



# Article Synthesis, Characterization, and Solar Photo-Activation of Chitosan-Modified Nickel Magnetite Bio-Composite for Degradation of Recalcitrant Organic Pollutants in Water

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Abstract: Photocatalysis is a promising process for decomposing harmful organic pollutants in water. In this study, solar/photocatalytic degradation of two model azo dyes, i.e., methylene blue (MB) and methyl red (MR), in water using a nanostructured chitosan-modified nickel magnetite (CS-NM) biocomposite was investigated. The CS-NM bio-composite was synthesized through a co-precipitation method and characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), thermogravimetry (TGA), and UV-Vis spectroscopy. FTIR analysis showed the uniform incorporation and conjugation of nickel magnetite (NM) into the chitosan (CS) polymer matrix. SEM showed that the average particle size was 0.5 µm. The TGA results revealed the good thermal stability of the prepared bio-composite at 300 °C. The point of zero charge was calculated as 7.5. The effect of water quality and process parameters, such as concentration of dyes, catalyst dose, solution pH, and temperatures, was investigated, for application purposes. The solar/CS-NM photocatalysis resulted in 99 and 96% degradation of individual MB and MR ( $C_0 = 50$  ppm), respectively, in 90 min. The degradation of MB and MR by solar/CS-NM photocatalysis followed pseudo-first-order kinetics, with observed rate constants (k) of 0.077 and  $0.072 \text{ min}^{-1}$ , respectively. The CS-NM photocatalyst showed high recyclability, represented by only a 4-6% loss in the photocatalytic efficiency, after four cycles. The results showed that solar/CS-NM photocatalysis is an efficient technique for degrading recalcitrant organic pollutants, such as azo dyes, in water environments.

**Keywords:** solar energy harvesting; water depollution; chitosan-modified nickel magnetite bio-composite; photocatalysis; advanced oxidation processes

## 1. Introduction

Water covers more than 70% of the Earth's surface, with more than 95% of water confined to the oceans, leaving only about 3% as fresh water. Meanwhile, clean water supply is critical for living a healthy life. Unfortunately, water resources are frequently polluted by various anthropogenic activities, mainly due to increasing population, extensive urbanization, and especially industrialization. A large variety of harmful organic pollutants, including pesticides, pharmaceuticals, and dyes are frequently introduced into the water system. Globally, about 70,000 tons of dyes are produced annually [1]. Azo dyes represent a significant proportion of the synthetic dyes that are widely used in thetextile, paper, latex, pharmaceuticals, plastics, leather, cosmetics, and food industries [2,3]. Many synthetic



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azo dyes with aromatic compounds are less biodegradable and more persistent in the environment, as well as highly toxic to human beings and animals [4,5].

For example, azo dyes are broken down by liver enzymes and intestinal flora into aromatic amine in human bodies, causing cancers [6]. Azo dye concentration in water bodies may also affect the food chain via light absorption, causing imbalances in the ecosystem [7]. Therefore, azo dye contaminated water must be treated before entering into the environment, for the sake of human beings and the ecosystem.

The removal of azo dyes from water canbe carried out using different methods, including adsorption, ultrafiltration, reverse osmosis, ion-exchange, biodegradation, electrochemical reduction, heterogeneous photocatalysis, photo-Fenton process, gamma irradiation, etc. [8–15]. Semiconductorphotocatalysis, employing titanium dioxide (TiO<sub>2</sub>), copper oxide  $(Cu_2O)$ , zinc oxide  $(ZnO_2)$ , magnetite  $(Fe_3O_4)$ , and tungsten oxide  $(WO_3)$ , has been extensively used for water decontamination, owing to the ease of use, high photostability, economy, environmentally friendly processing, and generation of harmless by-products [16–23]. The proposed mechanism of semiconductor photocatalyst activation by light, as well as the generation of reactive species, was shown in reactions (1)-(3) [16]. When light falls on the surface of the catalyst, an electronic transition occurs, from the valence band to the conduction band, resulting in the generation of conduction band electron and valence band hole pairs (reaction 1). The conduction band electron  $(e^{-})$  and valence band hole  $(h^{+})$ play a vital role in the formation of reactive radicals. For example, the valence band hole and conduction band electron react with water (or  $^{-}OH$ ) and  $O_{2}$  molecule, which results in the production of the hydroxyl radical ( $^{\bullet}$ OH) and superoxide radical anion ( $O_2^{\bullet-}$ ), respectively [16]. These reactive radicals are responsible for the photodegradation of dye. In recent years, Fe<sub>3</sub>O<sub>4</sub> photocatalyst has been extensively used in water treatment, owing to its novel properties, biocompatibility, chemical and structural stability, narrow band gap, visible light active, low cost, and sustainable nature [24,25]. The physical and chemical properties of Fe<sub>3</sub>O<sub>4</sub> towards heterogeneous photocatalysis can be further improved by merging with other metals, metal oxides, or polymers [26].

