



Article Photocatalytic Degradation of Organic Dyes Contaminated Aqueous Solution Using Binary CdTiO₂ and Ternary NiCdTiO₂ Nanocomposites

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Abstract: The synergistic effect of binary CdTiO₂ and ternary NiCdTiO₂ on the photocatalytic efficiency of TiO₂ nanoparticles was investigated. The SEM analysis demonstrates spherical TiO₂ NPs of different sizes present in agglomerated form. The structural analysis of the nanocomposites reveals a porous structure for TiO₂ with well deposited Cd and Ni NPs. TEM images show NiCdTiO₂ nanocomposites as highly crystalline particles having spherical and cubical geometry with an average particle size of 20 nm. The EDX and XRD analysis confirm the purity and anatase phase of TiO₂, respectively. Physical features of NiCdTiO₂ nanocomposite were determined via BET analysis which shows that the surface area, pore size and pore volume are $61.2 \text{ m}^2/\text{g}$, 10.6 nm and $0.1 \text{ cm}^3/\text{g}$, respectively. The absorbance wavelengths of the CdTiO₂ and NiCdTiO₂ nanocomposites have shown red shift as compared to the neat TiO₂ due to coupling with Ni and Cd that results in the enhanced photocatalytic activity. The photocatalytic activity demonstrated that TiO₂, CdTiO₂ and NiCdTiO₂ degrade methylene blue (MB) and methyl green (MG) about 76.59, 82, 86% and 63.5, 88, 97.5%, respectively, at optimum reaction conditions.

Keywords: TiO₂; nanocomposites; photocatalysts; photodegradation; methylene blue; methyl green

1. Introduction

Industrial effluents containing synthetic dyes is a formidable challenge for water remedy processes [1,2]. Dyes are used for the coloration of several materials such as textile fibers, cosmetics, paper, tannery, food, leather and pharmaceutical products [3]. These synthetic dyes are major water pollutants and cause serious environmental problems due to their high aromaticity, low biodegradability, toxicity, chemical stability and carcinogenic nature [4]. These dyes also reduce the light penetration which reduces the photosynthetic activity that causes a deficiency in dissolved O₂ content of the water [5]. Various approaches are applied for the remediation of these pollutants such as adsorption [6], nanofiltration [7], ozonation [8], coagulation [9], biodegradation [10] and phytoremediation [11] etc. These conventional approaches are expensive, destructive, difficult and transform pollutants into sludge [12].

Advanced Oxidation Processes (AOPs) generate and use powerful transitory species such as hydroxyl radicals [13] to eliminate the organic pollutants by final conversion into small and stable molecules such as H₂O and CO₂ [14]. Among the AOPs, photocatalytic degradation is believed to be the most appropriate low-cost approach to treat organic pollutants [15]. Photodegradation has advantages over other conventional approaches owing to its simplicity, complete pollutants mineralization, cost-effectiveness, no harmful



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). byproducts formation, ambient pressure and temperature operation [16]. Various semiconducting photocatalysts are used for the photodegradation of dyes such as ZnO [17], Fe₃O₄ [12], SnO₂ [18], TiO₂ [19] etc. Among these photocatalysts, titanium (IV) oxide has been the most investigated material for the environmental photocatalysis owing to its abundance, high specific surface area, nontoxicity, photostability, strong oxidation capability, low price, high photoactivity and chemical stability [20-22]. Titanium dioxide (TiO₂) as an intrinsically n-type semiconductor material with a band gap of around 3 eV [23,24] is extensively suggested for diverse applications such as lithium-ion batteries [25], supercapacitors [26], solar cells [27], sensors [28] and photocatalysts [29–31]. However, TiO₂ as photocatalyst represents low photocatalytic activity due to its high electron-hole pair recombination rate, wide band gap and its excitation only under UV light [32]. In order to retard these deficiencies, various approaches are developed such as doping [33], sensitization [34], supporting on a medium [35] and coupling with semiconductors [36–38]. Among these, coupling of TiO_2 with other semiconducting material having lower band gap energy forming a heterojunction is a strategic option. The semiconductor having lower gap energy plays the role of sensitizer by being excited first, and then inducing the excitation of TiO_2 by passing photoelectrons from its conduction band to that of TiO_2 [39].

