (D = 0.9 λ / β cos 2 θ).

Optical properties (Fig. 4a) like absorption spectrum of $g-G_3N_4$ and $g-C_3N_4/TiO_2$ nanocomposites were recorded. Compared to $-C_3N_4/TiO_2$, the $g-C_3N_4$ composite possesses higher absorption in the visible region. In order to evaluate the energy band gaps for the $g-C_3N_4/TiO_2$ composites, plots of $(\alpha h v)^2$ versus photon energy (hv) were obtained and are shown in Fig. 4b. The simple method for probing the band structure of



Fig. 4 - UV-vis of the of g-C₃N₄ and g-C₃N₄/TiO₂ (a) and the band gap of samples (b).

composite materials is to measure the absorption spectrum (Davis and Mott, 1970). Based on the calculation results, the band gap of $g-C_3N_4$ and $g-C_3N_4/TiO_2$ were 2.65 eV and 2.81 eV, respectively. The presence of $g-C_3N_4$ on TiO_2 leads to expanding to the visible light region.

The nitrogen adsorption-desorption isotherm of g- C_3N_4/TiO_2 nanocomposites is shown in Fig. 5a. It is a type IV isotherm with H3 hysteresis loop (indicated in the P/P₀ range of 0.4-0.95). The specific surface area of g-C₃N₄/TiO₂ calculated by the Brunauer-Emmett-Teller (BET) method was found to be about 40.17 m^2 /g. The pore size distribution curve (inset in Fig. 5a) calculated from the desorption branch of the N2 isotherms by Barrett-Joyner-Halenda (BJH) method and the plot BJH illustrates that most pores are in the mesoporous range with a peak among 9-20 nm. Fig. 5b shows the FTIR spectra of the bare g-C₃N₄ and g-C₃N₄/TiO₂ nanocomposites and the absorption band at $1636 \,\mathrm{cm^{-1}}$ can be ascribed to the C-N stretching vibration modes, while the four strong peaks at 1247, 1329, 1423 and 1569 cm^{-1} to the CN heterocycle stretching of g-C₃N₄. Broadband located in the range of 3600 to 3000 cm⁻¹ corresponds to the stretching modes of terminal NH2 or NH groups at the defect sites of the aromatic ring (Troppová et al., 2018).

3.2. Response surface methodology

The numerical value of main, interaction and quadratic effects correspond to factors were estimated by initial RhB and MB concentration, irradiation time and $g-C_3N4/TiO_2$ mass (4-factor in 5-level) based on CCD design, which their analysis leads to a second-order polynomial. The 3D surface response graph was plotted against two parameters to illustrate the combined effects of parameters on simultaneous photocatalytic degradation of mixture RhB and MB by $g-C_3N4/TiO_2$ (Figs. 6 and 7).

As it can be seen, the effect of initial RhB and MB concentration on the photo-degradation efficiency in reactor PTCs under solar irradiation and in batch mode under LED light reveals that lower concentration of dyes leads to more photo-degradation efficiency and vice versa (Figs. 6 and 7). The effect of photocatalyst mass on RhB and MB photodegradation reveals that a higher value of $g-C_3N_4/TiO_2$ supply more reactive sites and more feasible reaction which increases degradation efficiency owing to higher superoxide and hydroxyl radicals during dyes degradation. Higher content of $g-C_3N_4/TiO_2$ leads to enhancing their photo-degradation. The light irradiation time is an effective parameter in photocatalytic dyes degradation and UV energy of solar light was used by TPCs leads to increasing carrier generation (hole–electron pairs) and improved photo-degradation efficiency.

3.3. Optimization condition study

Based on numerical optimization, the desired aim for each parameter and response was calculated by the desirability function (DF). The values of desirability functions for each dependent parameter are combined into overall DF by computing their geometric mean of different $df_{\rm i}$ values $(DF = [df_1^{\nu 1} \times df_2^{\nu 2} \times df_3^{\nu 3} \times ... \times df_n^{\nu n}]^{1/n}, 0 \le \nu_i \le 1 (i = 1, 2, ..., N)$ n)). Where df_i is the desirability of each response and v_i is the importance of responses (Sabzehmeidani et al., 2019a). The DF of degradation of binary mixture MB and RhB dyes versus operational variables was calculated using STATISTICA software to achieve the optimum values of variables. The desirability response was used for optimization that varies from 0.0 (undesirable) to 1.0 (desirable situation). The profile desirable responses for a binary mixture of MB and RhB photodegradation by g-C₃N₄/TiO₂ under LED and solar irradiation was investigated and the current level of each variable $(X_1,$ X_2 , X_3 , and X_4) in the model was shown at the bottom of Fig. 8. The optimum values correspond to such result (74.84% MB and 93.13% RhB) is 11 (mg/L) MB, 17 (mg/L) RhB, photocatalyst mass of 0.02 (g) and irradiation time of 80 (min) for LED irradiation in batch mode. On the other hand, after 80 min for mixing 10 and 15 mg/L¹ of MB and RhB and photo-degradation via $0.02\,g\,C_3N_4/TiO_2$ lead to the achievement of 94.92 and 93.07% degradation of MB with DF = 0.91 in PTCs collector under solar irradiation, respectively.

