

Photodegradation of Methylene Blue in Fe₂O₃–Oxalate Suspension Under UV Light Irradiation

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To cite this article:

A. Z. M. Mainul Islam Mazumder, Md. Sofiul Alom, Tajmeri S. A. Islam. Photodegradation of Methylene Blue in Fe₂O₃–Oxalate Suspension Under UV Light Irradiation. *American Journal of Physical Chemistry*. Vol. 7, No. 1, 2018, pp. 6-11.

doi: 10.11648/j.ajpc.20180701.12

Received: April 7, 2018; **Accepted:** April 23, 2018; **Published:** May 18, 2018

Abstract: The aim of this study was to investigate the photodegradation of organic pollutants in natural environment with co-existence of iron oxides and oxalic acid. Methylene Blue (MB) was selected as a model pollutant while Fe₂O₃ was selected as iron oxide. Commercial Fe₂O₃ was calcined at 300°C, 400°C and 500°C and was used to degrade MB in oxalate solutions of different concentration under UV radiation. Adsorption of MB on the surface of calcined Fe₂O₃ was studied and 30 minutes was required to reach the adsorption equilibrium. The effect of the initial concentration of oxalic acid, initial concentration of MB and calcined temperature of Fe₂O₃ on photodegradation of MB in the Fe₂O₃–oxalate suspension under UV light irradiation was investigated. Oxalic acid plays a very important role, no significant degradation of MB was found in absence of oxalic acid in the suspension. But excess concentration of oxalic acid decreases the degradation. Photodegradation of MB increases with increasing calcined temperature of Fe₂O₃ and decreases with increase in MB concentration. Since this process does not require the addition of hydrogen peroxide and shows good efficiency under UV irradiation, it is an economically viable method for pre-treating wastewater containing dye.

Keywords: Methylene Blue, Photodegradation, Fe₂O₃–Oxalate Suspension, Adsorption

1. Introduction

Industrial wastewater contains dyes and other organic pollutants. The increasing diversity of manufactured products increases the complexity of wastewater particularly the dye house wastewater. Dye house wastewater usually contains about 10-50 mg/L of dyes [1] which is high enough concentration to induce a remarkable coloring of the receiving water bodies where they are discharged. Methylene Blue is very common among many azo dyes used in textile industries. Methylene blue [3,9-bis dimethyl-aminophenazothionium chloride] is a cationic dye containing a heterocyclic aromatic ring. It is a well-known animal mutagen and highly toxic through oral and intravenous routes. Dryness of mouth, flushed skin, rapid pulse, blurred vision, dizziness etc. could be the consequences of inhalation of methylene blue.

Colored effluents cannot be removed efficiently by

conventional biological methods. In most of the biological methods dyes are absorbed onto biomass without being degraded [2] which is a kind of pollution transfer. But the sludge should be discarded in a sustainable manner. Recently, there has been considerable interest in the utilization of advanced oxidation processes (AOPs) to destroy organic compounds. AOPs are based on the production of hydroxyl radicals as oxidizing agents to mineralize organic chemicals. Besides ozonation [3] and fenton reaction [4] many efforts have been directed at the photodegradation of organic dyes by different UV irradiation systems in combination with H₂O₂ [5, 6], fenton [4, 5] or with photocatalyst. The photocatalytic degradation of azoic dyes in a TiO₂ suspension has been investigated by several research groups [7-10] all over the world. The two main AOP methods to destroy organic pollutants are-(i) Oxidation in the presence of H₂O₂ and light, (ii) Semiconductor mediated photodegradation.

Different forms of iron oxides and hydroxides such as

hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite, magnetite (Fe_3O_4), goethite ($\alpha\text{-FeOOH}$) etc show semiconductor properties due to their narrow band gaps (2.0-2.3 eV). These oxides and hydroxides of iron should therefore be photoactive under solar radiation [11]. A photochemical system can be constructed by combining iron oxides and polycarboxylic acids to give a photo-fenton like reaction without the addition of H_2O_2 and with much higher quantum efficiency than with $\text{Fe}(\text{OH})^{2+}$ or iron oxides alone [12]. Both iron oxides and polycarboxylic acids are abundant in nature. Oxalic acid is an active polycarboxylic acid.