In the present work, TiO_2 nanoparticles were prepared by precipitation technique and then coupled with Cd and Ni to obtain CdTiO₂ and NiCdTiO₂ nanocomposites through co-precipitation method. The CdTiO₂ and NiCdTiO₂ nanocomposites are not reported in literature nor utilized as photocatalysts in the photodegradation of dyes to the best of our knowledge. These photocatalysts were prepared from economical materials and simple approach. The photocatalysts are very efficient toward the photodegradation of both dyes. The photocatalytic efficacy of the TiO₂, CdTiO₂ and NiCdTiO₂ was assessed by degradation of methylene blue (MB) and methyl green (MG) dyes in aqueous solution under UV-light irradiation. MB and MG are selected as model dyes because these are recalcitrant organic pollutants with carcinogenic and mutagenic nature with LD50 = 1180 mg/kg [40]. At higher concentration these dyes cause great damage to the human body and environment [41,42]. In the photodegradation of MB and MG dyes, the effect of irradiation time, catalyst dosage and pH were assessed.

2. Results and Discussion

2.1. Morphological and Elemental Analysis

The surface morphology of TiO₂, CdTiO₂ and NiCdTiO₂ was studied via SEM analysis and the images at different magnifications are shown in Figures 1–3, respectively. The images show spherical TiO₂ NPs of different shapes and sizes and present mostly in agglomerated form. The particles are also present and dispersed when highly magnified. The SEM analysis of CdTiO₂ shows that Cd NPs are deposited on the surface and embedded in the porous structure of TiO₂. The morphology of CdTiO₂ displayed that TiO₂ are present in porous nanotubes form and Cd NPs are dispersed on its surface, and inserted in the nanochannels. The CdNiTiO₂ nanocomposites are mostly agglomerated, and the Cd and Ni NPs significantly cover the pores and surface of TiO₂. The particles have different shapes and morphology.

The ternary NiCdTiO₂ nanocomposites were also examined via TEM analysis and the results are as shown in Figure 4 at different magnifications which support the SEM analysis. Images shows that Cd and Ni NPs are uniformly mixed with TiO₂ NPs. Highly crystalline NiCdTiO₂ nanocomposites of cubical as well as spherical geometry with an average particle size of 20 nm are confirmed by TEM images.



Figure 1. (**a**–**d**) SEM images of TiO₂ nanoparticles.



Figure 2. (a–c) SEM images of CdTiO₂ nanocomposite.



Figure 3. (a–d) SEM images of NiCdTiO₂ nanocomposite.



Figure 4. (a–d) TEM images of NiCdTiO $_2$ nanocomposite at different magnifications.

The composition of the ternary NiCdTiO₂ nanocomposite was ascertained via EDX and the spectrum along with %composition in tabulated form is presented in Figure 5. The EDX spectrum shows signals for the constituent elements (Ti, Ni, Cd and O). The carbon and silver signals are present due to their coating on samples prior to EDX analysis for obtaining good quality images.



Figure 5. (a) EDX spectra and (b) mapping of the ternary NiCdTiO $_2$ nanocomposite.

2.2. XRD Analysis

The XRD patterns of the photocatalysts are displayed in Figure 6. The observed signals can be related to the corresponding (101), (004), (200), (105), (211), (204) and (116) crystal planes. The identified diffraction signals can be allocated to the anatase TiO₂ (JCPDS-21-1272). Peaks for the Cd and Ni NPs are not observed owing to their minute quantity. However, (105) and (211) crystal plane peaks observed in the TiO₂ patterns are replaced by single broadened peaks in the CdTiO₂ and NiCdTiO₂ nanocomposites patterns.



Figure 6. XRD patterns of the TiO₂, CdTiO₂ and NiCdTiO₂.