3.4. Kinetic study

In order to investigate the photocatalytic degradation of binary mixture MB and RhB under LED and solar by g- C_3N_4/TiO_2 nanocomposites were carried out, as shown in Fig. 9a. These observations demonstrate that solar irradiation plays an important role in enhancing the catalytic activity of g- C_3N_4/TiO_2 because it can provide a higher separation efficiency of photogenerated electron-hole pairs. The kinetics of the photo-degradation process was expressed to a pseudo-first-order rate law using the equation $ln(C_0/C) = kt$, Where C_0 and C_t are the initial MB and RhB concentration at each time.



Fig. 5 – Nitrogen sorption isotherms of the g-C₃N₄/TiO₂ and BJH plot (inset figure) (a), FTIR of the bare g-C₃N₄ and g-C₃N₄/TiO₂ (b).



Fig. 6 - Response surface plots for photocatalytic degradation of binary mixture MB and RhB under LED by g-C₃N₄/TiO₂.

Fig. 9b and c shows the binary mixture MB and RhB simultaneous photo-degradation by the $g-C_3N_4/TiO_2$ samples under LED and solar light irradiation. The error bars in Fig. 9c represent standard deviations calculated from three experiments. The apparent rate constant values are 0.0231, 0.0191, 0.0179, and 0.0162 min⁻¹ by $g-C_3N_4/TiO_2$ for MB and RhB under solar light irradiation and for MB and RhB under LED light, respectively. The apparent rate constant under the solar light is higher than the LED light. The Langmuir–Hinshelwood (L–H) model which is the most common kinetic for the degradation process was exposed. The final kinetic rate equation based on the L–H model was: $\frac{1}{2}R = \frac{1}{2}\kappa_r \kappa_A c_0 + \frac{1}{2}\kappa_r$ (Sabzehmeidani et al., 2019b).



Fig. 7 - Response surface plots for photocatalytic degradation of binary mixture MB and RhB under solar g-C₃N₄/TiO₂.

The applicability of the L–H model was calculated by plotting the inverse of the initial rate (1/R) against the inverse of the initial concentration (1/C₀) of MB and RhB dyes (Fig. 9d). A linear plot provides the intercept and slope attributed to 1/kr and 1/k_rK_A, respectively. According to the above-mentioned equations, L–H kinetic model well fitted experimental data and understudy process approximated follow pseudo-first-order kinetics by g-C₃N₄/TiO₂ under soar and LED light. The reaction rate constant (k_r) represents the limiting rate of the reaction at maximum coverage and K_A represents the equilibrium constant for adsorption of mixture dyes on the illuminated g-C₃N₄/TiO₂. It seems that decreasing of MB and RhB concentration has a positive effect on the rate of photo-degradation efficiency, also the rate constant (k) decreases with raising dyes initial concentration.

3.5. Proposed mechanism

The degradation of binary mixture MB and RhB by $g-C_3N_4/TiO_2$ composite, pure TiO_2 and $g-C_3N_4$ were performed under sunlight irradiation. As seen from Fig. 10a, $g-C_3N_4/TiO_2$ composite indicated much higher degradation efficiency than that of pure TiO_2 and $g-C_3N_4$. That related to the contribution of both TiO_2 and $g-C_3N_4$ towards enhancement in the degradation activity. To explore the photocatalytic mechanism of the $g-C_3N_4/TiO_2$ composite taking the degradation of binary mixture MB and RhB under sunlight. In order to probe the active species

and identify the electron transfer mechanism of photocatalytic activity of g-C₃N₄/TiO₂, radical trapping experiments were conducted for the photo-degradation process. Various radical scavengers including isopropyl alcohol (IPA, 'OH scavenger), p-benzoquinone (BQ, scavenger) and ethylenediaminetetraacetic acid (EDTA, h⁺ scavenger) were applied (Fig. 10b). The results indicate that the degradation efficiency was decreased highly in the presence of IPA which tells that [•]OH radicals to play crucial role in the degradation of mixture dyes. The degradation decreased slightly in the presence of EDTA which is assigned to more h⁺ active species. In addition, the MB and RhB degradation decrease in the presence of BQ that 'O²⁻ radicals is an important active species in their degradation. The band gap energy of g-C₃N₄ and TiO₂ are calculated by Tauc plot of $(\alpha h v)^{1/2}$ vs photon energy as demonstrated in Fig. 4. The valence band (VB) position and the position of conduction band (CB) of g-C₃N₄ and TiO₂ were calculated in order to explain mechanistically the enhanced photocatalytic activity of the g-C₃N₄/TiO₂ composite nanocomposites under sunlight irradiation by the following equations (Mousavi and Habibi-Yangjeh, 2016; Shafafi et al., 2020):

$$E_{CB} = X - E_{C} - \frac{1}{2}E_{g}$$
 (1)

$$E_{VB} = E_{CB} + E_g \tag{2}$$



Fig. 8 – Profiles of predicated values and desirability functions for photocatalytic degradation of binary mixture MB and RhB under LED and solar by g-C₃N₄/TiO₂.

