

## SYNTHESIS OF Ag-Fe<sub>3</sub>O<sub>4</sub> NANOPARTICLES FOR DEGRADATION OF METHYLENE BLUE IN AQUEOUS MEDIUM

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**ABSTRACT.** Fe<sub>3</sub>O<sub>4</sub> known as magnetite is one of the oxides of iron which plays a major role in various fields of sciences. Fe<sub>3</sub>O<sub>4</sub> was synthesized by precipitation method using NH<sub>3</sub>.H<sub>2</sub>O, FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O as precursor materials. For synthesis of 5% Ag-Fe<sub>3</sub>O<sub>4</sub>, the green synthetic method was used for immobilization of Ag nanoparticles on Fe<sub>3</sub>O<sub>4</sub> using leaves extract of *Calotropis gigantea* plant. The synthesized Fe<sub>3</sub>O<sub>4</sub> and 5% Ag-Fe<sub>3</sub>O<sub>4</sub> were employed as catalyst in degradation of methylene blue. The photo catalytic activity of Fe<sub>3</sub>O<sub>4</sub> was remarkably enhanced by doping of Fe<sub>3</sub>O<sub>4</sub> with Ag nanoparticles. Advanced instrumental techniques including XRD, EDX, TGA and SEM were used for characterization of synthesized particles. The immobilization of Ag on Fe<sub>3</sub>O<sub>4</sub> enhanced the photo degradation of methylene blue from 40 to 72% at 40 °C which confirms that 5% Ag-Fe<sub>3</sub>O<sub>4</sub> is an active catalyst for treatment of dye contaminated water. Ag-Fe<sub>3</sub>O<sub>4</sub> exhibited almost same catalytic activity in two successive cycles.

**KEY WORDS:** Fe<sub>3</sub>O<sub>4</sub>, *Calotropis gigantea*, Degradation, Methylene blue

## INTRODUCTION

A large number of elements are known which are plentiful in occurrence and extensively used on earth. Iron, in the form of various oxides, is one of these known elements which has potential for different applications. Various types of oxides of Fe like Fe<sub>3</sub>O<sub>4</sub>, β-Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub> and FeO are known to exist. These polymorphs of iron oxide exhibit remarkable chemical and physical properties which are favorable in wide range of applications. These magnetic nanoparticles of iron oxides have many uses such as recording material, magnetic resonance imaging, magnetic drug target, environment and catalysts [1]. Fe<sub>3</sub>O<sub>4</sub> known as magnetite is one of the oxides of iron which plays a major role in various areas of chemistry, material sciences, physics and medical sciences. Fe<sub>3</sub>O<sub>4</sub> crystallizes in mixed oxidation state iron (Fe<sup>3+</sup> and Fe<sup>2+</sup>) inverse cubic spinel structure [2-4]. Fe<sub>3</sub>O<sub>4</sub> can be used in magnetic resonance imaging, in drug delivery systems, as sorbent for heavy metal, as antibacterial agents, as catalyst, as electrochemical biosensors, as shielding material in electromagnetic interference and for energy harvesting [5-9]. It has been reported that separation between valence band of Fe(4s) and O(2p) in Fe<sub>3</sub>O<sub>4</sub> is 4–6 eV (309-206 nm) [10]. Hence, Fe<sub>3</sub>O<sub>4</sub> can be confidently tested as photo catalyst for remediation of aqueous contaminants under ultra violet/visible irradiation. The photo catalytic activity of metal oxide, Fe<sub>3</sub>O<sub>4</sub>, can be further boosted up by doping it with metal atoms. In metal-metal oxide photo catalyst, the photo excited electron easily shifts to fermi level of doped metal atom via Schottky contact which prevents the de-excitation of electron and hence it improves the catalytic performance of metal oxide [11-13]. In this study we have made an attempt to develop an effective photo catalyst for degradation of methylene blue in aqueous medium.

