

Synthesis of TiO₂/g-C₃N₄ Hybrid Photocatalyst and its Application for Degradation of Chlorophenol as Organic Water Pollutant

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This study used a hydrothermal-calcination approach to make TiO₂/g-C₃N₄ hybrid photocatalysts, which were then used to degrade 2-Chlorophenol (2-CP) as organic water pollutants under solar irradiation. According to XRD and SEM studies, the high porosity TiO₂/g-C₃N₄ hybrid nanocatalyst was successfully synthesized. The band gap energies of g-C₃N₄, TiO₂, and TiO₂/g-C₃N₄ hybrid nanocatalysts were 2.58, 2.88, and 3.16 eV, respectively, according to optical studies. The decrease in band gap energy in TiO₂/g-C₃N₄ hybrid toward TiO₂ was evidence of facilitation in photo-excitation of charge carries using low energy, which can extend the light absorption spectrum into visible regions and holes and accelerate the transmission of the photogenerated charge carriers. Electrochemical analysis revealed that the TiO₂/g-C₃N₄ hybrid had a lower charge transfer resistance and a longer electron life time than pure g-C₃N₄ and TiO₂, signifying a low electron recombination rate, allowing for faster electron transport and higher photodegradation efficiency. The entire degradation of 100 ml of 25 mg/L 2-CP was obtained after 125, 110, and 65 minutes of sun irradiation, respectively, in the presence of g-C₃N₄, TiO₂, and TiO₂/g-C₃N₄ hybrid nanocatalysts. The practical application of a TiO₂/g-C₃N₄ hybrid nanocatalyst to treat 2-CP in genuine industrial wastewater samples was investigated, and the results revealed the produced photocatalyst's excellent effectiveness in treating 2-CP in industrial wastewater.

Keywords: Photocatalyst; Photodegradation; TiO₂/g-C₃N₄ hybrid; 2-Chlorophenol; Industrial wastewater

1. INTRODUCTION

Chlorophenols (CPs) are a class of compounds formed when phenol is electrophilically halogenated with chlorine [1, 2]. In businesses and goods, CPs are used to make insecticides, herbicides, medicines, and dyes. Some are used to kill algae and fungi as well as disinfect. Historically,

the compounds have been employed to preserve textile and leather products during storage and transportation [3, 4].

Industrial waste, herbicides, and insecticides, as well as the degradation of complex chlorinated hydrocarbons, all contribute to the proliferation of CPs as persistent and recalcitrant toxicants in the environment [5, 6]. The compounds are caustic and highly irritating or poisonous, and using respirators incorrectly can be deadly [7]. These substances are caustic and extremely irritating or poisonous [8]. CPs do not breakdown spontaneously and can easily accumulate in organs, tissues, and cells through food chains [9]. As a result, it is causing acute and chronic toxic effects on aquatic creatures, as well as the possibility of histopathological alterations, mutagenic, and carcinogenic effects [10, 11]. 2-Chlorophenol (2-CP), sometimes known as ortho-chlorophenol, is an organic chemical that is a phenol derivative. Disinfectants and insecticides containing related chemicals are utilized [12].

Many methods such as chemical and electrochemical oxidation [13], adsorption [14], ozonation [15], coagulation [16], Fenton and electro-Fenton oxidation [17-19], bacterial degradation [20], sonochemical [21, 22] and photocatalytic degradation [23-27] have been employed for the treatment of CPs contaminated wastewater. The photocatalytic degradation process is an interesting solution for the removal of organic water contaminants because it is both environmentally beneficial and affordable. As a result of this research, a $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid photocatalyst was synthesized utilizing a hydrothermal-calcination process and was used to degrade 2-CP as an organic water pollutant.

2. EXPERIMENT

2.1. Synthesis of TiO_2 , $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts

$\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts were synthesized using the hydrothermal-calcination technique [28]. In a nutshell, a dispersed aqueous mixture of 10 g/L melamine (99%, Sigma-Aldrich) and 10 g/L NH_4F ($\geq 98\%$) was ultrasonically created in an equal volume ratio. After that, 50 mL of the mixture was poured into 100mL Teflon-line autoclave and covered with a titanium foil (99.99%, 40mm x 30mm x 0.5mm, Sigma-Aldrich) that was vertically placed in the autoclave. The reaction was carried out at 160°C for 72 hours. After that, the product was collected and rinsed with deionized water before being heated for 5 hours at 530°C in a muffle furnace at a rate of $20^\circ\text{C}/\text{min}$. For synthesis of the pure TiO_2 , the above hydrothermal-calcination process was repeated without adding melamine and NH_4F , and for synthesis of the pure $\text{g-C}_3\text{N}_4$, the same process was performed without titanium foil.

