

Removal of trichlorophenol from wastewater using NiS/RGO/TiO₂ composite as an efficient photocatalyst under sunlight

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ABSTRACT

In this study, nickel sulfide-reduced graphene oxide-titanium dioxide (NiS/RGO/TiO₂) nanocomposite was synthesized by the hydrothermal method. Different tools such as scanning electron microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy, and photoluminescence spectroscopy were used to characterize the prepared nanocomposite. The application of NiS/RGO/TiO₂ nanocomposite was investigated for the degradation of trichlorophenol (TCP) under solar light irradiation. Results showed that the coupling of nickel sulfide and reduced graphene oxide with titanium dioxide has significantly enhanced the photocatalytic activity where the degradation of TCP reached 95% after 6 h under sunlight radiations. The total organic carbon was reduced to 4 mg L⁻¹ from its initial concentration (11 mg L⁻¹), which showed that up to 55% of organic carbon mineralization was successfully achieved. In general, the study revealed an efficient photocatalytic capability of NiS/RGO/TiO₂ nanocomposite under visible light.

Keywords: NiS/RGO/TiO₂ nanocomposite; Photocatalyst; Sunlight; Trichlorophenol; Wastewater

1. Introduction

Natural water resources such as a river, canals, groundwater, etc. are contaminated due to the presence of a variety of pollutants from chemical and microbial sources. Organic pollutants release from a variety of industrial and agricultural activities [1]. Many toxic contaminants can potentially impair the metabolic activity in living cells and thus affect biochemical processes [2,3]. Discharge from partially treated wastewater could serve as the primary source of toxic pollutants [4,5]. Besides this, suspended particles and are also

concentrated with contaminants. Conventional wastewater treatment plants are the less efficient incomplete treatment of pollutants from the wastewater and thus the need to choose innovative water treatment technology.

For the treatment of organic contaminants in wastewater, the use of powerful hydroxyl radicals (*OH) through advanced oxidation processes (AOPs) occurs via the means of chemical, photocatalytic, or photochemical methods [6]. Among various AOPs, photocatalysis has been recognized as a sustainable tool to state issues related to energy and water purification challenges by utilizing solar light [7–9]. There is enough proof that photocatalysis is the most significant and effective method to remove organic pollutants from water

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because it has low maintenance costs, simple to operate, and is highly efficient [10]. Most importantly, it generates fewer or no toxic substances at the end of the treatment process. titanium dioxide (TiO_2) is the most preferred photocatalyst due to its availability, superior photocatalytic performance, nontoxicity, and long-term stability [11]. However, one of the drawbacks that significantly limit many people from using TiO_2 is that it only utilizes the ultraviolet (UV) light that constitutes about 3%–5% of the solar spectrum [12]. Therefore, to broaden the TiO_2 absorption band, there is a need to modify TiO_2 with other semiconductors to achieve a change in its bandgap energy which might develop the material capability to absorb visible light. To increase the efficiency in the visible region, it is critical to overcoming the fast recombination of photogenerated holes and electrons that are generated under photocatalyst irradiation. Several methods have been brought forward to increase TiO_2 efficiency to absorb visible light. One of them is to develop TiO_2 based nano-based composites that are efficient in enhancing the photocatalytic performance through reduction in charge recombination [13–15]. Additionally, various techniques can be used to obtain these composites, namely, nonmetallic doping, doping with noble metals, and nonmetal/metal co-doping [16].