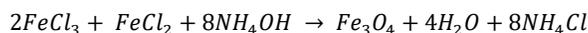
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## EXPERIMENTAL

### *Synthesis of Fe<sub>3</sub>O<sub>4</sub>*

Chemical coprecipitation method was used for synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles using NH<sub>4</sub>OH, FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O as precursor materials. A solution was prepared by suspending 16.25 g FeCl<sub>3</sub>.6H<sub>2</sub>O in 100 mL distilled water. Similarly, another solution was prepared by suspending 6.35 g FeCl<sub>2</sub>.4H<sub>2</sub>O in 100 mL distilled water. Both solutions were mixed in a glass beaker. Then, NH<sub>4</sub>OH was added dropwise to mixture formed by mixing of first two solutions of FeCl<sub>3</sub>.6H<sub>2</sub>O and FeCl<sub>2</sub>.4H<sub>2</sub>O under continuous stirring at 70 °C till pH 10. The resultant precipitate was filtered, washed and dried. The chemical reaction can be expressed as:



### *Synthesis of Ag-Fe<sub>3</sub>O<sub>4</sub>*

Green synthetic method using leaves extract of *Calotropis gigantea* was used for reduction of Ag ions in synthesis of 5% Ag-Fe<sub>3</sub>O<sub>4</sub>. For this purpose, a 50 mL plant extract obtained by boiling dried leaves (15 g) in distilled water was dropped to a suspension containing a predetermined amount of Fe<sub>3</sub>O<sub>4</sub> prepared in first step and AgNO<sub>3</sub>. After stirring the suspension for 120 min, the solid residue was filtered, washed and dried. The obtained powder consisting of 5% Ag-Fe<sub>3</sub>O<sub>4</sub> was preserved for further analyses.

### *Characterization*

Advanced instrumental techniques including XRD, EDX, TGA and SEM were used for characterization of Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> with JDX-3532 X-Ray Diffractometer (Japan), EDX JSM5910 (UK), Perkin Elmer 6300 TGA Analyzer (USA) and JSM-5910 (Japan), respectively.

### *Degradation procedure*

The photo degradation of methylene blue over Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> was conducted in a Pyrex glass beaker as batch reactor as we reported earlier [13]. For this purpose, a mixture of methylene blue solution and synthesized catalyst was stirred for 15 min in dark. Afterward, the photo reactor was irradiated with visible light in the presence of O<sub>2</sub>. A photo reacted suspension was taken periodically and analyzed with UV-visible spectrophotometer for concentration of methylene blue.

## RESULTS AND DISCUSSION

### *Characterization*

The crystalline structure of prepared nano particles of Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> were determined by powder X-rays analyses. The XRD of synthesized Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> is dominated with sharp peaks confirming the crystallinity of prepared particles (Figure 1). The XRD pattern shows diffraction peaks at 2θ 30.88, 35.47, 42.87, 54.28, 57.76 and 62.98° which correspond to (2-0-0), (3-1-1), (4-0-0), (4-2-2), (5-1-1) and (4-4-0) hkl planes of Fe<sub>3</sub>O<sub>4</sub>, respectively [3]. According to JCPDS No. 03-0863, all the diffraction peaks observed in XRD pattern can be indexed to cubic structure of Fe<sub>3</sub>O<sub>4</sub>. Wang *et al.* [14] have assigned these diffraction peaks to (1-0-4), (1-1-0), (2-0-2), (1-1-6), (1-2-2) and (1-1-4) planes of Fe<sub>2</sub>O<sub>3</sub>, respectively. On the basis of XRD pattern, it can be concluded that prepared Fe<sub>3</sub>O<sub>4</sub> is crystalline and pure in nature. In the XRD pattern of Ag-Fe<sub>3</sub>O<sub>4</sub> (Figure 1b) two additional diffraction peaks, one at 2θ 38.36 and other at

64.61°, can be observed. Furthermore, the intensity of diffraction peaks at 2θ 44.36° has been increased in XRD pattern of Ag-Fe<sub>3</sub>O<sub>4</sub>. These peaks are indexed to (3-1-1), (2-2-0) and (2-2-2) hkl planes of Ag face centered cubic unit cell. 33.5 nm was calculated as average crystallite size of synthesized material using Scherrer formula, Eq. 1, ( $\beta$ : width of peak,  $\theta$ : Bragg's angle) [3, 11, 13-15].