2.3. BET Analysis

The optimum porosity and high specific surface area are considered as essential parameters for the efficiency of nanocomposite materials used in photocatalysis. Figure 7a presents the BET and adsorption-desorption plot for NiCdTiO₂ nanocomposite. The adsorption/desorption of N₂ is important for investigating the surface area, average pore size and pore volume of the NiCdTiO₂ photocatalyst. The study revealed that the NiCdTiO₂ nanocomposite exhibit type IV isotherm with a sharp increase of the adsorbed volume starting from $P/P_0 = 0.84$, confirming the mesoporous nanosized nature of the nanocomposite. When the relative pressure approaches 1, the hysteresis loop shifts higher and shows that the microporous particles are also present. Figure 7b shows BJH plot for the porosity investigation of NiCdTiO₂ nanocomposite. Different surface parameters like BET surface area, pore size, volume and BJH average pore width of NiCdTiO₂ nanocomposite are represented in the Table 1.

Table 1. The specific surface area, pore size, pore volume and BJH average pore width of NiCdTiO₂ nanocomposite.

BET (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)	BJH Average Pore Width Ads/Des (nm)		
61.2	0.1	10.6	9.6/8.7		



Figure 7. (a) BET and adsorption desorption plot for NiCdTiO₂ (b) BJH plot showing porosity evaluation of NiCdTiO₂.

2.4. UV-Visible Analysis

The absorbance wavelength and band gap energy of the TiO_2 , $CdTiO_2$ and $NiCdTiO_2$ were recorded using UV–VIS spectroscopy. Figure 8 displays the UV–VIS absorption spectra of TiO_2 , $CdTiO_2$ and $NiCdTiO_2$. The UV–Visible absorption spectrum of TiO_2 shows absorption band at 265 nm. The maximum absorbance wavelengths of the $CdTiO_2$ and $NiCdTiO_2$ have shown slight red shifts. This shift can make nanocomposites better photocatalysts compared to pure TiO_2 .



Figure 8. UV–VIS absorption spectra of TiO₂, CdTiO₂ and NiCdTiO₂.

Figure 9a–c displays the Tauc plots: $(\alpha hv)^2$ versus energy of TiO₂, CdTiO₂ and NiCdTiO₂, respectively. The band gap was calculated applying Tauc plots, which represents the relation between the sample absorption edge with the energy of the incident photon.

$$\alpha hv = A(hv - E_g)^n \tag{1}$$

where α = molar extinction coefficient, h = Planck constant, v = photon's frequency, A = constant, E_g = band gap energy, and n = parameter associated with the electronic transition ($\frac{1}{2}$ in the present case). The results demonstrate 2.7 eV band gap energy for TiO₂. The band gap energy values for CdTiO₂ and NiCdTiO₂ are 2.64 eV and 2.52 eV, respectively, as shown in the Figure 9c inset. The results clearly show the effect of Cd doping and Ni, Cd co-doping on the band gap energy of TiO₂ which can further be correlated with the photocatalytic activity of the catalysts.



Figure 9. Tauc plots: $(\alpha hv)^2$ versus energy for the (**a**) TiO₂ (**b**) CdTiO₂ (**c**) NiCdTiO₂, inset; comparison of band gap energy.

2.5. Photodegradation of Methylene Blue (MB) Dye

2.5.1. Effect of Irradiation Time

The photocatalysts were utilized for the photodegradation of MB dye in aqueous medium under UV-light irradiation. Figure 10a-c displays the UV-VIS spectra of MB dye before reaction and after varying UV light-irradiation times in the presence of TiO₂, CdTiO₂ and NiCdTiO₂, respectively. The MB dye has shown maximum absorbance in the absence of catalysts. A sharp decrease in the absorbance was observed in the presence of catalysts due to photodegradation of the dye. The absorbance shows a regular decrease in the presence of catalysts with increasing irradiation time. The %degradation of MB dye by the synthesized catalysts as presented in Figure 10d shows higher photocatalytic activity for the ternary NiCdTiO₂ as compared to the binary CdTiO₂ and neat TiO₂. A 40, 48 and 65% degradation of the dye was observed within 20 min irradiation time with TiO_2 , CdTiO₂ and CdNiTiO₂, respectively. The degradation was increased to 76.59, 82 and 86% in the presence of TiO_2 , CdTiO₂ and CdNiTiO₂, respectively, by increasing irradiation time to 100 min. The increase in photodegradation of dye with an increase in irradiation time is due to the availability of more and more time to generate more hydroxyl radicals, which is a key species in dye degradation. The photocatalytic degradation experiments of MB using 30 ppm initial concentration were carried out under optimal reaction conditions and a pseudo first-order kinetics was observed. The results were in good agreement with the reported literature [42–50].