2.2. Characterization

The crystal structures and morphology of the produced nanocatalysts were studied using an X-ray diffractometer (XRD; Rigaku D/max-2400, Japan) and scanning electron microscopy (SEM). A UV-vis spectrophotometer was utilized to detect optical absorption spectra (Model Omega 10, Bruins Instruments, Puchheim, FRG). Electrochemical impedance spectroscopy (EIS) measurements were performed under visible-light illumination, for comparing electron-transfer rates in photocatalysts at a frequency range of 10^{-1} to 10^6 Hz and 10mV AC voltage into 0.5M Na_2SO_4 solution ($\geq 98\%$) by

potentiostat/galvanostat equipped with an electrochemical cell containing nanocatalysts modified fluorine doped tin oxide (FTO, Sigma-Aldrich) as working electrode, a Pt plate as counter, and Ag/AgCl as reference electrode. The obtained EIS data were fitted with an appropriate equivalent circuit using the software Z-view.

2.3. Study the photocatalytic Activity

The photodegradation activity of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts was evaluated for the treatment of 100 ml of 2-CP solution under solar illumination. The experiments were conducted on a reactor system consisted of a cylindrical Pyrex-glass cell with a 1000 mL capacity and a Philips tungsten-halogen lamp (250 W) was placed in a 8 cm just above the sample in the reactor. The mixture of 20 mg of nanocatalysts in 100 ml of prepared 2-CP solution with deionized water, as well as a prepared real sample of industrial wastewater. Before the photodegradation measurements, the mixture was magnetically stirred for one hour in a dark place to get an adsorption/desorption equilibrium between 2-CP molecules and the nanocatalysts. For photocatalytic experiments, the light source was irradiated on samples for a regular time interval, and irradiated samples were centrifuged at 10000 rpm for 8 minutes, filtered through a 0.22 μm membrane (MF-Millipore™, Merck, Germany) and collected. The concentration of 2-CP of the supernatants was measured by UV-vis absorbance (spectrophotometer, Bruins Instruments) at $\lambda_{\text{max}} = 275 \text{ nm}$ [29]. The 2-CP concentration corresponded to the absorbance intensity, which was used for the calculation of the degradation efficiency (η) by the following equation [26, 30]:

$$\eta (\%) = \frac{I_0 - I_t}{I_0} \times 100 = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where I_0 and I_t are absorbance intensity of initial and illuminated 2-CP solutions, respectively, and C_0 and C_t is corresponded 2-CP concentration in initial and illuminated 2-CP solutions, respectively.

3. RESULTS AND DISCUSSION

3.1. Study of morphology and structure of nanocatalysts

Figure 1 shows XRD patterns of powders of $\text{g-C}_3\text{N}_4$, TiO_2 , and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts. The (100) and (002) planes in $\text{g-C}_3\text{N}_4$ are related to the in-plane structure of tris-triazine units and the interlayer stacking of conjugated aromatic systems, respectively, in the XRD pattern [31-33]. According to the XRD patterns of TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid, there are diffraction peaks at 25.20° , 37.75° , 47.97° , 53.68° , 54.191° , and 62.65° , which correspond to the typical crystal facet of anatase TiO_2 with (101), (004), (200), (105), (211), and (204) planes, respectively (JCPDS card no. 21-1272) [34, 35]. However, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalyst diffraction peaks show an additional peak of (002) plane of $\text{g-C}_3\text{N}_4$, indicating the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalyst was successfully synthesized by the hydrothermal-calcination method.

