

Research Article

The Study of Photocatalytic Degradation Kinetics and Mechanism of Malachite Green Dye on Ni–TiO₂ Surface Modified with Polyaniline

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Synthetic organic dyes are coloring agents used in various industries. Despite the fact that they offer exciting colors and long-lasting effects, certain organic dyes can have harmful impacts on human health and aquatic ecosystems. This study investigates the photo-catalytic degradation of malachite green dye using Ni–TiO₂ nanoparticles (NPs) and Ni–TiO₂/PANI nanocomposites (NCs) in various reaction conditions. The surface and compositional change of synthesized photocatalysts were characterized by XRD, FTIR, AAS, and UV–vis spectrophotometer. Accordingly, the XRD results signify the crystal structure of photocatalysts found to be tetragonal anatase phase while the FT-IR spectra indicate the titanium has predominantly form a coordination compound upon reaction with nitrogen atom through weakening the bond strength between C=N, C=C, and C–N in the PANI. The UV–vis measurement shows that the energy bandgaps were decreased from 3.20 to 2.77 eV and 2.59 eV for Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs, respectively. From AAS data, the authors confirmed that Ni metal has significantly existed in the aforementioned photocatalysts after the calcination process. The photocatalytic degradation of Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs on the model dye has studied and their efficiency was 94.22% and 99.09%, respectively. The photocatalytic degradation follows pseudo-first order with 2.23 × 10⁻² min⁻¹ reaction rate at optimum conditions of pH 8.5, initial dye concentration of 0.2 g/L, catalyst load of 0.2 g/L, and irradiation time of 90 min. With this, the outstanding result recorded using Ni–TiO₂/PANI NCs is ascribed to the smaller particle size as compared to Ni–TiO₂ NPs, and it is found to be the promising photocatalyst for the removal of wastewater containing organic dyes.

1. Introduction

Water is one of the most worthy sources playing a vital role in sustaining life and keeping the environment safe, clean, and hygienic circumstances [1]. However, by virtue of the discharging hazardous organic and inorganic pollutants to natural water bodies without proper handling, human health and aquatic ecosystem are under serious conditions. In particular, synthetic organic dyes are the most toxic pollutants to human and aquatic species [2] which can be generated and discharged from paper, textile, plastic, cosmetics, and leather industries [3]. Mostly, such dyes are harmful and their stability would make them nonbiodegradable. Previous reports indicate that over 10% of organic dyes commonly find their way to effluents when they failed entirely bind to the targeted fibers and could creates serious environmental pollution [4]. With these wider applications in foods, cosmetics, drugs, and printing inks industries [5], the exposure to such organic dyes could pose the skin, eye, respiratory tract irritation, and reproductive impairment upon inhalations and direct contact [6]. For example, malachite green (MG) is an organic dyes contains the triphenylmethane group and commonly known as 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N dimethylaniline ($C_{23}H_{25}N_2Cl$) could serve as coloring agent in various industries [7, 8] and cause severe health effect to human beings. Nevertheless, MG dye along with its reduced form (leuco MG) has an unpleasant effect on reproductive and immune system [9]. Consequently, it is indispensable to develop an effective treatment techniques

species.

A few decades back, scientists developed the most common wastewater treatment methods including chemical coagulation, flocculation [11], photocatalytic degradation, microbial degradation, advanced oxidation process (AOP), UV/H2O2, membrane separation, and adsorption process [12]. Among the aforementioned techniques, advanced oxidation process has received enormous attention because of its effective generation of hydroxyl free radicals ('OH) which can attack the target contaminants. The active HO[•] can be generated by chemical oxidants in the presence of energy sources such as ultraviolet (UV) light. Recently, photocatalysts have been established as one of the most important UV light assisted catalytic materials for successful degradation of environmental contaminants with kinetically feasible rates [13]. This photocatalytic degradation process use the heterogeneous semiconductor substrate including metal oxide such as ZnO, Fe₂O₃, V₂O₅, WO₃, NiO, CuO, and TiO₂. It is most preferable technique as a result of its inexpensiveness, versatility, and environmentally friendly [14]. Predominantly, TiO_2 is one of the valuable photocatalyst in addition to its various applications such as gas sensors, antifogging, surface coating, solar energy cells, surface cleaning, and sterilizing materials. Furthermore, this semiconductor is inexpensive, nontoxic, corrosion-resistant, and own enormous oxidative capacity [15]. The photocatalytic activity of TiO_2 is pronounced when it does exist in anatase than in the rutile and brookite phase [16]. As a result of high bandgap of anatase phase (3.20 eV), it can absorb only a small portion of the solar spectrum.

Besides its advantages, photocatalytic techniques are facing the challenges such as the wide bandgap, limited photoresponse, and difficulties in posttreatment recovery of the metal oxide nanoparticles (NPs) [17]. To overcome these limitations and produce photocatalysts responsive to visible light, surface-tuning strategies and modification of oxides at nanometer (nm) scale have been developed through doping, surface treatment, and multilayer oxide preparation [18]. Consequently, the semiconductors have been doped with metals/nonmetals such as N, C, S, Ag, Au, and Pt to extend its activity toward the visible region [19].

For instance, TiO₂ was doped with ceramics via sol-gel method for the degradation of Rhodamine B (RhB) under UV light irradiation [20]. The result showed that the modification of TiO₂ not only prevents phase transfer but also provides facile recovery of the catalyst after degradation of RhB. Among various dopants, Ni metal is most widely used for surface reengineering so as to enhance the photocatalysis of semiconductors. It is more attractive due to its abundant, low cost, exist in acceptable toxicological levels, and may bring about alternative reactivity profiles in order to generate novel chemical transformation [21]. Recently, the photodegradation of organic dyes using Ni-ZnO NPs and the composite with p(AAc) microgels have been studied [22]. The energy bandgap of ZnO has lowered from 3.31 to 3.16 eV when its surface has been treated, and the model dye has been degraded as compared to the corresponding pure NPs. Furthermore, the conjugated polymers (CPs) are receiving great attention in modifying photocatalyst because of their plausible applications environmental remediation [23, 24]. CPs also have shown remarkable advantages in renewable energy devices [25, 26] due to their unique behavior [27].