Iron is the fourth most abundant element of the earth's crust (5.1 mass %). Iron oxides are kind of natural minerals and geocatalysts. Soils, lakes and rivers are major sources of iron oxides [13]. On the other hand, oxalic acid is discharged by plant roots in natural environment [14]. It can also be found as a byproduct of oil manufacturing [15, 16]. Oxalic acid shows strong chelating ability with multivalent cations. Ligand-to-metal charge transfer ability of Fe^{3+} -oxalate is very strong [17]. Hence, it can be expected that Fe^{3+} -oxalate complexes could undergo photochemical reactions in surface soil and surface water. In the past decade, several studies had reported the photochemical process of $\text{Fe}(\text{III})$ -oxalate and iron oxide-oxalate systems for degradation of organic pollutants [18-23]. For iron oxide-oxalate suspension system, $\text{Fe}(\text{III})$ -oxalate complexes includes dissolved ones and adsorbed ones [21, 22]. $\text{Fe}(\text{III})$ -oxalate complexes produces superoxides and hydroperoxyl radicals ($\text{O}_2^{\cdot-}/\text{O}_2\text{H}^{\cdot}$) when illuminated with UV and/or visible light [24].

2. Experimental

Fe_2O_3 , obtained from Merck, Germany were calcined at three different temperatures (300°C, 400°C and 500°C) to use as photocatalyst. Oxalic Acid was also obtained from Merck, Germany. All the aqueous solutions were prepared with deionized water. 1.0×10^{-3} M methylene blue (Dyester, Germany) solution was prepared in 100.0 mL volumetric flask. Required dilute solutions were prepared from this stock solution. The absorbance of each solution was measured at $\lambda_{\text{max}} = 664$ nm using UV-visible spectrophotometer (UV-1650PC, Shimadzu, Japan). The concentration range of MB used in this experiment was 0.5×10^{-5} M to 5×10^{-5} M.

In case of photodegradation of MB, the reaction mixture containing MB, oxalic acid (OA) and Fe_2O_3 were kept in dark (with continuous stirring) for 30 minutes to reach the adsorption equilibrium and then the reaction mixture was irradiated with UV light. Aliquot portion of the reaction mixture was collected at different time intervals during irradiation. It was then centrifuged (Laboratory centrifuge machine-3000 cps, Heka, BHG) and analyzed using UV-visible spectrophotometer to determine the concentration of MB. The reactor in which experiments were carried out was a beaker of inside diameter of 4.3 cm and height of 5.5 cm. The source of radiation was comprised of a lamp emitting monochromatic radiation of 254 nm. The reactor was placed on a magnetically stirred plate and the distance of the

solution surface from the lower part of the lamp was fixed at 5.0 cm by adjusting the plate height. The total system was enclosed in a wooden box called lamp house. Inside surfaces of the lamp house was covered by aluminium foil to avoid the absorption of light.

3. Results and Discussion

3.1. Adsorption of MB on Fe_2O_3 Surface

Adsorption is a prerequisite for photodegradation. MB molecules can be adsorbed on the Fe_2O_3 surface. To examine the adsorption of MB on Fe_2O_3 surface and to determine the time required to reach the adsorption equilibrium an experiment was performed by stirring MB solution in 0.5 g/L of Fe_2O_3 suspension in absence of any light source. After 30 minutes adsorption attained equilibrium condition (Figure 1). Shiva et al. found that adsorption of the MB to magnetic-modified Fe_3O_4 nanoparticles reached equilibrium after 25 min [25]. For photodegradation of MB, reaction mixtures were kept in dark (with continuous stirring) for 30 minutes before it was exposed to the light source to allow the MB to be adsorbed on the Fe_2O_3 surface.

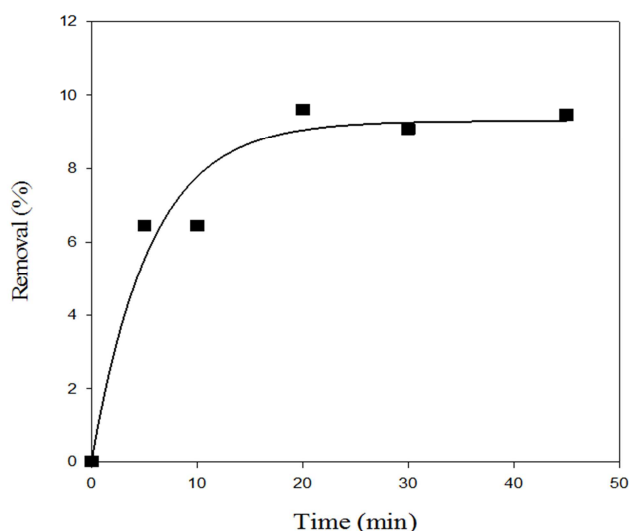


Figure 1. Percentage removal of MB by adsorption on 0.5 g/L Fe_2O_3 ; where, initial concentration of MB = 1.0×10^{-3} M and initial concentration of oxalic acid = 1.0×10^{-3} M.