$$CS - NM \xrightarrow{h\nu} CS - NM (h^+ + e^-)$$
 (1)

$$h^+ + H_2 O \to {}^{\bullet}OH + H^+$$
(2)

$$e^- + O_2 \to O_2^{\bullet -} \tag{3}$$

$$Dye + O_2^{\bullet -} \rightarrow Degradable \text{ products}$$
(4)

$$Dye + {}^{\bullet}OH \rightarrow Degradable \text{ products}$$
(5)

Nickel-modified Fe<sub>3</sub>O<sub>4</sub> hybrid materials have gained much attention, owing to theirnovel photocatalytic properties [27,28]. The properties of nickel-modified  $Fe_3O_4$  caneven be improved by integrating with bio-polymers [29]. Chitosan (CS) is a bioactive polymer that is widely used in the field of photocatalysis, due to its biocompatibility, biodegradability, and non-toxicity [30]. Chitosan is a N-deacetylated chitin derivative, composed of  $\beta$ -Dglucosamine and acyl- $\beta$ -D glucosamine residues with 1, 4- $\beta$  bonds [31,32]. It is a partially crystalline polymer with strong intermolecular and intramolecular hydrogen bonds. The presence of reactive amino and hydroxyl groups has been proven to improve the photocatalytic properties of photocatalysts. Kumar et al. [33] reported a CS-ZFN composite that was very effective in the degradation of crystal violet and brilliant green in water. Aziz et al. [26] found that CS-ZnS-NPs efficiently degraded Acid black 234 and Acid brown 98 in an aqueous medium. Similarly, ternary ferrites-CS nanocomposite was reported as a 93% efficient photocatalyst for the degradation of MB under visible light [34]. Likewise, methyl pyrazolone functionalized magnetic CS composite was found to be 99.8% efficient for visible light decomposition of MB [35]. Despite the extended use of modified CS, further research is needed, in order to improve its mechanical, physical, and biological properties for degradation of persistent organic pollutants in the water environment. In addition,

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other major challenges include the preparation and safe implementation of a low-cost, efficient, reusable, and eco-friendly photocatalyst for the treatment of dye-polluted water and wastewater, for application purposes.

In this study, the synthesis of an efficient chitosan-modified nickel magnetite (CS-NM) bio-composite for degradation of two model azo dyes, i.e., methylene blue (MB) and methyl red (MR) in water was investigated. The synthesized CS-NM bio-composite was characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive x-ray (EDX), ultraviolet-visible (UV-Vis), and thermogravimetric analysis (TGA). The effect of water quality and process parameters, such as the concentrations of dyes, catalyst dose, solution pH, and temperature, on the contaminants removal was investigated for practical applications. The recyclability of the synthesized photocatalyst was investigated for reusability purposes. The obtained data provided useful information on the applicability of chitosan-modified nickel magnetite (CS-NM) bio-composite photocatalytic advanced oxidation processes for the treatment of water contaminated with methylene blue and methyl red or other azo dyes.

## 2. Results and Discussion

## 2.1. Characterization Studies

The synthesized CS-NM bio-composite was analyzed using FTIR, SEM, EDX, TGA, and UV-Vis spectroscopy, for structural and morphological characterization, and the results are discussed in the following sections.

## 2.1.1. FTIR

The synthesis of CS-NM bio-composite was confirmed by comparing the FTIR spectrum of synthesized bio-composite with the data in the literature. As shown in Figure 1, the FTIR spectrum obtained for the chitosan (CS) has characteristic peaks: 3435 cm<sup>-1</sup>, corresponding to the stretching of the  $NH_2$  and OH groups; 1649 cm<sup>-1</sup>, corresponding to the C=O group of amide; 1384 cm<sup>-1</sup>, due to deformation of CH<sub>3</sub> in chitosan; and 1083–1020 cm<sup>-1</sup>, due to the stretching of C-C. As shown in Figure 2, the FTIR spectrum of CS-NM bio-composite showed two characteristic bands, corresponding to two metaloxygen bands. One band is due to Ni-O bond stretching around 567  $\rm cm^{-1}$ , which represents tetrahedral sites, whereas the second is attributed to Fe-O bond stretching at  $664 \text{ cm}^{-1}$ , which is related to the octahedral sites of the spinel structure of NM-CS. These two bands showed the interaction of chitosan with NM. These findings were in good agreement with the results reported in the literature [36]. The wide band at  $3400 \text{ cm}^{-1}$  was assigned to O-H stretching and overlapped with N-H stretching in the chitosan. The peak at 2850 cm<sup>-1</sup> corresponded to aliphatic C-H stretching, the peak at around 1610 cm<sup>-1</sup> indicated the stretching vibration of C=O, arising from an acetylated group of chitosan. The band at 1384 cm<sup>-1</sup> was contributed by CH<sub>3</sub> deformation in the chitosan structure [37,38]. Hence, the presence of Ni, Fe, and other characteristic bands of chitosan confirmed the validity of the synthesized CS-NM bio-composites.



