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Light-induced Photocatalytic Degradation of Methylene Blue observed using Mg-Cu-Cd Ferrite Nanoparticles

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ABSTRACT

A major issue in the industrial sector is the highly efficient and economical treatment of hazardous dye-based colour effluents. Spinel ferrite nanoparticles are more prominent for their unique qualities, such as their optical, catalytic, electrical, and magnetic properties. Moreover, physical characteristics of ferrites may be influenced as well as their catalytic properties by substituting metals like magnesium. In this context, herein, $Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and Δx=0.1) nano-ferrites were employed to examine the photodecomposition of methylene blue (MB) under visible light. To optimize the reaction conditions, the effects of different operational parameters including irradiation time span, catalyst amount, initial dye concentration, and pH for the degradation of MB dye were investigated. The maximum degradation efficiency of 93.54% was obtained by using 1 g/L catalyst and 10 ppm MB dye at pH 10 within 120 min reaction time. These results demonstrate the applicability of the Mg^{2+} doped Cu-Cd ferrite samples for water remediation.

Keywords: Mg-Cu-Cd ferrites, Photocatalyst, MB degradation, Environmental remediation, Recyclability.

INTRODUCTION

Because different dyes have carcinogenic properties, the industrial waste water that contains them is to account for water pollution[1]. Numerous studies have found that the textile industry uses 10-12% of dyes annually, including Methyl orange, Congo red, Rose Bengal, Thymol blue, Indigo Red, Rhodamine B, Red 120, Eriochrome Black-T (EBT), and Methylene Blue (MB) of which a significant portion (20%) is lost during synthesis and treatment processes and enters the water through effluents[2]. When such coloured effluents are released into the environment, they significantly contribute to eutrophication and non-esthetic pollution[3]. Moreover, the oxidation, hydrolysis, and other chemical processes that occur during the wastewater phase can produce hazardous byproducts[4].

As a result, decolorization of dye effluents has drawn more attention. Traditional physical methods (such as ion exchange on synthetic adsorbent resins, adsorption on activated carbon, reverse osmosis, ultrafiltration, ozonation, and coagulation by chemical agents) may typically be utilized effectively to eradicate colour contaminants[5]. The fact that these methods just move organic chemicals from one phase of water to another and so cause secondary contamination makes them non-destructive[6]. Moreover, these methods have high operational costs. Adsorption, for instance, results in physical removal rather than degradation, which causes an issue with waste management[7], while ozonation only has a very small impact on the carbon content[8]. Traditional biological treatment procedures are inadequate for decolorization and degradation because of the stability of modern dyes and the high degree of aromaticity contained in dye molecules[9]. Thus, the development of efficient water processing methods is urgently needed by the textile industry.

In recent years, advanced oxidation processes (AOPs) have drawn attention because they exhibit high efficacy in the treatment of wastewater[10]. The degradation of dyes and other hazardous materials from polluted water sources is commonly accomplished by the photocatalytic process, one of the AOPs techniques. The most often utilized photocatalysts for the breakdown of organic dyes from wastewaters are ferrite nanoparticles, which have high surface areas and great chemical stability[11].

Three types of dyes—cationic, anionic, and non-ionic (disperse dyes)—are recognized[12,13]. Methylene blue (MB), a cationic dye, is the most prevalent synthetic dye utilized in the bulk of the textile industries. Its particular qualities of strong thermal and light withstanding behaviour are the main reasons it is used[14]. When MB gets drained out with wastewater and causes damage, it is incredibly challenging to remove it from the water[15].

In this context, herein, $Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and Δx=0.1) ferrite nanoparticles were employed to study the photodecomposition of methylene blue (MB) under visible light.

MATERIALS AND METHODS

Materials

Magnesium sulphate [$MgSO_4.7H_2O$], Copper sulphate [$CuSO_4.5H_2O$], Ferrous sulphate [$FeSO_4.7H_2O$] and Cadmium sulphate [$3CdSO_4.8H_2O$] were purchased from Merck, India. Potassium oxalate monohydrate [$C_2H_2K_2O_5$] was procured from Spectrochem chemicals, India. All chemicals were of analytical grade. The chemicals received were used as such without additional purification. Distilled water is used throughout this investigation.

