Photodegradation of Malachite Green Dye Over Sol-gel Synthesized Nanocrystalline α-Fe₂O₃

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ABSTRACT

Photocatalysis is a rapidly growing field for degradation of organic compounds including dyes. This paper describes the synthesis of nanocrystalline α-Fe₂O₃ by sol-gel method and its photoactivity for degradation of malachite green (MG) dye. α-Fe₂O₃ samples were synthesized at different temperatures; 450, 550 and 650ºC. At 550ºC, the α-Fe₂O₃ nanocrystals were formed with crystallite size 19.9 nm and specific surface area 177.4m²/g. The 200 mg of the catalyst sample showed high photoactivity at 100 ppm dye concentration in alkaline medium at pH 10.

Keywords: Nanocrystalline α-Fe₂O₃, Sol-gel method, Malachite green dye, Effect of pH, Photodegradation.

INTRODUCTION

Malachite green (MG) is widely used as antifungal, anti-bacterial and anti-parasitical therapeutic agent in aquacultures and animal husbandry. Also, it is widely used as a direct dye for silk, jute, paper, leather etc. [1]. MG can also be used as a saturable absorber in dye lasers, or as a pH indicator between pH 0.2–1.8. Moreover, due to its low manufacturing cost, malachite green is still used in certain countries with less restrictive laws for non-aquaculture purposes. MG was classified a Class II Health Hazard. It shows toxic effects on kidney, liver, gill and gonads of aquatic animals [2]. It causes irritation and even cancer in human when inhaled or ingested [3]. Therefore, removal of MG has become an important topic for the environmental safety.

The traditional methods such as adsorption, flocculation, osmosis etc. which have been used for removal of dyes from aqueous solution are associated with certain drawbacks. Semiconductor photocatalysis is a rapidly developing multidisciplinary research field with potential applications in mineralization of organic pollutants, disinfection of water and air, photo assisted electrolysis of water etc. The advanced oxidation processes (AOPs) have been considered as an effective technology in treating organic chemicals including dyes in wastewater [4]. AOPs include photocatalysis using semiconductors such as TiO_2, Fe_2O_3, ZnO, Al_2O_3, WO_3, etc. and UV light. Fe_2O_3 (iron oxide) is a well known *n*-type semiconductor which exists in nature in many forms in which hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_2O_3) are the most common [5]. Hematite is the most stable iron oxide under ambient condition and has significant scientific and technological importance [6]. Moreover, due to stability and interesting band gap of 2.2 eV, it is also used as a photocatalyst [7]. The present work describes the sol-gel synthesis of nanocrystalline α-Fe_2O_3 and its use in photodegradation of malachite green dye.

EXPERIMENTAL SECTION

All chemicals used are of analytical grade and used as received without further purification. To the aqueous solution of iron (III) nitrate ($Fe(NO_3)_3$ .9H₂O), con. Nitric acid was added slowly in stoichiometric amounts. The resultant solution was stirred at 70ºC for 90 min. After the 30 min of stirring, the calculated amount of stearic acid was dissolved in small quantity of deionized water and added to the ferric solution. The stirring was continued for next 30 min. Then, a certain amount of ethylene glycol was added to the above mixture and was allowed to stir. The

obtained slurry was divided in three parts and heat treated for 4 h at 450 ℃ (R-I), 550 ℃ (R-II) and 650℃ (R-III) to get the final material. This process presents the quickest and simplest way to synthesize nanocrystalline α-Fe$_2$O$_3$.

All the materials are characterized by various analytical and spectroscopic techniques. The crystalline structure of the samples was determined by an X-ray diffraction (XRD) measurement. The target used in the diffractometer is copper (λ = 1.54 Å), and the scan rate is 1.2 deg./min. The average grain size (*D*) was calculated from XRD pattern according to the Scherrer equation $D = k\lambda/\beta\cos\theta$, where, k is constant (about 0.9), λ is the wavelength (1.54 Å), β is the full width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle. A scanning electron microscope (SEM; Hitachi, S-4700) was used to analyze the morphology of the materials. The specific surface area of the powders was measured by the dynamic Brunauer-Emmet-Teller (BET) method.

