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Solar degradation of malachite green using nickel-doped TiO_2 nanocatalysts

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ABSTRACT

Malachite green (MG) is one of the most used dyes in textile industries. The aim of this research work was to degrade MG, a model dye, using nickel-doped TiO_2 nanocatalysts. Nickel-doped TiO_2 nanocatalysts were fabricated under mild hydrothermal conditions (p = autogenous, $T = 100^\circ C$, and $t = 12$ h). Nickel oxide and *n*-butylamine were used as dopant and surface modifier, respectively. The samples dried were characterized using powder X-ray diffraction, zeta potential, SEM, and electron diffraction X-ray analysis. The batch experiments of MG degradation were performed under UV light and sunlight irradiation. The effect of operational parameters including nanocatalyst dosage, pH, contact time, initial concentration of dye solution, and light source were investigated systematically. It was found that nickel-doped TiO_2 nanocatalysts had better solar degradation efficiency compared with bare TiO_2 under both UV light and sunlight irradiation. The optimum solar degradation efficiency for MG dye solution was achieved at pH 8, nanocatalyst dosage = 1.2 g/l, contact time = 120 min, and initial dye concentration = 250 mg/l.

Keywords: Nanocatalysts; Hydrothermal technique; Sunlight; SEM; Dye

1. Introduction

Discharging dye-containing effluents into water bodies not only results in esthetic and landscape issues but also brings about water pollution [1]. Multi-applications of dyes in various industries have made them inseparable part of industries, which demand increasing dye synthesis [2,3]. Some of dyes and the dye degradation products are reported to be carcinogenic and mutagenic in nature [4]; therefore, the effluent has to be treated before discharging into the receiving environments. Malachite green (MG) is a triphenylmethane dye with various applications; it is very toxic and soluble in aqueous media [5]. Although its application has been internationally forbidden [6], it is illegally used in many developing countries. Dyes could be removed through different techniques including adsorption [7], electrocoagulation [8], sonochemical [9], biological treatment [10], reverse osmosis [11], and photocatalytic degradation [12]. The latter is one of the eco-friendly and cost-effective methods creating no sludge. TiO_2 nanocatalysts have

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established their role as a promising option in this regard. However, bare TiO_2 is active only under UV irradiation due to its band gap energy. For designing highly efficient and low-cost photocatalytic systems, many approaches, such as doping with various transition metal cations, have been introduced to extend the optical absorption of TiO_2-based systems to the visible-light region [13,14]. Transitional metals, ions, and metal oxides are well-known dopants, which can change the band gap energy of semiconductors such as TiO_2 in order to make it active under sunlight irradiation, a free natural light source. Using different precursors, nickel-doped TiO_2 has been fabricated; however, the size of nanomaterials reported is not in nanorange [15–17]. Moreover, instability and low dispersion of nanocatalysts in aqueous media, tendency to agglomeration, and lack of control over the crystal growth direction are some drawbacks of nanomaterials, which limit the efficiency of nanomaterials. Hence, applying suitable amount of surface modifier was introduced as an effective strategy in this regard [18]. Based on the authors' best knowledge of the literature review, there was no report on applying *n*-butylamine as surface modifier in fabricating Ni:TiO_2 NCs.

Thus, the main objectives of the present work were to synthesize nickel-doped TiO_2 nanocatalysts (Ni:TiO_2 NCs) under mild hydrothermal conditions and to investigate their application in photodegradation of MG as a model dye.

2. Materials and methods

Ni:TiO_2 NCs were fabricated under mild hydrothermal conditions (p = autogenous, $T = 100$°C, and $t = 12$ h). In brief, 1 mol (1 M) of bare TiO_2 was taken as starting material and the dopant, nickel oxide, at 0.5, 1, and 2 mol% was added into it. Then, 10 ml of 1 N HCl was taken as solvent. The mixture was gradually blended with 1.0 ml of *n*-butylamine as surface modifier. All of the reagents used were from Merck (AG, 99%). No calcination was performed. The rest procedure was as presented in our previous work [19].