Figure 1. FTIR spectrum of chitosan.



Figure 2. FTIR spectrum of CS-NM bio-composite.

## 2.1.2. EDX

EDX is a method used to determine the composition and proportion of elements in a sample. Qualitative analysis involves the identification of the lines with corresponding energies in the EDX spectrum. The elemental composition of synthesized CS-NM biocomposite showed clear peaks of iron and nickel, with corresponding energy values for the EDX spectrum in Figure 3. The presence of chitosan was confirmed from the carbon peak, which revealed the successful synthesis of the CS-NM bio-composite [39]. The percentage of elements in the prepared bio-composite is shown in Table 1.



Figure 3. EDX spectrum of CS-NM bio-composite.

Table 1. Elemental composition of CS-NM bio-composite.

Element	Weight %	Atomic %
С	36.35	49.67
0	43.24	43.36
Fe	18.91	5.56
Ni	1.50	1.41
Total	100	100

# 2.1.3. SEM

The surface morphology and average particle size of the synthesized NM- and CS-NM biocomposite were characterized by SEM, and the results are shown in Figure 4a,b. The micrographs revealed that nickel magnetite were irregular shaped micro-particles with an average particle size of 0.5  $\mu$ m. A tendency for agglomeration of nickel magnetite was observed in Figure 4a. In Figure 4b, SEM images of the CS-NM biocomposite show that the chitosan coating led to a smoother appearance and less particle aggregation.



Figure 4. (a) SEM image of nickel magnetite and (b) CS-NM biocomposite.

## 2.1.4. TGA-DTGA

Thermal studies and differential thermal gravimetry (DTG) were performed, to determine the amount of chitosan attached chemically or physically with nickel magnetite in the prepared CS-NM bio-composite. For TGA-DTG analysis, a 30–600 °C range of temperature was used at a heating rate of 10 °C per minute in an inert atmosphere. The TGA curve of pure chitosan in Figure 5a shows the two stages of weight loss in the range 47–450 °C, the first (I) occurring in the range of 50–150 °C, due to loss of water molecules with a weight loss of about 12%. The primary degradation of chitosan started at 247 °C (II) and it was completely degraded at about 450 °C, with a weight loss of about 15 °C. Figure 5b showed a two-step (I, II) mass loss in the CS-NM bio-composite. The initial mass (I) loss was about 12% at 50–150 °C, attributed to vaporization of trapped water molecules and unreacted oxygen moieties in the CS-NM sample. The second (II) mass loss was about 15% at around 300–500 °C, and was ascribed to the disintegration of organic compounds from the hydroxyl group at the sample surface, as well as the degradation of chitosan present in the bio-composite. The results demonstrated that the thermal stability of the chitosan wasless than the CS-NM bio-composite.



Figure 5. (a) TGA, (b) DTG, and (c) DSC curves of pure chitosan and CS-NM bio-composite.

Moreover, in the DTG curve of the pure CS and CS-NM bio-composite (i.e., Figure 5c), there were two endothermic peaks, i.e., afirst peak at about 100 °C, which showed the elimination of moisture from the sample, and the second peak at around 300–400 °C, representing the decomposition of chitosan from the CS-NM sample. Similar results were reported by other researchers in the literature [40,41]. The DSC analysis of CS-NM bio-composite showedafirst endothermic peak at 75 °C, which signified the loss of water from the sample. A second peak was around 240 °C, which represented the melting point of the sample. For chitosan, the first peak wasat 65 °C, with the second around 245 °C.

## 2.1.5. Optical Analysis

The light absorption of the synthesized CS-NM bio-composite was recorded using an UV-Vis spectrophotometer. The CS-NM was dispersed in isopropanol for 30 min by sonication, and the absorbance was scanned in a wavelength range from 200 to 800 nm. Figure 6 shows the spectrum of light absorption of the CS-NM bio-composite. Peaks at 200 nm originated from the  $n-\pi^{\times}$  transition, whereas peaks positioned at 365 nm were due to the  $\pi$ - $\pi^{\times}$  transition. Compared with the UV-Vis spectrum in the literature, the presence of more peaks, with their shift towards alonger wavelength (bathochromic shift), in the spectra of CS-NM bio-composite provides evidence of a higher extent of  $\pi$ -electronic conjugation in the polymer. The enhanced  $\pi$ -electronic conjugation resulted in more  $\pi$ bonds, and thus an improvement in delocalization of the electron along the  $\pi$ -bond of the synthesized CS-NM bio-composite was recorded [26].



Figure 6. UV-Vis spectrum of CS-NM bio-composite.

Moreover, the optical band gap ( $E_g$ ) of the prepared bio-composite was determined using the Tauc equation from the plot of  $[(\alpha h\nu)^2 v/s (h\nu)]$ , displayed in Figure 7. The tangent drawn on the *X*-axis of the "Tauc plot" was used to determine the  $E_g$  value. The  $E_g$  was found to be as low as 2.49 eV, which was expected to help in the photocatalytic degradation process.



