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ENHANCED PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN ON SPINEL FERRITE (NICKEL/ MAGNESIUM FERRITE) UNDER DIRECT SUN LIGHT

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ABSTRACT

$Ni/MgFe_2O_4$ (NMF) nanocomposite were synthesized by solution combustion method and tested its activity under visible active photocatalyst for degradation of malachite green dye (MG). The structure and morphology of ferrite catalyst were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The formation of cubic spinel structure was confirmed by powder x-ray diffraction (XRD). The morphology of the photocatalyst were shown by SEM, which have flakes like structure. The nanoparticles showed an excellent sunlight driven photocatalytic activity to malachite green in water. The efficiency of photodegradation and mineralization studies was optimized by varying parameters such as concentration of H_2O_2, pH and catalyst weight. The mineralization of MG has been confirmed by COD measurements. The results give a clear idea that NMF can be utilized as promising photocatalyst under visible light for organic pollutant degradation.

KEY WORDS: **Ferrite, Visible light driven catalyst, Photodegradation, Advanced oxidation process.**

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INTRODUCTION

The high amount of water waste expelled from the industry has lead to a situation where it has to be recycled or the renewable water resources will be contaminated.[1] Effluent treatment of industrial wastes has become a headache for environmental scientist. Recent studies had proved the increased success rate of advanced oxidation process (AOP) and had become highly efficient environmentally friendly tool than the other traditional method.[2] The commonly used photocatalytic materials are TiO_2 based composites, they have certain drawbacks like utilization of Ultra-Violet region due to large band gab (3.2 eV) which has limited its role as photocatalyst. The usage of enormous amount visible light region along with ultra violet region had triggered the development of novel photocatalyst to next level.[3] In this regard spinel ferrites are stable, cost-effective, reusable heterogeneous catalysts with narrow band gab energy which can be effectively utilized for visible region in natural sun light. Moreover its ferromagnetic nature allows using in magnetic separable performance.[4] Magnesium ferrite ($MgFe_2O_4$) is a typical photocatalyst with less electronic conductivity and fast electron hole recombination property it reduces photocatalytic efficiency under visible light region.[5] But photocatalytic effect can be further enhanced by doping or intermixing $MgFe_2O_4$ with transition metal oxide.[6] Nickel is found to possess high ferromagnetic property among the commonly used transition metal which improves the photocatalytic performance in visible region.[7] To best of our knowledge, no literatures have concentrated on Nickel/Magnesium Ferrite (Ni/$MgFe_2O_4$) as photocatalyst. Here in this work, we have synthesized Ni/$MgFe_2O_4$ (NMF) with spinel structure which improves the catalytic efficiency. Various studies have been performed on NMF catalyst which implies that it is a very highly efficient photocatalyst for the removal of malachite green under direct sunlight.

MATERIALS AND METHODS

Synthesis of Ferrite

We have synthesised the photocatalyst NMF according to our previous report.[8,9] In this study required stoichiometric ratio of nickel and magnesium nitrates Ni/$MgFe_2O_4$ (NMF) as aqueous solution. To the aqueous solution add citric acid as a combustion fuel and then the solution was sonicated by ultrasonicator bath for 5 min. The resultant solution about 30 ml was taken in a china dish and placed in muffle furnace heated upto 450 °C for 5 min and simultaneously another study has been conducted with aqueous solution which contains of magnesium and iron nitrate. The obtained foamy material was grounded into fine powder and characterized using high resolution scanning electron microscopy (HRSEM) image AU_Quanta250FEG and x-ray diffraction (XRD) was carried out on G.E Inspection Technologies, XRD 3003 TT with CuKα, λ=0.1541 nm. The specific surface areas of the samples were determined through nitrogen adsorption at -196 °C on the basis of BET equation using a micrometrics ASAP 2020 V3.00 H.