EXPERIMENTAL

$Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and Δx=0.1) ferrites nano-particles [Mg-Cu-Cd NPs] were previously synthesized by oxalate co-precipitation approach and have already reported elsewhere[16]. The batch mode photocatalytic degradation experiments were conducted for 180 min in visible light (160 W lamp with 535 lux). Adsorption-desorption equilibrium was obtained in dark using 25 mL of a 10 ppm MB dye solution and 25 mg of catalyst. The sample (3 mL) were sampled every 30 min after the solution was exposed to light. The following equation[17] is used to determine the photocatalytic degradation using a UV-Vis spectrophotometer.

$$\% D=(C_0-C_t)/C_0 \times 100 \quad (1)$$

Where, C_o and C_t stand for initial and absorbance after time t, respectively, and %D for percent degradation.

RESULTS AND DISCUSSION

The detailed structural, magnetic, and optical properties of Mg-Cu-Cd NPs by oxalate co-precipitation approach has already been published elsewhere[16]. The photocatalytic property of Mg-Cu-Cd NPs against MB dye is discussed as follows.

Photocatalytic activity of Mg-Cu-Cd NPs

Due to their extremely low band gap (1.66 eV)[16], Mg-Cu-Cd spinel ferrites are advantageous materials for photocatalytic activity because they may be employed in MB photocatalytic degradation without the usage of an extra oxidant. The breakdown of MB in an aqueous solution was tested utilizing studies on the photocatalytic activity of $Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and Δx=0.1) ferrite powders under visible light. Since the concentration (C) and absorbance (A) are proportional, the

C_o/C_t equation can be employed in place of the A_o/A_t equation[18]. The photocatalysts use light energy ($h\nu$) to carry out the oxidation and reduction reactions ($h\nu$). When light energy is irradiated, one electron (e^-) is transferred from the valence band of catalyst into the conduction band, generating a photogenerated hole (h^+). Because more e^- and h^+ pairs are formed as a result of extending the exposure time for each sample, the dye degrades more quickly. Cu^{2+} ions have a (d^9) electronic configuration, but Mg^{2+} ions have a ($2s^2,2p^6$) electronic structure and can thereby reduce electron availability. Because it restricts the availability of electrons, x=0.5 produces the fewest electron-hole pairs. In the current ferrite system, the band gap decreases as Mg^{2+} substitution in $Cu_{0.5}Cd_{0.5}Fe_2O_4$ ferrite increases[16] and as a consequence, it is expected to be a more advantageous material for MB photodegradation. However, the results of the current investigation support the idea that other factors contribute to photodegradation. The basic factors that affect photodegradation are the temperature of the reaction medium, the quantity of the photocatalyst, the pH of the solution, the nature of the photocatalyst and substrate, the intensity and duration of the light source, the surface area of the photocatalyst, the doping of non-metals or metals, and the structural characteristics of the photocatalyst, such as surface defects, particle size, band gap, etc[3]. K. M. Jadhav *et al.,*[19] also reported the opposite outcome. For the photocatalytic degradation of MB, Mg-Cu-Cd NPs were proposed and discussed below, according to the literature[20].

Step-I: Mg-Cu-Cd ferrite will produce electrons and holes in valence and conduction bands in response to the absorption of an efficient photon ($h\geq E_g$).

$$Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4+h\nu \longrightarrow Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4 (e^-+h^+) \quad (2)$$

Step-II: Anionic super-oxide radicals are generated when conduction band electrons and oxygen from the environment interact.

$$e^-+O_2 \longrightarrow O_2^{\bullet-} \quad (3)$$

The aforementioned it is super-oxide radicals react with H^+ to produce $HO_2^{\bullet}$, which subsequently reacts with an electron to form OH•:

$$O_2^{\bullet-}+H^+ \longrightarrow HO_2^{\bullet} \quad (4)$$

$$HO_2^{\bullet}+e^- \longrightarrow OH^{\bullet} \quad (5)$$

Valence band holes produce OH• free radicals when they interact with OH- ions or surface-bound water, as seen below.

$$h^+ + H_2O \longrightarrow OH^{\bullet} + H^+ \quad (6)$$

$$h^+ + OH^- \longrightarrow OH^{\bullet} \quad (7)$$

Step-III: MB dye molecules oxidized by active species:

$$OH^{\bullet}, O_2^{\bullet-}, HO_2^{\bullet} + MB \longrightarrow \text{Oxidation products} \quad (8)$$

The following operational factors affect the photocatalytic degradation of MB:

Effect of irradiation time

The photodegradation in the presence of the Mg-Cu-Cd nano-ferrite photocatalyst was determined using the UV-Vis absorption spectra of the MB at different irradiation periods. The impact of irradiation time on the extent of degradation was examined using UV-Vis absorbance spectra. The results indicate that increasing the irradiation period significantly increases the degradation efficiency of MB. This is because initially more MB molecules were involved in the breakdown, but over time, this number reduced. This may be because the MB molecule is first attacked by a considerable number of oxidizing radicals in the solution, but as time passes, the number of oxidizing radicals in the solution diminishes, slowing the rate of degradation. The effect of irradiation duration on MB degradation was investigated using 25 mL of a 10-ppm solution and 25 mg of the photocatalyst. Fig. 1 depicts the MB degradation of using $Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and Δx=0.1) as a function of exposure time. According to Fig. 1, the MB photodegradation rate drastically increases for all Mg-Cu-Cd ferrites up to 120 min before gradually decreasing after optimized irradiation time. When the irradiation period was increased from 30 to 120 min, the percentage of degradation for $Mg_{0.1}Cu_{0.4}Cd_{0.5}Fe_2O_4$ increased from 53.58 to 83.50 per cent.

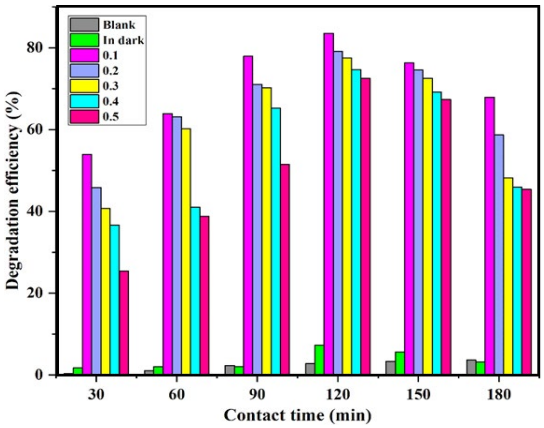

Fig. 1. Effect of contact time on the photocatalytic degradation of MB dye

Effect of Mg-Cu-Cd ferrite dosage

The amount of catalyst used in the photocatalysis method is an important factor from an economic standpoint[21]. $Mg_xCu_{0.5-x}Cd_{0.5}Fe_2O_4$ (x=0.1 to 0.5, and ∆x= 0.1) nano-ferrites were tested in 25 mL of MB dye (10 mg/L) for a constant time of 120 min to determine the effect of photocatalyst quantity on degradation. The outcomes show that MB dye degradation was accelerated when the catalyst dosage was raised to 25 mg, as depicted in Fig. 2.

The efficiency of photodegradation is improved when the amount of photocatalyst is increased because Mg-Cu-Cd nano-ferrite and reactive radicals possess more active reaction sites[22]. When the dosage of Mg-Cu-Cd ferrites was increased from 10 to 25 mg, the percentage of degradation increased from 54.38 to 90.53 per cent. As a consequence, the catalyst used in future testing was 25 mg. Increased turbidity in the reaction fluid from an excess of photocatalyst reduces light penetration[23]. M. Swaminathan *et al.,* similarly demonstrated a comparable drop in MB degradation efficacy beyond the optimal amount of photocatalyst[24].

Effect of dye concentration

The dye concentration is one of the key factors that significantly influence how well photocatalytic degradation functions. Initial MB concentrations (5-25 mg/L) were changed while the Mg-Cu-Cd ferrite dosage (25 mg), contact time (180 min), and dye volume (25 mL) were constant to evaluate the photocatalytic degradation of MB dye. When the initial dye concentration is increased from 5 to 10 mg/L, as shown in Fig. 3, the degradation percentage of MB increases from 83.00 to 87.42 per cent. As the dye concentration increases, the breakdown process gets slower. The obvious answer is that when the concentration of dye molecules increases on the active surfaces of catalyst, visible light penetration decreases, reducing the generation of $OH^{\bullet}$ radicals.