Figure 7. Tauc plot of the CS-NM bio-composite.

## 2.2. Point of Zero Charge $(pH_{PZC})$

The point of zero charge in degradation is the pH value which indicates that the surface charge of the catalyst is zero. Figure 8 shows the plot of pH<sub>i</sub> vs.  $\Delta$ pH. The pH <sub>PZC</sub> for the NM-CS composite was found to be 7.5. This means that the surface of the catalyst is positively charged when the pH is below 7.5 and negatively charged when the pH is above 7.5 [33].



Figure 8. Plot of pH<sub>PZC</sub> for the prepared bio-composite.

#### 2.3. Photocatalytic Degradation of MB and MR

The degradation of methylene blue and methyl red in water by solar/CS-NM photocatalysis was carried out, and the results areshown in Figure 9. The results showed a 99 and 96% removal of the individual methylene blue and methyl red, respectively ( $C_0 = 50$  ppm, each) by solar/CS-NM photocatalysis ([CS-NM] $_0$  = 0.5 g), in 90 min, at pH 10. The hydroxyl radical ( $^{\bullet}$ OH) and superoxide radical ( $O_2^{-\bullet}$ ), produced in Equations (4) and (5), were the major species responsible for the degradation of methylene blue and methyl red in water [16]. The results also showed that, initially, the degradation rate (i.e., calculated by the change in dye concentration within the specific time interval) was high, probably due to the large number of dye molecules exposed to the reactive species. However, since the concentration of dyes decreased with time, the degradation rate was also decreased. Shah et al. [42] reported that acid black was completely degraded by 0.2 g CoCrFeO<sub>4</sub>-CB catalyst in 2 h, while 93% and 85% of acid brown and Congo red was degraded, respectively, after 2 h. Similarly, Vadivel et al. [43] reported that 94% of methylene blue was degraded by visible light/CaFe<sub>2</sub>O<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysis ( $[dye]_0 = 10 \text{ ppm}$ ,  $[catalyst]_0 = 100 \text{ mg in}$ 50 mL), in 120 min. Meanwhile, the degradation efficiency of methylene blue and methyl red was less than 4% during 90 min direct solar photolysis (Figure 9). Soltani and Mohammad observed a negligible degradation of methylene blue during 1-h sunlight photolysis, at the natural and acidic pH conditions [44]. Ahmed et al. reported only 0.40% decolorization of methylene blue with the exposure of 1 h visible-light irradiation [45]. Singh et al. observed no change in the concentration of methyl red during a 1-h UV photolysis [46]. Singh et al. observed a 7% degradation of methylene red ( $C_0 = 30$  ppm) during 1-h solar photolysis [47]. In the subsequent experiments, the effects of water quality and process parameters such as dye concentrations, catalyst dose, solution pHs, and temperatures on solar/CS-NM photocatalysis of MB and MR wereinvestigated, and the results are discussed in the following sections.



**Figure 9.** Degradation of MR and MB by solar/CS-NM and solar photolysis.  $[MB]_0 = [MR]_0 = 50$  ppm,  $[CS-NM]_0 = 0.5$  g, pH = 10.

## 2.3.1. Kinetics Studies

The degradation kinetics of methylene blue and methyl red by solar/CS-NM photocatalysis were studied, and the results are shown in Figure 10, indicating pseudo first-order kinetics, according to Equation (7) [48]. The observed rate constant (k) for methylene blue  $(C_0 = 50 \text{ ppm})$  was found to be 0.077 min<sup>-1</sup>, with a correlation coefficient (R<sup>2</sup>) value of 0.98. The observed rate constant (k) of methyl red ( $C_0 = 50$  ppm) was found to be 0.072 min<sup>-1</sup>, with an  $\mathbb{R}^2$  value of 0.99. Yatmaz et al. showed that the photocatalytic decolorization of an azo reactive dye in aqueous ZnO suspensions followed pseudo first-order kinetics [49]. Da Silva et al. also reported that the photocatalytic degradation of an azo dye in aqueous solution by  $UV/AC-TiO_2$  followed pseudo first-order kinetics, consistent with our results [48]. Furthermore, it was seen that the observed rate constant (k) of methylene blue and methylene red decreased with increasing concentrations of the dyes, consistent with the literature reports [50,51]. The results shown in Figure 11 revealed that the observed rate constant (k) of methylene blue decreased from 0.087 to 0.082, 0.077, and 0.071 min<sup>-1</sup>, while that of methyl red was reduced from 0.082 to 0.076, 0.072, and 0.067 min<sup>-1</sup>, when the initial concentration of the dyes was increased from 10 to 30, 50, and 70 ppm, respectively. A possible reason for this could be the increased formation of reaction by-products, causing greater competition with the parent dye compounds for the reactive radicals [43].