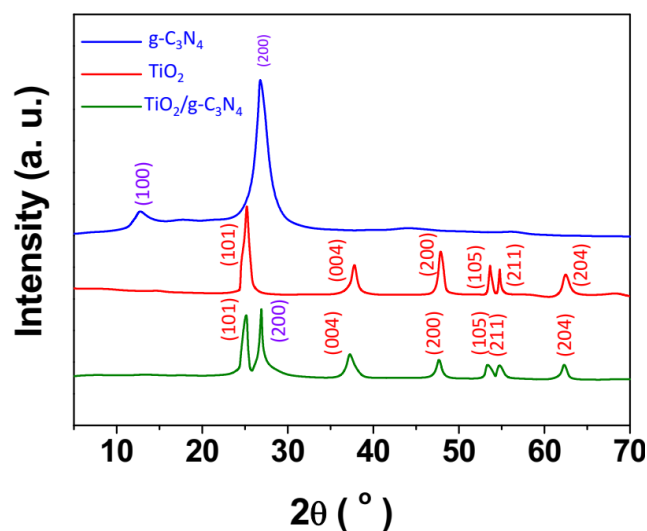


Figure 1. XRD patterns of powders of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts.

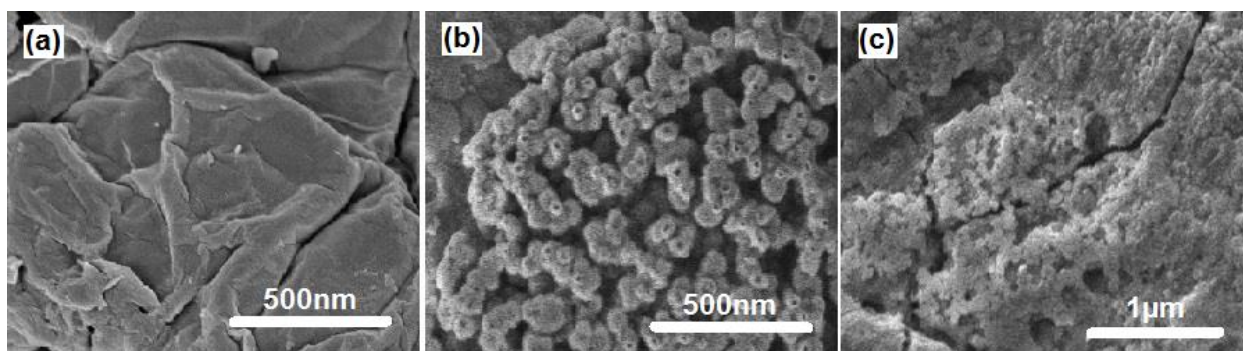


Figure 2. SEM micrographs of (a) g-C₃N₄, (b) TiO₂ and (c) TiO₂/g-C₃N₄ hybrid nanocatalysts.

Figure 2 shows SEM micrographs of g-C₃N₄, TiO₂, and TiO₂/g-C₃N₄ hybrid nanocatalysts. The surface of g-C₃N₄ has a layered sheet structure (Figure 2a). Surface morphology of the sheets is smooth. Figure 2b shows a significant number of irregularly spherical shaped nanoparticles with an average size of 60nm in a SEM micrograph of TiO₂. The hydrothermal-calcination process produces a minor aggregate. TiO₂ nanoparticles are equitably bonded in g-C₃N₄ sheet-like structure, creating heterojunction with high rough and porous hybrid structure, as shown in SEM micrograph of TiO₂/g-C₃N₄ hybrid nanocatalyst. This porosity contains more surface flaws and can increase the effectiveness of light absorption [36, 37].

3.2. Study of optical absorbance spectra

The optical absorbance spectra of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts are depicted in Figure 3a. It is observed that the spectrum of g-C₃N₄ shows an absorption wavelength up to 450 nm. It is suggested that g-C₃N₄ has good visible light response. Its UV response is lower than that