The photoactivity of the prepared samples was evaluated by photodecomposition of Malachite green. For a typical photocatalytic experiment, 200 mg of the prepared catalysts was added to the 100 cm^3 of the 100 ppm malachite green aqueous solution. The solution was stirred for 30 min in dark. A Photoreactor equipped with a 400 W halogen tungsten UV lamp was used for photodegradation experiment. The decolorization of MG dye was calculated by formula;

$$\text{Decolorization} = (C_o\text{-}C)/C_o$$

Where, Co and C are the concentrations of primal and decomposed dye solution. The absorbance of was measured with a UV-vis spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of α-Fe$_2$O$_3$ nanoparticles calcined at 550℃. XRD patterns showed the presence of crystal phases of both γ-Fe$_2$O$_3$ and α-Fe$_2$O$_3$. At 550℃, the complete transformation of γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$ can be seen. These results are contradictory to those obtained by *Sahoo et al*. where they had reported the complete transformation at 850℃ [8]. The phases present and crystallite size of various samples are listed in Table 1. Average crystallite size is calculated using broadening of most intense peaks from XRD pattern and Scherrer equation. The effect of heat treatment was observed on the crystallite size and specific surface area. In the present synthetic method, 550℃ is the temperature at which the α-Fe$_2$O$_3$ particles with size 19.9 nm and specific surface area of 177.5m^2/g were obtained.

It can be seen from the surface area measurement data given in Table 1 that, as the calcination temperature increases, the surface area gets reduced onwards 550℃. However, a noticeable increase in surface area was observed as the calcination temperature increases from 450 to 550℃. This might be explained by the phase transformation from γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$ in this range of temperature.
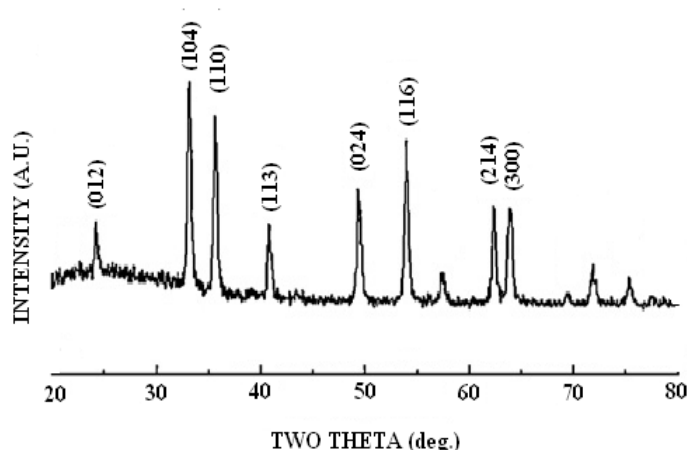

Figure 1. XRD pattern of α-Fe$_2$O$_3$ calcined at 550℃.

Table 1. Calcination temperature (ºC), phases present, crystallite size (nm) and specific surface area (m²/g) for synthesized samples

Sample	Calcination temperature (ºC)	Phases present	Crystallite size D_{XRD} (nm)	Specific surface area (m²/g)
R-I	450	γ-Fe_2O_3, α-Fe_2O_3	28.9	103.7
R-II	550	α-Fe_2O_3	19.9	177.4
R-III	650	α-Fe_2O_3	25.3	98.9