Figure 10. UV–Visible absorption spectra of MB photodegraded by (**a**) TiO₂ (**b**) CdTiO₂ (**c**) NiCdTiO₂ (**d**) Comparison of %degradation of MB dye inset kinetic model of degradation.

The photocatalytic degradation of dye depends upon the light-harvesting efficiency, the efficiency of the reaction of the photogenerated electron/hole charges and the reaction of photogenerated charges with substrate molecules. Photodegradation of the dye is achieved when UV-light interacts with the photocatalyst. Photons having energy equal to or greater than the band gap of the catalyst, excite the electrons from their valence band (VB) to the conduction band (CB) and produce positive holes (h⁺) in the VB. The h⁺ of the VB

react with the water molecules and produce hydroxyl radicals (\cdot OH) while the excited electrons present in the CB react with oxygen molecules and generate superoxide anion radicals (O_2^{--}) [43,44]. These radicals are highly reactive species and effectively degrade dye molecules into simple and small species such as H₂O and CO₂. In the case of pristine TiO₂, a major portion of the separated electron–hole pairs recombine and reduces the photocatalytic activity. However, in CdTiO₂ and NiCdTiO₂ nanocomposites, the electrons present in the VB of TiO₂ get captured by the coupled Cd and Ni so the electron–hole pairs recombination rate decreases. This makes the nanocomposites more efficient photocatalysts compared to the neat TiO₂. The suggested mechanism for the photodegradation of MB dye by ternary NiCdTiO₂ nanocomposite is presented in Figure 11.



Figure 11. Proposed mechanism of photodegradation of MB dye by NiCdTiO₂.

2.5.2. Effect of Photocatalyst Dosage

As photocatalytic activity is greatly affected by the available active sites, the effect of catalyst dosage on the dye degradation was, therefore, also investigated. Different amounts of catalysts (0.010, 015, 0.020, 0.025 and 0.030 g) were taken with a fixed irradiation time (30 min) and dye amount (10 mL) and the results for the degradation process as monitored by UV-Vis spectroscopy are shown in Figure 12a–c for TiO₂, CdTiO₂ and NiCdTiO₂ NPs, respectively. The %degradation of MB dye by TiO₂, CdTiO₂ and NiCdTiO₂ is compared in the Figure 12d. With an increase in catalyst dosage, the %photodegradation was also increased. Maximum photodegradation was achieved with 0.030 g of the catalyst. With this amount, 76.5, 83.5 and 86% dye was degraded by TiO₂, CdTiO₂ and NiCdTiO₂, respectively. Further increases in catalyst dosage beyond the limit (0.030 g) had no significance on the enhancement of the photocatalytic activity for the degradation process. No further increase in the catalytic activity could be attributed to the agglomeration of photocatalysts beyond the optimum dosage [16].



Figure 12. UV-VIS absorption spectra of MB dye before and after different dosage of (**a**) TiO_2 (**b**) $CdTiO_2$ (**c**) $NiCdTiO_2$ (**d**) Comparison of %degradation of MB dye photodegraded by different dosage of photocatalysts.