Nickel sulfide (NiS) is known as an important member of metal sulfides with the benefit of high electronic conduction, ease of fabrication, low cost and low toxicity [17]. NiS is a simple binary semiconductor of *p*-type, which can be used to develop a novel *p-n* heterojunction catalyst with titania, because of its high electronic conductivity, low bandgap energy, earth-abundant elements, environmentally friendly and has a large absorption coefficient [18]. There is no doubt inefficient *p-n* heterostructure, however, the selection of *p*-type semiconductors that matched with energy levels of TiO_2 , NiS plays an ideal role. A study reported that the synthesis of a novel NiS/ TiO_2 nanosheet composite via the hydrothermal synthesis process. The improvement in the degradation of organic pollutants under visible light has been reviewed by Chatterjee and Dasgupta [17] using modified TiO_2 photocatalyst. Contrary to this, the outstanding properties of graphene such as high adsorption capacity, high electron mobility, and stability has compelled to be used as an electron co-catalyst and sustenance photocatalysis [19]. Graphene is a two-dimensional sp^2 -hybridized carbon nanosheet that has unique properties. They include high mobility of charge carriers, a high theoretical surface area, and good mechanical strength [20–23]. Due to the excellent electron mobility of graphene, it has the efficiency to separate and transfer photogenerated electrons from holes to be recombination [24]. The practical application of graphene is usually hindered by inherent problems of restacking under the action of the Van der Waals force which leads to losing effective surface area, therefore the low value of capacitance [25]. Recently, some researchers have put their attention in studying photocatalytic or catalytic properties of reduced graphene oxide (RGO) and graphene to understand them deeply since they are essential in the formation of efficient composites [24,26].

Keeping in view the above mention concerns of low visible light activity and electron recombination, the present study was conducted to develop nanocomposite using

NiS, RGO with TiO_2 to achieve a visible light active nickel sulfide-reduced graphene oxide-titanium dioxide (NiS/RGO/ TiO_2) nanocomposite photocatalyst. The photocatalyst was characterized by using various tools such as scanning electron microscopy (SEM), photoluminescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (XRD). The photocatalytic efficiency of the catalyst was evaluated using trichlorophenol (TCP) as a model pollutant in wastewater under visible light (direct sun exposure). Notably, TCP is a renowned example of an aromatic contaminant in an aqueous solution [27]. The degradation efficiency was measured by analyzing the concentration of TCP at various intervals using high-performance liquid chromatography (HPLC).

2. Materials and methods

2.1. Chemicals

For the synthesis of catalyst, TiO_2 powder (P-25 Degussa Co., Ridge-Field Park, NJ, USA) sodium hydroxide (Panreac Quimica SLU, Spain), NiCl_2 , sodium sulfite (BDH Chemicals, England) and graphite powder (Sigma Aldrich, USA) were used. The model pollutant used for testing photocatalytic activity was pure TCP (Fisher Scientific, USA). The solution and reagents were prepared using deionized water.

2.2. Synthesis of NiS/RGO/ TiO_2 nanocomposite

The preparation of the NiS/RGO/ TiO_2 nanocomposite involved two sequential steps. In the first step, P25 was hydrothermally modified using a 10 M NaOH solution. Thus, 2 g P25 was mixed with 100 ml 10 M NaOH solution and stirred for 2 h. Thereafter, the P25 solution was transferred in the hydrothermal reactor and heated at 120°C for 18 h. The modified P25 was washed with deionized water, acetone and 0.1 HCl solutions to remove the excess of sodium ions and dried at 105°C.

In the second step for the synthesis of NiS/RGO/ TiO_2 nanocomposite, 1 g modified P25 was dispersed in 70 ml deionized. Thereafter, 30 ml graphene oxide (GO) (1 mg ml^{-1}) solution and 0.474 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was mixed with P25 solution and stirred for 2 h. Then, 20 ml Na_2S (2 M) was added and the prepared mixture was further stirred for 2 h and transferred to the hydrothermal reactor and heated at 140°C for 24 h. The added Na_2S reagent is a reducing agent. It not only converts Ni into NiS, but also convert GO to RGO. The synthesized precipitate was filtered, washed thoroughly with deionized water, acetone and dried at 105°C.