Among several CPs, polyaniline (PANI) [28] is one of the most frequently used polymers as a result of its decent stability, low synthesis cost, nontoxicity, good optical, and electrical properties. The PANI hybrid NCs are photocatalytically active under UV-vis because of HOMO-LUMO excitation and increased electron-hole pairs separation [24]. Therefore, the incorporation of such CPs into NPs is mostly used to stabilize via surface capping of the catalyst [29]. For instance, PANI/CdO NCs were developed for the photocatalytic degradation on methylene blue (MB) and MG dyes [30] and the result indicated that the degradation performance of the catalyst was enhanced after the surface treatment with polymer. For instance, Pandiselvi et al. [31] modified TiO₂ NPs with ceramic and PANI (n-TiO₂/C/PANI) using sol-gel method for the photodegradation of MB and crystal violet (CV). The study indicated that an addition of ceramic and polymer to TiO₂ enhances its photocatalytic efficiency under visible light illumination. Recently, Alemu et al. [32] synthesized Ag doped CdO/PANI NCs using sol-gel method in order to investigate the photocatalytic degradation of BPB dyes under UV-vis illumination. The reports signify that the degradation efficacy was recorded 97.30% at pH 6 and 210 min irradiation time while the photodegradation kinetics followed pseudosecond order reaction rate.

To our best of knowledge, the photodegradation of MG with the aid of Ni–TiO₂ NPs modified with PANI homopolymer under UV–vis light irradiation has not reported yet to resolve the aforementioned challenges. Thus, the current study mainly focuses on the synthesization of Ni–TiO₂/ PANI NCs using sol–gel method and surface characterization of photocatalyst by FT-IR, XRD, and UV–vis spectroscopic techniques for the investigation of photodegradation of MG dyes under visible light illumination. Furthermore, the effect of operating parameters such as pH of media, catalyst load, nature of catalysts, and initial dye concentration for photodegradation of model dye and the degradation mechanism has also been proposed. In general, we have established the novel method which could be applicable for the treatment of wastewater samples containing cationic dyes.

2. Materials and Methods

2.1. Experimental Site. The as-synthesized photocatalysts' degradation performance study, optical bandgap determination, and data analysis were carried out at Wollega University, Chemistry Department Research Laboratory; surface composition and exploratory its functional group were conducted at Addis Ababa University. In addition, the crystalline structure was carried out at Adama Science and Technology University, Ethiopia.

2.2. Materials. UV-visible spectroscopy (UV-vis, Cary 60 UV-Vis, Agilent Technologies, China), X-ray diffractometer (XRD, Shimadzu XRD-7000, German), Fourier-transform infrared spectroscopy (FT-IR, Shimadzu 8,400 S, German),

and atomic absorption spectroscopy (AAS, AA-10 Varian manufacturing Co. Ltd, Australia) were among the critical instruments used for photocatalytic surface characterization of this work. Photoreactor (PUV-PR, Peschl Ultraviolet, GmbH, Germany) with two LED lamps emit 400 luminous light intensity between 360 and 625 nm wavelength, pH meter, air (oxygen) pumper, muffle furnace, centrifuges, magnetic stirrer, electronic balance, and oven were the most apparatus used for this purpose.

2.3. Chemicals. All chemicals used for this study were analytical grade which were applied without additional refinements. Titanium tetrachloride (99%), nickel nitrate hexahydrate, aniline (99%), ammonium peroxysulphate (APS), ethanol (99.7%), sulfuric acid (98%), sodium hydroxide, hydrochloric acid (37%), distilled water, and MG dye were chemicals used in this work. The aforementioned chemicals were supplied by Loba Chemical except APS which was procured from Micron Chemical agent.

2.4. Experimental Parts

2.4.1. Synthesization of Ni-TiO₂ NPs. Nickel-doped TiO₂ (Ni-TiO₂) NPs are prepared via sol-gel method. Twenty milliliters of TiCl₄ (99%) has added drop-wise to 200 mL ethanol (99.7%) at ambient temperature. It was performed in a fume hood since the Cl₂ and HCl were exhausted in a very large amount during the mixing process and the mixture changed to yellowish solution. A 100 mL of the sol-gel was added into beaker A and 10 mL isopropyl alcohol and 6 mL of distilled water were mixed to obtain a new solution (Solution A). Another solution (Solution B) is prepared from 0.2 g of 2 wt% Ni(NO₃)₂·6H₂O which is engendered through mixing with the solution containing 10 mL of isopropyl alcohol (99%) followed by the addition of 1 mL conc. HNO₃ and 6 mL of DI water. A sol-gel was formed upon slowly adding Solution A to Solution B under continuous stirring for 5 hr while the pH was adjusted to 1-2 through adding conc. HNO₃. Then, the dry-gel was obtained upon vaporizing for 3 hr at 80°C which then calcinated for 2 hr in the furnace at 500°C. After calcinations, the powder with gray colored is obtained and grinded from which the fine powder is prepared. Finally, about 0.5 g of the grinded powder was obtained and stored for further surface characterization and study its catalytic activity [15].

2.4.2. Synthesization of Ni–TiO₂/PANI NCs. A 2 g of Ni–TiO₂ is added into 100 mL of 1 M H₂SO₄ to beaker A and continuously stirred for 30 min. A 1.85 mL of aniline monomer was supplemented to the same beaker which was stirred for 20 min. To beaker B, 4 g of APS was added to 100 mL of H₂SO₄ and stirred for 10 min. The mixture in beaker B was added slowly to the mixture of beaker A. This step was helpful to prepare the conductive polymer and avoid the formation of oligomer. Then after, a dark green precipitate was obtained. The acquired suspension has been kept for 24 hr at room temperature. Finally, the above suspension is filtered, washed with ethanol as well as water until the filtrate changes to colorless and dried at 100°C for 5 hr. The mixture changed to green color indicating the formation of conductive polyaniline (PANI). Finally, the dried powder is grinded till the fine powder is created for actual characterization and study of catalytic activity [33].