of TiO_2 [38]. It is in agreement with the reports which indicated that the two-dimensional planar structure of $\text{g-C}_3\text{N}_4$ with π -conjugated system benefits the transport of charge carriers, and the narrow bandgap energy with visible-light absorbing ability [39]. Optical absorbance spectra of TiO_2 shows notable absorption edge in the UV region ($\lambda \leq 390 \text{ nm}$) and poor absorption in the visible light region, which associated with the intrinsic band-gap energy of pure TiO_2 and is indicting to great photocatalytic response to UV light [40-42]. Meanwhile, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid exhibits not only a broader absorption edge than TiO_2 and distinctly enhanced in the visible light region, but also it has the highest optical absorption in comparison to that both of the $\text{g-C}_3\text{N}_4$ and TiO_2 nanostructures which can be related to the introduction of Ti^{3+} and the oxygen vacancies [43]. It is reported that introduction of Ti^{3+} and oxygen vacancies into the TiO_2 lattice can form local states at the bottom of the conduction band of TiO_2 which results in visible-light absorption performance while eliminating the recombination effect [44-46]. As depicted in Figure 3b, the band-gap energy (E) value can be obtained from the intercept of linear portion of the $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) to the energy axis, where α is the absorption coefficient, h is the Planck's constant ($4.1357 \times 10^{-15} \text{ eV.s}$), and ν is the light frequency. The values of band gap energy of $\text{g-C}_3\text{N}_4$, TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts are determined at 2.58, 2.88 and 3.16 eV, respectively. Thus, introducing Ti^{3+} and oxygen vacancies can form the local states and a series of discrete energy levels which reduce the edge of the conduction band create a disordered assembly [47]. The $\text{g-C}_3\text{N}_4$ in $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid also creates a new impurity levels by the upshifted of the TiO_2 valence band edge [48]. As results, formation these local states and impurity levels could considerably decrease the forbidden band width of TiO_2 , accordingly, decrease of band gap energy in $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid toward TiO_2 is evidence of facilitation in photo-excitation of charge carries using low energy, which can extend the light absorption spectrum into the visible region, and accelerate the transmission of the photogenerated charge carriers [49-51]. Eventually, it leads to the production of further electron and hole pairs and melioration of the photocatalytic treatment of the pollutants [48, 52].

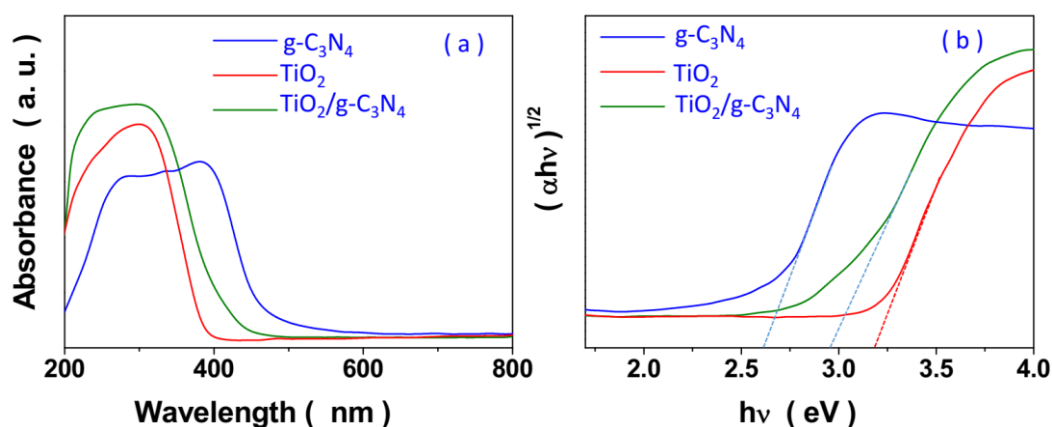


Figure 3. (a) The optical absorbance spectra of $\text{g-C}_3\text{N}_4$, TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts and (b) corresponded plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$).

3.3. Electrochemical analyses

The electrochemical kinetics process in photocatalysts has traditionally been evaluated using EIS experiments. Figure 4 shows Nyquist and Bode diagrams of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts, respectively. Figure 5 and Table 1 illustrate the equivalent circuit and the acquired parameters by fitting the EIS spectra with the equivalent circuit. The parameters of the corresponding circuit are included. R_{ct} is the first semicircle into the middle-frequency region that is related to charge-transfer resistance and reflects the facility of electron transfer at the electrode/solution interface, and R_s is the series impedance as the nonzero intersection of the semicircle with the real axis at high frequency from the Nyquist plots in Figures 4a [53-55]. Z_N is Nernst diffusion impedance which related to second semicircle at the low-frequency region. C_{dl} presents the chemical capacitance at the interface of photocatalyst/electrolyte. Results indicate that the R_{ct} values of TiO₂/g-C₃N₄ hybrid is remarkably less than pure g-C₃N₄ and TiO₂, implying that merger g-C₃N₄ and TiO₂ provides high porosity and great effective surface area, and more reaction sites to promote the transfer of electrons at the interface of the photocatalyst and electrolyte. As consequence it can enhance the photocatalytic reaction rate [56, 57]. Moreover, the TiO₂/g-C₃N₄ hybrid shows the lowest Z_N value that it is indicated to good diffusion ability in the electrolyte. The depicted Bode plots Figures 4b shows the peak frequency (f_{max}) of TiO₂/g-C₃N₄ hybrid toward g-C₃N₄ and TiO₂ are shifted to low frequency. According to the formula $\tau_n = 1 / (2\pi f_{max})$, f_{max} is inversely related to the electron life time (τ_n). Thereby, the decrease in f_{max} implies an increased electron life time which participates in the electrocatalytic reaction, and a decreased rate for the charge-recombination process for TiO₂/g-C₃N₄ hybrid [58, 59]. These results are in agreement with SEM and optical analyses and confirm the lower charge resistance, an efficient injection of electrons into the TiO₂/g-C₃N₄ hybrid, and its low electron recombination rate which provide the rapid electron transport and higher photodegradation efficiency.