2.3. Characterization

The prepared materials TiO_2 , NiS, and NiS/RGO/ TiO_2 were characterized by different tools and instrumentations like XPS, SEM, XRD, and PL spectroscopy. For structural characteristics, XRD Ultima IV X-ray diffractometer was used. The absorbance (optical) properties were analyzed by (PL; Kimon, 1K, Japan), and morphological properties by SEM JEOL-JSM7600 F, (Japan). The chemical state of the catalyst was analyzed by XPS (SPECS GmbH, Germany)

2.4. Photocatalytic activity

The catalyst NiS/RGO/TiO₂ nanocomposite was examined in solar light photocatalysis experiments using TCP as an organic pollutant in aqueous solution. A pyrex reactor was developed to conduct photocatalytic activity under the illumination of natural sunlight. The reactor is set outdoor to harvest sunlight for activation of the photocatalyst. A mass of 1 g of the photocatalyst was dispersed in an aqueous solution containing TCP. The pH of the solution was mentioned in a range of 4.0–5.0 until the end of the experiment using 0.1 M H₂SO₄ and NaOH. The samples (3 ml) were collected after every hour for a total of 6 h illumination under solar radiation. The degradation amount of TCP was measured by an HPLC equipped with a UV detector. For the measurement of mineralization efficiency of the photocatalyst, total organic carbon (TOC) was measured by the C.O.T. type CA-10 TOC analyzer.

3. Results and discussion

3.1. Characterization

3.1.1. SEM analysis

To study the morphological characteristics of the prepared catalysts, SEM analysis was performed. The results showed that the modified TiO₂ particles were sheet-shaped and distributed uniformly. However, they might have contributed to the agglomerations of some smaller particles (Figs. 1a and b). Similarly, Figs. 1c and d portray that NiS occurs as a particle-like structure with some fiber-like structure. SEM micrographs of NiS/RGO/TiO₂ nanocomposite shows the NiS and RGO sheets decorated on modified TiO₂ particles (Figs. 1e and f).

3.1.2. X-ray diffraction analysis

The structural characteristics of the NiS, TiO₂ and NiS/RGO/TiO₂ were analyzed by XRD and are depicted in Fig. 2. The XRD pattern of NiS indicated the diffraction peaks at 2θ of 18.3°, 32.3° and 37.4° which are corresponded with 110, 300, and 220 planes respectively. These diffraction peaks are associated with the rhombohedral structure of NiS. Other diffraction peaks include 2θ at 55° which is associated with the existence of nickel oxide due to air oxidation in the NiS powder. In the case of modified TiO₂ nanoparticles, the XRD pattern showed the presence of a mixture of rutile and anatase phases (modified-TiO₂). The peaks at (101), (004), and (200) that corresponds to 2θ of 24.45°, 48.35°, and 63° respectively are due to anatase. Whereas, the rutile peaks occurred at (110) and (101) corresponds to the 2θ of 28.25° and 45.45° respectively. The XRD pattern of NiS/RGO/TiO₂ nanocomposite showed similar peaks like NiS and modified TiO₂. However, the intensity of the diffraction peaks has been changed partially due to composite formation. A similar phenomenon has been reported in the previous studies which evidence the formation of composites of NiS and TiO₂ [12,14–15].

3.1.3. XPS analysis

The chemical states and surface composition of NiS/RGO/TiO₂ photocatalyst were examined by XPS analysis. It was observed that elements Ni, S, Ti, O C and O with 6.673%, 2.377%, 29.936%, 35.26% and 25.754% mass concentrations were present in the composite. Fig. 3 shows the wide scan spectra NiS/RGO/TiO₂ composite and the peaks for Ni 2p_{3/2}, Ti 2p_{3/2}, S 2p, O 1s, and C1s were appeared at the binding energy 856.24, 458.49, 169.14, 530.14 and 284.99 eV, respectively. The presence of the peaks for Ni 2p_{3/2}, Ti 2p_{3/2}, S 2p, O