3.2. Role of Oxalic Acid and UV-light on Photodegradation of MB

Several experiments were performed to examine the role of oxalic acid and light source during photodegradation of MB under different experimental conditions. When MB was irradiated with UV light in a suspension that contains 0.5 g/L Fe_2O_3 , decrease in concentration of MB was very small. But presence of oxalic acid in 0.5 g/L suspension increases the degradation of MB significantly. Again, almost no decrease in concentration of MB was occurred when the same system was kept in dark. This results support that the photodegradation of MB proceed by the formation of iron-

oxalate complex, which eventually generates. O_2^- , O_2H and. OH radicals in the solution in presence of UV light.

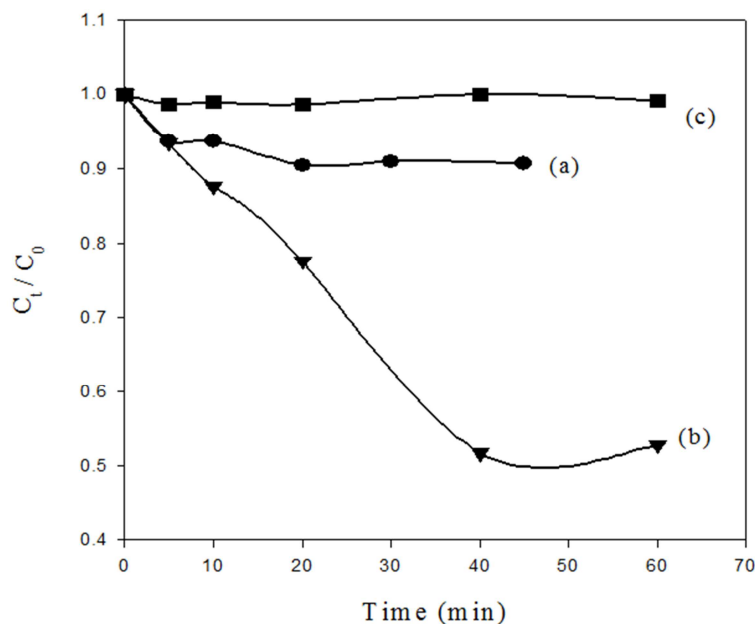


Figure 2. Photodegradation of MB ($1.0 \times 10^{-5} \text{ M}$) under different conditions (a) $0.5 \text{ g/L Fe}_2\text{O}_3 + \text{UV-light}$; (b) $0.5 \text{ g/L of Fe}_2\text{O}_3 + \text{UV light} + 1.0 \times 10^{-3} \text{ M oxalic acid}$ & (c) $0.5 \text{ g/L Fe}_2\text{O}_3 + 1.0 \times 10^{-3} \text{ M oxalic acid}$.

3.3. Effect of Initial Concentration of Oxalic Acid

A series of experiments were performed to investigate the effect of the initial concentration of oxalic acid. To perform these experiments concentration of oxalic acid was varied

from $0.1 \times 10^{-3} \text{ M}$ to $5.0 \times 10^{-3} \text{ M}$ in presence of a fixed concentration of MB ($1 \times 10^{-5} \text{ M}$) and a fixed amount of Fe_2O_3 (0.5 g/L) calcined at 400°C under UV-light irradiation (Figure 3).