$$\text{Particle size} = \frac{0.89 \times 0.154}{\beta \cos \theta} \quad (1)$$

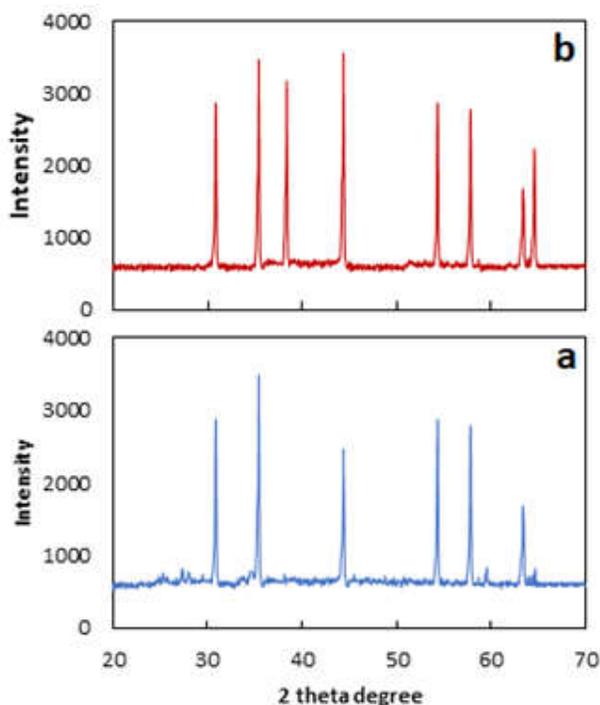


Figure 1. X-Rays analyses of Fe<sub>3</sub>O<sub>4</sub> (a) and Ag-Fe<sub>3</sub>O<sub>4</sub> (b).

The formation of Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> was further supported by EDX analyses. Two peaks were observed in EDX spectrum of Fe<sub>3</sub>O<sub>4</sub> as given in (Figure 2a) which represent the existence of iron and oxygen only with 70.76 and 29.24 weight percentage. The observed results of EDX analysis confirm the formation of Fe<sub>3</sub>O<sub>4</sub>. It is also confirmed that the synthesized material does not contain any other impurities. The results of both techniques, XRD and EDX, support each other. Similarly, in EDX spectrum of Ag-Fe<sub>3</sub>O<sub>4</sub> (Figure 2b) peaks for iron, oxygen and silver can be observed indicating the purity of prepared material.

Thermal stability of the prepared Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> was studied by thermal gravimetric analysis (TGA) (Figure 3). It is concluded that the prepared photo catalyst is stable over a wide range of temperature as no appreciable loss on weight of the sample was noted with temperature over 30-600 °C. About 8% weight loss was observed in TGA analysis of Fe<sub>3</sub>O<sub>4</sub> (Figure 3a) up to 250 °C which corresponds to evaporation of moisture. Similarly, two weight losses were observed in TGA analysis of Ag-Fe<sub>3</sub>O<sub>4</sub> (Figure 3b). First weight loss of about 12% up to 250 °C can be attributed to evaporation of adsorbed water content while the other weight loss of 47% up to 350 °C represent the degradation of unwashed plant material.