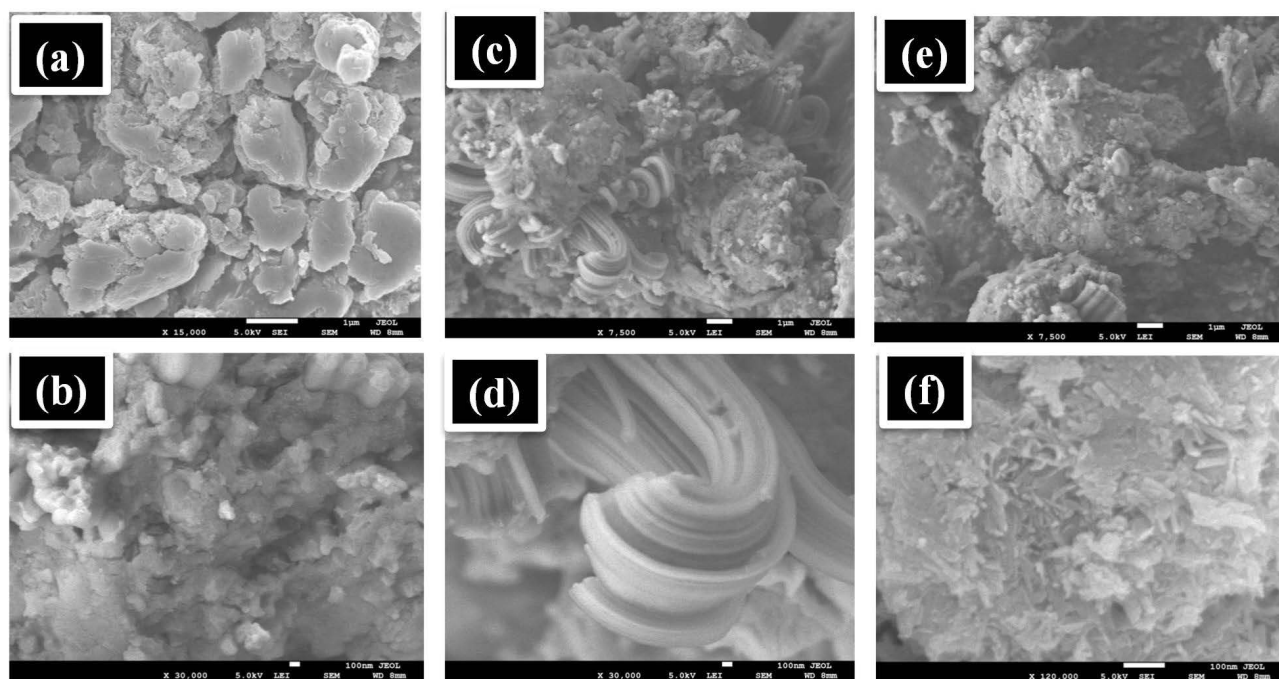


Fig. 1. SEM images of the prepared materials using LEI and SEI detectors, (a,b) TiO₂, (c,d) NiS and (e,f) NiS/RGO/TiO₂.

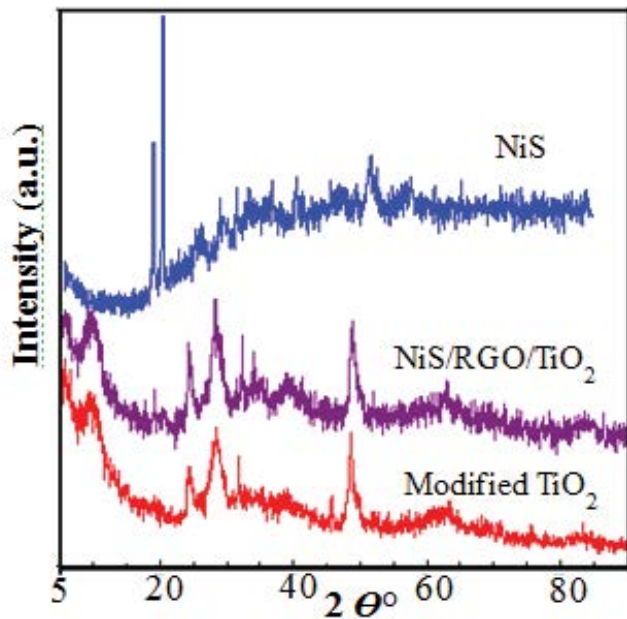


Fig. 2. XRD patterns of NiS, modified TiO₂ and NiS/RGO/TiO₂ nanocomposite.

