



Effective Heterogeneous Photocatalytic Degradation of Crystal Violet Dye Using Manganese Ferrite Nanoparticles

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Abstract

A novel catalyst of MnFe_2O_4 manganese ferrite nanoparticles (MFN) was synthesized by simple co-precipitation method and successfully used as an efficient heterogeneous photocatalyst following Langmuir-Hinshelwood kinetic approach for the rapid photocatalytic degradation of organic dyes such as Crystal Violet (CV). Several techniques like, Fourier transform infrared (FTIR), X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) were used to characterize the synthesized heterogeneous photocatalyst. The outcomes of the characterization established that the MFN can be competently synthesized with the size ranging between 20 to 50 nm, using sodium dodecyl sulphate (SDS) as stabilizer. UV-visible spectrophotometer was used for monitoring CV dye photodegradation. Different controlling analytical parameters such as dosage of MFN photocatalyst, concentration of CV dye, time and pH were optimized to explore the potential application of newly synthesized catalyst MFN for the maximum photodegradation of CV dye. The kinetics of reaction mechanism was also analyzed by plotting Eley-Rideal model and Langmuir-Hinshelwood model. The MFN was found to be an environmental friendly, highly economical and effective heterogeneous photocatalyst with rapid >90% efficiency to degrade the dye under investigation and easily could be regenerate with the help of magnet for successive uses.

Keywords: MnFe_2O_4 nanoparticles, Heterogeneous photocatalyst, Crystal violet degradation, UV light.

Introduction

The residues of various dye-based industries are the chief toxins to make water polluted and cruelly affect all living organism in ecosystem by resulting health hazardous substances [1-2]. Colored organic dyes generally have complex aromatic molecular structures, which make them more stable and non-biodegradable. Crystal Violet (CV), a cationic triphenylmethane (Fig. 1) is a very popular dye and has been employed in veterinary medicine as a biological stain. It is also used to provide deep violet color in textiles, cosmetics, paint and varnishes, food, pulp and paper, plastics and ink

industry [3-6]. Despite many uses, CV has been reported as having unfavourable effects. It acts as a mitotic poison, potent carcinogen and clastogene promoting tumor growth in some species of fish [7]. Hence, CV is of great concern to be effectively removed from industrial wastewaters to save the environment.

This organic dye can be decolorized by several methods including electrochemical, filtration, coagulation and adsorption, precipitation [8]. Currently, heterogeneous photocatalysis with

hydrogen peroxide (H_2O_2) in presence of light is an advanced oxidant process (AOP). AOP is a very successful technique to remove toxic contaminant from water [9-15]. In this method the H_2O_2 decompose to highly reactive hydroxyl radicals (HO^\bullet) which decolorized the organic dyes in the presence of heterogeneous photocatalyst. The ferromagnetic material, iron-based nano catalyst is the emerging application in AOP that is widely examined due to its successful use in removing a broad range of common ecological organic and inorganic pollutants [16-19]. Ferrite catalysts due to its magnetic property can be reused and regenerated effortlessly [20-21].

In the current study, a simple and direct co-precipitation method for the synthesis of manganese ferrite nanoparticles (MnFe_2O_4) and its nano-photocatalytic potential to degrade organic dye (crystal violet) was investigated. The characterization of the newly synthesized heterogeneous nano-photocatalyst MFN was made by Fourier transform infrared (FTIR), X-ray diffraction (XRD), energy dispersive X-ray (EDX) and scanning electron microscope (SEM). The percent degradation of the crystal violet dye was observed through UV-visible spectrophotometer. The effect of controlling analytical parameters such as dosage of MFN photocatalyst, concentration of CV dye, time and pH were also studied for the maximum percent degradation of CV dye. Approximately 92% degradation of organic dye within a short time period was obtained. Due to simple synthesis and heterogeneous catalytic approach the MFN can be used as a low cost, environmental friendly and effective catalyst to photodegrade the dye under investigation.

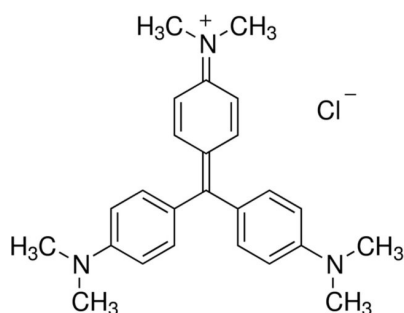


Figure 1. Structure of crystal violet

Materials and Methods

Chemicals

All chemicals used in the experiment were analytical grade and purchased from well know suppliers and used as received without any further purification. Metal precursors salts including manganese chloride (MnCl_2) and ferrous chloride (FeCl_2), sodium borohydrate (NaBH_4) and sodium dodecyl sulphate (SDS) were purchased from Sigma Aldrich. CV and H_2O_2 (30%, w/v) were obtained from Merk (Germany). Ultrapure milli-Q water was used to prepare all standard solutions. The milli-Q water was obtained from milli-Q water purification machine (Elga Co. USA). The apparatus were soaked in 10% solution of nitric acid for 24 h. Next day, the glassware were washed thoroughly with de-ionized water and dried at 110°C in an oven.