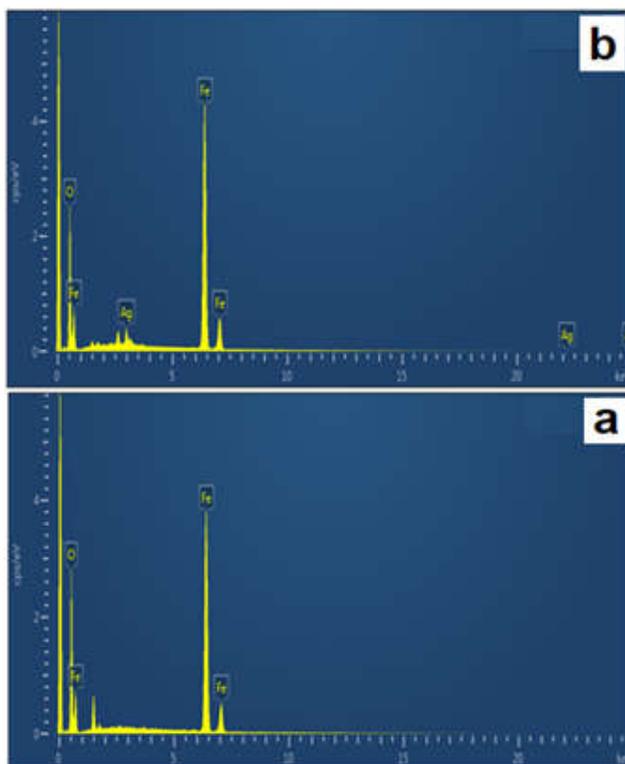


Figure 2. EDX spectrum of  $\text{Fe}_3\text{O}_4$  (a) and  $\text{Ag-Fe}_3\text{O}_4$  (b).

The shape of the prepared  $\text{Fe}_3\text{O}_4$  and  $\text{Ag-Fe}_3\text{O}_4$  NPs was investigated by SEM analyses. Considering the micrographs given in Figure 4, it is concluded that prepared particles are dispersed and non-agglomerated. Furthermore, the particles are homogeneous and spherical in shape.

#### *Catalytic activity of synthesized $\text{Fe}_3\text{O}_4$ and $\text{Ag-Fe}_3\text{O}_4$*

The catalytic activity of synthesized  $\text{Fe}_3\text{O}_4$  and  $\text{Ag-Fe}_3\text{O}_4$  was evaluated by visible light assisted photo degradation of methylene blue. The catalytic activity of prepared  $\text{Fe}_3\text{O}_4$  and  $\text{Ag-Fe}_3\text{O}_4$  on degradation of methylene blue was estimated from measurement of absorbance/optical density of reaction mixture after every 10 min. It was found that absorbance at  $\lambda = 630$  nm continuously decreased as it is treated with  $\text{Fe}_3\text{O}_4/\text{Ag-Fe}_3\text{O}_4$ . The decrease in absorbance shows the degradation of dye. The degradation of dye is expressed in a plot of  $A_t/A_0$  ( $A_t$  = absorbance of reaction mixture treated with photo catalyst for different time,  $A_0$  = absorbance of un-treated reaction mixture) against time as given in Figure 5. It is suggested that photo catalytic degradation of methylene blue dye reported here takes place in two stages. First, the degradation of dye proceeds slowly with generation of the OH radicals as suggested by slight decrease in absorbance with an induction period. The second stage of reaction is dominated with a significant decrease in absorbance. This stage represents degradation reaction where OH radicals mineralize the dye molecules [16]. The degradation of 0.0188 M (50 mL) dye solution

obtained after treatment of dye with Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> for 120 min was 41 and 73%, respectively. To confirm the photo chemical reaction, degradation procedure was repeated in the absence of irradiation under similar conditions. It was observed that treatment of dye solution in the absence of light did not cause any significant change in concentration as given in Figure 6. A small decrease in concentration of dye in the dark is due to adsorption of dye on the surface of catalyst. Therefore, the reaction mixture was stirred for 15 minutes in dark to get the adsorption equilibrium. Moreover, methylene blue was degraded in the presence of Fe<sub>3</sub>O<sub>4</sub>/Ag-Fe<sub>3</sub>O<sub>4</sub> catalyst due to OH radical. Irradiation of photo catalyst leads to formation of OH radical by a series of reactions of positive hole and photo excited electron pair ( $h^+/e^-$ ). These OH radical are active and unstable species which react with methylene blue and mineralize it. The proposed mechanism is described by following reactions [13, 17, 18]:

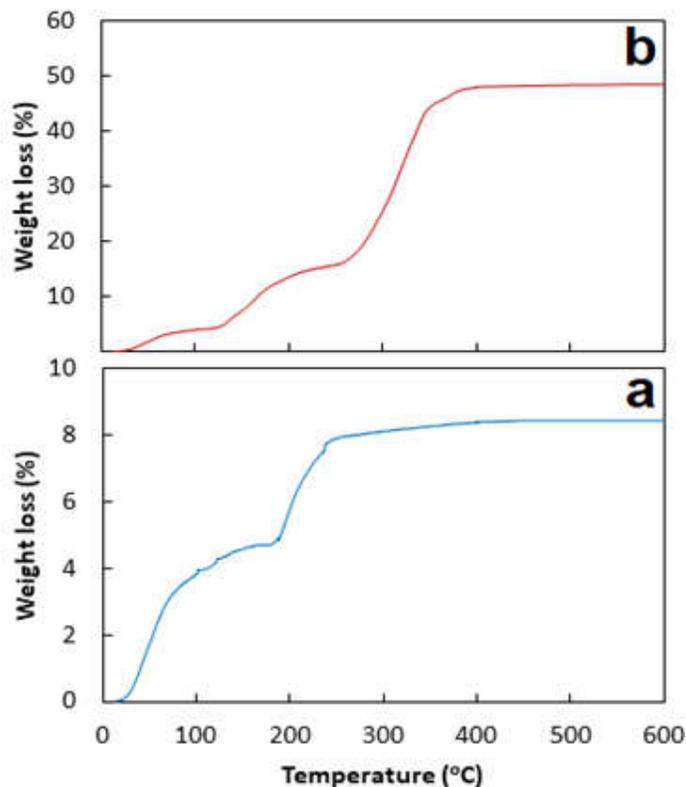
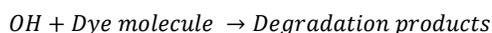
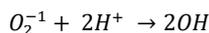
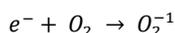
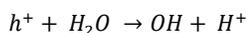
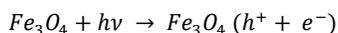


Figure 3. Thermal analysis of Fe<sub>3</sub>O<sub>4</sub> (a) and Ag-Fe<sub>3</sub>O<sub>4</sub> (b).