Photodegradation of malachite green dye was chosen as a probe to investigate the photocatalytic activity of synthesized α-Fe_2O_3 nanoparticles. Figure 2 shows the results of photodegradation of MG over the synthesized samples at various calcination temperatures. It can be seen that the photoactivity is reduced for the sample calcined at 650ºC and the sample calcined at 550ºC showed highest photoactivity among all the samples. It can be seen from Table 1, that with elevation in calcination temperature beyond 550ºC, the specific surface area as well as crystallite size decreases. The reduction in specific surface area reduces number of active sites available for adsorption of dye particles. The sample calcined at 450ºC showed the lowest photoactivity. This might be due to presence of a non photoactive maghemite phase (γ-Fe_2O_3) along with α-Fe_2O_3.
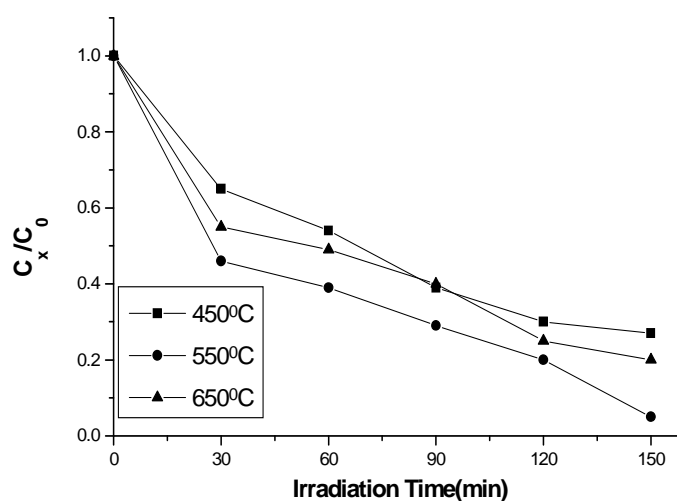

Figure 2. Photodegradation of Malachite green over α-Fe_2O_3 calcined at various temperatures
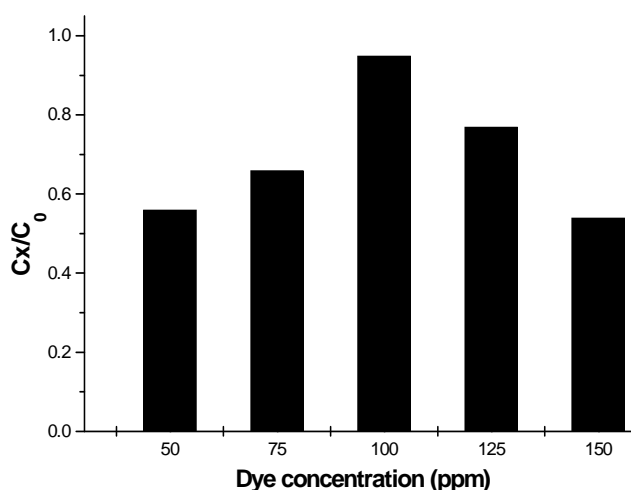
Figure 3. Effect of dye concentration on the photodegradation of MG dye over sample R-II (catalyst dosage 200 mg)

The effect of the dye concentration on photodegradation of MG dye was studied (Figure 3). The rate of photodegradation was found to increase with increase in dye concentration up to 100 ppm. This might be due to the availability of more dye molecules for degradation. At further increase in dye concentration (above 100 ppm), the

rate of photodegradation falls. An explanation to this behavior is that, at high dye concentration the path length of incident light entering the solution decreases which retards the photoformation of hydroxyl radicals (OH•) on the catalyst surface [9, 10]. Previous studies have proposed that photoformation of OH• radical at the catalyst surface is the key step in photodegradation of organic compounds [11]. Moreover, as the concentration of dye increases, instead of OH• radicals, dye molecules will occupy the catalyst surface which will retard the rate of photodegradation.
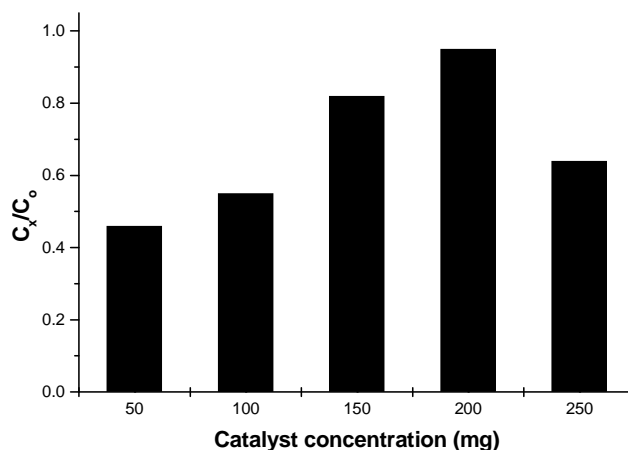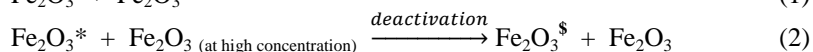