Synthesis of MFN

Manganese ferrite nanoparticles (MFN) with standard shape and size of 20-50 nm have been synthesized by simple co-precipitation method. In typical method suitable mass of precursor salts, FeCl_2 and MnCl_2 were mixed in 50 mL of 10 mmol solution of SDS to form 2:1 mole ratio solution. The clear solution is obtained after 15 minutes sonication. After that 50 mg of NaBH_4 and 10 mL of 0.1 M NaOH was added. Then solution was sonicated for 30 minutes and sample was dried on electronic hot plate at 100°C . Furthermore it was calcinated in the furnace at 600°C .

Photocatalytic degradation study of CV dye

For photodegradation studies, 100 ppm stock solution of CV was prepared in milli Q water. For each dye degradation study, different amount of stock solution of CV were taken in glass container with the diameter 8cm and treated with 1 mL of H_2O_2 (30%, w/v) and known amount (50-200 mg) of newly synthesized nano-photocatalyst MFN. The total volume of the mixture was adjusted to 100 mL with milli Q water. The reaction mixture was sonicated for 30 min in dark to obtain the adsorption-desorption equilibrium between CV dye and MFN. Finally,

the reaction dispersion was placed under 50 W Philips Mercury vapor lamp with constant stirring. The reaction mixture was irradiated by focusing the light directly onto the suspension at a distance 10 cm. At a given time period, 5 mL of clear solution was taken out from the reaction mixture, separated with help of magnet and the decreased absorbance at λ_{max} 588 nm was monitored by UV-visible spectrometer model Biochrom Libra S22. The following formula was used to calculate the percentage of dye degraded:

$$\% \text{ Degradation} = (C_0 - C/C_0) 100 = (A_0 - A / A_0) 100$$

Here C_0 is representing the initial concentration of dye, C is the variable concentrations, A_0 is the initial absorbance, and A is denoting the variable absorbance. The experiment was repeated by varying the parameters such as dosage of MFN photocatalyst, concentration of CV dye and pH. Calibration curves were constructed for CV degradation, and all experiments were performed three times to verify the reproducibility of the results.

Results and Discussion

Characterization

Initially IR spectra of synthesized nanophotocatalyst MFN was recorded by employ the ATR of a Thermo Nicolet Model Avatar 330 FT-IR spectrometer with Omnic software and prepared with ZnSe cell (Fig. 2). The FT-IR spectrum shows broad absorption band approximately on 3400 cm^{-1} and the small band at 1300 cm^{-1} is due to stretching vibration of hydrogen bonding groups and C=O stretching mode from the absorption of atmospheric moisture and CO_2 on the surface of MFN [22-23]. The absorption bands appeared in between 500 to 1000 cm^{-1} is because of the metal-oxygen bond [23].

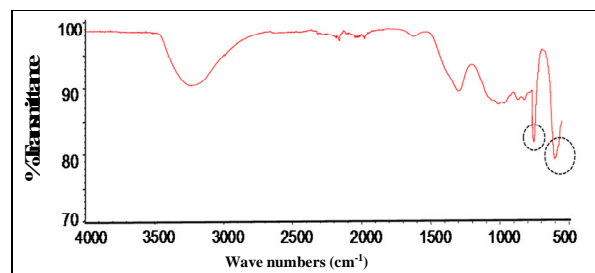


Figure 2. FTIR spectrum of manganese ferrite nanoparticles

The successful synthesis of MFN, its crystallinity and phase of particles was checked by using Advanced system (Bruker D8) with $10^\circ \text{ min}^{-1}$ scan rate and Cu $K\alpha$ irradiation ($\lambda = 1.541 \text{ \AA}$) X-ray diffraction microscopy. The diffractogram pattern shown in Fig. 3. The patterns present the bragg reflection planes (111), (311), (222), (400), (422) and (440), which verify the existence of single phase MFN with a face-centered cubic structure. All the peaks well coordinated with the reflections of the MFN in published research papers [24] and (JCPDS card No. 10-0319).