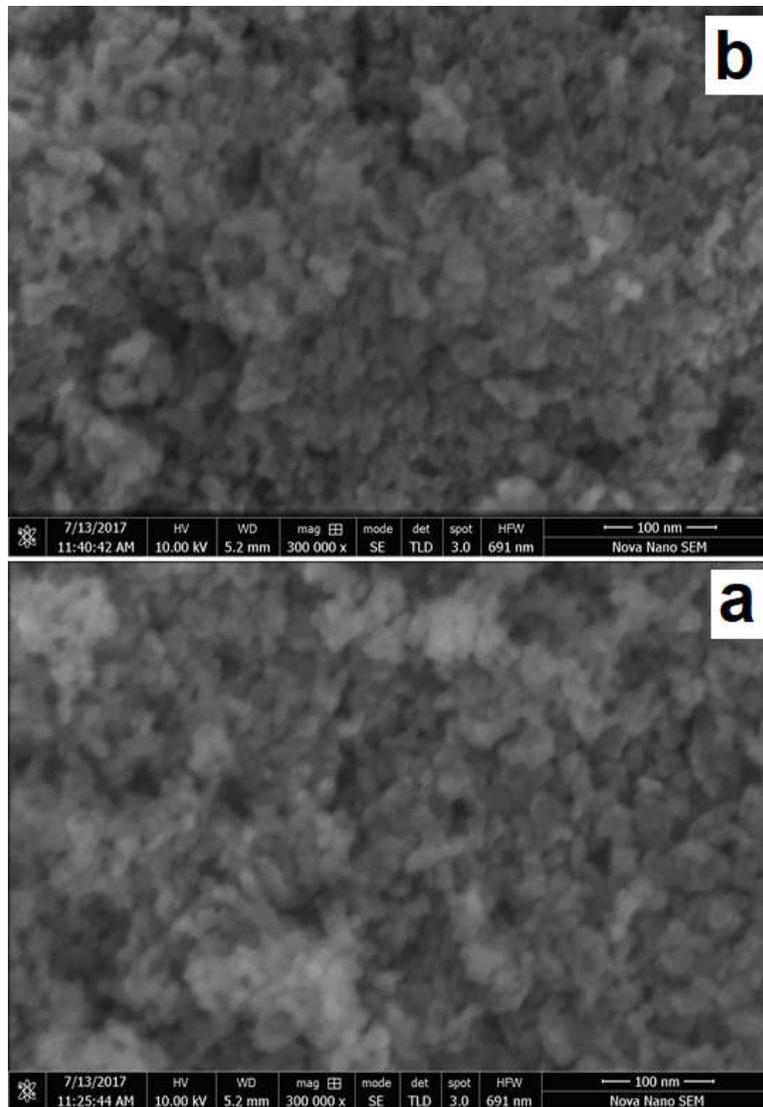


Figure 4. Scanning electron micrograph of Fe<sub>3</sub>O<sub>4</sub> (a) and Ag-Fe<sub>3</sub>O<sub>4</sub> (b).

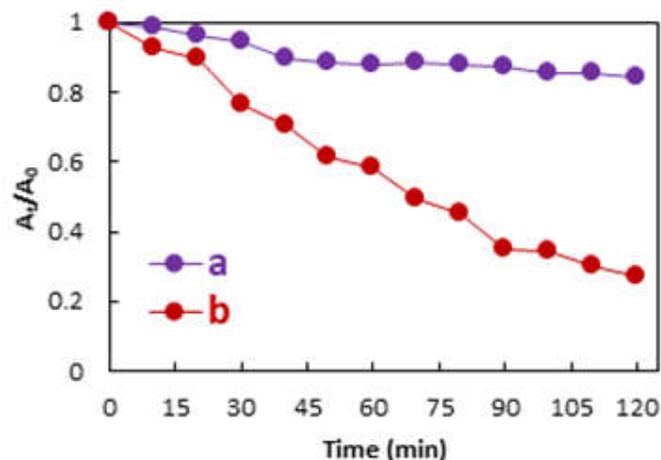


Figure 5. Decolorization of methylene blue treated with Fe<sub>3</sub>O<sub>4</sub> (a) and Ag-Fe<sub>3</sub>O<sub>4</sub> (b) under visible irradiation (50 mL of 0.0188 M of methylene blue solution was irradiated over 0.1 g of catalyst at 40 °C).

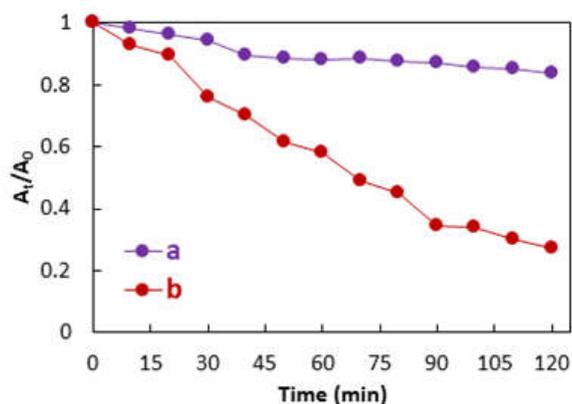


Figure 6. Decolorization of methylene blue treated with Ag-Fe<sub>3</sub>O<sub>4</sub> in dark (a) and light (b) (50 mL of 0.0188 M of methylene blue solution was treated over 0.1 g of Ag-Fe<sub>3</sub>O<sub>4</sub> at 40 °C).

Immobilization of Ag boosts up the catalytic performance of Fe<sub>3</sub>O<sub>4</sub> towards degradation of methylene blue dye. These Ag nanoparticles immobilized on Fe<sub>3</sub>O<sub>4</sub> act as electron traps resulting in decreasing the recombination of positive holes and electrons [19]. Hence the deposition of Ag on Fe<sub>3</sub>O<sub>4</sub> improves the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>. The possibility of proposed mechanism was confirmed by using isopropyl alcohol as OH radical scavenger [20].