2.1. Photocatalytic degradation experiments

Photodegradation of MG was studied using synthesized nanocatalysts. Different dye concentrations (20–200 mg/l) were prepared using the stock solution. The reaction suspension was prepared by adding different amounts (0.4–1 g) of photocatalyst powder per a liter of the dye solution. Prior to the irradiation, the reaction mixture was kept in darkness for 30 min under continuous shaking ($\omega = 100$ rpm) to ensure balanced adsorption–desorption equilibrium. The mixture was then irradiated with the sun (mean luminance was 650 ± 25 lux) and UV light separately. Each experiment was carried out during 12:30 am–2:00 pm (June 2014). In order to utilize the sunlight more efficiently, the outdoor experiments were carried out using a 250-ml Pyrex glass reservoir placed on a shaker exposed to the sunlight directly on the roof of the laboratory building. The ambient temperature was about 38 ± 3°C while carrying out the experiments. All the Pyrex glass beakers containing dye sample and nanocatalysts were covered with a very thin transparent cellophane cover. For comparison purpose, a blank experiment was carried out along with other experiments. Each suspension was sampled at specific time intervals (30, 60, 90, and 120 min) in order to monitor the changes in the MG concentration. Ni:TiO_2 NCs were removed from suspensions sampled through centrifuging at 4,500 rpm for 30 min and then each sample was analyzed using a double beam UV–vis spectrophotometer at 616 nm (λ_{max}) corresponding to the maximal absorption of the dye.

3. Results and discussion

3.1. Structural and morphological analysis

As it was mentioned in the introduction, synthesized nanomaterials need to be stable and get dispersed in the aqueous media, having less agglomeration property with control over the crystal growth direction. Such requirements were met by applying *n*-butylamine as surface modifier. This research found that Ni:TiO_2 NCs are well dispersed in dye solution and had less agglomeration. Fig. 1 shows the powder X-ray diffraction (XRD) patterns (Bruker, USA) of surface-modified Ni:TiO_2 NCs. It revealed that the diffraction peaks correspond to the anatase phase of TiO_2. The existence of secondary new peaks ($2\theta = 27.47$ and 44.75°) of Ni confirms its doping and incorporation into TiO_2 nanocatalysts [20]. Shifting the peak position in patterns indicates the changing in lattice parameter values. Table 1 represents the cell parameters and cell volume calculated using freely available Chekcell software (Collaborative Computational Project No. 14) for different Ni contents of the synthesized nanocatalysts. The Ni:TiO_2 NCs belong to the space group $I41/\text{amd}$. As Table 1 indicates, nickel oxide has resulted in decreasing the cell parameters and cell volume of Ni:TiO_2 NCs.

Attachment of functional groups was recorded using FTIR (Bruker, Tensor 27, USA). As Fig. 2(a)

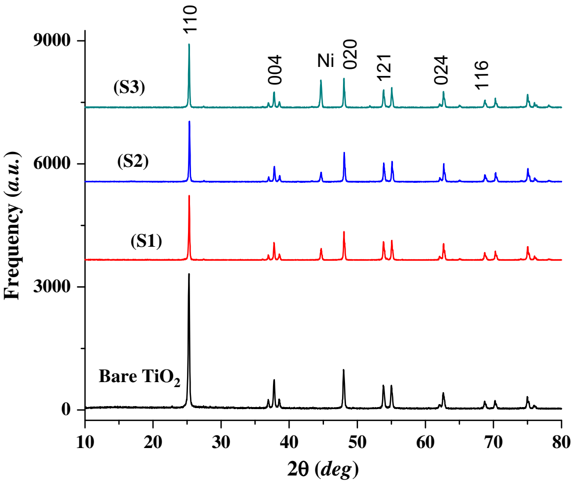

Fig. 1. Powder XRD plots of Ni:TiO_2 NCs (S1 = 0.5, S2 = 1.0, and S3 = 1.5% dopant added).

Table 1
Cell parameters of Ni:TiO_2 NCs

Catalyst	*a* (Å)	*c* (Å)	*a*:*c* ratio	*V* (Å^3)
Bare TiO_2	3.7845	9.5143	0.3977	136.27
Ni:TiO_2 (S1)	3.7824	9.4985	0.3982	135.89
Ni:TiO_2 (S2)	3.7811	9.5002	0.3980	135.82
Ni:TiO_2 (S3)	3.7808	9.4976	0.3980	135.76

indicates, in order to highlight the new peaks of the surface modifier (*n*-butylamine) added, we extracted C=O=C and O–H peaks from the ATR spectra. Hence, new peaks at 3,000 and 1,600 cm^{-1} are ascribed to N–H and NH_3 ion bands, respectively [21]. The broad band centered at 500–600 cm^{-1} is likely due to the vibration of the Ti–O bonds in the TiO_2 lattice [22]. The role of *n*-butylamine is just to control the crystal growth direction and to prevent agglomeration of the nanocatalysts fabricated. On the other hand, it has no direct effect on photodegradation properties [14]. The ATR spectrum of *n*-butylamine is presented in Fig. 2(b); this spectrum could not be overlaid with ATR spectra of Ni:TiO_2 NCs due to its high intensity.