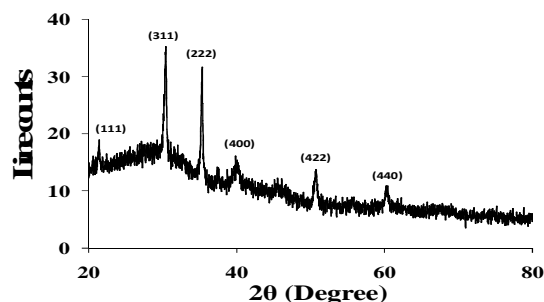


Figure 3. XRD pattern of manganese ferrite nanoparticles

The morphological features and topography of synthesized catalyst were studied by a Hitachi S2300 SEM at 25 kV accelerating voltage. The microscope was equipped with an EDX analyser to examine the elemental composition of nano catalyst. The samples were carbon coated using an Edwards Scancoat Six machine to reduce the charging effect. The Fig. 4(A-B) shows low and high resolution SEM images. The particles are homogeneously distributed in size, having semispherical smooth surface and diameter of nanoparticles obtained from SEM micrograph are about 20-50 nm with greater distribution is 35 nm.

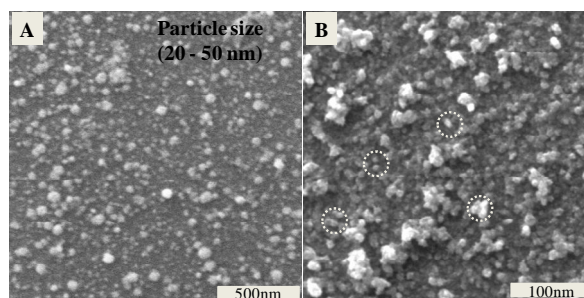


Figure 4. (A, B) SEM images of manganese ferrite nanoparticles with different magnification

The EDX spectroscopy technique further contributes the valuable information about atomic concentration of various composite on top surface layers of the solid examined. The energy dispersive X-ray spectrum of newly synthesized MFN (Fig. 5) authenticates the presence of Fe, Mn and O elements with the C substrate peak. The observed atomic percent of Fe, Mn and O are 23.21, 13.57 and 49.97, respectively.

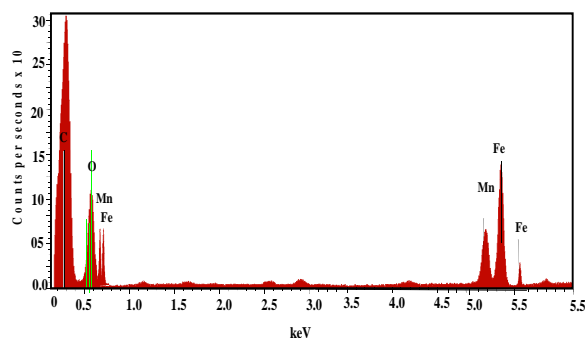


Figure 5. EDX spectrum of manganese ferrite nanoparticles

Heterogeneous catalytic application of MFN for photodegradation of CV

The catalytic activity of the MNF has been investigated for the degradation of toxic organic dye CV in aqueous solution in the presence of the H_2O_2 . In a typical process, manganese ferrite nanocatalyst was added in 100 mL aqueous solution of 10 mgL^{-1} CV and 1 mL of H_2O_2 (30%, w/v). After every 5 minute degradation of CV was monitored by recording the absorption spectra using the UV-Visible spectrophotometer (Fig. 6). Fig. 6 shows almost complete degradation of CV dye within 60 minutes time period.

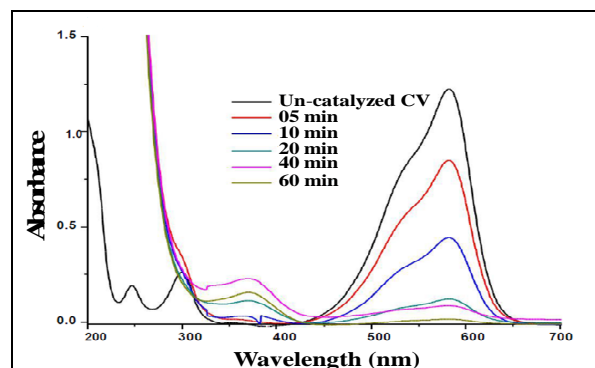


Figure 6. Effect of time for the photocatalytic degradation of CV dye

Initially to achieve the maximum degradation of CV, different parameters including concentration of CV, pH of reaction solution, reaction time and the dose of catalyst were optimized. Also, the kinetics of reaction was analyzed by plotting Eley-Rideal model and Langmuir-Hinshelwood model.