The dependency of catalytic activity of Ag-Fe<sub>3</sub>O<sub>4</sub> on temperature was also studied. Typically, separate degradation reactions of methylene blue were conducted with 0.1 g Ag-Fe<sub>3</sub>O<sub>4</sub> and 0.0188 M (50 mL) solution of methylene blue at 30, 40 and 50 °C under visible

irradiation. The analyses of reaction mixtures after 120 min showed that about 56, 67 and 78% of dye degraded at 30, 40 and 50 °C, respectively. The degradation data obtained at different temperatures is given in Figure 7.

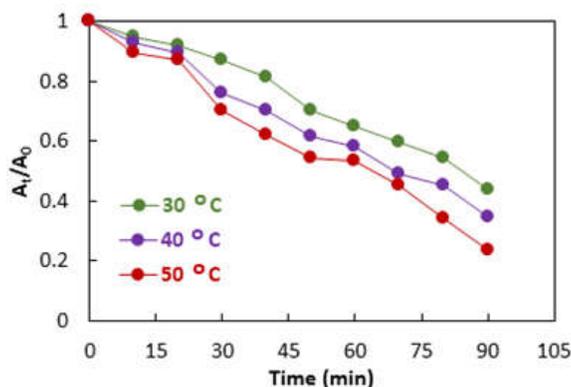


Figure 7. Ag-Fe<sub>3</sub>O<sub>4</sub> catalyzed photo degradation of methylene blue at various temperatures (50 mL of 0.0188 M of methylene blue solution was irradiated over 0.1 g of Ag-Fe<sub>3</sub>O<sub>4</sub>).

The degradation kinetics in present study is described by Eley–Rideal mechanism which suggests that the molecule of methylene blue dye reacts with adsorbed oxygen [21-26]. The proposed mechanism can be expressed mathematically in Eq. 2 as given below. Considering the constant pressure of oxygen, Eq. 2 can be written as Eq. 3, which changes to Eq. 4 on integration. The final mathematical expression, Eq. 4, is first order kinetics equation

$$-\frac{d[MO]}{dt} = k_r O_{2(ad)}[MB] \quad (2)$$

$$-\frac{d[MO]}{dt} = k[MB] \quad (3)$$

$$\ln \frac{MB_0}{MB_t} = kt \quad (4)$$

The degradation data of methylene blue at various temperatures was analyzed according to kinetic expression, Eq. 4. The results obtained by this analysis are given in Figure 8. On the basis of best straight lines in this figure (Figure 8), we conclude that photo degradation of methylene blue over Ag-Fe<sub>3</sub>O<sub>4</sub> in this study follow the pseudo-first-order kinetic model. The apparent rate constants determined from the slopes of straight lines are 0.0076, 0.0102 and 0.0131 per min at 30, 40 and 50 °C, respectively. Other researchers have also reported similar kinetics analyses [27-34]. 22.2 kJ/mol was calculated as energy of activation using the Arrhenius plot. As photo reactions are not much temperature dependent, therefore the activation energy is low.

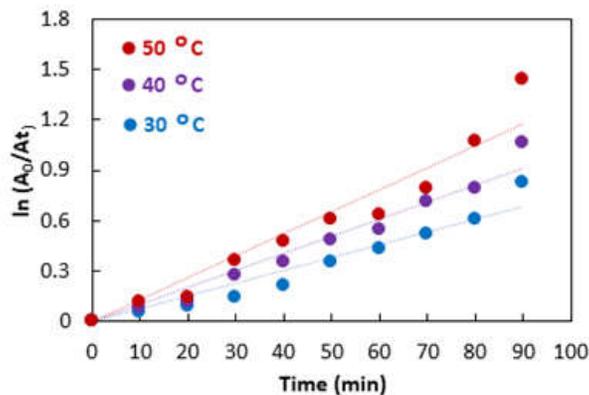


Figure 8. Kinetics analysis of Ag-Fe<sub>3</sub>O<sub>4</sub> catalyzed photo degradation of methylene blue at various temperatures.