Photodegradation Experiment

The photocatalytic activity measurements were conducted by degradation of malachite green under direct sun light.[10] In a typical reaction, 50 mL of 0.8 g/L malachite green solution was added to 30 mg of NMF and placed in dark room for 30 min to attain adsorption equilibrium between dye and photocatalyst. Further degradation studies were performed under direct sunlight at given irradiation time intervals, from the suspension solution about 2mL were collected and centrifuged to separate the photocatalyst particles [9]. The centrifugation was used to monitor the colour removal of MG by determining its absorbance at λ_{max}=619 nm using Shimadzu UV-3600 Model.

RESULT AND DISCUSSION

XRD pattern of MNF catalyst

The XRD pattern of the assynthesized NMF catalyst was shown in Figure 1. The crystalline peaks at 30.22°, 35.69°, 43.03°, 53.62°, 57.21° and 62.58° are corresponding to (220), (311), (400), (422), (511) and (440) reflection planes, respectively. The peak at 35.69° corresponds to the formation of spinel and face centered cubic structure which is in good agreement with previous report.[11] No diffraction peaks of other impurities such as α-Fe_2O_3, NiO, MgO are observed.

SEM image of NMF photocatalyst

The morphology of the assynthesized NMF catalyst was shown in Figure 2, it indicates that the NMF catalyst are almost having homogenous structure and also clearly resembles a flake like structure with many smaller particles spread over the flakes. Figure 2 of HRSEM image at higher magnification which infer that the particles embedded on the surface and also identify the pores on the surface of the catalyst.

N_2 physisorption studies

The catalytic activity depends on the surface of the catalyst.[12] The surface area of catalyst was determined using the nitrogen physisorption studies. N_2 adsorption–desorption isotherm was shown in Figure 3. BET surface area ($5.45 m^2 g^{-1}$) and total pore volume ($0.017 cm^3 g^{-1}$) of the NMF catalyst were also determined. From this study, we confirm that the ferrite catalyst could act as a good photocatalyst and shows greater activity due to the effect of surface area.

Photocatalytic studies

Figure 4(a) shows the photodegradation of malachite green with different catalyst for comparative study in an aqueous solution under sun light. NMF photocatalyst removes 92% of malachite green dye within a short period of time 90 min and the result has been compared with magnesium ferrite catalyst which degrades 58% and also other catalyst ZnO (39%) this is due to effective utilization of sun light. Ni^{2+} capture the photo generated electron reduce the rate of recombination of electron-hole pair which improves the performance of photocatalytic activity.[13] The degradation studies were also done without catalyst under sunlight, it clearly illustrate that there is no degradation without catalyst (Figure 4(a)). The absorption spectrum of malachite green in presence of NMF was in shown in Figure 4(b).

The two peaks absorbed at 617 and 368 nm which corresponds to MG. The peak absorbed at 617 nm gradually decreases when increase in the irradiation time without formation of other peak which clearly proved that MG totally decompose rather than the formation of other byproduct.

Influence of H_2O_2 concentration

The degradation of MG with NMF catalyst (0.8 g) was studied at pH 4.0 by varying H_2O_2 concentration (2 to 8 ml/L). Figure 5 shows the degradation efficiency increases significantly when increase in hydrogen peroxide 2 to 4 ml/L. Further increase in H_2O_2 the degradation efficiency decrease this is due to hydroxyl radical scavenging effect of H_2O_2.[14] The reason for choosing H_2O_2 as an oxidant rather than other oxidants, it is easily decomposed and it does not produce any toxic products.

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^-$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + {}^{\bullet}OOH$$

$${}^{\bullet}OOH + {}^{\bullet}OH \longrightarrow H_2O + O_2$$

Influence of catalyst concentration

The impact of the catalyst concentration against time is illustrated in Figure 6. The results indicated that the decolorization of MG was significantly affected by the quantity of catalyst. By increasing the catalyst dosage from 0.6 to 0.8 g/L, has enhanced the dye decolorization to a greater extend. It is mainly due to the presence of high amount of catalyst increases the available active sites to wide range. However, a dosage exceeding saturation increase the turbidity it could also prevent UV from penetrating into the solution and scattering of light it reduces the hydroxyl radical production.[15] So, decolorization efficiency slightly decreased with increase in the catalyst dosage from 0.8 to 1.2 g/L.