where E_{CB} and E_{VB} are the VB and CB potentials, respectively. In addition, E_C is the energy of free electrons vs. hydrogen (4.5 eV) and E_g is the band gap of semiconductor. Besides, X is the electronegativity of the semiconductor is determined by geometric mean of the electronegativity of the constituent atoms which is estimated by the following equation.

$$X = \left[X^{a}_{(A)} X^{b}_{(B)} X^{c}_{(C)} \right]^{\frac{1}{a+b+c}}$$
(3)

where a, b, and c are the number of constituent atoms of A, B and C in the compounds. The VB and CB energies for g- C_3N_4 are +1.58 and -1.13 eV and whereas they are +2.7 and -0.5 eV for TiO₂, respectively. In addition, the g-C₃N₄ with the band gap of 2.65 eV can be excited under the visible light irradiation, while the TiO₂ with the band gap of 3.13 eV can only be activated by the UV light irradiation (Shafafi et al., 2020; Abbasi et al., 2020). Based on density functional theory (DFT) calculations, several authors have demonstrated that



Fig. 9 – Photocatalytic degradation of dyes as a function of irradiation time (a), plots of kinetic model $\ln(C_0/Ct)$ vs. irradiation time by using g-C₃N₄/TiO₂ (a), rate of constants (c) and Plots of the L-H kinetic model 1/R vs. 1/C₀ (d).



Fig. 10 – Degradation of binary mixture MB and RhB by g-C₃N₄/TiO₂, TiO₂ and g-C₃N₄ (a), scavenger study for the degradation of mixture dyes and schematic illustration of the proposed mechanism for g-C₃N₄/TiO₂ solar light irradiation (c and d).

the formation of S-scheme heterojunction can be validated (Fei et al., 2021; Yan et al., 2020). Based on the band structure of g-C₃N₄ and TiO₂ as well as the results of scavengers experiment, the mechanism of simultaneous photo-degradation of MB and RhB under solar and LED irradiation in the presence of the g-C₃N₄/TiO₂ reveals the start of the process by photoexcitation which leads to the creation of a charge carrier pair. The hybridization among C and N atoms in g-C₃N₄ leads to the formation of π conjugate structure. Fig. 10c illustrates a schematic representation of the band energy levels of n-type TiO₂ and n-type g-C₃N₄ with the conduction and valence band edge. In sunlight irradiation, the electrons get promoted from the VB to the CB in TiO_2 and $g-C_3N_4$ due to UV energy of solar light. In addition, electron transfer between the CB and the VB edge of TiO₂ is more positive than that of g-C₃N₄ allow comfortable and facile transfer of the excited hole on the surface of TiO₂ to g-C₃N₄ through the formed heterojunction. The CB edge potential of g-C₃N₄ is more negative than TiO₂ and allow transport of the excited electron on the surface of $g-C_3N_4$ to TiO₂ via the well-built heterojunction. Fig. 10d illustrates the charge transfer mechanism of the S-scheme heterojunction between n-type TiO₂ and n-type g-C₃N₄. Thus, this electron transfer process leads excellent redox capacity that has been confirmed by the radical trapping experiments (Xie et al., 2020; Xu et al., 2020). The good coupling of TiO_2 and $g-C_3N_4$ leads to well-contacted solid-solid heterojunction interface particles that improving photo-generated charge carriers and increasing photocatalytic activity. Under solar irradiation, the photo-induced holes tend to transfer from the CB of TiO₂ to VB of g-C₃N₄ and it leads to the formation of S-scheme photocatalytic system. The VB holes in TiO₂ locate at lower position than the OH⁻/ $^{\bullet}$ OH, which could oxide H₂O to form \cdot OH. Then, the electrons stored in CB of g-C₃N₄ are reacted by O₂ to form a reactive superoxide radical ion (*O2-). Eventually, the dyes can be degraded by these highly active radical species into carbon dioxide and water (Lu et al., 2018; Hu et al., 2019).

4. Conclusions

In this study, the S-scheme g-C₃N₄/TiO₂ heterojunction photocatalyst was successfully synthesized annealing method and characterized by FE-SEM, EDS, Ft-IR, XRD, BET, elements mapping and DRS. The photocatalytic degradation under solar irradiation by PTC collector and LED irradiation in batch mode, has been proven. PTCs are an efficient technology for the degradation of high concentrations of contaminants in continuous mode by solar energy. The best operation and performance for $g-C_3N_4/TiO_2$ photocatalyst by PTC collector based on CCD was achieved at 10 mg/L MB, 15 mg/L RhB 0.02 g photocatalyst and 80 min irradiation time for MB and RhB which supply about 94.92 and 93.07%, respectively. The photocatalytic degradation obeys pseudo-first-order kinetics. In addition, the UV energy of solar light leads to an increase in the apparent rate constant of photo-degradation of the MB and RhB. The PTC reactors as continuous flow loop photoreactors are promising technology and comfortably handled for industrial applications.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. No financial interests/personal relationships

Acknowledgment

The work of H. H. was supported by the EPSRC, UK, under grant EP/R511705/1.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cherd.2021.08.015.

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