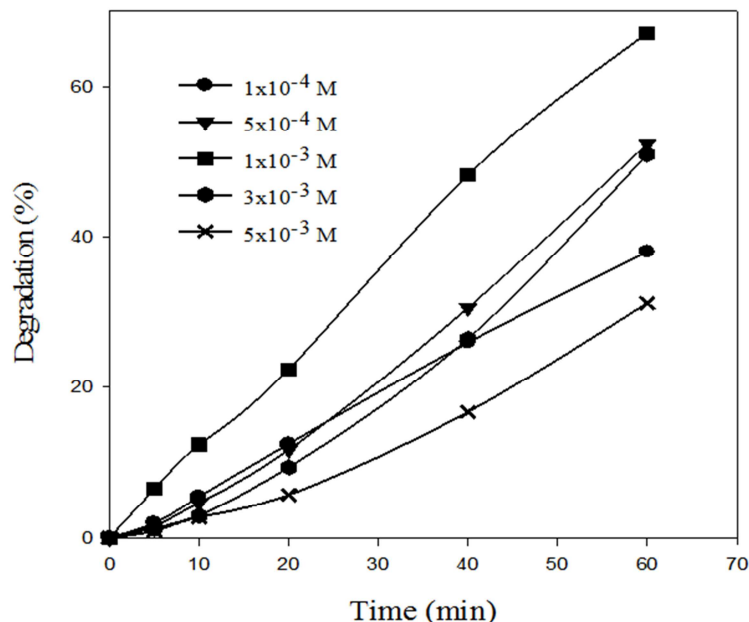


Figure 3. Percentage degradation of MB as a function of time with the variation of concentration of oxalic acid. Where initial concentration of MB = $1.0 \times 10^{-5} \text{ M}$ in $0.5 \text{ g/L Fe}_2\text{O}_3$ suspension, light source = UV light.

It was observed that with the increase of concentration of oxalic acid degradation of MB increases to a maximum and then gradually decreases. Maximum degradation of MB was found to be 67% and the optimum oxalic acid concentration has been found to be $1.0 \times 10^{-3} \text{ M}$ (Figure 4). When the concentration of oxalic acid is greater than $0.18 \times 10^{-3} \text{ M}$, in

the Fe_2O_3 -oxalate system Fe^{3+} exists mainly as $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ [19]. Photolysis of these complexes is much more efficient than other Fe^{3+} species [24] and thus, production of oxidizing intermediates is also prominent. For this reason, presence of oxalic acid is expected to greatly enhance the photodegradation of MB. The present

observation shows that photodegradation of MB has been enhanced when concentration of oxalic acid was increased from 0.1×10^{-3} M to 1.0×10^{-3} M suggesting the effective formation of complex ions $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

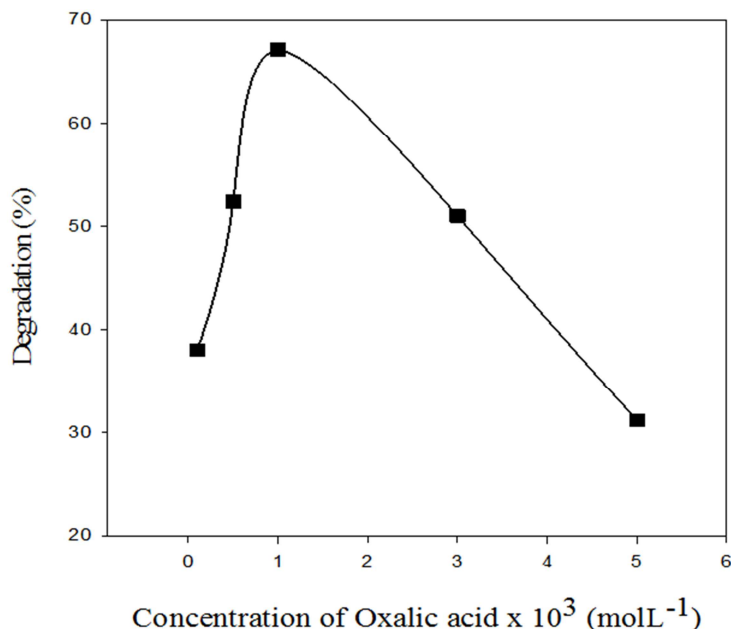
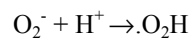
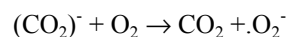
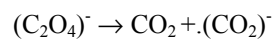
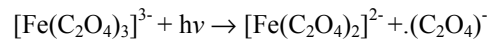
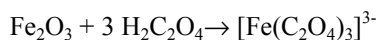


Figure 4. Percentage degradation of MB as a function of oxalic acid concentration for 60 minutes under UV irradiation. Where, initial concentration of MB was 1.0×10^{-5} M in 0.5 g/L Fe_2O_3 suspension.

When oxalic acid concentration exceeds 1.0×10^{-3} M degradation of MB starts to decrease. The reason would be that the excess oxalic acid may compete with MB in two ways, firstly for the adsorption sites on ferric oxide surface and secondly, in the reaction generating. OH radicals [23, 24]. That means oxalic acid itself can also be degraded by. OH radicals.