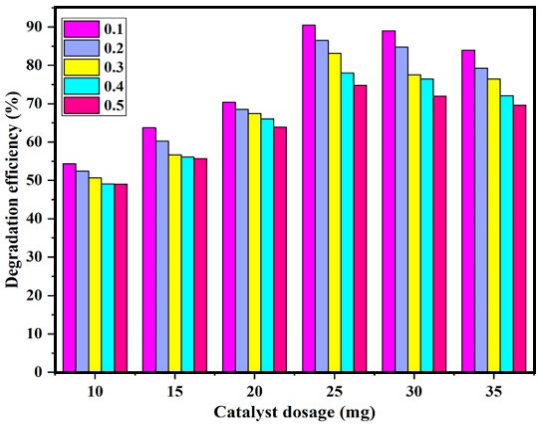

Fig. 2. Effect of photocatalyst dosage on the photocatalytic degradation of MB dye

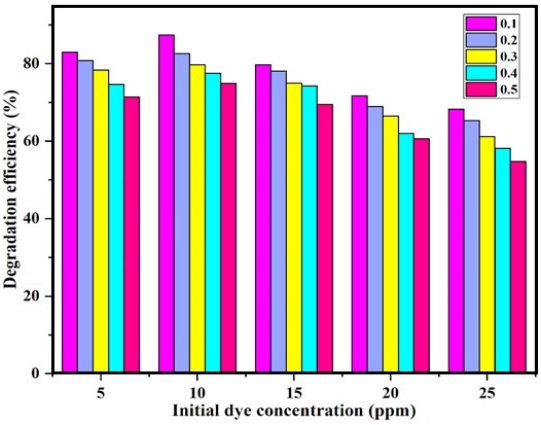

Fig. 3. Effect of initial dye concentration on the photocatalytic degradation of MB dye

Effect of pH

Although pH is a useful parameter that determines the surface state, the surface charge of catalyst has the greatest influence on the adsorption and degradation of MB[25]. Experiments were conducted at various pH (4, 7, and 10) to find the optimal pH for the breakdown of MB while maintaining constant dye concentrations (10 mg/L), catalyst concentrations (1 g/L), contact periods (180 min), and dye volumes (25 mL). The results are displayed in Fig. 4.

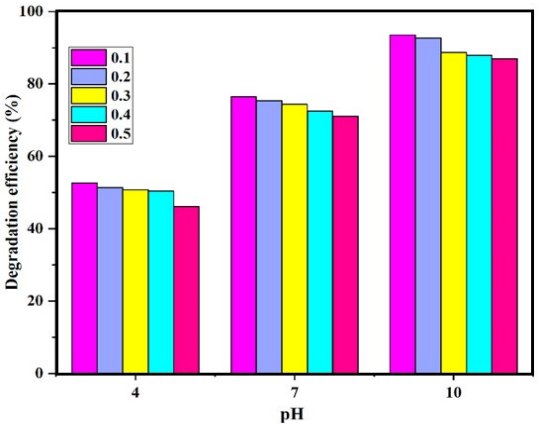

Fig. 4. Effect of pH on photodegradation of methylene blue

The MB was successfully degraded in a basic medium[26], with pH 10 showing the highest rate of degradation. Fig. 4 demonstrates that from pH 4 to pH 10, the rate of MB degradation under visible light substantially increased. The percentage of degradation increased from 52.56 to 93.54 per cent at the optimal pH for this experiment, which was 10. L. Zhang *et al.,* found that the isoelectric point (pzc) of $CdFe_2O_4$ is 5.4[27]. Because cationic dye molecules and the catalyst surface are both positively charged at an acidic pH, electrostatic repulsions occur, resulting in minimal degradation. The surface of the Mg-Cu-Cd NPs turns negative if the pzc value is surpassed. Because the cationic dye MB is directed to the negatively charged Mg-Cu-Cd ferrite species, the pollutant can be rapidly destroyed.

Effect of different acids

Investigations were conducted to determine how different acids would affect photocatalytic MB degradation. We were able to study the degradation process by varying the amounts of each acid (HCl, HNO_3, and H_2SO_4) to the various reaction mixtures ranging from 2 mL to 8 mL. The findings of research are shown in Fig. 5. The fastest degradation occurred in the solution with 0.01 mol/L of HNO_3, followed by 0.01 mol/L of H_2SO_4. The slowest rate of degradation was seen in the solution with the lowest concentration of HCl (0.01 mol/L).