Adeel et al. observed that the photocatalytic efficiency of Co-ZnO decreased with anincreasing initial concentration of methyl orange. As the initial concentration of methyl orange was increased from 100 to 400 ppm, the photocatalytic degradation efficiency reduced from 77 to 42% [50]. Similarly, Saeed et al. reported that the photocatalytic activity of ZnO catalyst decreased from 80 to 44, 29, and 19% as the initial concentration of methyl orange was increased from 50 to 100, 150, and 200 ppm, respectively [51].



**Figure 10.** Pseudo first-order kinetics of photocatalytic degradation of dyes by solar/CS-NM photocatalysis.



**Figure 11.** Variation of observed rate constants (*k*) of methylene blue and methyl red with increasing concentrations of dyes.

## 2.3.2. Effect of pH

The photocatalytic degradation efficiency of pollutants is a function of the solution pH [52]. The photocatalytic degradation of methylene blue and methyl red was carried out at various solution pHs, i.e., 3, 6, 8, and 10, and the results areshown in Figure 12. The results show that the degradation efficiency of the dyes was enhanced as the pH of the solution was increased, until the maximum degradation efficiency was achieved at pH 8. These results might indicate that the overall degradation efficiency was higher in the basic medium than the acidic condition. The point of zero charge for CS-NM bio-composite was calculated as pH = 7.5. The results indicated that at above pH 7.5 (i.e.,  $pH_{PZC}$ ), the CS-NM bio-composite will be negatively charged, while below pH 7.5, it will be positively charged. The higher degradation efficiency in the basic medium was attributed to the enhanced creation of the hydroxyl radical (\*OH), responsible for the dye degradation [52].

The electrostatic attraction of methylene blue and methyl red molecules (i.e., cationic dye) on the CS-NM bio-composite surface may have been high due to the creation of negative charge at the higher pH. Literature studies showed that photocatalytic degradation was high in the basic medium, attributed to enhanced electrostatic interactions [53]. At low pHs, the attraction of methylene blue and methyl red to the CS-NM bio-composite decreased, which might have lowered the degradation efficiency of the dyes as well.



Figure 12. Effect of pH on the solar/CS-NM photocatalytic degradation of dyes.

Saeed et al. [54] reported that Ag-TiO<sub>2</sub> photocatalytic degradation of rhodamine B and methylene blue washigh at pH 10. However, Siddique et al. [55] reported the maximum photocatalytic degradation of rhodamine B on bismuth ferrite catalyst was at pH 7. Nisar et al. [56] reported the highest degradation efficiency of methylene blue by ZnO-rGO photocatalysis was achieved under neutral pH conditions.

## 2.3.3. Effect of Catalyst Dose

The photocatalytic degradation of methylene blue and methyl red was studied using various dosages of the catalyst, i.e., between 0.1–0.7 g, and the results are shown in Figure 13. As can be seen, the degradation efficiency of methylene blue and methyl red increased with anincreasing dosage of the catalyst, up to 50 ppm, and then it decreased. The maximum degradation efficiency of methylene blue and methyl red was achieved using 0.5 g CS-NM photocatalyst, represented by a 99 and 96% degradation, respectively, in 90 min. When increasing the catalyst dosage, the number of electron-hole pairs increased, thereby enhancing the generation of reactive radicals, and hence the photocatalytic degradation efficiency was increased. However, further increasing the catalyst dosage beyond 50 ppm could increase the turbidity of the solution, which in turn decreased the penetration of sunlight to the catalyst surface, thereby reducing the number of electron-hole pairs, as well as the generation of reactive radicals. Consequently, the photocatalytic degradation efficiency of MB and MR decreased as well. Thus, 0.5 g was the optimum catalyst dosage for the further experiments. Kumar et al. [33] showed that the removal efficiency of crystal violet and brilliant green increased from 17 to 75% and 25 to 97%, respectively when the ZFN–CS catalyst dosage was increased from 0.1 to 0.5 g. Ajithkumar et al. [57] reported that the degradation efficiency of MB decreased when the concentration of CZFY, i.e.,  $Cu_yZn_1-yFe_{2-x}Y_xO_4$  (x = 0.1, y = 0.5) was increased from 10 to 50 mg, represented by a 99.0% MB removal at 10 mg CZFY.



**Figure 13.** Influence of catalyst dosage on the degradation of methylene blue and methyl red dye in an aqueous system.

#### 2.3.4. Effect of Temperature

To study the effect of temperature on the solar/CS-NM photocatalytic degradation of MB and MR, separate photocatalytic reactions were conducted at 35, 40, and 45 °C, under identical reaction conditions. As shown in Figure 14, the degradation efficiency of MB and MR was high at 35 °C, represented by a 99 and 96% degradation, respectively, in 90 min. However, the photocatalytic degradation efficiency of MB and MR decreased with increasing temperature, represented by a 92 and 87% degradation of MB, with 87 and 85% degradation of MR, at 40 and 45 °C, respectively, in 90 min. A possible reason for this could be the enhanced recombination of electron-hole pairs at the higher temperature. Thus, the optimal temperature was 35 °C for further experiments. Saeed et al. [58] reported that, on increasing the temperature from 30 to 40 °C, the photocatalytic degradation of methylene blue on Ag-Al<sub>2</sub>O<sub>3</sub> was enhanced, attributed to the increasing kinetic energy of the molecules. However, the degradation efficiency decreased whenfurther increasing the temperature, attributed to the increased electron-hole pair recombination.