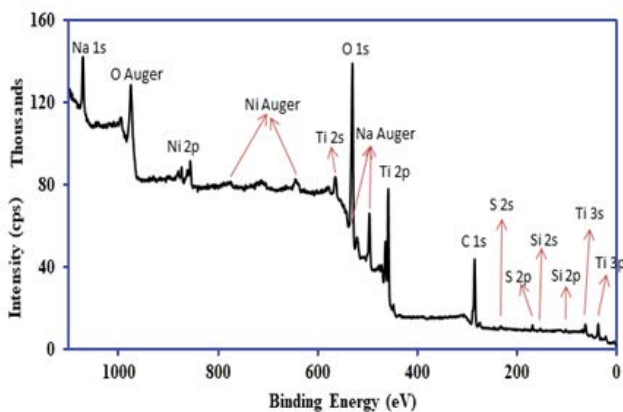


Fig. 3. A wide scan XPS survey spectrum of NiS/RGO/TiO₂ composite.

1s, and C1s at their respective binding energies revealing the successful synthesis of the NiS/RGO/TiO₂ composite.

3.1.4. Optical properties

The optical properties of NiS, TiO₂ and NiS/RGO/TiO₂ were studied using PL spectroscopy and UV-visible spectroscopy. The PL spectra are shown in Fig. 4a and PL which indicated that the TiO₂ has higher PL intensity. On the other hand, the NiS/RGO/TiO₂ nanocomposite attained a lower PL intensity than the modified TiO₂, and higher than NiS. The lower PL intensity of NiS/RGO/TiO₂ compared to modified TiO₂ leads to lower electron and holes recombination under the visible region. Thus, there is no doubt that the resulting nanocomposite possessed good photocatalytic in the visible range (solar light) as compared to that of NiS and TiO₂. The

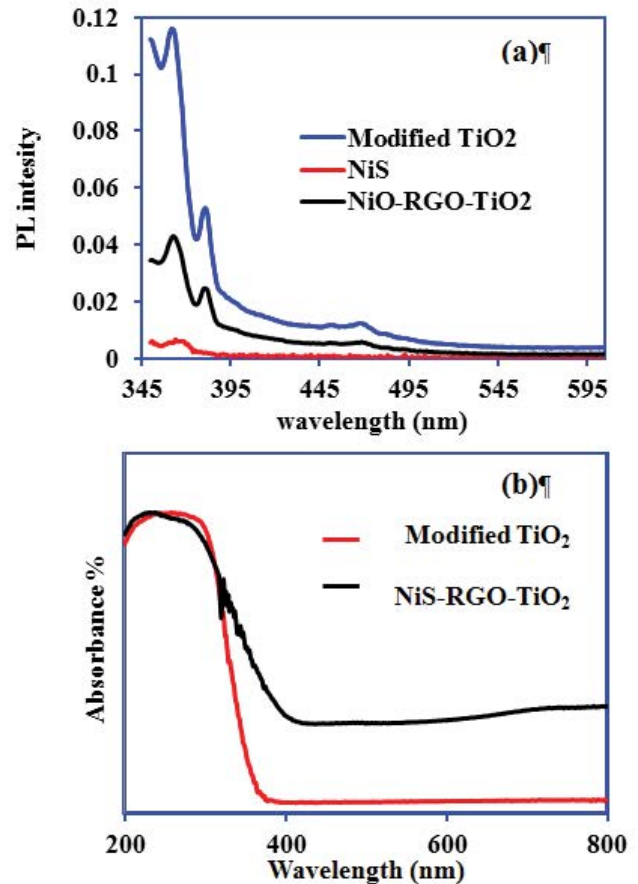


Fig. 4. (a) Normalized photoluminescence spectra of modified TiO₂, NiS, and NiS/RGO/TiO₂ nanocomposite and (b) UV visible DR_S spectra of TiO₂ and NiS/RGO/TiO₂ nanocomposite.

UV visible absorption spectrum of the prepared catalyst is described in Fig. 4b. The TiO₂ spectra show the absorption of light higher in UV range 250–380 nm while a redshift in the wavelength for NiS/RGO/TiO₂ composite in the visible range was observed. These results showed that NiS/RGO/TiO₂ composite is a visible light active photocatalyst.