2.5. Characterization Methods

2.5.1. Study of Crystalline Structure. The crystal phase and sizes of Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs were studied by X-ray diffractometer (XRD). The samples were measured in the angular range (2θ) of 10°–80° at the scan rate of 4°/min with the help of Cu K α radiation (λ = 0.154060 nm) operating at 40 kV and 30 mA accelerated voltage and applied current, respectively. The diffraction pattern is used to determine the average crystallite size of particles using Equation (1) [34]:

$$D = \frac{K\lambda}{\beta\cos\theta},\tag{1}$$

where K—Scherrer's constant = 0.9, β is the full width at half maximum (radians), λ is the X-ray wavelength (0.154060 nm), D is the average crystallite size, and θ is *the* Braggs angle.

2.5.2. Study of Functional Group. The functional groups of each photocatalyst are characterized by FT-IR spectrometry. The measurement is performed with pressed pellets using paraffin as diluents while its spectrum is collected between the wave numbers of 400 and $4,000 \text{ cm}^{-1}$ [35].

2.5.3. Determination of Energy Bandgap. The capacities of light harvesting and absorption of the aforementioned NPs and NCs are determined by UV–vis absorption spectra measured in 200–800 nm wavelengths. A 0.2 g/L of both Ni–TiO₂ and Ni–TiO₂/PANI samples were taken during the measurement. Thus, the bandgap energy of each photocatalyst is obtained from the following equation [36]:

$$E_g = \frac{1,240}{\lambda} \,\mathrm{eV},\tag{2}$$

where E_g is the energy bandgap and λ is wavelength in nm.

2.5.4. Determination of Ni in Nanocomposite Using AAS. Determination of Ni in Ni–TiO₂/PANI NC was done in replicates using computerized atomic absorption spectrometer (AAS, AA-10 Varian manufacturing Co. Ltd., Australia). The calibration of the instrument using standards and blank was frequently done between samples to ensure stability of the baseline.

2.6. A Study of Photocatalytic Degradation. A 0.2 g MG dye is dissolved in 1 L of DI water. Then, 100 mL of dissolved dye is taken to 250 mL beaker. A 0.2 g of Ni–TiO₂ NPs and Ni–TiO₂/ PANI NCs powders are dissolved in 100 mL of dye solution while the pH of the mixtures is adjusted to 8.5 and continuously stirred for 30 min till adsorption–desorption equilibrium is achieved. Throughout the irradiation process, the photoreactor was sustained under magnetic stirring to achieve a homogeneous suspension to encourage the adsorption of dye at the surface of photocatalysts. Two LED lamps that primarily emit the definite

power of 30 W (about 400 luminous light intensity) and 220 V were applied as source of visible light and situated parallel to the reactor [32, 37]. Then after, the absorbance of the solutions has recorded every 15 min using UV–vis spectrophotometer. Percentage degradation efficiency of the photocatalysts has been calculated as follows [38]:

Degradation (%) =
$$\frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100,$$
 (3)

where C_0 is the dye initial concentration, *C* is the concentration of dye at time "t," A_0 is the absorbance at initial stage, and A_t is the absorbance of dye at time "t." The wavelength of light corresponds to maximum absorbance of MG is found to be 617 nm and measured accordingly. The degradation kinetics of MG dye was studied using the initial concentrations of 0.1, 0.2, 0.3, and 0.4 g/L. The catalytic activity of as-synthesized photocatalysts under UV–vis light can be evaluated by comparing the apparent rate constants [39]. Accordingly, the degradation kinetics is also described using pseudo-first order (Equation (4)) and pseudo-second order kinetics (Equation (5)):

$$\ln\left(\frac{C}{C_{\rm o}}\right) = K_1.t,\tag{4}$$

$$\frac{1}{[C]} = \frac{1}{C_0} + K_2.t,$$
(5)

where C_0 and C are the concentration of MG at initial and after time t, K_1 and K_2 are respective rate constants for pseudo-first and -second order reactions, respectively [40].

2.7. Study of Operational Parameters

2.7.1. UV–Vis Irradiation Time. The relationship between the degradation efficiency with UV–vis irradiation time on MG was studied for 90 min reaction time keeping the fixed concentration of dye to 0.2 g/L, catalyst load of 0.2 g, and pH at 8.5.

2.7.2. Effect of Catalyst Dose. The effect of catalyst dosage on the degradation efficiency of photocatalytic against MG dye was observed by adding 0.1-0.5 g of Ni–TiO₂/PANI NCs at constant concentration of dye (0.2 g/L) and 8.5 pH values.

2.7.3. Effect of pH. The variation of pH on photocatalytic degradation efficiency and its effects was investigated from 5 to 10 through maintaining the other parameters constant such as dye concentration of 0.2 g/L, photocatalyst load of 0.2 g which lasts for 90 min.

2.7.4. Effect of Initial Concentration of Dye. The initial concentration of MG is varied from 0.1 to 0.4 g/L in order to investigate the photocatalysts' degradation performance through fixing the other parameters constant such as photocatalyst load to be 0.2 g and pH to be 8.5 [41].



FIGURE 1: The XRD pattern of Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs.

3. Results and Discussion

3.1. Surface Characterization of Photocatalysts

3.1.1. Study of Crystalline Structure. Figure 1 shows XRD spectrum of Ni-TiO₂ NPs and Ni-TiO₂/PANI NCs. From the graph, the diffraction pattern at angle $2\theta = 25.33^{\circ}, 28.45^{\circ}, 38.57^{\circ},$ 48.05°, 54.18°, 55.05°, 62.70°, 70.26°, and 76.02°; the respective Miller indices are (101), (004), (200), (105), (211), (204), (220), and (215) for Ni-TiO₂ NPs; the diffraction peaks at angle $2\theta =$ 25.28°, 28.35°, 38.46°, 47.99°, 53.91°, 55.03°, 62.20°, 62.67°, 70.34°, and 75.02°; and the corresponding miller indices of (101), (004), (200), (105), (211), (213), (204), (301) and (215) for Ni-TiO₂/PANI NCs. The previous report indicates that the XRD peaks observed at 25.33 and around 48.00° were ascribed to the formation of pure TiO_2 in anatase phase [42]; however, in addition to those peaks, there are few spectra observed around 38.50° and it realizes the presence of nickel metal within NP and NC [43]. Similarly, the crystallographic planes validated the current nanomaterial's crystalline phase and are very well aligned to specifications of JCPDS card No. 21-1272 [44] which signifies that all the XRD peaks are corresponding to the anatase phase structure of TiO₂ doped with Ni and modified with PANI while there are no peaks matching to rutile and brookite phase formation.

