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Green Synthesis of Fe_2O_3 Nanoparticles and its Application towards Kinetic Studies on Degradation of Methyl Orange

Yogesh. B. More[1] and Hemant. P. Narkhede[2*]

1. Department of Chemistry, M. J. College, Jalgaon- 425 001 (M. S.) **INDIA**
2. Smt. P. K. Kotecha Mahila Mahavidyalaya, Bhusawal-425201 (M. S.) **INDIA**

Email: narkhede.hemant@rediffmail.com

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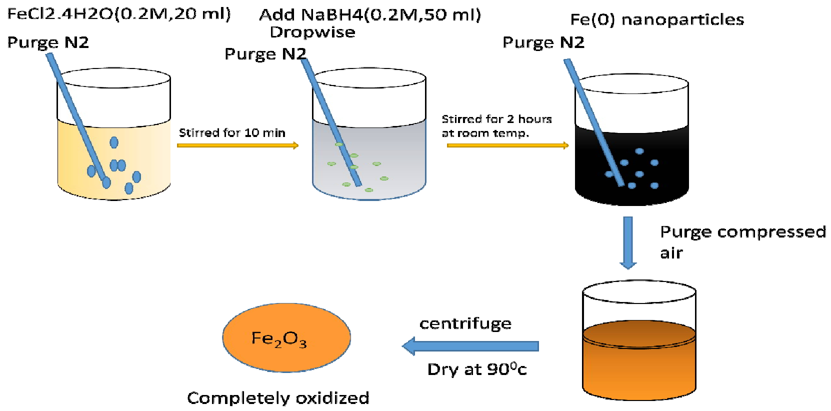
ABSTRACT

Worldwide researchers have been engaged in developing and improving a more efficient method to deal with increasingly rigorous organic dye pollution. In the present work, focus was on benign synthesis of iron oxide (Fe_2O_3) nanoparticles and environmental remediation by degradation of dyes like methyl orange found in waste water of dyes, textile, and pharmaceutical and chemical industries using synthesized iron oxide nanoparticles. These Fe_2O_3 nanoparticles were found to be acts as a prospective catalyst for the degradation of methyl orange in the presence of sodium borohydride. Rate constants for the catalyzed and uncatalyzed reactions were determined. The catalyzed reaction spectrum had shown abrupt fall in absorbance value confirming catalytic effect of Iron oxide nanoparticles. No significant change in the absorbance in case of uncatalyzed reaction was observed, indicating very slow reduction rate of methyl orange.

Graphical abstract



Schematic Representation of Synthesis of Fe_2O_3 Nanoparticles.

Keywords: Methyl orange, Iron nanoparticles, UV-Visible Spectroscopy, Rate Constant.

INTRODUCTION

In latest years, nanoparticles have been the center of attention of researchers in the field as the conversion from microparticles to nanoparticles was seen to lead to massive changes in the physical and chemical properties of a material. Recently, the application of nanomaterials in wastewater treatment has attracted significant attention due to the advantages of large surface areas and more activated functioned sites [1]. Among the different pollutant released to the environment from a variety of industrial applications are dyes which can be considered as dangerous water contaminants. They cause many health disorders such as dysfunction of the kidney, reproductive system, liver, brain, central nervous system even presents at low concentrations [2]. The field of nanoscience has blossomed over the last two decades and the importance of nanotechnology increases in areas such as computing, sensors, biomedical and many other applications. In the past decade, magnetic iron oxide micro and nanoparticles have attracted much consideration because of their distinctive magnetic properties and well-known application in different fields. Magnetic iron oxide nanoparticles are proficient, readily available and have high surface-area resulting in high catalyst loading capacity and excellent stability to heterogeneous supports for catalysts preparation [3]. Accordingly, the application of magnetic nanoparticles catalysis has become an interesting filed of research besides other advantages of nanocatalysts. A series of functionalized Fe_2O_3 nanoparticle have been employed in a range of organic transformations, showing excellent catalytic activities in oxidation [4], dihydroxylation of olefins [5] and amination [6].