Figure 14. Influence of temperature on the degradation efficiency of the dyes.

The Arrhenius equation (i.e., Equation (6)) was used to determine the activation energy  $(E_A, \text{ J mol}^{-1})$  for the dye degradation process [59].

$$ln k_a = ln A - \left[\frac{E_A}{RT'}\right].$$
(6)

where  $k_a$  (min<sup>-1</sup>) is the rate constant, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant, A is the preexponential factor, and T (K) is the temperature. For the photocatalytic degradation of MB and MR, the  $E_A$  was determined as 10.82 kJ mol<sup>-1</sup> and 11.64 kJ mol<sup>-1</sup>, respectively (Figure 15a).



**Figure 15.** (**a**) Arrhenius plot and (**b**) Eyring plot for the photocatalytic degradation process of MB and MR.

The Eyring equation (i.e., Equation (7)) was used to estimate the entropy of activation ( $\Delta S^{\#}$ , J mol K<sup>-1</sup>) and enthalpy of activation ( $\Delta H^{\#}$ , kJ mol<sup>-1</sup>) from the intercept and slope of the graph between  $ln(k_a/T)$  and 1/T (Figure 15b) [59].

$$ln\frac{k_a}{T} = ln\frac{k_B}{h} + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT}$$
(7)

where, *k* is transmission coefficient,  $k_B$  (J K<sup>-1</sup>) is Boltzmann constant and *h* (J s) is Planck's constant. The  $\Delta S^{\#}$  was -5.9 J mol K<sup>-1</sup>, whereas  $\Delta H^{\#}$  was determined as 37.73 kJ mol<sup>-1</sup> for MB. For MR decomposition, the  $\Delta S^{\#}$  and  $\Delta H^{\#}$  were -6.14 J mol K<sup>-1</sup> and 41.23 kJ mol<sup>-1</sup>, respectively. From these results, it can be concluded that the photocatalytic degradation of the selected dyes on the CS-NM surface was an endothermic process, accompanying a decrease in the entropy at the solid–liquid interface. The details of various thermodynamics parameters, including activation *energy* ( $E_a$ ), entropy of activation ( $\Delta S^{\#}$ ), and enthalpy of activation ( $\Delta H^{\#}$ ) for the solar/CS-NM photocatalytic degradation of MB and MR are provided in Table 2.

Table 2. Kinetics and thermodynamics parameters of solar/CS-NM photocatalysis of MB and MR.

Dye	Rate Constant, <i>k</i> (min <sup>-1</sup> )	Activation <i>Energy, E</i> a (kJ mol <sup>-1</sup> )	Entropy of Activation (ΔS <sup>#</sup> , J mol K <sup>-1</sup> )	Enthalpy of Activation (ΔH <sup>#</sup> , kJ mol <sup>-1</sup> )
Methylene blue	0.077	10.82	-5.9	37.73
Methyl red	0.072	11.64	-6.14	41.23

#### 2.3.5. Recycling of the CS-NM Bio-Composite

The synthesized CS-NM bio-composite was recovered from the solution, reused for four successive runs, and the results are shown in Table 3. The results showed that the photocatalytic ability of the photocatalyst was largely maintained during four runs, represented by a 99, 97, 94, and 93% removal efficiency of MB and 96, 95, 93, and 92% removal efficiency of MR during the 1st, 2nd, 3<sup>rd</sup>, and 4th runs, respectively. From the results it was revealed that even after four cycles, the efficiency of chitosan-modified nickel magnetite was significantly high in removing MB and MR from the water environment.

**Table 3.** Reusability of CS-NM bio-composite for the two selected dyes under optimum conditions, i.e.,  $[MB]_0 = [MR]_0 = 50$  ppm,  $[CS-NM]_0 = 0.5$  g, pH = 7.5.

Number of Batches	1st	2nd	3rd	4th
Dyes	Photocatalytic degradation of azo dyes (%)			
Methylene blue	99	97	94	93
Methyl red	96	95	93	92

2.3.6. Comparison with Other Bio-Composite-Based Photocatalysts

Bio-composite-based photocatalysis is a widely used technique for the degradation of toxic azo dyes in water. Various azo dyes, including methylene blue, methyl red, methyl orange, malachite green, acid brown, acid black, Congo red, etc. [42,60–62], were degraded in the literature via bio-composites photocatalysis and the results are shown in Table 4. From Table 4, it can be seen that the degradation efficiency of methylene blue and methyl red using the CS-NM bio-composite was significantly high compared to the literature reports.