2.5.3. Effect of pH of the Medium

pH has an important role in the production of hydroxyl radicals responsible for the photodegradation process. Therefore, the effect of pH variation (2, 4, 6, 8, and 10) for a constant photocatalyst dosage (0.02 g) and irradiation time (30 min) on the photodegradation process was investigated and the results are shown in Figure 13a–c. The %degradation of the MB dye in different pH media are compared for the catalysts in the Figure 13d. The degradation process was low in acidic media and at pH 2 only 15, 22.07 and 26% MB dye was degraded by TiO₂, CdTiO₂ and NiCdTiO₂, respectively. However, in basic media the degradation percentages of the MB dye were quite high and at pH 10 about 79, 80.1 and 85.71% dye was degraded by TiO₂, CdTiO₂ and NiCdTiO₂, respectively. The cationic MB dye favors a high pH value for the adsorption process, which leads to an improved photocatalytic degradation [16].



Figure 13. UV–VIS spectra of MB dye photodegraded in different pH medium in the presence of (a) TiO₂ (b) CdTiO₂ (c) NiCdTiO₂ (d) Comparison of %degradation of MB dye.

2.6. Photodegradation of Methyl Green (MG) Dye

2.6.1. Effect of Irradiation Time

The photodegradation efficacy of the synthesized catalysts was also investigated against methyl green (MG) dye in aqueous solutions in the presence of UV light. Figure 14a–c demonstrates the UV–VIS spectra of MG dye before reaction and after different UV light irradiation times in the presence of TiO₂, CdTiO₂ and NiCdTiO₂, respectively. Figure 14d represents the %degradation of MG dye at varying irradiation times in the presence of catalysts. The graph clearly demonstrates that MG photodegradation increases effectively with increasing UV irradiation time. The %degradation results show that about 28, 45 and 59.5% of the MG dye was photodegraded by TiO₂, NiTiO₂ and CdNiTiO₂, respectively, within 20 min. The %degradation was increased to 63.3, 88 and 97.5% by TiO₂, NiTiO₂ and CdNiTiO₂, respectively, when irradiation time was increased to 100 min. The results clearly demonstrate that an increase in irradiation time results in an increased dye degradation due to availability of more and more time for dye adsorption followed by photodegradation.



Figure 14. UV–VIS absorption spectra of MG degraded in the presence of (**a**) TiO₂ (**b**) CdTiO₂ (**c**) NiCdTiO₂ (**d**) Comparison of %degradation of MG dye.

2.6.2. Effect of Photocatalyst Dosage and Medium pH

The effect of catalyst dosage was evaluated by applying different dosages of photocatalysts keeping another parameters constant. Figure 15a represents the %degradation of MG dye photodegraded by different dosages of the catalysts The results show increased percent degradation of the dye with increased photocatalyst dosage. A 68, 87 and 98% degradation was achieved by 0.030 g (maximum dosage) of the TiO₂, CdTiO₂ and NiCdTiO₂, respectively, within 30 min. The effect of pH on Mg dye degradation was also evaluated by degrading dye in different pH solutions keeping other parameters constant. Figure 15b represents the %photocatalytic degradation of MG dye in different pH media. At pH 2, the TiO₂, NiTiO₂ and CdNiTiO₂ degraded about 12, 20 and 26% MG dye, respectively. The efficiency of MG dye degradation increases and about 67, 85 and 96.5% dye degraded at pH 10 by TiO₂, NiTiO₂ and CdNiTiO₂, respectively, within 30 min. The increased degradation of MG dye at higher pH is due to the production of more hydroxyl radicals in the basic medium.



Figure 15. %degradation of MG dye photodegradation (**a**) by different dosage of photocatalysts and (**b**) at different pH.

2.7. Photocatalytic Activity Comparison

The comparative photocatalytic efficiency of the catalysts in the photodegradation of MB and MG dyes is shown as %degradation in the Figure 16. The dyes were irradiated for 100 min in the presence of catalysts. The data shows that neat TiO_2 is more efficient in degrading MB compared to MG dye. However, the nanocomposites are more effective in degrading MG dye compared to the MB dye. The ternary NiCdTiO₂ has shown the highest photocatalytic efficiency and degrades about 97.5% and 86% of MG and MB dye, respectively. The present study shows supremacy over the reported results [45–51] due to the photodegradation capability in correlation with band gap energy as presented in Table 2.