Fig. 3 shows SEM images of surface-modified Ni:TiO_2 NCs taken using VEGA TS5130MM, USA. The images indicate monodispersity in size of the Ni:TiO_2 NCs, which could be attributed to the effect of applying surface modifier. Moreover, it was found that increasing weight percentage (wt.%) of nickel oxide was proportional with the reducing size of nanocatalysts.

The elemental analysis of Ni:TiO_2 NCs was performed using electron diffraction X-ray (EDAX). The EDAX data confirmed the existence of Ti, O_2, and Ni atoms. However, in some cases, a small amount of other elements (Cu, Si, and Fe) were observed, which could be attributed to the impurity of the distilled water used. Table 2 shows EDAX data and corresponding percentage. The EDAX data also revealed that Ni dopant was homogeneously distributed in the matrix of TiO_2.

Stability of Ni:TiO_2 NCs in the medium is required for achieving higher photodegradation efficiency. Malvern instrument was used to measure the characteristic zeta potential (Fig. 4) and size distribution (Fig. 5) of Ni:TiO_2 NCs. The zeta potential of all samples synthesized was almost the same (−33.1 mv), indicating the good stability of the nanocatalysts in distilled water. Moreover, the size distribution analysis supports the results achieved by SEM images.

Band gap energy of semiconductors is an important property, which plays a crucial role in photodegradation of pollutants using TiO_2 as a catalyst. UV–vis spectrophotometer (DR 5000, Hach, Germany) was used to measure band gap energy. For this purpose, a pinch of bare TiO_2 and different samples of Ni:TiO_2 NCs were dissolved in methanol. The reading of wavelength was from 300 to 600 nm. Doping TiO_2 with different molar ratios of nickel oxide resulted in reducing band gap energy of Ni:TiO_2 NCs. However, as Fig. 6 indicates, the reduction in band gap energy was not proportional with molar percentage of nickel oxide. On the other hand, the order of reduction was as $S2 > S1 > S3$ (Fig. 6) [19]. Decreasing band gap energy of Ni:TiO_2 NCs could enhance the visible light absorption ability under sunlight irradiation as it was confirmed by solar degradation of MG. This change in band gap would affect the formation or recombination of electron–hole pairs and separation in a photocatalytic application under light radiation. Such effect of doping with nickel was reported in the literature [23].

3.2. Photodegradation studies of MG

3.2.1. Effect of pH

For photodegradation studies, determining optimum pH is a crucial factor. Before conducting experiments with different pH ranges, a pretest was conducted using three different Ni:TiO_2 NCs samples; S2, i.e. 1 mol% Ni:TiO_2 NCs presented higher photodegradation efficiency under both sunlight and UV irradiations. Hence, the rest degradation experiments were conducted using S2. A series of experiments were carried out by adjusting pH of the dye solution using 0.1 N NH_4OH or HCl solutions. Fig. 7 shows the effect of initial pH on MG removal efficiency. It was found the higher pH, the higher color removal