**Table 4.** Comparison of the various bio-composite based photocatalysts for the photocatalytic degradation of azo dyes.

Catalyst	Light Source	Dye	Conc. mg/L	%D & <i>k</i> (min <sup>-1</sup> )	Reaction Time (min)	Ref.
CS-ZnS-NPs	UV light	Acid black 234 acid brown 98	10	97, 0.04096 93, 0.01464	100	[26]
ZnO-PVP	UV light	Methyl orange Congo red	100	82, 0.20 (g.min <sup>-1</sup> .mol <sup>-1</sup> ) 76, 14.3 (g.min <sup>-1</sup> .mol <sup>-1</sup> )	120	[53]
CdS	UV light	Methyl orange	10	99	90	[36]
CoCrFeO <sub>4</sub> -CB	Sunlight	Acid brown, acid black Congo red	50	100 93 85	100	[42]
yttrium doped zinc ferrite (ZFY) and yttrium and copper co-doped zinc ferrite (CZFY)	Visible light	Methylene blue	10	95, 0.00497 89, 0.00471	180	[57]
Ag-Al <sub>2</sub> O <sub>3</sub>	Visible light	Methylene blue	100	100, 0.08	120	[58]
Ni/TiO2 (UV)	UV light	Methyl orange	5	85, 0.0098	120	[61]
copper sulfide nanoparticles chitosan beads (CuS-CB)	Sunlight/Day light	Malachite green	50	95, 0.033	180	[62]
Co-CCMN, Ni-CCMN Fe-CCMN	UV light	Bromophenol blue	30	85, 0.0047 83, 0.0034 95, 0.0040	600	[63]
Ag/PET TeMs	Visible light	Methylene blue	1	61, 0.9	60	[64]
Ni-Fe <sub>3</sub> O <sub>4</sub> -CS	Sunlight	Methylene blue Methyl red	50	99, 0.077 96, 0.072	90	This work

## 3. Materials and Methods

## 3.1. Materials

Methylene blue and methyl red were received from Chem Dyes Corporation Ltd., Pakistan. Ferrous (II) ammonium sulfate  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ , 99%), ferric (III) chloride hexa hydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 98%), acetic acid (CH<sub>3</sub>COOH, 99%), and chitosan powder (C<sub>56</sub>H<sub>103</sub>N<sub>9</sub>O<sub>39</sub>) were purchased from Merck, (Merck KGa, Darmstadt, Germany). Sodium hydroxide (NaOH, >99.8%) and nickel sulfate (NiSO<sub>4</sub>.6H<sub>2</sub>O, ≥98%) were purchased from Sigma-Aldrich, St. Louis, MO, USA). The pH of the solution was adjusted using 0.1 N NaOH or HCl. All solutions were prepared using Milli-Q water. All chemicals were used as received.

#### 3.2. Synthesis of Nickel Magnetite Nanoparticles

The synthesis of nickel magnetite was carried out by a co-precipitation method, as described elsewhere [53]. Nickel sulfate (0.25 M), ferrous ammonium sulfate (0.25 M), and ferric chloride (1 M), 50 mL each, were mixed together under rigorous stirring for 1 hr. Then, 30 mL NaOH (2 M) was added to the resulting solution, drop wise, until the pH reached 11. After 30 min, the obtained product was washed thoroughly with Milli-Q water till at neutral pH. The resulting product was dehydrated at 120 °C for 20 min in an oven, and then stored for further processing.

## 3.3. Synthesis of Chitosan-Modified Nickel Magnetite (CS-NM) Bio-Composite

Nickel magnetite (0.5 g) contained in 50 mL water was mixed with 50 mL of 10% acetic acid in chitosan. The mixture was sonicated for 30 min at room temperature, until the nanoparticles were uniformly dispersed. Then,30 mL sodium hydroxide (2 M) was added, and CS-NM bio-composite was precipitated out. The precipitate of CS-NM bio-composite was separated by filtration, carefully washed with Milli-Q water until a neutral pH, and dried at 100 °C.

## 3.4. Characterizations

The synthesized CS-NM bio-composite was analyzed by FTIR, SEM, EDX, TGA, and UV–Vis techniques, for structural and morphological characterization. A Fourier transform infrared spectrometer (FTIR) (Schimadzu IR Prestige-21, Kyoto, Japan) was used in the wavenumber range of 4000 to 400 cm<sup>-1</sup>. The average particle size, as well as surface morphology and composition of the CS-NM bio-composite, were investigated by Scanning Electron Microscopy (SEM) (JEOL, JSM5910, Tokyo, Japan) and Energy Dispersive X-Ray (EDX) spectroscopy (INC-200, Oxford Instruments, Oxford, UK), respectively. Thermogravimetric Analysis (TGA) of CS-NM was performed using a thermogravimeter (Perkin Elmer, Walthman, MA, USA), operating at 10 °C/min from 30 to 600 °C. The absorbance of the dispersed nanocomposite in isopropanol was measured usingUV-Vis (Shimadzu, Tokyo, Japan) spectroscopy and the band gap was determined.