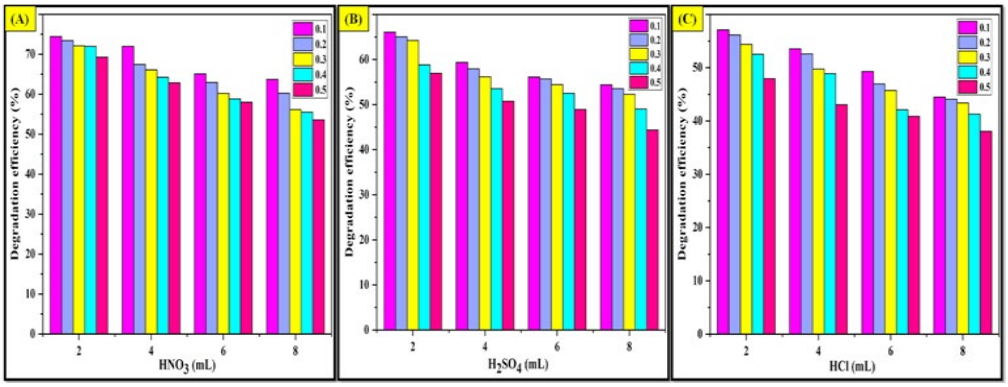

Fig. 5. Effect of (A) HNO_3, (B) H_2SO_4, and (C) HCl on photodegradation of methylene blue

These observations can be explained by the following aspects:

Ability of HNO_3 to produce a lot of hydrogen ions (H^+) in the MB dye solution. The hydrogen ions H^+ and electrons in the aqueous medium react to generate hydrogen radicals $H^\bullet$, which finally demolish the MB dye.

$$H^+ + e_{aq}^- \rightarrow H^\bullet \quad (9)$$

The degradation of MB dye is slower with H_2SO_4 than with HNO_3, as can be seen from the graph below. Sulphate (SO_4^{2-}) ions produced by H_2SO_4 scavenge radicals.

$$SO_4^{2-} + OH^\bullet \rightarrow SO_4^{\bullet-} + OH^- \quad (10)$$

In the MB solution, HCl generates Cl^- ions that largely consume $OH^\bullet$ radicles and ultimately result in a minimal breakdown of MB.

$$Cl^- + OH^\bullet \rightarrow ClOH^- \quad (11)$$

Similar observations and reasons for these acids were provided by N. Ali *et al.,*[28].

Reusability and stability

For long-term photocatalytic applications, the recycling of prepared photocatalytic materials is

required[22]. The following parameters were used in the experiments: pH 10, catalyst (25 mg), contact time (180 min), MB dye concentrations (10 mg/L), and dye volume (25 mL). Fig. 6 displays the results. After irradiation, a magnet was used to separate the catalyst from the mixture. The magnetic properties of ferrites make it simple to extract them from solutions with a magnet. To assure its stability in the current investigation, the separated photocatalyst was washed five times with water, dried, and recycled. The photocatalytic activity of the Mg-Cu-Cd nano-ferrites modestly decreases from 90.53 to 82.49 per cent after the five runs, as shown in Fig. 6.

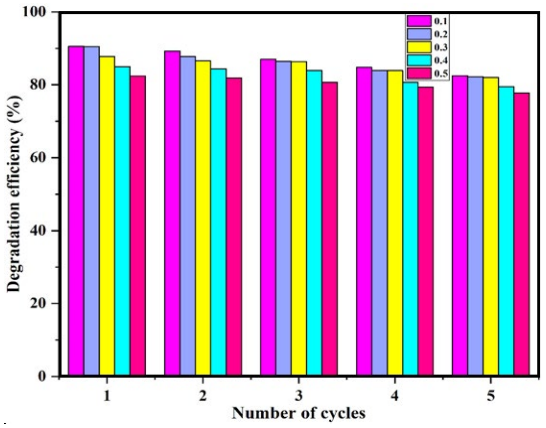

Fig. 6. Recyclability of photocatalyst for photodegradation of methylene blue

CONCLUSION

The most promising approach for degrading organic dyes is heterogeneous photocatalysis using Mg-Cu-Cd NPs. At a dosage of 1 g/L photocatalyst, it was discovered that a 10 ppm MB solution could be degraded to its maximum extent (93.54%) under visible light irradiation in 120 minutes. The $Mg_{0.1}Cu_{0.4}Cd_{0.5}Fe_2O_4$ photocatalyst shown effectiveness in MB dye degradation. The photocatalysts performed remarkably in an alkaline media (pH 10), which may have been influenced by the characteristics of the surface charge.

Declaration of competing interest

The authors affirm that they have no known financial or personal conflicts that might have looked to have influenced the research presented in this study.

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Conflict of interest

The author declare that we have no conflict of interest.

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