Using the Debye–Scherrer formula indicated in Equation (1), the average crystallite size of photocatalysts is calculated using the most intensive peaks [45] observed at 25.33° , 38.57° , and 48.05° for both samples, and their values are shown in Table 1. In this graph, the XRD diffraction peak of Ni–TiO₂/PANI NCs has slightly shifted to the lower angle when related to Ni–TiO₂ NPs, indicating that the NCs' crystallite size is getting smaller than pure NPs. These results further indicate that Ni ions have been successfully doped into TiO₂ in the process of synthesis which shows the successful surface treatment with polymer.

Ti ions are partly replaced by Ni ions in the crystallization process so that they occupy the sites in the crystal lattice.

Journal of Nanomaterials

| Photocatalyst | 2θ (degree) | β (degree) | β (radian) | D (nm) | Average (nm) |
|---------------------------|--------------------|------------------|------------------|--------|--------------|
| | 25.3258 | 0.39200 | 0.006842 | 21.71 | |
| Ni–TiO ₂ | 48.0532 | 0.44520 | 0.00777 | 20.42 | 19.88 |
| | 27.4601 | 0.48810 | 0.00856 | 17.51 | |
| | 25.2811 | 0.40970 | 0.007151 | 20.77 | |
| Ni–TiO ₂ /PANI | 47.9950 | 0.45600 | 0.00796 | 19.93 | 19.17 |
| | 27.4191 | 0.50890 | 0.008882 | 16.80 | |

TABLE 1: The calculated crystallite size of Ni-TiO₂ NPs and Ni-TiO₂/PANI NCs.



FIGURE 2: The FTIR spectra of Ni-TiO₂ NPs and Ni-PANI/TiO₂ NCs.



SCHEME 1: The Ni-TiO₂/PANI NCs interactions with N in PANI and Ti in TiO₂.

From the result, it could be recognized that Ni doping does not significantly influence the structure of TiO_2 , rather reduces the grain size and widens the peaks in its XRD pattern [15]. Both photocatalysts displayed the XRD peaks which correspond the standard diffraction data and signify that TiO_2 before and after modification own the tetragonal anatase crystalline structure (JCPDS card no. 21-1272) and agree with the prior report [44].

3.1.2. Study of Functional Group. The FTIR spectra of Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs are shown in Figure 2. As observed from the graph, the vibrational bands observed at 621 and 678 cm⁻¹ represented the stretching modes for Ti–O–Ti in Ni–TiO₂ NPs [46] while the peaks located at 593 and 563 cm⁻¹ indicate the symmetric stretching modes in –O–Ti–O–. In addition, the broadband at 520 cm⁻¹ illustrates the vibration of metal–oxygen bond (Ti–O) or (Ni–O) in Ni–TiO₂ NCs [47]. In this study, the distinct bands of

1,500–1,587 cm⁻¹ and 1,492–1,502 cm⁻¹ represent the C=N and C=C stretching modes of quinoid (Q) and benzoid (B) units [46]. Meanwhile, the FTIR spectrum observed at 1,129 cm⁻¹ ascribes the Ti–N vibration which originated from the coordination compound formed between Ti and N atoms and confirmed the bands shifted to higher wavenumber corresponding to weakening spectra of C=N, C=C, and C–N in PANI. Thus, in Ni–TiO₂/PANI NCs, the shift in peaks indicates that there is a significant Ti–N interaction after surface modification with polymer. The structures represent the bond formation between PANI and Ni–TiO₂ where B is benzoid and Q is quinoid group of polymeric chains [46], as shown in Scheme 1.

3.1.3. Determination of Energy Bandgap. The UV–vis absorption spectrums of Ni–TiO₂ NPs as well as Ni–TiO₂/PANI NCS are revealed in Figure 3. The absorption edges for both photocatalysts are found to be 447 and 478 nm, respectively.



FIGURE 3: The UV-vis absorption spectrum of (a) Ni-TiO₂ NPs and (b) Ni-TiO₂/PANI NCs.

TABLE 2: Summary of energy bandgap of Ni–TiO $_2$ NPs and Ni–TiO $_2/PANI$ NCs.

| Photocatalysts | Wavelength (nm) | Energy gap (eV) |
|---------------------------|-----------------|-----------------|
| Ni–TiO ₂ | 447 | 2.77 |
| Ni–TiO ₂ /PANI | 478 | 2.59 |

The intrinsic absorption peak of TiO2 was observed at 440 nm; red shifted comparing with the bulk exciton in consequence of the size effect of the nanostructures. Obviously, the absorption wavelength of Ni-TiO₂ NPs and Ni-TiO₂/PANI NCs powders are shifted to higher wavelength with the increase of its absorption intensity with narrowing the energy gap due to the delocalized N2p states in PANI, thus greatly contribute to the creation of VB with the O2p and 3d metal states which agree with the previous report [36]. Such effect is attributed to the transitions between the VB and CB as well as the exchange interaction between d electrons of Ni ions which can mix with Ti d-orbital. The energy gaps (E_g) of the synthesized photocatalysts were calculated (Equation (2)) and the corresponding results for Ni-TiO₂ NPs and Ni-TiO₂/PANI NCs are 2.77 and 2.59 eV, respectively, as indicated in Table 2.

3.1.4. Atomic Absorption Spectroscopic Analysis. Figure 4 shows the calibration curves of absorbance with respect to samples' concentrations at a specific wavelength of metal constructed through analysis of the instrument blank and standards. As shown in curves, the instrument response was found to be linear and sensitive with $R^2 = 0.9996$. The plotted calibration curve was used to determine the concentrations of Ni metal (Table 3) in the samples of Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs using standard solution for Ni metal.

The AAS data confirmed the existence of Ni in both photocatalysts after the calcination process and polymerization reaction with Ni–TiO₂. Therefore, the incorporation of Ni participates in the nanoparticles and nanocomposites



FIGURE 4: The calibration curve for nickel metal from AAS data.

TABLE 3: The concentrations of Ni metal in Ni–TiO $_2$ NPs and Ni–TiO $_2/PANI$ NCs.

| | | A1 1 () |
|---------------------------|---------------------|----------------------|
| Photocatalysts | Concentration (ppm) | Absorbance (a.u.) |
| Ni–TiO ₂ | 12.59 | 5.79×10^{3} |
| Ni–TiO ₂ /PANI | 3.21 | 2.99×10^{4} |

with the appropriate amount were very good for photocatalytic degradation.