Effect of dose of heterogeneous photocatalyst

The effect of different amounts 0 to 200 mg of heterogeneous photocatalyst was investigated for the degradation of 10 mgL^{-1} CV solution with 1 mL of H_2O_2 (30%, w/v) at pH 7.5 for 120 minutes. The percentage degradation of CV dye only in presence of H_2O_2 , without catalyst is just 35% (Fig.7). It shows that in the absence of heterogeneous photocatalyst, H_2O_2 alone is not effectively work to oxidize the CV dye. Therefore, MFN as a catalyst is needed to activate H_2O_2 . On the basis of these results, following reaction mechanism for the degradation of CV is proposed.



Oxygen and free radicals are generated with the aid of MFN which further reacts with CV dye to degrade it.

Furthermore, Fig. 7 shows that CV photodegradation increases with increases the heterogeneous photocatalyst concentration upto 150 mg but decreases at 200 mg. It could attribute to the dosage of MFN increases the exposed surface area for adsorption of number of CV molecules also increases. Increased amount concentration of MFN is also effected by dimension of glass vessel. Increasing collision between molecules with increased amount of MFN may also cause to obstruct the light strike on MFN which ultimately reduces the efficiency of MFN to produce HO^\bullet . Secondly, the increase MFN concentration above the optimal range may cause the agglomeration of MFN particles which lead less active sites of MFN for degradation of CV.

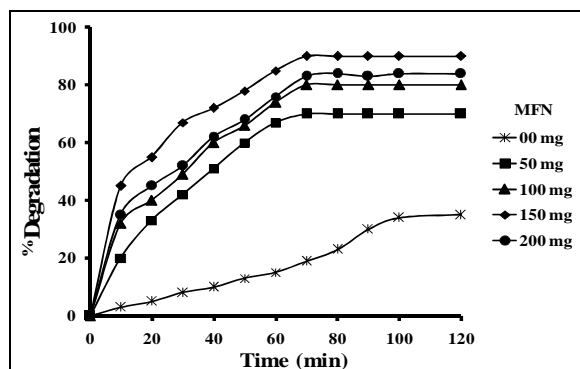


Figure 7. Effect of dose of MFN photocatalyst on the CV degradation

Effect of CV dye concentration

100 mL CV solutions of 10 to 50 mgL⁻¹ with 150 mg of MFN at pH 7.5 were used to examine the effect of initial CV dye concentration on photodegradation performance for 120 minutes. Fig. 8 shows that approximately 92% degradation for 10 to 40 mgL⁻¹ CV dye, but the percentage degradation decreased for 50 mgL⁻¹ CV solution. The decrease in degradation of CV dye can be explained by adsorption capacity of MFN catalyst, as the concentration of CV increases the active sites of MFN decreases. At higher concentration of dye more CV molecules are adsorbed at the surface of MFN catalyst which ultimately also hindered the production of HO[•] and the light incident.

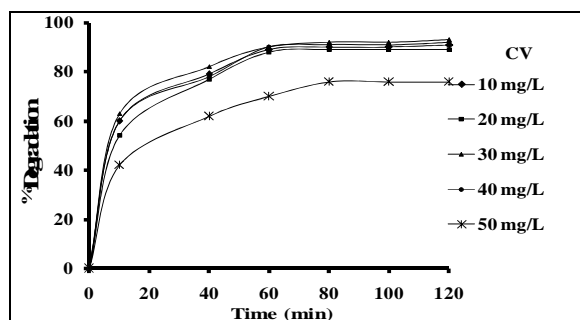


Figure 8. Effect of concentration of crystal violet on photodegradation

Effect of the pH

The pH effect on the photodegradation rate of CV dye was studied by taking 100 mL solution of 10 mgL⁻¹ CV dye with 150 mg of MFN for 120 min and the pH was varied from 3 to 9 by adding

0.1N NaOH and HCl. The percentage degradation is shown in Fig. 9. The percentage degradation was observed to increase rapidly from initial pH 3 - 5 and maintained constant on further increase in pH range from 5 to 9. This fact can be explained on the basis of adsorption behavior of MFN, usually affected by the pH of the solution. At pH < 5 the MFN exist in cationic form so they less interacted with the cationic CV dye due to electrostatic repulsion. On the other hand, at pH > 5 MFN exist in anionic form so they maximally interacted with cationic CV dye molecules due to electrostatic force of attraction. Additionally, only the CV dye molecules adsorbed at the surface of MFN catalyst can be degraded successfully. Consequently, the higher pH value can improve the adsorption capability of MFN for cationic CV dye molecules and so their catalytic potential.