Figure 4. Effect of catalyst concentration on photodegradation of MG dye over sample R-III (dye concentration 100 ppm)
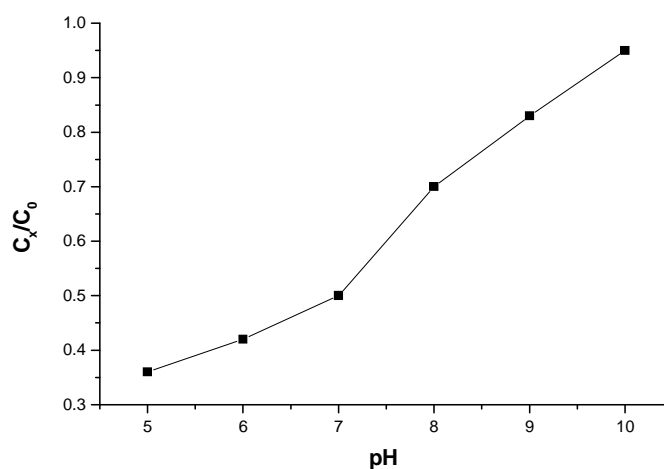
Figure 5. Effect of pH on the photodegradation of MG dye over sample R-III (catalyst concentration: 200 mg, dye concentration: 100ppm).

Addition of optimum amount of catalyst is essential in order to avoid the usage of excess catalyst. The effect of catalyst concentration on the photodegradation of MG dye under UV irradiation has been examined (Figure 4) by varying the amount of catalyst from 50-250 mg of the catalyst at 100 ppm dye concentration. The rate of photodegradation immediately increases with increase in the catalyst concentration from 50 to 200 mg. At catalyst concentration less than 150 ppm, minimum degradation was observed. This may be due to transmittance of incident UV light at low catalyst concentration [12]. The highest rate of photodegradation was observed at the catalyst concentration of 200 mg. With increasing the concentration above 200 mg, the photoactivity decreased. The reason for this decrease in rate of photodegradation may be due to the factors viz. i) decrease in number of surface active sites, ii) increase in the opacity and iii) deactivation of activated catalyst molecules at high catalyst concentration (Eq. 1and 2)

$$Fe_2O_3 \xrightarrow{h\nu} Fe_2O_3* \tag{1}$$

$$Fe_2O_3* + Fe_2O_3 \text{ (at high concentration)} \xrightarrow{deactivation} Fe_2O_3^\$ + Fe_2O_3 \tag{2}$$

where, Fe_2O_3* is the activated molecule and $Fe_2O_3^\$$ is the deactivated molecule.

Figure 5 shows the effect of pH on photodegradation of MG dye over sample R-III. The findings were revealed that as the pH values increase from 3 to 10, the rate degradation of dye increases slightly in acidic medium and immediately in alkaline medium. At pH 10, the concentration of OH^- is high at catalyst surface which increases the coulombic attraction of cationic dyes with negatively charged catalyst surface. Therefore, at high pH, the rate of photodegradation increases.

CONCLUSION

Nanocrystalline α-Fe_2O_3 catalyst with surface area 177.5 m^2/g and considerably high photoactivity was synthesized by simple sol-gel method at 550ºC. About 95% of the malachite green dye was decomposed in 150 min at catalyst concentration of 200 mg. The photoactivity of α-Fe_2O_3 can be further improved by adopting novel synthetic methods and contamination with other oxides.

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