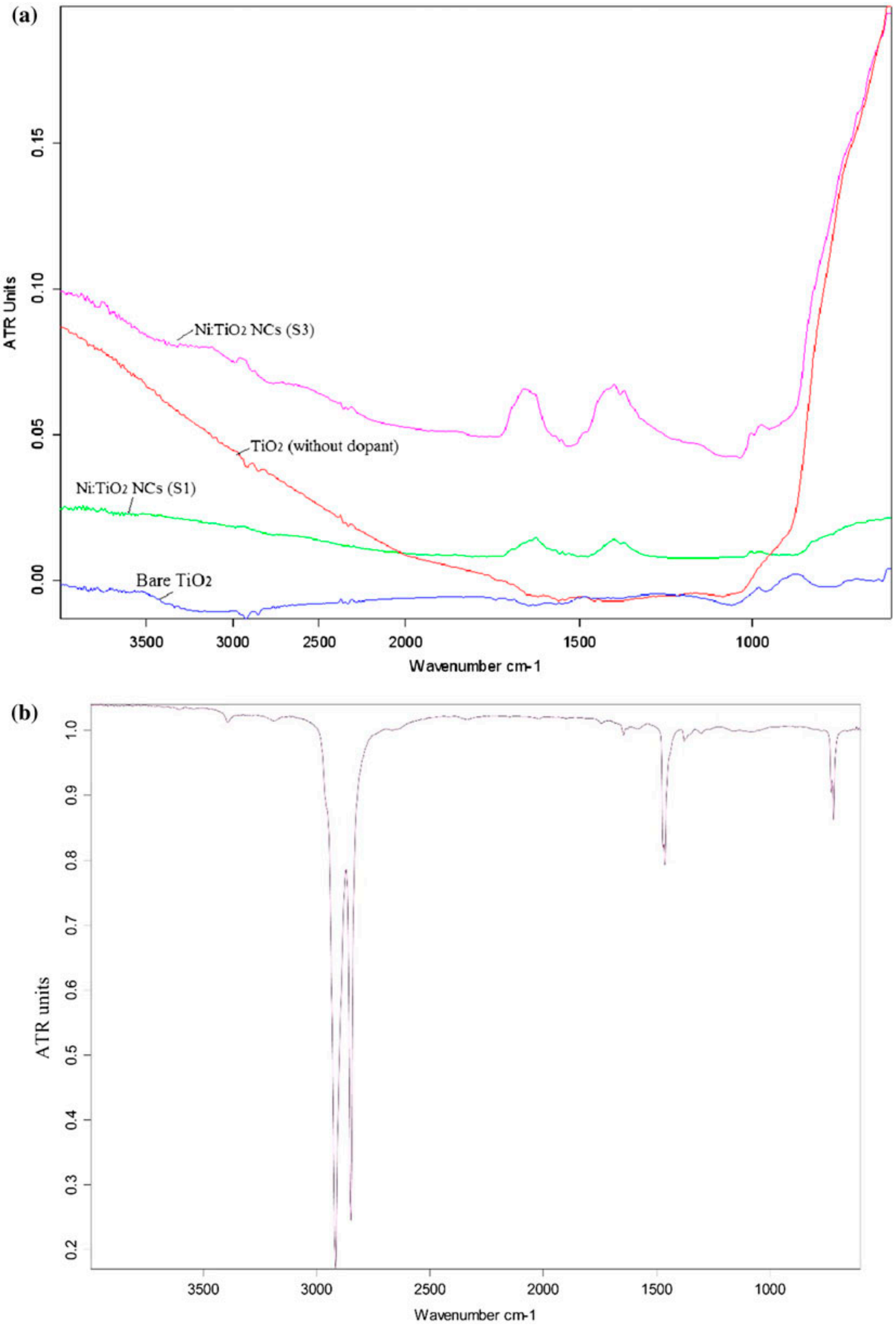

Fig. 2. ATR spectra of (a) different Ni:TiO_2 NCs samples and (b) *n*-butylamine.