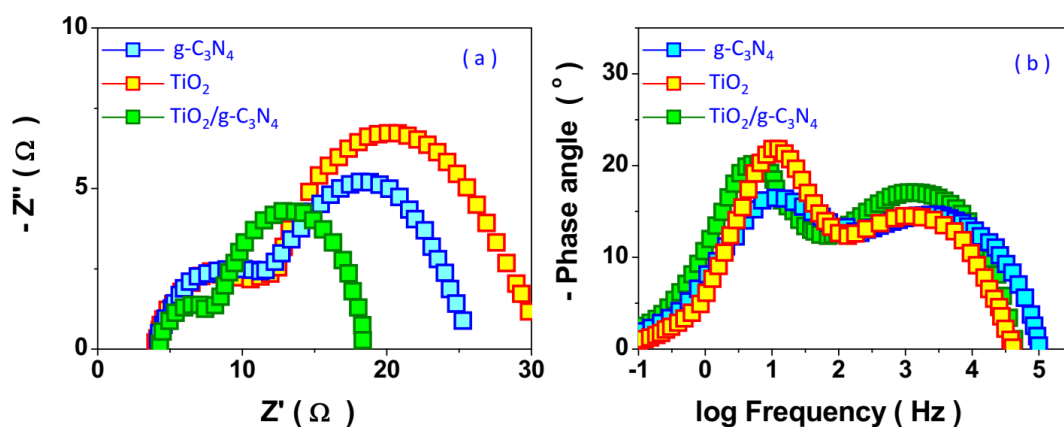


Figure 4. (a) Nyquist and (b) Bode plots of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts.

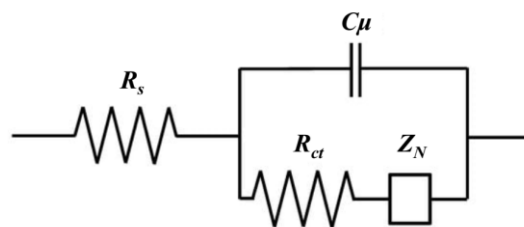


Figure 5. The equivalent circuit.

Table 1. The obtained parameters by fitting the EIS spectra with the equivalent circuit.

Sample	R_s (Ω)	R_{ct} (Ω)	Z_N (Ω)
TiO ₂	4.42	5.77	19.28
g-C ₃ N ₄	4.35	2.37	17.20
TiO ₂ /g-C ₃ N ₄	4.33	1.25	12.09

3.4. Photodegradation activity

Figure 6 shows the findings of a study comparing the photodegradation activities of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid photocatalysts for the treatment of 100 ml of 25 mg/L 2-CP solution to degradation in a control sample without photocatalyst and photodegradation activity in the dark. As can be shown, control sample degradation efficiencies in the dark (first hour) and under solar illumination (for 130 minutes) are 0.09% and 0.8%, respectively. For all photocatalysts, the degradation efficiency after one hour in darkness reaches $\leq 0.9\%$, and it is drastically increased under solar illumination in first minutes. Accordingly, the degradation efficiency is obtained at 12%, 15% and 25% using g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts after 5 minutes of solar illumination, respectively. These observations confirm the great photocatalytic activity of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts under solar illumination [60]. Furthermore, Figure 6 also shows that total degradation of 2-CP is obtained after 125, 110 and 65 minutes of solar illumination in the presence of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid nanocatalysts, respectively. Therefore, the TiO₂/g-C₃N₄ hybrid nanocatalyst illustrates a faster degradation rate of 2-CP than that g-C₃N₄ and TiO₂ which is associated with three factors in good agreement with SEM, EIS and optical analyses: (i) its larger effective surface area and further active sites for photocatalytic processes [61], (ii) more efficient photo-generated electron-hole separation and quick charge transfer than g-C₃N₄ and TiO₂, (iii) its narrow band-gap which can explain the improved photocatalytic elimination of 2-CP under solar illumination.