3.1.5. Photocatalytic activity

The photocatalytic activity for pure NiS, modified TiO₂ and NiS/RGO/TiO₂ nanocomposite for degradation of TCP under sunlight irradiation was evaluated and results are illustrated in Fig. 5. It was found that the decomposition of TCP gradually increased with the increase in light exposure time. Moreover, pure TiO₂ and NiS showed a lower efficacy for TCP degradation compared to NiS/RGO/TiO₂ photocatalyst. The degradation kinetics for TCP is presented in Fig. 5b. Specifically, the order of reaction differs for the distinctive photocatalysts used in the present study where the higher values for degradation constant *k* was observed for NiS/RGO/TiO₂. However, all photocatalyst were close to first-order reactions.

From the results, it is clear that TCP was rapidly degraded in the presence of the NiS/RGO/TiO₂ composite

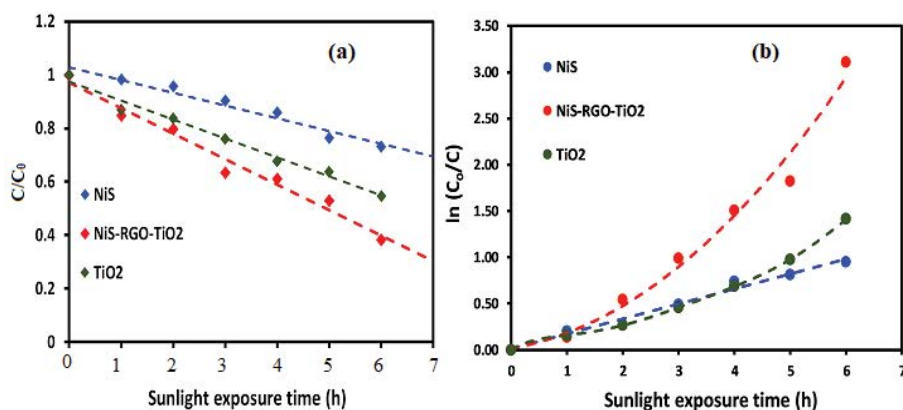


Fig. 5. Variation of C/C_0 (A) and $\ln(C_0/C)$ vs. sunlight exposure time for the TCP degradation over NiS, TiO₂, and NiS/RGO/TiO₂ photocatalysts under the illumination of natural sunlight.

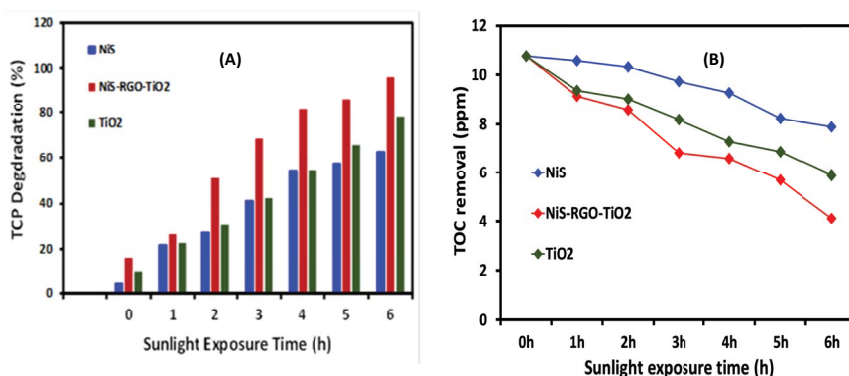


Fig. 6. Comparison of the percentage TCP degradation (%) (a) and TOC removal (b) over NiS, TiO₂ and NiS/RGO/TiO₂ photocatalysts under the illumination of natural sunlight.

photocatalyst and photocatalytic activity was superior compared to that of NiS and TiO₂. The good photocatalytic performance of NiS/RGO/TiO₂ can be attributed to the effective dispersion of NiS particles and RGO onto TiO₂. This prevents the restacking and agglomeration of graphene during the charging and discharging processes under light luminance. Moreover, the presence of graphene in the composite photocatalyst provides increased surface area for the adsorption of the pollutant over the surface of the catalyst which maintains its mechanical integrity and offers a high electrical conductivity of electrons.