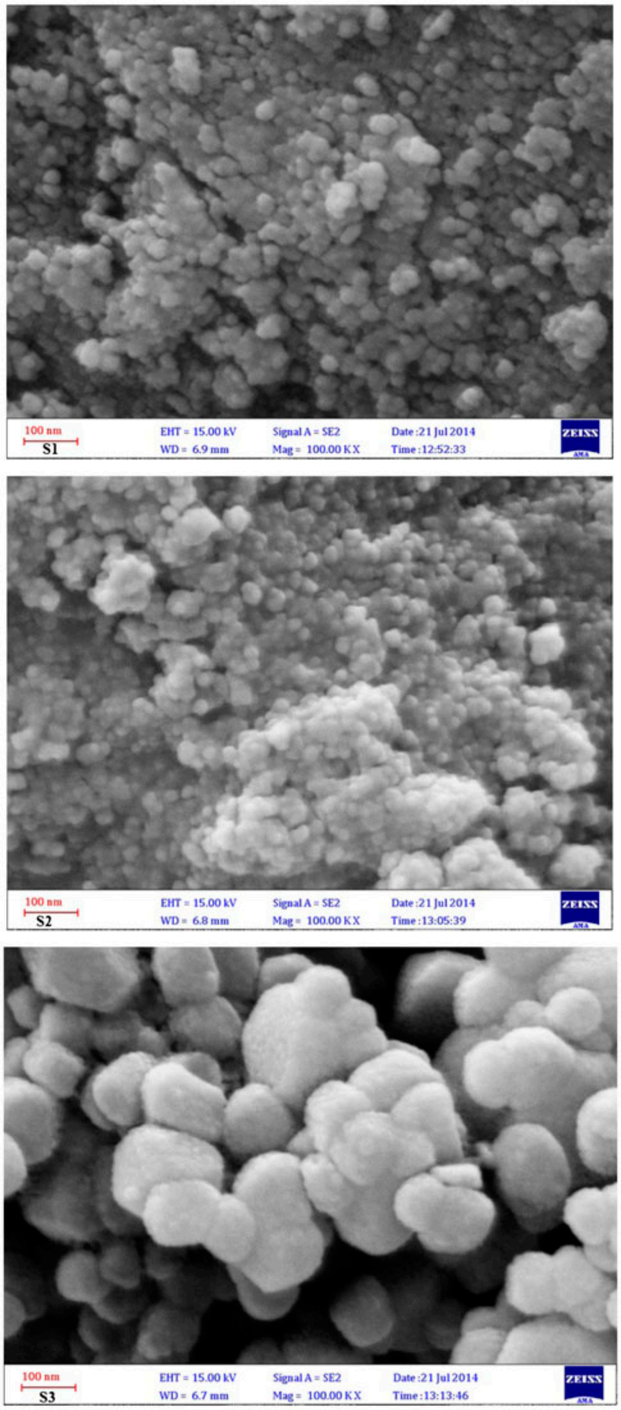

Fig. 3. SEM images of different Ni:TiO_2 NCs.

Table 2
Elemental analysis (EDAX) of different Ni:TiO_2 NCs

	Ni:TiO_2 NCs		
Element	S1	S2	S3
Ti	79.85	79.68	79.90
O	18.18	18.85	18.46
Ni	1.97	1.2	1.22
Cu	0.0	0.15	0.22
Si	0.0	0.12	0.0
Fe	0.0	0.0	0.42
Total	100	100	100

efficiency (the MG removal efficiency at pH 11 and 2 was 99.98 and 80% respectively in the case of sunlight irradiation). These findings match well with other research works reported [24]. Such effect was observed for both sunlight and UV light irradiation. This phenomenon could be attributed to the nature of Ni:TiO_2 NCs and MG dye solution; surface of Ni:TiO_2 NCs is negatively charged under alkaline conditions and, therefore, can easily retain positively charged compounds such as MG [25]. It is well known that under acidic conditions, the electron–hole pairs recombination prevents the formation of a large number of hydroxyl radicals [26]; however, in the case of Ni:TiO_2 NCs, the dye removal efficiency was good (97%), which could be attributed to the effect of doping on limiting electron–hole recombination. Since the photodegradation efficiency of MG dye solution was acceptable and affordable at near neutral pH, we conducted the photodegradation studies at pH 8 as optimum pH in order to make the technique more eco-friendly. As Fig. 7 reveals, bare TiO_2 had negligible photodegradation efficiency under both sunlight (less than 15%) and UV light irradiation. Therefore, bare TiO_2 was not considered for comparison purpose in determining the effect of the other operational parameters.

3.2.2. Effect of MG dye concentration

Fig. 8 shows the effect of MG dye initial concentration on the color removal efficiency. The dye concentration used was in the range of 30–300 mg/l for a maximum reaction time of 3 h. Dye concentration is a limiting factor in most of the removal techniques, especially in photodegradation. As the dye concentration increases, it prevents the penetration of light irradiation into the medium, so that the dye photodegradation would be reduced remarkably. On the other hand, the higher the dye concentration, the lower the dye photodegradation.

3.2.3. Effect of nanocatalyst dosage

A dosage of 0–1.5 g/l Ni:TiO_2 NCs was used to find out the nanocatalyst effect on MG photodegradation efficiency. Fig. 9 shows that Ni:TiO_2 NCs exhibit