Similarly, the dependency of catalytic activity of Ag-Fe<sub>3</sub>O<sub>4</sub> on initial concentration of dye was also studied. Typically, separate degradation reactions of methylene blue were conducted at 40 °C with 0.1 g Ag-Fe<sub>3</sub>O<sub>4</sub> using a 50 mL solution of methylene blue having concentration 0.0063, 0.0125 and 0.0188 M. The analyses of reaction mixtures after 120 min showed that about 93, 85 and 73% of the dye degraded with 0.0063, 0.0125 and 0.0188 M, respectively. The data obtained is given in Figure 9. The degradation data with various initial concentrations of methylene blue was analyzed according to Eq. 4 and the obtained results are given in Figure 10. The best straight lines suggest the pseudo first order kinetics in this study as stated earlier. The apparent rate constants determined from the slopes of straight lines are 0.0207, 0.0138 and 0.0102 per min with 0.0063, 0.0125 and 0.0188 M, respectively. High concentration of dye imparts an intense color to solution which suppress the infiltration of photon to the solution resulting a decrease in rate of reaction. Hence increase in concentration of dye decreases the rate of reaction [35, 36].

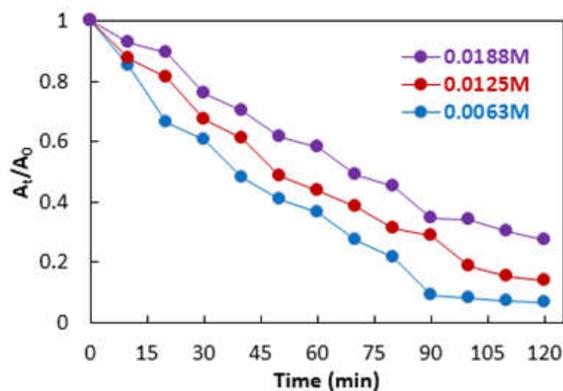


Figure 9. Ag-Fe<sub>3</sub>O<sub>4</sub> catalyzed degradation with various concentration of methylene blue (50 mL of methylene blue solution was irradiated over 0.1g of Ag-Fe<sub>3</sub>O<sub>4</sub> at 40 °C).

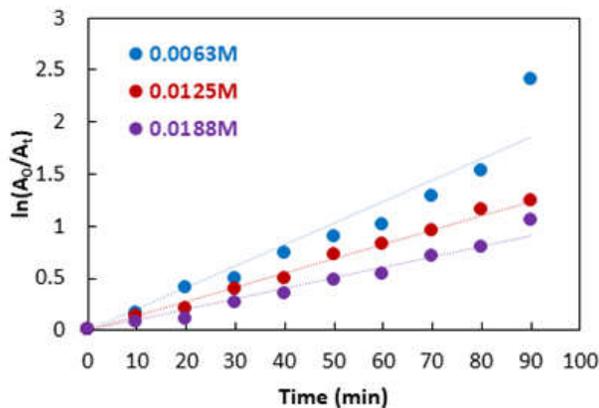


Figure 10. Kinetics analysis Ag-Fe<sub>3</sub>O<sub>4</sub> catalyzed photo degradation with various concentration of methylene blue dye.

### CONCLUSION

Ag-Fe<sub>3</sub>O<sub>4</sub> were successfully synthesized and characterized by various techniques. The synthesized Ag-Fe<sub>3</sub>O<sub>4</sub> was used as photo catalyst for degradation of methylene blue dye in aqueous medium. The immobilization of Ag nanoparticles on Fe<sub>3</sub>O<sub>4</sub> remarkable enhanced the photo catalytic activity of Fe<sub>3</sub>O<sub>4</sub> towards photo degradation of methylene blue dye. It was found that 41 and 73% of 0.0188 M degraded under visible irradiation in 120 min over Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> as photo catalysts, respectively.

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