3.2. Mineralization

The mineralization efficiency of NiS/RGO/TiO₂ was measured by analyzing TOC content. The results presented in Fig. 6 depict TCP degradation and TOC removal as mineralization. The TOC was used as a function of irradiation time and initial concentration of TCP removal, which was 0.5 mmol L⁻¹ and corresponds to TOC at 11 mg L⁻¹. In Fig. 6a the degradation of TCP reached 95% after 6 h light exposure when the NiS/RGO/TiO₂ composite was used. However, the removal of TCP did not exceed 75% when using pure TiO₂ and 60% when using NiS alone. In Fig. 6b the TOC concentration reached 4 mg L⁻¹ after 6 h with NiS/RGO/TiO₂ photocatalyst

which corresponded to the mineralization efficiency up to 55%. The yield difference was attributed to the TCP oxidation and the production-degradation of intermediates such as pyrocatechol and chlorohydroquinone in the solution.

3.3. Comparison of degradation percentages of TCP with available literature

The results of the present study are compared with previously reported photocatalyst materials that have been presented in Table 1. The photocatalytic activity of NiS/RGO/TiO₂ was evaluated under visible light sources and other studies with distinctive light sources for various organic pollutants. It can be observed that the various nanomaterials developed previously have lower catalytic efficiency, for instance, the use of mixture 0.5 g anatase + 2 g AC-NO showed 91% removal of TCP of pollutant removal after 300 min while the photocatalysis was performed under UV light [28]. In another study, up to 88.74% degradation of the pollutant was achieved [29], however, the light source was UV region which is more costly as compared to visible light. In the case of the present study, visible light was used where degradation of the pollutant was achieved up 95%. Overall, the present study was highly promising because sunlight is a renewable source and could offer a proper replacement

Table 1
Comparison of photo-degradation percentages of trichlorophenol with literature

Catalyst	Light source	TCP concentration	Time (min)	Deg. (%)	References
NiS/RGO/TiO ₂	Solar light	11 mg L ⁻¹	360	95	This study
Mixture 0.5 g anatase + 2 g AC-NO NHZr	UV light (Hg lamp 100 W)	40 mg L ⁻¹	300	91	[28]
CdS	UV light (254 nm)	10 mg L ⁻¹	180	96	[30]
gC ₃ N ₄	UV light (high pressure Hg lamp)	65 mg L ⁻¹	180	88.74	[29]
Fe ₃ O ₄ @TiO ₂ @Au	300 W Xe lamp >420 nm	1 × 10 ⁻⁴ M	120	100	[31]
Cobalt doped TiO ₂	Xe lamp	7.5 × 10 ⁻⁵ M	48	98	[32]
	UV radiation, 254 nm	400 mg L ⁻¹ (mixed halophenol solution)	240	95.1	[33]

to a conventional high-power source for the photocatalytic degradation of organic pollutants.

4. Conclusion

The above study significantly contributed to the development of a novel NiS/RGO/TiO₂ nanocomposite and its photocatalytic application for the treatment of organic pollutants in wastewater under solar light. The photocatalyst NiS/RGO/TiO₂ was prepared by two steps hydrothermal method and characterization proved its successful synthesis as the visible light active material. Indeed, the photocatalyst showed its advantage for the mineralizing of organic pollutants in wastewater. The outcomes of the experiment show that the NiS/RGO/TiO₂ photocatalyst exhibits a high photocatalytic activity for TCP degradation under natural solar light. The organic matter reduction by 55% has been observed as a mineralization yield and 95% degradation of TCP was obtained after exposure of 6 h under sunlight. Therefore, the results indicated that NiS/RGO/TiO₂ photocatalyst is a highly suitable material for various large-scale environmental applications. Due to the efficiency of material to harvest solar light, the process could reduce the treatment cost due to the extensively available gift of solar light.

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