Influence of pH

The effect of pH were studied on the decolorization of MG by varying the pH from 2–10 and the results were shown in Figure 7. The maximum degradation was achieved at pH 4 against 0.2 g/L of dye which is a good achievement than the previous report.[16] This is because at alkaline medium pH due to the accumulation of ferric oxyhydroxides the reactive surface area for formation of hydroxyl radical is reduced.[17] At very low pH dissolution of ferrite occurs which reduces the penetration of sunlight.

COD Analysis

To confirm the photocatalytic degradation of malachite green by NMF under sun light, we have carried out COD analysis the results are shown in Figure 8 which clearly infers that the MG has been completely decolorized after 90 min and 90% COD reduction was obtained. This indicates that NMF can be effectively used in removal of the pollutant from aqueous solution.

Possible mechanism of photocatalytic degradation

To explain the possible mechanism for the malachite green photodegradation over NMF can be proposed, as illustrated by Scheme.1. When ferrite was irradiated in sun light electrons get excited from the valence band to the conduction band which creates electron hole.[18]

$$Mg_{(1-x)}Ni_{(x)}Fe_2O_4 + h\nu \longrightarrow Mg_{(1-x)}Ni_{(x)}Fe_2O_4(h^+_{VB} + e^-_{CB})$$

These generated holes (h^+) react with water to form hydroxyl oxide.

$$h^+_{CB} + H_2O \longrightarrow {}^{\bullet}OH + H^+$$

Meanwhile the excited electron (e^-_{CB}) captured by Ni^{2+} reduces the rate of h^+/e^- recombination.

$$Mg_{(1-x)}Ni_{(x)}Fe_2O_4(e^-_{CB}) \longrightarrow Ni^{2+}(e^-_{CB})$$

These trapped electrons react with H_2O_2 and O_2 to generate O_2^- and hydroxyl radicals respectively.

$$Ni^{2+}(e^-_{CB}) + O_2 \longrightarrow {}^{\bullet}O_2^-$$

$$H_2O_2 + e^-_{CB} \longrightarrow OH^- + {}^{\bullet}OH$$

All the reactive species such as O_2^- and hydroxide radicals could have been involved in degrading the dye molecules