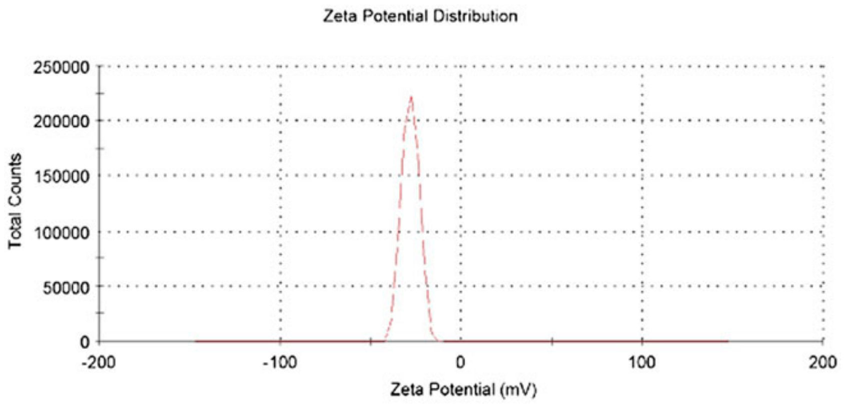

Fig. 4. Characteristic size distribution analysis of Ni:TiO_2 NCs (S3).

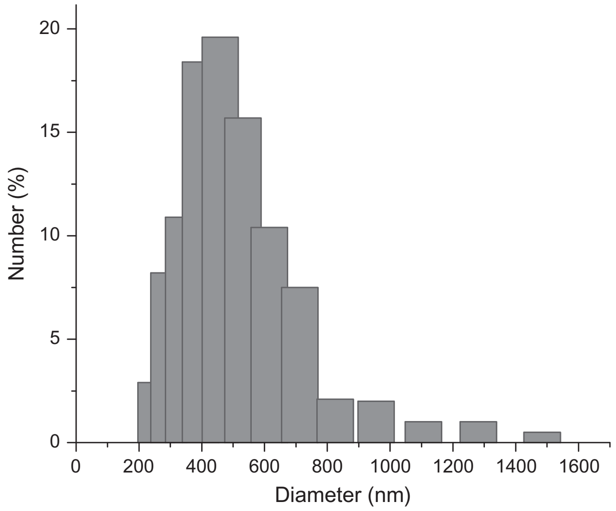

Fig. 5. Characteristic zeta potential of Ni:TiO_2 NCs (S2).

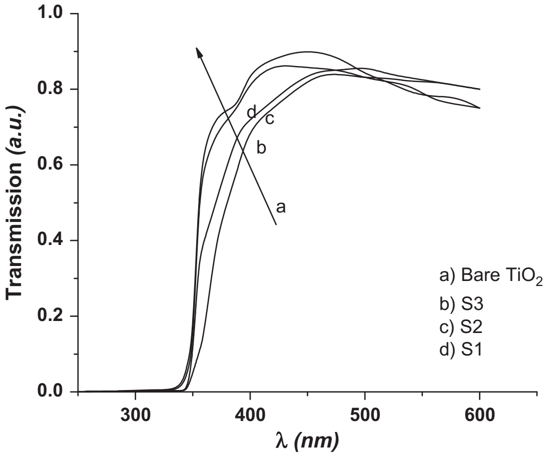

Fig. 6. Band gap energy of different Ni:TiO_2 NCs.

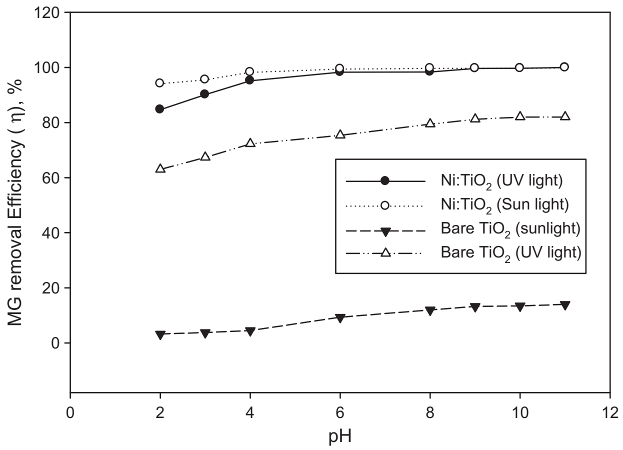

Fig. 7. Effect of pH on the MG photodegradation efficiency.