3.4. Effect of Initial Concentration of MB

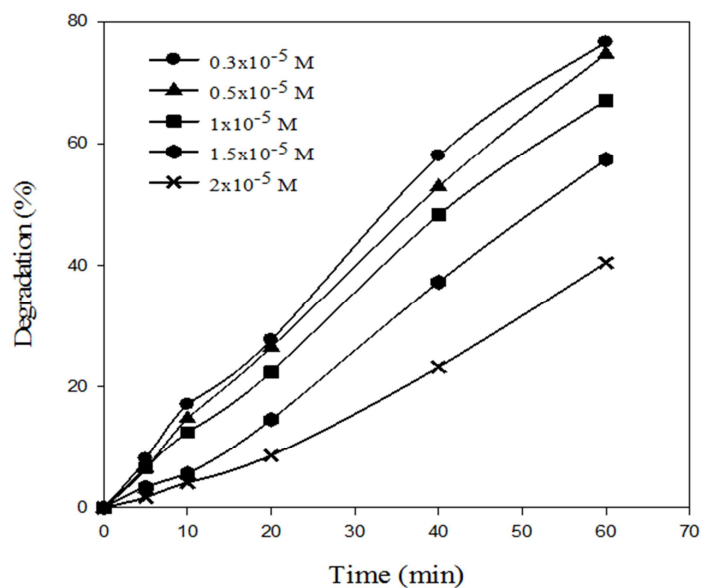


Figure 5. Percentage degradation of MB as a function of time for different initial concentrations of MB. Where, initial concentration of oxalic acid = 1.0×10^{-3} M, amount of Fe_2O_3 = 0.5 g/L and light source = UV light.

The effect of concentration of MB on its photodegradation was investigated by performing several experiments with

different initial concentration of MB ranging from 0.3×10^{-5} M to 2.0×10^{-5} M at a fixed concentration of oxalic acid (1.0×10^{-3} M) in 0.5 g/L of Fe₂O₃ calcined at 400°C under UV light illumination. It was observed that, with the increase of initial concentration of MB, degradation gradually decreases (Figure 6). Since, a definite amount of Fe(III) catalyst produces definite amount of superoxides and hydroperoxyl radicals, these radicals can only attack a proportional amount of MB species. Accordingly, as the concentration of MB increases the number of available MB species to be attacked by the radicals also increases. Hence the percentage degradation falls. Foad Kazemi et al. found the same pattern while studying photodegradation of methylene blue with a titanium dioxide/polyacrylamide photocatalyst under sunlight [26].

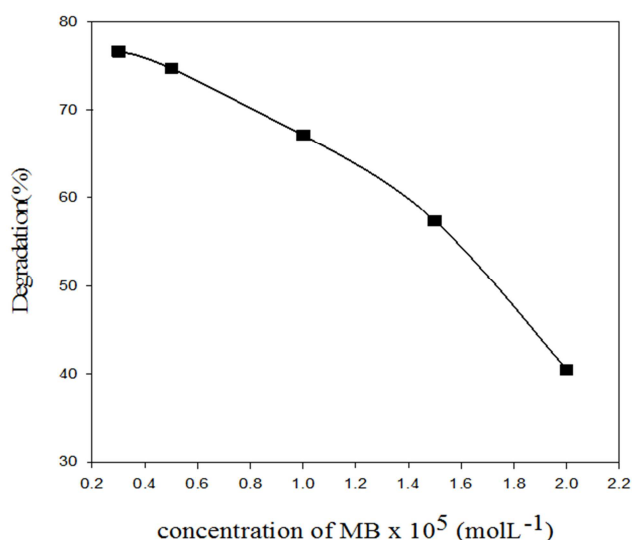
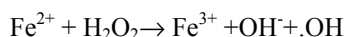
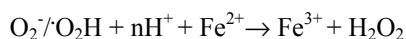
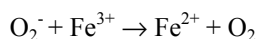


Figure 6. Percentage degradation of MB as a function of initial concentration of MB. Initial concentration of oxalic acid = 1.0×10^{-3} M, amount of Fe₂O₃ = 0.5 g/L and light source = UV light.

3.5. Effect of Calcination Temperature of Fe₂O₃

Several experiments were carried out to investigate the effect of different calcined temperatures of Fe₂O₃ (0.5g/L) with 1.0×10^{-3} M of oxalic acid and 3.0×10^{-6} M of MB (Figure 7). Photodegradation increases with increasing calcined temperatures of Fe₂O₃ (Figure 8) due to the increase in dissolution of Fe³⁺ in the suspension that favors the generation of .OH via following reactions:



The experimental results of Abdullah et al. also showed that with increasing calcination temperature the photodegradation efficiency of a catalyst increases [27].