$${}^{\bullet}OH + {}^{\bullet}O_2^- + MG \longrightarrow CO_2 + H_2O$$

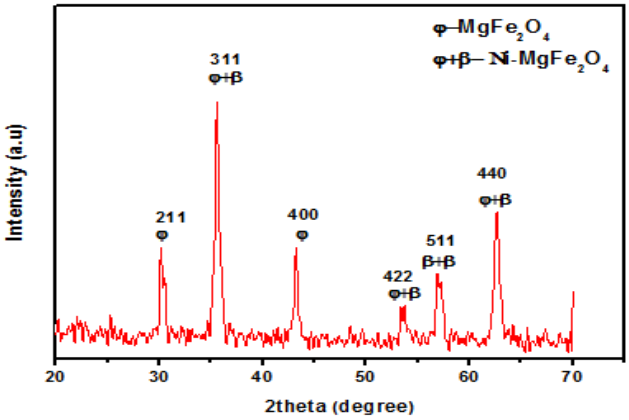


Figure 1
XRD of MNF catalyst

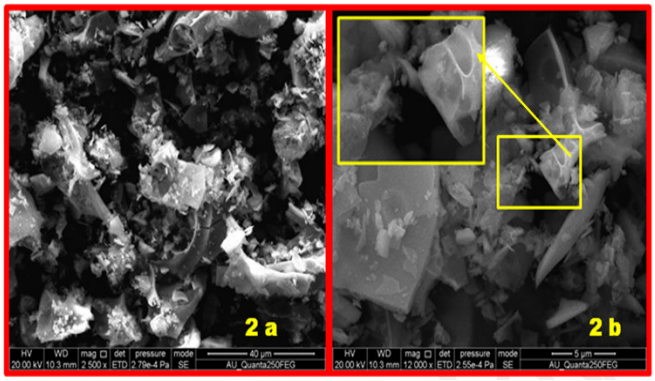


Figure 2
SEM image of assynthesized MNF catalyst

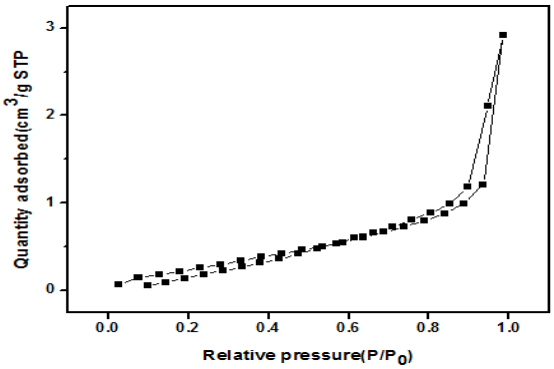


Figure 3
N_2 physisorption studies

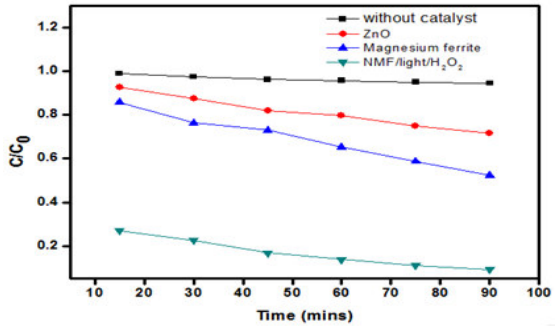


Figure 4(a)
Photocatalytic degradation profile of MG with different catalyst

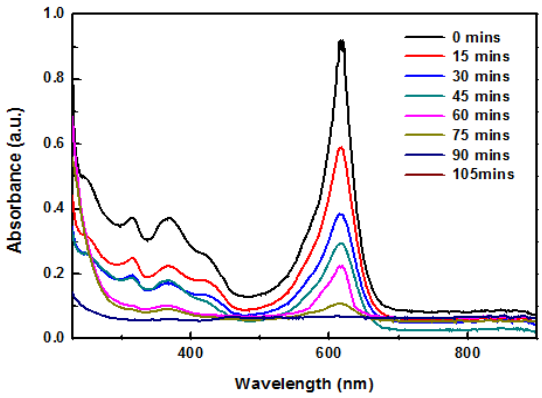


Figure 4(b)
Absorption spectra of MG at different irradiation times

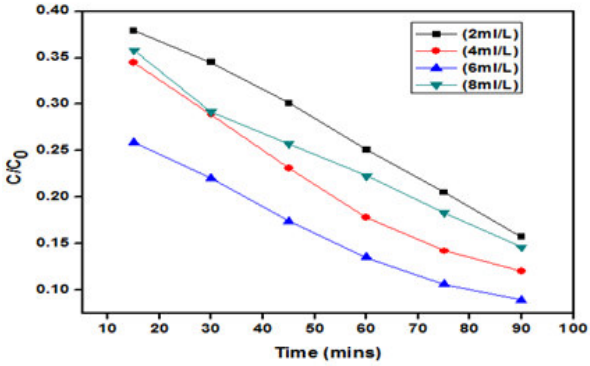


Figure 5
Effect of H_2O_2 concentrations

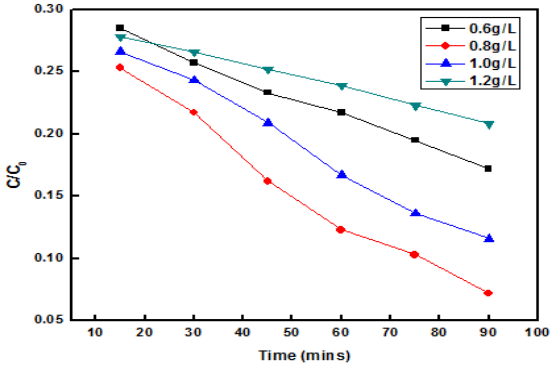


Figure 6
Effect of catalyst weight

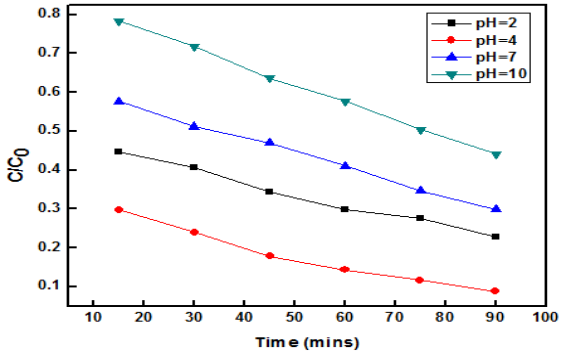


Figure 7
Effect of pH catalyst amount

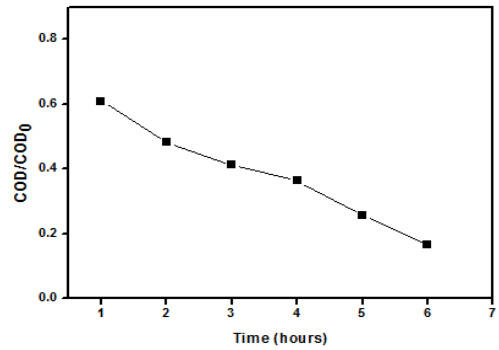


Figure 8
COD removal curve of NMF photocatalyst

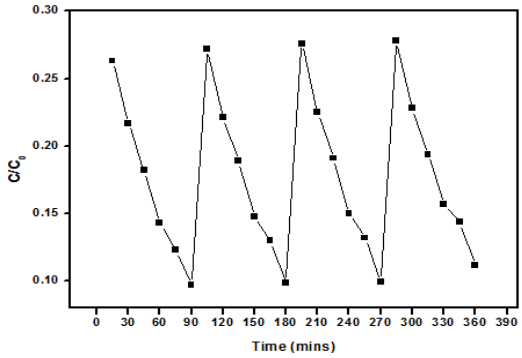
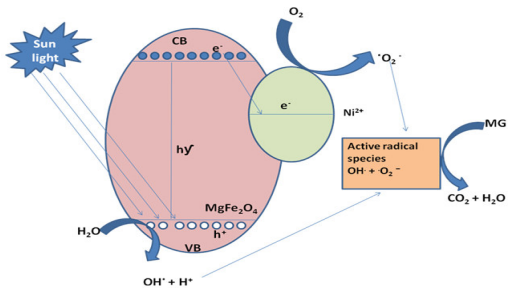


Figure 9
The reusability of nickel magnesium ferrite



Scheme 1
Mechanism of photodegradation of malachite green

Reusability

Reusability is an important tool of heterogeneous catalyst for industrial application. To evaluate the photostability of the NMF photocatalyst we carried out recycle experiment for the degradation of malachite green. The typical photodegradation efficiency of the MG in presence of ferrite for four successive cycles has been shown in Figure 9. After that the fourth cycle the efficiency of the MG degradation will slightly get reduced, this is due to the formation of intermediate products in the active sites of the catalyst. Finally the results indicate that the catalyst shows good reproducibility and high stability for longer time duration.[19]

CONCLUSION

In this present work, we have synthesized photocatalyst NMF by a simple solution combustion technique. The synthesized catalyst exhibits excellent photocatalytic activity against MG dye in presence of sunlight due to strong absorption of visible light region. We found that by varying the parameters such as H_2O_2, catalyst weight and pH. The efficiency of NMF catalyst for the removal of dye is 92.8 % at pH=4 with 0.8 g/L of NMF. This proves that NMF catalyst acts to be a very good photocatalyst for removal of organic pollutant.

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CONFLICT OF INTEREST

Conflict of interest declared none.

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