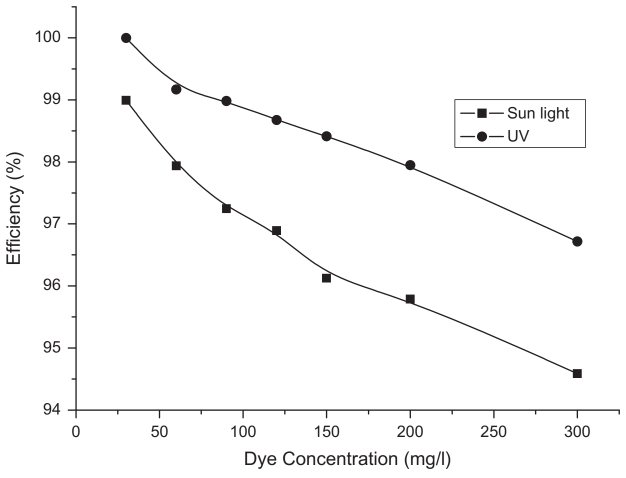

Fig. 8. Effect of MG initial concentration on the photodegradation efficiency.

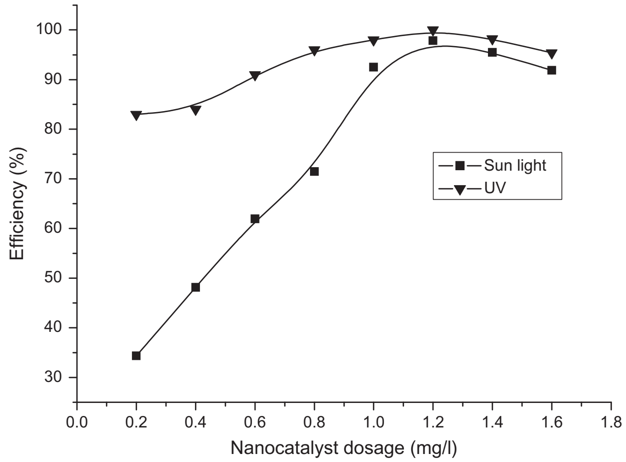

Fig. 9. Effect of Ni:TiO_2 NCs dosage on MG photodegradation efficiency under sunlight and UV light irradiation.

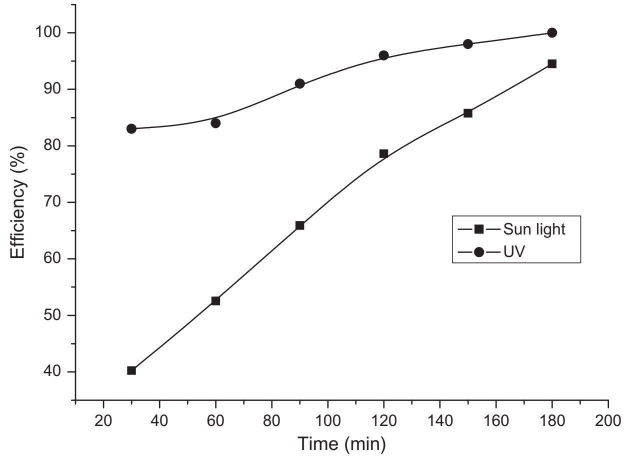

Fig. 10. Effect of contact time of Ni:TiO_2 NCs on MG photodegradation efficiency under sunlight and UV light irradiation.

excellent photodegradation property for MG decolorization. It was found that the optimum dosage of Ni:TiO_2 NCs is 1.2 g/l. However, at higher dosage, the efficiency again decreased, which might be contributed to the effect of turbidity and inhibiting light penetration [27].

3.2.4. Effect of contact time

Time is another operational parameter, which must be investigated in photodegradation studies. The photodegradation experiments were conducted at different time intervals (0–180 min). Fig. 10 shows the effect of contact time on photodegradation efficiency. As Fig. 10 indicates, there is a log phase at the beginning and later, it becomes stationary. Hence, 120-min contact time was considered as optimum contact time. This contact time is acceptable for most of the industries.

4. Conclusion

Ni:TiO_2 NCs were fabricated under mild hydrothermal conditions. The characterization results confirmed the doping of Ni into TiO_2 lattice. Moreover, it was found that Ni and surface modifier have crucial effect on reducing band gap energy, the crystal growth, and cell parameter values. The effect of different operational parameters were studied on the photodegradation properties of the synthesized nanocatalysts. The comparison of photodegradation properties of Ni:TiO_2 NCs with bare TiO_2 indicated that Ni:TiO_2 NCs show higher efficiency than bare TiO_2 in terms of photodegradation. The optimum conditions were found to be pH 8, NCs loading dosage = 1.2 g/l, contact time = 120 min, and dye initial concentration = 250 mg/l.

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