3.2. Study of Photocatalytic Activity and Degradation Mechanism

3.2.1. Study of Photocatalytic Activity. The photocatalytic activity as-synthesized photocatalysts; Ni–TiO₂ NPs and Ni–TiO₂/PANI NCs were investigated under visible irradiation on the model MG dye by optimizing the catalyst load, initial concentrations of dyes, pH of solution, and irradiation time. The percent degradation was also calculated using Equation (3). In this study, the effective type of catalyst in degradation efficiency was determined using 0.2 g/L concentration of each catalyst. Accordingly, among the two catalysts, Ni–TiO₂/PANi NCs were offered the high degradation

Journal of Nanomaterials

| Photocatalyst for MG dye degradation | A _o | Α | Degradation (%) |
|--------------------------------------|----------------|--------|-----------------|
| Ni-TiO ₂ | 0.2602 | 0.0150 | 94.22 |
| Ni-TiO ₂ /PANI | 0.2602 | 0.0024 | 99.09 |





FIGURE 5: The schematic representation of photocatalytic degradation mechanism of MG dye using Ni-TiO₂/PANI NCs.



SCHEME 2: The photocatalytic degradation mechanism of MG dye using Ni-TiO₂/PANi NCs.

performance on MG (Table 4). This catalytic performance is ascribed to its lower particle size and narrow energy gap (shown in the results of XRD and UV–vis spectrum) so that the MG dye molecules could adsorb to the catalyst's active sites.

3.2.2. Degradation Mechanism. Figure 5 represents the photocatalytic degradation mechanism using Ni–TiO₂/PANI NCs. In this process, TiO₂ could absorb UV light and generate electron–hole pairs which then react with surface adsorbed O₂ to form O₂. The electron–hole pairs generation within the catalysts is mainly caused by the direct absorption of photons that further cause the diffusion of the charge carriers to the surface of photocatalysts. This is owing to the lowering bandgap as a result of the formation of the dopant's energy levels below conduction band [10]. The delocalized electrons of Ni3d energy state account for the narrowing energy bandgap of TiO_2 NPs to 2.77 eV upon doping with Ni metal. The codoping of PANI further promotes shifting wavelength to the higher value from 447 to 478 nm and lessening an energy bandgap to 2.59 eV in Ni–TiO₂/PANI NCs. However, there is possibility where some holes created in the HOMO of PANI as a result of electron transfer from HOMO of PANI to VB of Ni–TiO₂ NCs.

Scheme 2 shows the photocatalytic degradation mechanism of MG dye using Ni–TiO₂/PANi NCs.

This is due to the fact that the HOMO of PANI (2.8 eV) [48] is at wider energy compared to VB of Ni–TiO₂/PANI (2.59 eV). In Ni–TiO₂/PANI NCs, the photosensitized polymer performs the electrons excitation from HOMO-to-LUMO which further jumped to CB of Ni–TiO₂ NCs. An electron accepted part would then combine with an adsorbed O₂ to form O₂^{••} radicals, while *OH is formed due to the



FIGURE 6: The effect of catalyst load on photodegradation of MG dye under UV-vis light.

interaction of the holes react with H_2O [49]. Accordingly, the activated free radicals could effectively split the pollutant (MG dye) into H_2O and CO_2 [50].

3.3. Study of Operational Parameters

3.3.1. Effect of Catalyst Dose. The amount of catalyst on photodegradation of MG dye was studied with different concentration 0.1, 0.2, 0.3, 0.4, and 0.5 g/L fixing the initial concentration of MG at 0.2 g/L and pH 8.5. Accordingly, the optimum amount of catalyst was found to be 0.2 g/L with the highest photodegradation efficiency (Figure 6). At 0.2 g/L concentrations of catalyst, the degradation efficiency has decreased along with increase in catalyst load is attributed to the aggregation of the catalyst so that it leads to lowering the total active sites of the catalyst prior adsorption of dye molecules. Furthermore, as the amount of photocatalyst is getting higher, it can generate turbidity which tackles the penetration of light results in the inactivation of the available active sites [9].

3.3.2. Effect of Irradiation Time. The influence of irradiation time against degradation of MG dye has been determined over a reaction time of 20–90 min at concentration of all catalyst load, initial dye concentration of 0.2 g/mL, and pH of 8.5. As observed in Figure 6, at visible light irradiation time of 90 min, the highest degradation rate of the MG dye was achieved. This achievement is due to the rapid adsorption rate prior to the equilibrium that is determined by increased availability in the number of active surface of Ni–TiO₂/PANI NCs. Attachment-controlled process like adsorption is expected at the equilibrium stage of the reaction because of fact that there are sorption sites available [51].

3.3.3. The Effect of Initial Concentration of Dye. The study of the degradation efficiency of Ni–TiO₂/PANI NCs on the MG dye with varying its initial concentration from 0.05 to 0.4 g/L and fixing the catalyst load to 0.2 g/L was studied. The result



FIGURE 7: Effect of initial concentration of dye on the photocatalytic degradation of Ni-TiO₂/PANI NCs at pH 8.5 and 0.2 g/L catalyst load.



FIGURE 8: The effects of pH on photodegradation of Ni–TiO₂/PANI by fixing catalyst load and dye concentration to 0.2 g/L.

reveals that the degradation performance of the aforementioned photocatalyst has increased with increasing dye concentration till the maximum value of 0.2 g/L (Figure 7). With this optimum concentration, it is anticipated that more dye molecules could adsorbed at all active sites of Ni–TiO₂/PANI NCs accompanied by electron donation to the conduction band. Nevertheless, as the concentration of dye exceeds 0.2 g/L, the degradation performance has decreased so that the adsorption between dye molecules and O_2 at the catalyst surface is more competitive. Since O_2 is one of the electron acceptor; it would loosely adsorbed at surface than the dye molecules so that it lowers the degradation efficiency and also reaction rate [9]. Otherwise, the applied Ni–TiO₂/PANI NCs deliver a fixed amount of free radicals which is insufficient to degrade a higher amount of dye.