Figure 16. Comparison of %degradation of MB and MG dyes photodegraded by all the photocatalysts.

No.	Catalysts	Dye	Band Gap (eV)	Irradiation (nm)	Time (min)	Conversion (%)	Ref
1	Ni-Cr/TiO ₂	methylene B	2.45	Sunlight	90	95.6	1
2	B-La/TiO ₂	methyl O	-	Sunlight	90	98	2
3	Ag-MoO ₃ /TiO ₂	methyl O	2.89	UV	330	95.6	3
4	Sn-La/TiO ₂	rhodamine B	3.17	UV	180	98	4
5	Ce-B/TiO ₂	malachite G	3.42	UV	120	90	5
6	CdS/TiO ₂	Acid B	2.55	UV	90	84	6
7	Ni/TiO ₂	methylene B	2.92	UV	240	99	7
8	Ni-Cd/TiO ₂	methylene G	2.52	UV	100	97.5	Work

Table 2. Comparative analysis of the synthesized catalysts with the reported studies.

2.8. Lifespan of the Catalyst

The catalyst was regenerated from the reaction medium by simple centrifugation process and washed and dried in an oven overnight. The regenerated catalysts were utilized subsequently for five experimental runs under the optimum reaction conditions with no significant loss of activity as shown in Figure 17. The extended lifespan of the catalysts revealed the industrial scale applicability of the catalysts.



Figure 17. Recycling of catalyst for five experimental runs.

3. Experimental Work

3.1. Materials

Titanium (IV) isopropoxide ($C_{12}H_{28}O_4$ Ti) (97%), cadmium (II) chloride hemi(pentahydrate) (CdCl₂·2.5H₂O) (98%), and nickel (II) chloride hexahydrate (NiCl₂·6H₂O) (98%) were purchased from Riedel-de Haen, Germany. Analytical grade sodium hydroxide (NaOH) (98%), methylene blue (98%), and methyl green (97.5%) were obtained from Sigma Aldrich, USA.

3.2. Synthesis of TiO₂ Nanoparticles

The precipitation procedure was utilized for the preparation of TiO_2 NPs by titanium (IV) isopropoxide precursor. A careful addition of 5 mL of titanium (IV) isopropoxide to 8 mL deionized water at 45 °C was followed by constant stirring for 1 h and resulted in white precipitate formation. The precipitates were centrifuged and washed three times

with deionized water followed by methanol washings. The resultant powder was dried in an oven at 80 $^{\circ}$ C for 8 h followed by calcination at about 450 $^{\circ}$ C for 5 h.

3.3. Synthesis of Binary CdTiO₂ Nanocomposites

CdTiO₂ nanocomposites were synthesized via co-precipitation method. Cadmium (II) chloride hemi(pentahydrate) (0.030 mol, 6.85 g) was added to the deionized water (250 mL) and the mixture was stirred for 30 min at room temperature. The pH (9–10) of the mixture was adjusted by dropwise addition of 1 M NaOH solution. The precipitates formed during the process were centrifuged, separated and washed with deionized water followed by ethanol washing. The precipitates were dried in an oven at 80 °C for 5 h and annealed at 500 °C for 4 h. The resultant CdO NPs (0.01 M) were dispersed in methanol (5 mL) via sonication for 30 min. The dispersion was added to the TiO₂ (1 M) dispersion made in 5 mL methanol. The mixture was stirred at 80 °C for 30 min and the precipitates formed were separated via centrifuge. The CdTiO₂ binary nanocomposites obtained were kept overnight and oven dried at 100 °C for 2 h.