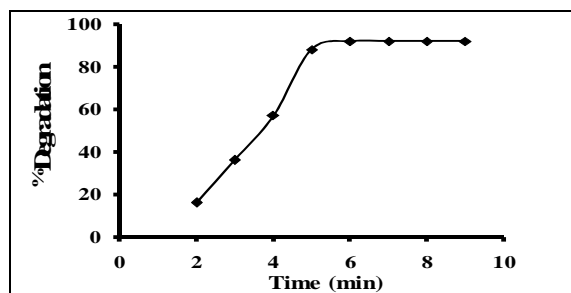


Figure 9. Effect of pH of reaction solution on photodegradation of crystal violet

Kinetics mechanism of photocatalytic degradation

Eley-Rideal model and Langmuir-Hinshelwood models were applied to determine the surface reaction mechanism. First Eley-Rideal model explains that during the course of reaction any one reactant is adsorbed at the surface of the catalyst and reacted with the other reactant present in the reaction mixture [25-26]. Then commonly applied kinetic model, Langmuir-Hinshelwood model was also studied for the heterogeneous catalytic reactions. Reaction followed Langmuir-Hinshelwood mechanism, once both reactants (CV and H₂O₂) adsorbed simultaneously onto the surface of catalyst and take a part in reaction. The rate determining step in the Langmuir-Hinshelwood mechanism is the surface reaction. Therefore, reactants adsorption at the surface of catalyst and the products dispersion from the

surface of the catalyst should be faster than the reaction mechanism itself.

In typical method for Langmuir-Hinshelwood a broad concentration range of CV (5 to 60 mgL⁻¹) was treated with a constant concentration of 1 mL of hydrogen peroxide H₂O₂ (30% w/v) (Fig. 10A). In addition, for Eley-Rideal model, different concentrations of hydrogen peroxide H₂O₂ (0.3 to 2.1 mL of 30% w/v of H₂O₂) were examined with constant concentrations of CV (10 mgL⁻¹) (Fig. 10B).

Figure 10 illustrated that the rate constant depends on the concentration of H₂O₂ and CV it was decreasing with increasing concentration of CV. Therefore, this reaction of degradation of CV followed a Langmuir-Hinshelwood mechanism. Since in the rate determining step, the reactants (hydrogen peroxide H₂O₂ and CV) adsorbed on the surface of catalyst MFN so the reaction starts between the generated free radicals HO[•] and CV and at the end of this step reaction, the product desorbs from the catalyst surface to reproduce free active sites on the catalyst surface. Moreover, the diffusion of the reactants to the surface of the catalyst MFN and adsorption-desorption equilibrium are assumed to be very fast.

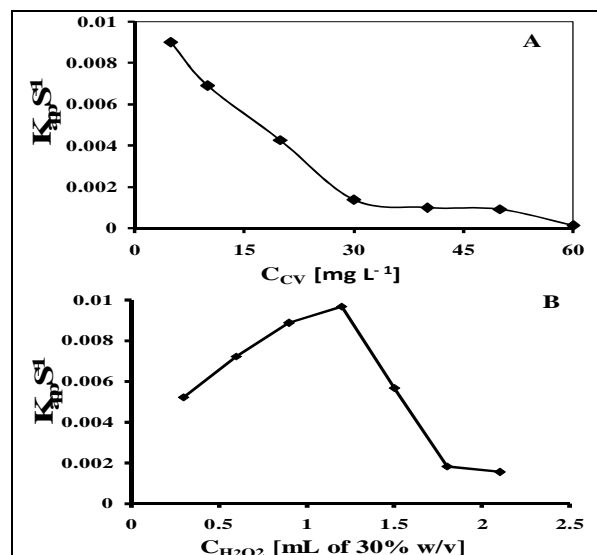


Figure 10. Kinetics mechanism of photocatalytic degradation

(a) Apparent rate constant K_{app} versus concentration of CV

(b) Apparent rate constant K_{app} versus concentration of H₂O₂

Conclusion

In the current research work, effective heterogeneous photocatalyst MFN were successfully produced by a simple co-precipitation strategy. The synthesized MFN was characterized by FTIR, XRD, EDX and SEM for their component analysis, crystalline structure, phase, elemental analysis, size and morphology. The MFN explained semi sphere-shaped geometry with an average particle size range 20 to 50 nm. The photocatalytic results reveals that MFN explain very fast photodegradation of CV dye with the degradation rate of >90% within the time period 60 min. The kinetic analysis established that the photodegradation reaction was following the Langmuir-Hinshelwood approach.

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