The point of zero charge (pH<sub>PZC</sub>) of the CS-NM bio-composite was determined by the salt addition method, using 0.1 M NaCl solution [12]. Next, 20 mL NaCl (0.1 M) and 0.1 g CS-NM was mixed in different vessels. The initial pH (pH<sub>i</sub>) of the mixture was determined using a pH meter. The suspension was stirred for 24 h in a shaker (120 rpm) at 30 °C. The final pH (pH<sub>f</sub>) of each suspension was recorded, and thepH<sub>PZC</sub> was obtained from the graph between  $\Delta$ pH verses pH<sub>i</sub> [53].

#### 3.5. Photocatalytic Degradation Experiments

The photoreactor used for the degradation experiments consisted of a 100-mL beaker, containing 0.5 g CS-NM, and 30 mL of 50 ppm methylene blue or methyl red at 35 °C, under uniform stirring. To achieve adsorption/desorption equilibrium, the dye solution with a specific quantity of photocatalyst was continuously stirred for 30 min in the dark, before exposing to sunlight irradiation. The concentration of methylene blue and methyl red at specific intervals of solar irradiation was measured at the  $\lambda_{max}$ , i.e., 664 and 425

nm, respectively, using UV-Vis spectrophotometer (Schimadzu, UV-1800, Japan). Before UV-Vis spectrophotometer analysis, the photocatalyst was separated from the dye solution by centrifugation. The percent degradation of dyes was calculated from the concentrations using Equation (8) [26].

Percent Degradation % = 
$$\left[\frac{C_o - C_f}{C_o}\right] \times 100$$
 (8)

where  $C_o$  and  $C_f$  indicate the concentration of the dyes before and after the solar radiation [26].

#### 3.6. Kinetics Studies

Kinetics studies of the degradation of methylene blue and methyl red by solar/CS-NM photocatalysis were carried out, and the degradation rate constants were determined using the kinetics model shown in Equation (9) [65].

$$In\frac{A_o}{A_t} = kt (9)$$

where "k" is the pseudo first-order rate constant,  $A_o$  is the absorbance of dye solution before irradiation, while  $A_t$  is the absorbance at time "t".

#### 3.7. Recycling Test

To test the recyclability of the synthesized CS-NM, the photocatalyst was recovered from the solution by centrifugation, washed with deionized water, and dried in an oven. The recovered photocatalyst was reused for four successive runs.

## 4. Conclusions

In this study, an innovative chitosan-modified nickel magnetite (CS-NM) bio-composite was synthesized using a co-precipitation method and characterized by various techniques, such as SEM, FTIR, EDX, UV/Visible, TGA, and UV–Vis spectroscopy. The synthesized photocatalyst was a nanostructured material, and it had a considerably low band gap energy (i.e.,  $E_g = 2.49 \text{ eV}$ ), which was efficiently activated by the solar light. The solar/CS-NM photocatalysis ([CS-NM]<sub>0</sub> = 0.5 g) resulted in a 99 and 96% degradation of MB and MR  $(C_0 = 50 \text{ ppm})$ , respectively, in 90 min, at pH 8. The photocatalytic efficiency was high in the basic medium, as compared to in acidic conditions. The hydroxyl radical (•OH) and superoxide radical  $(O_2^{\bullet-})$  were the major species responsible for the degradation of methylene blue and methyl red using the CS-NM bio-composite. Water quality and process parameters, such as initial dye concentrations, catalyst dose, temperature, and solution pH, had a moderate effect on the efficiency of the solar/CS-NM photocatalysis. The catalyst showed a significantly high photoactivity, even after four consecutive cycles. The data fit well into the pseudo first-order kinetics equation. The kinetics and thermodynamics parameters of the solar/CS-NM photocatalysis of MB were found to be as follows: rate constant,  $k = 0.077 \text{min}^{-1}$ , activation *energy*,  $E_a = 10.82 \text{ kJ mol}^{-1}$ , activation entropy,  $\Delta S^{\#} = -5.9$  J mol K<sup>-1</sup>, and activation enthalpy,  $\Delta H^{\#} = 37.73$  kJ mol<sup>-1</sup>. Similarly, the values of the rate constant (k), activation energy ( $E_a$ ), activation entropy ( $\Delta S^{\#}$ ), and activation enthalpy ( $\Delta H^{\pm}$ ) for the solar/CS-NM photocatalytic degradation of MR were  $0.072 \text{ min}^{-1}$ ,  $11.64 \text{ kJ mol}^{-1}$ ,  $-6.14 \text{ J mol} \text{ K}^{-1}$ , and  $41.23 \text{ kJ mol}^{-1}$ , respectively. The results suggested that the CS-NM bio-composite can potentially contribute to the decomposition of recalcitrant organic pollutants, such as azo dyes, from water environments.

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