3.3.4. The Effect of pH. Figure 8 shows the effects of pH on degradation efficiency of Ni–TiO₂/PANI NCs by varying the



FIGURE 9: Photodegradation kinetics of Ni–TiO₂/PANI nanocomposite against MG dye (a) pseudo-first order rate and (b) pseudo-second order rate.

pH from 5 to 10, catalyst load of 0.2 g/L, initial dye concentration of 0.2 g/L, and light irradiation for 90 min. The result signifies that the degradation performance is found minimum (58.59%) at pH 5. Conversely, the degradation power is increased up to pH 8.5 and records the maximum value of 99.09%. This result is directly dependent on the catalyst surface charge. The catalyst surface is positively charged in acidic environment (lower pH) which decreases the available active sites for adsorption of a cationic dye (MG). In the range of pH greater than zero point charge, the catalyst surface becomes negatively charged (at pH > 8). Therefore, in alkaline environment, the number of OH at Ni–TiO₂/PANI NCs has increased so that it facilitates the adsorption of MG; the degradation capacities become higher [52].

3.4. Degradation Kinetics

3.4.1. Pseudo-First Order Kinetics. Figure 9 illustrates the photocatalytic activity of Ni–TiO₂/PANI NC which was evaluated by comparing the respective rate constants (Equations (4) and (5)) for the degradation of MG dye. The degradation kinetic was studied using the initial concentrations of 0.1, 0.2, 0.3, and 0.4 mg/L of MG dye. The result corresponds to pseudo-first order kinetics (Figure 9(a)) indicates that the photocatalytic activity of Ni–TiO₂/PANI NCs recorded and supported by the regression coefficient of $R^2 = 0.9697$ while its rate constant (K_1) has a value of 2.23 × 10⁻² min⁻¹.

3.4.2. Pseudo-Second Order Kinetics. Figure 9(b) represents pseudo-second order kinetics for the degradation of MG dye at optimum conditions. The regression coefficient $R^2 = 0.7404$ for Ni–TiO₂/PANI NCs while the corresponding rate constant (K_2) is 4.13×10^{-3} M⁻¹ min⁻¹. Comparing the values of both R^2 and K of pseudo-first and -second order kinetics, the pseudo-first order is an appropriate kinetic model that provided the best fit to an experimental data. This kinetic model signifies the model dye could be adsorbed to the catalyst surface [32] following the optimum working condition following pseudo-first order kinetics.

4. Conclusion

In this research work, the photocatalysts (Ni-TiO₂ NP and Ni-TiO₂/PANI NC) were synthesized via sol-gel technique for photodegradation of MG. The synthesized photocatalysts were characterized using XRD, FTIR, UV-vis, and AAS for the determination of crystalline size, functional group, bandgap, and surface composition of Ni-TiO₂ NPs and Ni-TiO₂/PANI NCs. From the characterization techniques, the result reveals that the average particle size of Ni-TiO2 and Ni-TiO2/PANI was found to be 19.88 and 19.17 nm while their optical band gaps are 2.77 and 2.59 eV, respectively. The effects of different operational parameters such as catalyst load, initial concentration of dye, pH of solution, and irradiation time were also investigated. Consequently, from the two catalysts, Ni–TiO₂/PANI NCs provided the best degradation capacity and taking this catalyst, optimum degradation efficiency was recorded at pH 8.5, initial dye concentration of 0.2 g/L and 0.2 g of catalyst load. Thus, with these optimum conditions, the percentage degradation of MG dye was obtained 99.09% degradation efficiency. In general, Ni-TiO₂/PANI NCs have shown outstanding photocatalytic performance which could be applicable and desirable for the decompositions of other environmentally hazardous molecules, particularly organic dyes under UV-vis light.

Data Availability

All the data are incorporated in the manuscript.

Disclosure

The author only allowed getting an experimental facilities and instrumental analysis through the employer, Ambo University.

Conflicts of Interest

The authors declare that there is no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Authors' Contributions

The authors' significant scientific contribution is as follows: Girmaye Asefa—substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work. Dunkana Negussa contributed to drafting the work or revising it critically for important intellectual content. Gemechu Lemessa contributed to final approval of the version to be published. Tibebu Alemu contributed to agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved, design graphical abstract, and dye decomposition mechanism.

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References

- J. Bartram, C. Brocklehurst, M. B. Fisher et al., "Global monitoring of water supply and sanitation: history, methods and future challenges," *International Journal of Environmental Research and Public Health*, vol. 11, no. 8, pp. 8137–8165, 2014.
- [2] A. Tkaczyk, K. Mitrowska, and A. Posyniak, "Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: a review," *Science of the Total Environment*, vol. 717, Article ID 137222, 2020.
- [3] A. Ahmad, S. H. Mohd-Setapar, C. S. Chuong et al., "Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater," *RSC Advances*, vol. 5, no. 39, pp. 30801–30818, 2015.
- [4] M. Yusuf, "Synthetic dyes: a threat to the environment and water ecosystem," in *Textiles and Clothing*, M. Shabbir, Ed., pp. 11–26, Wiley, 2019.
- [5] R. Azmat, Z. Khalid, M. Haroon, and K. Mehar, "Spectral analysis of catalytic oxidation and degradation of bromophenol blue at low pH with potassium dichromate," *Advances in Natural Science*, vol. 6, no. 3, pp. 38–43, 2013.
- [6] A. Giwa, P. Nkeonye, K. Bello, and K. Kolawole, "Photocatalytic decolourization and degradation of C. I. basic Blue 41 using TiO₂ nanoparticles," *Journal of Environmental Protection*, vol. 3, no. 9, pp. 1063–1069, 2012.
- [7] A. Mohamed, M. M. Ghobara, M. K. Abdelmaksoud, and G. G. Mohamed, "A novel and highly efficient photocatalytic degradation of malachite green dye via surface modified polyacrylonitrile nanofibers/biogenic silica composite nanofibers," *Separation and Purification Technology*, vol. 210, pp. 935–942, 2019.
- [8] N. P. Raval, P. U. Shah, and N. K. Shah, "Malachite green "a cationic dye" and its removal from aqueous solution by adsorption," *Applied Water Science*, vol. 7, no. 7, pp. 3407– 3445, 2017.
- [9] L. Saikia, D. Bhuyan, M. Saikia, B. Malakar, D. K. Dutta, and P. Sengupta, "Photocatalytic performance of ZnO nanomaterials for self sensitized degradation of malachite green dye under solar light," *Applied Catalysis A: General*, vol. 490, pp. 42–49, 2015.