3.4. Synthesis of Ternary NiCdTiO₂ Nanocomposites

Ternary NiCdTiO₂ nanocomposites were prepared via co-precipitation method. Nickel (II) chloride hexahydrate (0.030 mol, 7.13 g) and cadmium (II) chloride hemi(pentahydrate) (0.030 mol, 6.85 g) were dissolved separately in deionized water (250 mL) and stirred for 30 min at ambient temperature. The pH (9–10) of the solutions were adjusted via dropwise addition of 1 M NaOH solution. The precipitates formed during the process were centrifuged and washed with deionized water followed by methanol three times. The obtained precipitates were oven dried at 80 °C for 6 h and annealed at 550 °C for 4 h. The synthesized Ni (0.001 M) and Cd (0.01 M) NPs were dispersed separately in 5 mL aqueous methanol via sonication for 30 min. The Ni and Cd dispersions were mixed with TiO₂ (1 M) solution made in aqueous methanol. The mixture was sonicated continuously at 80 °C for 30 min. The precipitates were centrifuged and the product NiCdTiO₂ was kept overnight and then dried at 100 °C for 5 h.

3.5. Characterization

The morphology and surface analysis were achieved through SEM (Model No. JEOL-5910; company Japan) and TEM (Tecnai F-20 FEI, USA). The elemental analysis was carried out via EDX (model INCA 200/oxford instrument, UK), while the size and phase of crystals were evaluated through XRD measurements (Model JEOL-300). The surface area and the porosity of the materials were evaluated applying a N₂ adsorption instrument (Micrometrics ASAP 2020). The photocatalytic degradation of the dyes was monitored using UV-VIS spectrophotometer (UV-1800, Shimadzu, Japan).

3.6. Dyes Photodegradation

The photocatalytic activity of the prepared catalysts was evaluated for the photodegradation (PD) of methylene blue (MB) and methyl green (MG) dyes in aqueous media under UV-light. The photocatalysts were individually added to 5 mL deionized water and sonicated constantly for 30 min, followed by an addition of 10 mL dye solutions (30 ppm) to each beaker. The beakers were covered with transparent plastic sheets. The mixtures were again sonicated for 30 min, kept in the dark to attain the adsorption/desorption equilibria and then kept under UV light (UV lamp (254 nm, 15 W)) with constant stirring for specific times. The catalysts were carefully removed through centrifugation (1200 rpm, 10 min). The study was completed by evaluating the effect of irradiation time (20, 40, 60, 80 and 100 min with a 0.03 g of catalyst), photocatalyst dosage (0.010, 0.015, 0.020, 0.025 and 0.03 g at 30 min irradiation time) and medium pH (2, 4, 6, 8 and 10 with 0.03 g catalyst and 30 min irradiation time) on dyes degradation. The degradation study was followed by UV-Vis spectrophotometer and the %degradation was found by applying the equation:

Degradation rate (%) =
$$\left(\frac{A_o - A}{A_o}\right) \times 100$$
 (2)

where A_o and A show dye absorbance before and after UV light irradiation, respectively. While for photocatalytic degradation, a pseudo first-order kinetic model was proposed.

$$-\frac{\mathrm{dC}}{\mathrm{dt}} = k_{ap}\mathrm{C} \tag{3}$$

$$\ln\left(\frac{C}{C_0}\right) = k_{ap}t\tag{4}$$

where C_0 : initial concentration, C: final concentration, k_{ap} : apparent rate constant and t: time in minutes.

4. Conclusions

In the present study, neat TiO₂ nanoparticles and its binary CdTiO₂ and ternary NiCdTiO₂ nanocomposites were synthesized by precipitation method. The synthesis of the TiO₂ and their binary and ternary nanocomposites were confirmed through various instrumental techniques. The synthesized materials have shown significant photocatalytic degradation of MB and MG dyes. The photodegradation results demonstrate that the dyes degradation increases with increasing irradiation time, catalyst dosage and pH of the medium. The increase in the degradation of the dyes with increasing photocatalyst dosage is due to more available active sites for dye adsorption followed by photodegradation. Similarly, the rapid photodegradation of the dyes at higher pH values could be a result of more reactive hydroxyl radicals formation. The coupled CdTiO₂ and NiCdTiO₂ nanocomposites result in the synergistic effect and have shown better photocatalytic efficiency compared to the neat TiO₂ nanoparticles. The NiCdTiO₂ nanocomposite is the most efficient photocatalyst for the degradation of MG (97.5% degraded in 100 min) as compared to MB (86% degraded in 100 min).

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