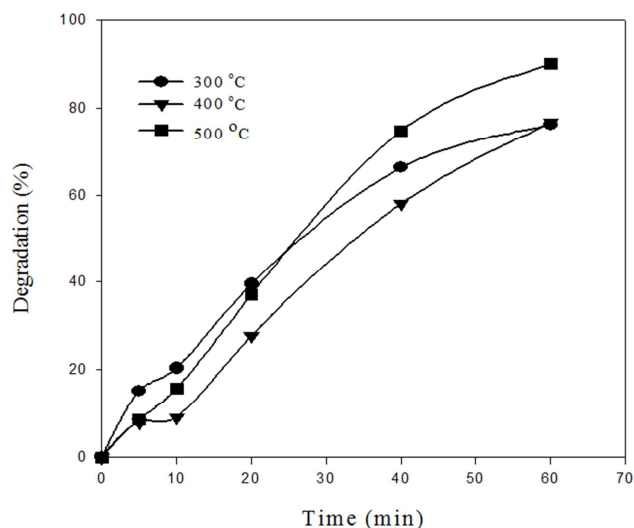


Figure 7. Percentage degradation of MB in a suspension of 0.5 g/L Fe₂O₃ as a function of time. Where, initial concentration of oxalic acid = 1.0×10^{-3} M, Initial concentration of MB = 3.0×10^{-6} M and light source = UV light.

In addition to this, increase in temperature may also enhance the process of complexation between Fe(III) and oxalic acid. Maximum degradation of MB was found to be 90% with Fe₂O₃ calcined at 500°C.

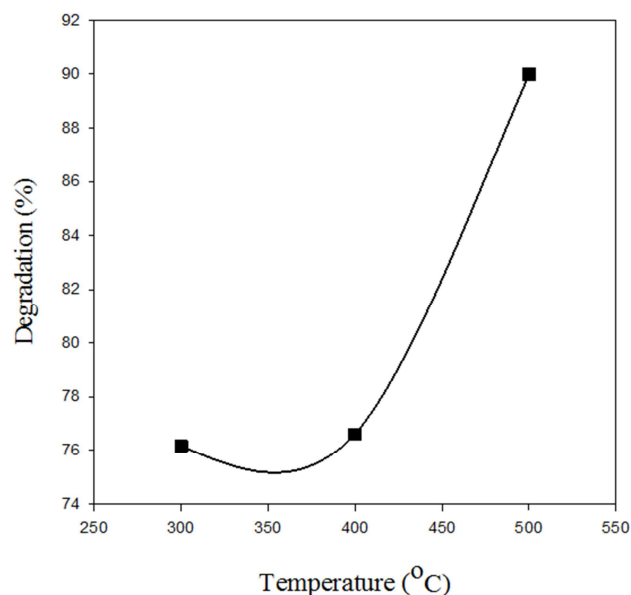


Figure 8. Percentage degradation of MB in a suspension of 0.5 g/L Fe₂O₃ as a function of calcined temperatures of Fe₂O₃. Where, initial concentration of oxalic acid = 1.0×10^{-3} M, initial concentration of MB = 3.0×10^{-6} M and light source = UV light.

4. Conclusion

The photodegradation behavior of methylene blue was investigated using calcined commercial iron oxides in oxalate solution, illuminating with UV radiation. From the investigations it can be concluded that, the combination of iron oxide, oxalic acid and UV light illumination is necessary for the photodegradation of MB. For 0.5 g/L Fe₂O₃ 30 minutes were required to reach adsorption equilibrium.

Under experimental conditions (MB concentration = 1.0×10^{-5} M and iron oxide 0.5 g/L) the optimum oxalic acid concentration is 1.0×10^{-3} M. Under experimental conditions (oxalic acid concentration = 1.0×10^{-3} M and iron oxide 0.5 g/L) with the increase of MB concentration photodegradation decreases. Fe_2O_3 calcined at higher temperature shows better photocatalytic activity. 90% of the methylene blue can be degraded when all the optimum conditions are maintained. Hence we can conclude that Fe_2O_3 in combination with oxalic acid in presence of UV light can be used as an efficient wastewater treatment procedure.

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