Azo dyes are characterized by one or more Azo group (-N=N-) are leading class of colorants used in tattooing, cosmetics, foods and consumer products [7]. Textile industries produce large volume of colored dye effluents, which are toxic and non-biodegradable. These dyes create rigorous environmental pollution problems by releasing toxic and potential carcinogenic substances into aqueous phase [8]. In many applications, once dying is complete a large amount of dye contaminated wastewater must be disposed and because of their high solubility in water, they are transported over long distances when discharged into water. Colored waste water in the ecosystem is a source of artistic pollution, eutrophication and perturbations in aquatic life [9]. Many dyes are cleverly designed to be highly stable towards light, aerobic biodegradation, and common oxidants such as hydrogen peroxide or even hypochlorite, making chemical removal extremely difficult. The traditional physical, chemical and biological methods of waste water treatment have very little degradation effect on this type of pollutants. On the contrary, the technology at nanoscale using spectroscopy techniques, especially UV-visible spectroscopy for degradation study has proved to be effective as compared with any conventional waste water treatment technique [10].

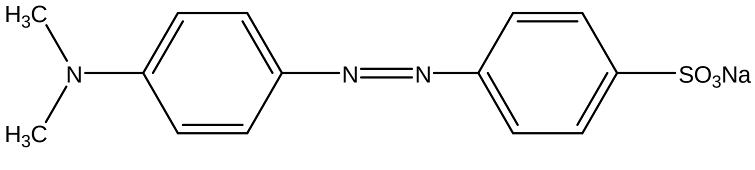


Figure 1: Molecular Structure of Methyl Orange as Azo dye

Methyl orange, being a typical Azo dye for the one Azo bonds (-N=N-) chromophores in its molecular structure is selected as a model dyeing pollutant to evaluate the catalytic activity of the iron nanoparticles. The molecular structure of methyl orange is shown in figure1. It is soluble in water to give intense orange color and used to dye wool, silk etc. and also used as stain as well as an indicator [11]. In present work, we report the degradation of methyl orange by synthesized iron nanoparticles through green approach, with help of UV–Visible spectroscopy. The rate constants for catalyzed and uncatalyzed reactions have been determined. The high catalytic behavior of iron nanoparticles is also confirmed.

MATERIALS AND METHODS

All chemicals used in the study were reagent grade without further purification. Sodium borohydride (99.99 %), sodium carboxymethyl cellulose (CMC) (MW = 90,000), sodium borohydride ($NaBH_4$), methyl orange were purchased from Aldrich, USA. All chemicals have high percentage of purity.

Synthesis of Fe_2O_3 Nanoparticles: Iron oxide (Fe_2O_3) nanoparticles were prepared by controlled oxidation of iron nanoparticles in the aqueous phase. Typically, stabilizer 0.5 g of carboxy methyl cellulose was dissolved in 100mL of deionized water followed by addition of $FeCl_2$ (0.2 M,20 mL) N_2 was purged for 15 min to promote the formation of Fe^{2+} - CMC complex. 50 mL of $NaBH_4$ (0.2 M) was then added into this precursor solution drop wise (5 mL min^{-1}) and the black iron NPs were formed immediately [12]. After $NaBH_4$ was consumed, the compressed air was bubbled into the solution at a flow rate of 40 mL min^{-1}. The solution turned brown due to the oxidation. To stop the oxidation, the particles were centrifuged and washed with ethanol twice. After washing, the particles were redistributed in ethanol and dried in the oven at 90^0C.

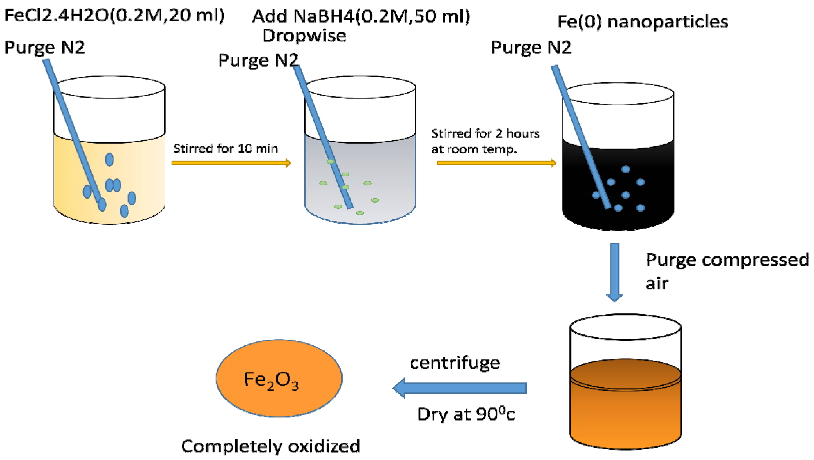


Figure 2. Schematic Representation of Synthesis of Fe_2O_3 Nanoparticles.