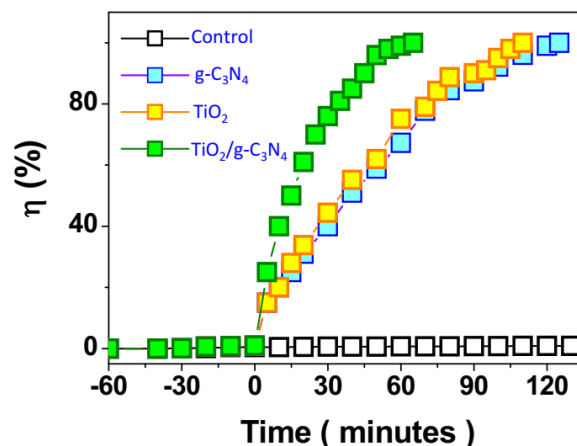
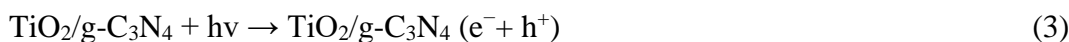


Figure 6. Degradation efficiency of g-C₃N₄, TiO₂ and TiO₂/g-C₃N₄ hybrid photocatalysts for the treatment of 100 ml of 25 mg/L 2-CP solution in dark and under solar irradiation.

Equations 3 to 8 demonstrate the photocatalytic reaction mechanisms for degradation of 2-CP under solar illumination [62, 63]. First, the electron and hole pairs are created on TiO₂/g-C₃N₄ under solar irradiation (Equation 3) in the conduction and valence band, respectively. The electrons are captured by O₂ to form •O₂⁻ (Equation 4), and further cause the formation of •OH (Equation 6). At the same time, H₂O molecules can be oxidized by photogenerated holes to form •OH (Equation 5). Eventually, 2-CP is degraded by these reactive oxygen species and even mineralized (Equation 7) [64].



The effect of initial 2-CP concentrations (10, 25, 50, and 100 mg/L) on TiO₂/g-C₃N₄ hybrid nanocatalyst degrading efficiency was investigated. Figure 7 shows that as the initial 2-CP concentration rises, the degrading effectiveness decreases considerably. Under solar irradiation, total degradation of 10, 25, 50, and 100 mg/L of 2-CP takes 40, 65, 90, and 115 minutes, respectively. Table 2 compares the photocatalytic activity of the photocatalyst in this study to that of various published photocatalysts for the treatment of 2-CP, demonstrating that the TiO₂/g-C₃N₄ hybrid nanocatalyst has a high photocatalytic efficiency due to the creation of intermediate states in the energy band-gap of the hybrid nanocatalyst and efficient separation of electron-hole pairs [65].

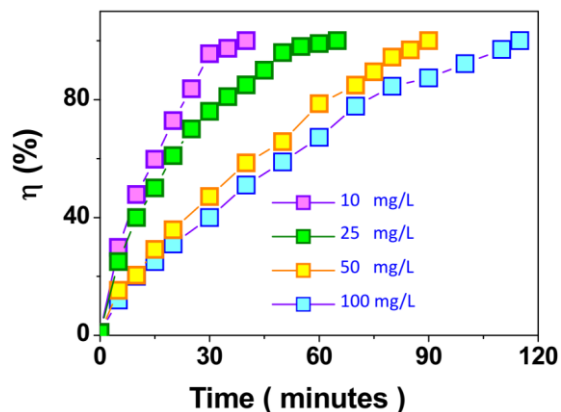


Figure 7. The effect of initial 2-CP concentrations (10, 25, 50 and 100 mg/L) on the degradation efficiency of TiO₂/g-C₃N₄ hybrid nanocatalyst under solar irradiation.

Table 2. Comparison the photocatalytic activity of photocatalyst in this study with that of various reported photocatalysts in the literature for the treatment of 2-CP.