- [10] R. Gusain, K. Gupta, P. Joshi, and O. P. Khatri, "Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: a comprehensive review," *Advances in Colloid and Interface Science*, vol. 272, Article ID 102009, 2019.
- [11] S. Sadri Moghaddam, M. R. Alavi Moghaddam, and M. Arami, "Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology," *Journal of Hazardous Materials*, vol. 175, no. 1–3, pp. 651–657, 2010.
- [12] B. Hayati, N. M. Mahmoodi, M. Arami, and F. Mazaheri, "Dye removal from colored textile wastewater by poly(propylene imine) dendrimer: operational parameters and isotherm studies," *CLEAN—Soil, Air, Water*, vol. 39, no. 7, pp. 673–679, 2011.
- [13] S. Bagheri, A. TermehYousefi, and T.-O. Do, "Photocatalytic pathway toward degradation of environmental pharmaceutical pollutants: structure, kinetics and mechanism approach," *Catalysis Science & Technology*, vol. 7, no. 20, pp. 4548–4569, 2017.
- [14] C. Byrne, G. Subramanian, and S. C. Pillai, "Recent advances in photocatalysis for environmental applications," *Journal of Environmental Chemical Engineering*, vol. 6, no. 3, pp. 3531– 3555, 2018.
- [15] M. Hasan Shahriari and M. Hosseini-Zori, "Synthesis and characterization of Ni–doped TiO₂ nanostructures as an active self-cleaning cover on floor-tile surface," *Journal of Cluster Science*, vol. 28, no. 4, pp. 2253–2267, 2017.
- [16] B. Roose, S. Pathak, and U. Steiner, "Doping of TiO₂ for sensitized solar cells," *Chemical Society Reviews*, vol. 44, no. 22, pp. 8326–8349, 2015.
- [17] H. Dong, G. Zeng, L. Tang et al., "An overview on limitations of TiO₂-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures," *Water Research*, vol. 79, pp. 128–146, 2015.
- [18] S. Linic, P. Christopher, and D. B. Ingram, "Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy," *Nature Materials*, vol. 10, no. 12, pp. 911–921, 2011.
- [19] E. Grabowska, A. Zaleska, S. Sorgues et al., "Modification of titanium(IV) dioxide with small silver nanoparticles: application in photocatalysis," *The Journal of Physical Chemistry C*, vol. 117, no. 4, pp. 1955–1962, 2013.
- [20] B. Wang, G. Zhang, Z. Sun, and S. Zheng, "Synthesis of natural porous minerals supported TiO₂ nanoparticles and their photocatalytic performance towards Rhodamine B degradation," *Powder Technology*, vol. 262, pp. 1–8, 2014.
- [21] J. E. Dander and N. K. Garg, "Breaking amides using nickel catalysis," ACS Catalysis, vol. 7, no. 2, pp. 1413–1423, 2017.
- [22] M. Javed and S. Hussain, "Synthesis, characterization and photocatalytic applications of p (Aac) microgels and its composites of Ni doped ZnO nanorods," *Digest Journal of Nanomaterials and Biostructures*, vol. 15, pp. 217–230, 2020.
- [23] A. Almasian, N. M. Mahmoodi, and M. E. Olya, "Tectomer grafted nanofiber: synthesis, characterization and dye removal ability from multicomponent system," *Journal of Industrial and Engineering Chemistry*, vol. 32, pp. 85–98, 2015.
- [24] Y. Xiang, J. Li, X. Liu et al., "Construction of poly(lactic-coglycolic acid)/ZnO nanorods/Ag nanoparticles hybrid coating on Ti implants for enhanced antibacterial activity and biocompatibility," *Materials Science and Engineering C*, vol. 79, pp. 629–637, 2017.
- [25] T. Alemu, S. A. Pradanawati, S.-C. Chang et al., "In operando measurements of kinetics of solid electrolyte interphase formation in lithium-ion batteries," *Journal of Power Sources*, vol. 400, pp. 426–433, 2018.