Degradation of Methyl Orange by Fe_2O_3NPs: A mixture containing 1.5 ml of 1 x 10^{-5} M Methyl Orange Solution and 1 ml of 0.01M sodium borohydride, 2mg of Fe_2O_3 nanoparticles was added in a quartz cuvette. Total volume of the mixture was made up to 3.2 ml by adding the required amount of double distilled water. The reaction was studied in a spectrophotometer cuvette using Shimadzu UV-1800, UV-Visible spectrophotometer at 303K temperature.

RESULTS AND DISCUSSION

FESEM Analysis: The particle size of the Fe_2O_3 particles was in the range of 50-100 nm (Fig.3). The FE-SEM image also reveals that iron nanoparticles tend to from a chainlike aggregate due to the magnetic attractive force between particles. These chain-like Fe_2O_3 Nanoparticles aggregates were also observed by others [13].

Analysis of degradation of methyl orange by sodium borohydride: The reduction of organic dyes by excess of $NaBH_4$ is widely used for evaluating the catalytic efficiency of metal nanoparticles provided their reduction reaction is thermodynamically favorable but not kinetically and their major spectral bands do not overlap with the SPR band of metal nanoparticles [14]. The aqueous solution of methyl orange shows strong absorptions UV–visible spectrum at 464 nm and 260 nm. The λmax at 464 nm is due to the absorption of azo group and 260nm is due to absorption of formed amino group. This catalytic reaction can be easily followed spectrophotometrically, since the λmax of methyl orange is well separated from the surface Plasmon absorption of Fe_2O_3 Nanoparticles.

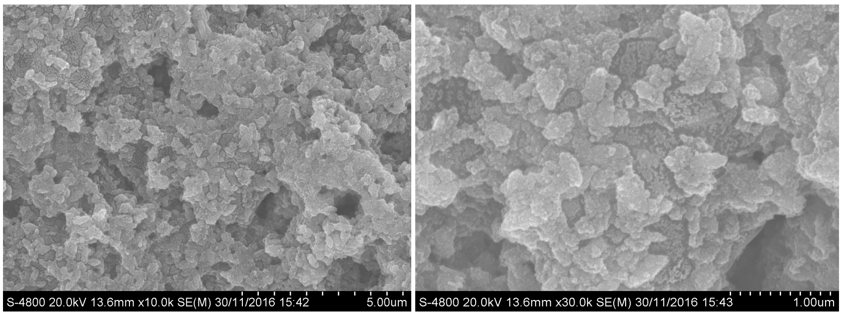


Figure 3. FESEM Images of Fe_2O_3 Nanoparticles.

The reduction of methyl orange by $NaBH_4$ in the absence of Fe_2O_3 Nanoparticles catalyst is extremely slow. This is evident from the observation that the intensity of λmax at 464 nm remains almost unchanged for several hours when a blank experiment is carried out without Fe_2O_3 nanoparticles catalyst. Thus, this reaction is not kinetically favorable in the absence of the catalyst and could not be realized only with $NaBH_4$. But the degradation reaction started immediately upon the addition of Fe_2O_3 nanoparticles as catalyst. The kinetics of Fe_2O_3 Nanoparticles catalyzed degradation of methyl orange by $NaBH_4$ was studied spectrophotometrically by monitoring the change in intensity of the absorption peak at 464 nm. As soon as the catalyst was added, the absorbance at 464 nm decreased continuously with time. The reaction was completed in 10 min as was evident from almost zero absorption at 464 nm. Electron transfer plays the crucial role in the degradation of methyl orange. The large difference in redox potential between the donor borohydride ion and the acceptor methyl orange hinders the electron transfer between them [15]. Thus, the reduction of methyl orange by $NaBH_4$ in the absence of the nanocatalyst is thermodynamically favorable and not kinetically. Fe_2O_3 Nanoparticles catalyst provides an alternative path of low activation energy for the reaction and hence reduces the kinetic barrier thereby making it thermodynamically as well as kinetically favorable [16].