Treatment method	Material	2-CP content (mg/L)	Light source	Degradation time (minute)	η(%)	Ref.
Photocatalyst	TiO ₂ /g-C ₃ N ₄	10	Solar	40	100	This work
		25		65	100	
		50		90	100	
		100		115	100	
Photocatalyst	TiO ₂ (P25)	100	UV	120	95	[66]
Photocatalyst	Ru-doped TiO ₂	100	Visible	180	53	[67]
Photocatalyst	ZrO ₂ -doped ZnCo ₂ O ₄	50	Visible	180	91.7	[68]
Photocatalyst	S-doped TiO ₂	25	Visible	180	71.4	[69]
Photocatalyst	N-doped TiO ₂	25	Visible	150	79.8	[70]
Photocatalyst	Co(III)-doped TiO ₂	25	UV	180	93.4	[71]
liquid/solid–ozone	Silica gel	50	---	50	100	[72]
liquid/solid–ozone	Zeolitic	50	---	65	100	[72]
Electrochemical oxidation	Graphite	100	---	20	60	[73]
Electrochemical oxidation	Copper	100	---	20	51.85	[73]
Electrochemical oxidation	Iron	100	---	20	41.90	[73]

The feasibility of using a TiO₂/g-C₃N₄ hybrid nanocatalyst to treat 2-CP in real-world industrial wastewater samples (IWS) was investigated. Under solar irradiation, Figure 8 shows the degrading efficacy of 100mL of 10mg/L 2-CP solution prepared from the actual sample (industrial effluent) and a

control sample (CS) made from deionized water. Total 2-CP treatment takes 40 and 60 minutes in the control sample and industrial wastewater samples, respectively, revealing that total 2-CP treatment takes longer (20 minutes) in industrial wastewater samples due to the presence of inorganic and organic contaminants. However, the results show that the developed photocatalyst is extremely effective at treating 2-CP in industrial effluent [65, 74, 75].

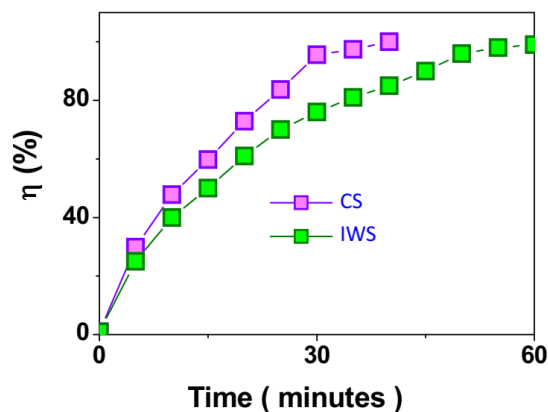


Figure 8. The degradation efficacy of 100mL of 10mg/L 2-CP solution made from actual sample (industrial wastewater) and a control sample made from deionized water under solar irradiation.

4. CONCLUSION

In conclusion, this study described the synthesis of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid photocatalysts utilizing a hydrothermal-calcination approach, as well as their use in the degradation of 2-CP as organic water pollutants under solar irradiation. According to structural analysis, the high porosity $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalyst was successfully synthesized. The band gap energies of $\text{g-C}_3\text{N}_4$, TiO_2 , and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts were 2.58, 2.88, and 3.16 eV, respectively, according to optical studies. The decrease in band gap energy in $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid toward TiO_2 was evidence of facilitation in photo-excitation of charge carriers using low energy, which can extend the light absorption spectrum into the visible region, hinder the recombination of charges, Electrochemical analysis revealed that the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid had a lower charge transfer resistance and a longer electron life time than pure $\text{g-C}_3\text{N}_4$ and TiO_2 , signifying a low electron recombination rate, allowing for faster electron transport and higher photodegradation efficiency. Total degradation of 2-CP was achieved after 125, 110, and 65 minutes of sun exposure in the presence of $\text{g-C}_3\text{N}_4$, TiO_2 , and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalysts, respectively. Because of the production of intermediate states in the hybrid nanocatalyst's energy band-gap and effective separation of electron-hole pairs, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalyst demonstrated a high photocatalytic efficiency when compared to several published photocatalysts for the treatment of 2-CP. The practical use of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hybrid nanocatalyst to treat 2-CP in genuine industrial wastewater samples (IWS) was studied, and the results revealed the produced photocatalyst's excellent effectiveness in 2-CP treatment in industrial wastewater.

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