- [26] F.-M. Wang, T. Alemu, N.-H. Yeh et al., "Interface interaction behavior of self-terminated oligomer electrode additives for a Ni-rich layer cathode in lithium-ion batteries: voltage and temperature effects," ACS Applied Materials & Interfaces, vol. 11, no. 43, pp. 39827–39840, 2019.
- [27] Y.-Z. Long, M.-M. Li, C. Gu et al., "Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers," *Progress in Polymer Science*, vol. 36, no. 10, pp. 1415–1442, 2011.
- [28] J. Xu, Y. Hu, C. Zeng, Y. Zhang, and H. Huang, "Polypyrrole decorated BiOI nanosheets: efficient photocatalytic activity for treating diverse contaminants and the critical role of bifunctional polypyrrole," *Journal of Colloid and Interface Science*, vol. 505, pp. 719–727, 2017.
- [29] H. Helmi, F. Falaki, M. Karimi, and F. Babaloii, "Highly facile removal of acid red 88 from aqueous samples by using synthesized iron oxide magnetic nanoparticles and 1-butyl-3methylimidazolium tetrachloroferrate magnetic ionic liquid," *Desalination and Water Treatment*, vol. 90, pp. 331–340, 2017.
- [30] H. Gülce, V. Eskizeybek, B. Haspulat, F. Sarı, A. Gülce, and A. Avcı, "Preparation of a new polyaniline/CdO nanocomposite and investigation of its photocatalytic activity: comparative study under UV light and natural sunlight irradiation," *Industrial & Engineering Chemistry Research*, vol. 52, no. 32, pp. 10924–10934, 2013.
- [31] K. Pandiselvi, H. Fang, X. Huang, J. Wang, X. Xu, and T. Li, "Constructing a novel carbon nitride/polyaniline/ZnO ternary heterostructure with enhanced photocatalytic performance using exfoliated carbon nitride nanosheets as supports," *Journal of Hazardous Materials*, vol. 314, pp. 67–77, 2016.
- [32] T. Alemu, G. Taye, G. Asefa, and L. B. Merga, "Surface modification of Ag–CdO with polyaniline for the treatment of 3', 3", 5', 5"-tetrabromophenolsulfonphthalein (BPB) under UV–visible light irradiation," *Heliyon*, vol. 8, no. 11, Article ID e11608, 2022.
- [33] M. T. Ramesan, V. Santhi, B. K. Bahuleyan, and M. A. Al-Maghrabi, "Structural characterization, material properties and sensor application study of in situ polymerized polypyrrole/silver doped titanium dioxide nanocomposites," *Materials Chemistry and Physics*, vol. 211, pp. 343–354, 2018.
- [34] X. Li, Y. Zhang, L. Jing, and X. He, "Novel N-doped CNTs stabilized Cu₂O nanoparticles as adsorbent for enhancing removal of Malachite Green and tetrabromobisphenol A," *Chemical Engineering Journal*, vol. 292, pp. 326–339, 2016.
- [35] N. M. Mahmoodi, "Equilibrium, kinetics, and thermodynamics of dye removal using alginate in binary systems," *Journal of Chemical* & Engineering Data, vol. 56, no. 6, pp. 2802–2811, 2011.
- [36] Y. Brhane and A. Tadesse, "Synthesis and characterization of Cr-NP-TRI doped ZnO nanoparticles for photocatalytic degradation of Malachite Green under visible radiation," *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, vol. 9, no. 3, pp. 10–22, 2018.
- [37] T. Alemu, L. B. Merga, A. Amente, and G. Asefa, "Treatment of wastewater dye using Ag–CdO–based nanocomposites surface modified with polyaniline," *Applied Nanoscience*, pp. 177–189, 2024.
- [38] N. M. Mahmoodi, M. Ghezelbash, M. Shabanian, F. Aryanasab, and M. R. Saeb, "Efficient removal of cationic dyes from colored wastewaters by dithiocarbamate-functionalized graphene oxide nanosheets: from synthesis to detailed kinetics studies," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 81, pp. 239–246, 2017.

- [39] G. Sharma, Z. A. ALOthman, A. Kumar, S. Sharma, S. K. Ponnusamy, and M. Naushad, "Fabrication and characterization of a nanocomposite hydrogel for combined photocatalytic degradation of a mixture of malachite green and fast green dye," *Nanotechnology for Environmental Engineering*, vol. 2, no. 1, pp. 1–7, 2017.
- [40] S. Iyyapushpam, S. T. Nishanthi, and D. P. Padiyan, "Enhanced photocatalytic degradation of methyl orange by gamma Bi₂O₃ and its kinetics," *Journal of Alloys and Compounds*, vol. 601, pp. 85–87, 2014.
- [41] A. M. Saad, M. R. Abukhadra, S. Abdel-Kader Ahmed et al., "Photocatalytic degradation of malachite green dye using chitosan supported ZnO and Ce–ZnO nano-flowers under visible light," *Journal of Environmental Management*, vol. 258, Article ID 110043, 2020.
- [42] Y. Liu, Z. Wang, W. Fan, Z. Geng, and L. Feng, "Enhancement of the photocatalytic performance of Ni-loaded TiO₂ photocatalyst under sunlight," *Ceramics International*, vol. 40, no. 3, pp. 3887– 3893, 2014.
- [43] X. Li, J. Yao, F. Liu et al., "Nickel/copper nanoparticles modified TiO₂ nanotubes for non-enzymatic glucose biosensors," *Sensors and Actuators B: Chemical*, vol. 181, pp. 501– 508, 2013.
- [44] B. Rajamannan, S. Mugundan, G. Viruthagiri, N. Shanmugam, R. Gobi, and P. Praveen, "Preparation, structural and morphological studies of Ni doped titania nanoparticles," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 128, pp. 218–224, 2014.
- [45] R. A. Janjua, C. Gao, R. Dai et al., "Na⁺-driven nucleation of NaYF₄:Yb,Er nanocrystals and effect of temperature on their structural transformations and luminescent properties," *The Journal of Physical Chemistry C*, vol. 122, no. 40, pp. 23242– 23250, 2018.
- [46] V. Gilja, K. Novaković, J. Travas-Sejdic, Z. Hrnjak-Murgić, M. Kraljić Roković, and M. Žic, "Stability and synergistic effect of polyaniline/TiO₂ photocatalysts in degradation of azo dye in wastewater," *Nanomaterials*, vol. 7, no. 12, Article ID 412, 2017.
- [47] N. M. Mahmoodi, M. Bashiri, and S. J. Moeen, "Synthesis of nickel–zinc ferrite magnetic nanoparticle and dye degradation using photocatalytic ozonation," *Materials Research Bulletin*, vol. 47, no. 12, pp. 4403–4408, 2012.
- [48] Q. Zhou and G. Shi, "Conducting polymer-based catalysts," *Journal of the American Chemical Society*, vol. 138, no. 9, pp. 2868–2876, 2016.
- [49] C. H. Nguyen, M. L. Tran, T. T. Van Tran, and R.-S. Juang, "Efficient removal of antibiotic oxytetracycline from water by Fenton-like reactions using reduced graphene oxide-supported bimetallic Pd/nZVI nanocomposites," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 119, pp. 80–89, 2021.
- [50] B. Jana, S. Bhattacharyya, and A. Patra, "Conjugated polymer P3HT–Au hybrid nanostructures for enhancing photocatalytic activity," *Physical Chemistry Chemical Physics*, vol. 17, no. 23, pp. 15392–15399, 2015.
- [51] M. A. Karimi, A. Hatefi-Mehrjardi, A. Askarpour Kabir, and M. Zaydabadi, "Synthesis, characterization, and application of MgO/ZnO nanocomposite supported on activated carbon for photocatalytic degradation of methylene blue," *Research on Chemical Intermediates*, vol. 41, no. 9, pp. 6157–6168, 2015.
- [52] D. Pathania, D. Gupta, A. H. Al-Muhtaseb et al., "Photocatalytic degradation of highly toxic dyes using chitosan-gpoly(acrylamide)/ZnS in presence of solar irradiation," *Journal* of Photochemistry and Photobiology A: Chemistry, vol. 329, pp. 61–68, 2016.