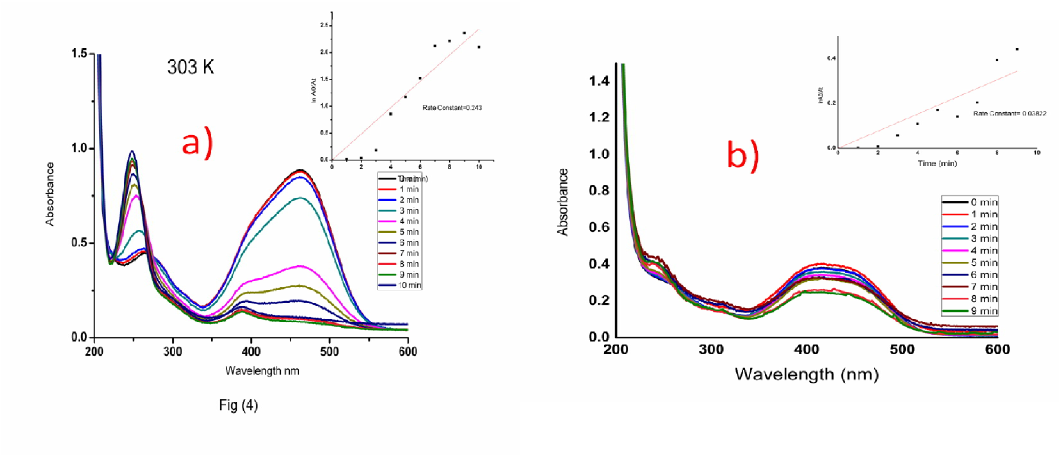


Figure 4. Pane (a) shows Decrease in Methyl Orange absorbance at 465 nm over time using Fe_2O_3 nanoparticles as catalyst in the presence of $NaBH_4$ at 303 K temperature and panel (b) shows decrease in methyl orange absorbance at 465 nm over time by uncatalyzed reaction with $NaBH_4$.

Kinetics and catalytic activity of Fe_2O_3 nanoparticles: The kinetics study was performed by using Langmuir-Hinshelwood mechanism [17]. The interaction of NaBH4 on the surface of Fe_2O_3 nanoparticles took place and which ultimately led to the liberation of hydrogen. In general, the rate law for degradation of methyl orange by $NaBH_4$ is given by Equation (1),

$$-d\,[MO]/\,dt = k\,[MO]^a\,[BH_4^-]^b \quad -(1)$$

In the Eq. (1) k is the pseudo-first order rate constant, calculated from Langmuir-Hinshelwood equation given by equation (2).

$$\ln(A_o/A_t) = kt \quad -(2)$$

n the Eq. (2), A_0 and A_t are the initial and final absorptions monitored for fixed wavelength at time t, k is the pseudo-first order rate constant for Fe_2O_3 nanoparticles. Hence, for the constant catalyst concentration, a plot of ln(A0/At) with respect to time gives straight line having slope k showing in figure 5. The rate constant of degradation on methyl orange by $NaBH_4$ in presence of Fe_2O_3 Nanoparticles at 303 K was estimated to be 0.243 min^{-1}.

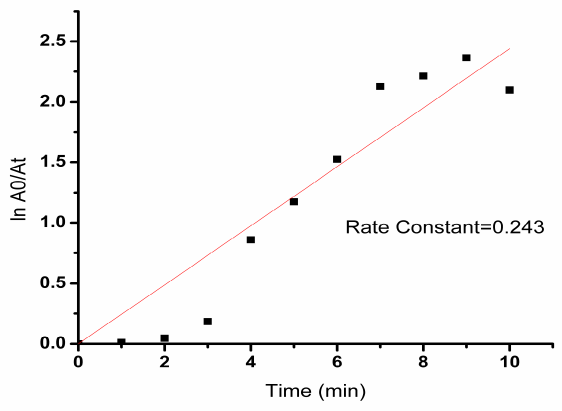


Figure 5. The Pseudo-first order reaction rate constant determined using Langmuir-Hinshelwood model by plotting $\ln(A_0/At)$ vs Time.

Table 1. shows rate constants for degradation of methyl orange.

Degradation of methyl orange	Rate Constant (k) min^{-1}
By $NaBH_4$	0.038
By $NaBH_4$ + Fe_2O_3 Nanoparticles	0.243

APPLICATION

Fe_2O_3Nps can be used as catalyst for removal of rigorous environmental pollutant dyes such as methyl orange. In the present investigation, it was observed that the Fe_2O_3Nps performed better for catalytic activity for degradation of methyl orange. The use of Fe_2O_3Nps will discover its use in various fields in years to come.

CONCLUSIONS

The catalytic activities of Fe_2O_3Nps have been determined by measuring the rate constant (k) using UV–Visible spectroscopy for the degradation of methyl orange in presence of $NaBH_4$. On the addition of Fe_2O_3NPs into methyl orange dye, rate of degradation is boost significantly indicating the improved catalytic behavior of Fe_2O_3NPs but in absence of Fe_2O_3NPs, the rate of degradation of methyl orange dye is very negligible.

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