International Journal of Environmental Science and Development, Vol. 7, No. 5, May 2016

Photocatalytic Degradation of Methylene Blue by Magnetite+H_2O_2+UV Process

Khan M. Reza, Asw Kurny, and Fahmida Gulshan

***Abstract*—The photocatalytic degradation of Methylene Blue (MB) dye has been investigated by locally available Magnetite with H_2O_2. Parameters such as Magnetite dosage, concentration of dye pH effect, light intensity and oxidizing agent (H_2O_2) were used to study the degradation of MB. The degradation rates were found to be strongly influenced by all the above parameters. The Magnetite/ H_2O_2/UV process proved to be capable of decolorizing Methylene Blue.**

***Index Terms*—Photocatalytic degradation, magnetite, oxidizing agent, methylene blue.**

I. INTRODUCTION

At present, 100000 different types of dyes with annual production rate of 7×10^5 tons are produced. Among them textile industries consume about 36000 ton/year dye. Up to 20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [1], [2]. These synthetic dyes can cause considerable environmental pollution and are injurious to health due to their stability and toxicity. A wide range of physical methods has been developed for the removal of synthetic dyes. Conventional water treatment technologies such as physical methods mainly provide a phase transter of the contaminants from waste water to solid waste which require further treatments. On the other hand chemical oxidation methods include a family of processes that may be appropriate for treating dye pollutants.

Advanced oxidation processes are promising technologies which aim at the decolorization and mineralization of a wide range of dyes and transform dyes into biodegradable or harmless products [3]. Photo-Fenton's oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The addition of UV or artificial light to Fenton's process accelerate dye decolorization as it influences the direct formation of $^{\bullet}OH$ radicals. The major reactions in the photo-fenton process for the formation of $^{\bullet}OH$ radical include fenton reaction, photolysis of hydrogen peroxide and photoreduction of ferric ion, as shown in following equations respectively [4].

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^{-} \quad (1)$$

$$H_2O_2 + UV \rightarrow 2OH^{\bullet} \quad (2)$$

$$Fe^{3+} + UV + H_2O \rightarrow {}^{\bullet}OH + Fe^{2+} + H^{+} \quad (3)$$

Magnetite (Fe_3O_4) is a semimetal semiconductor with bandgap 0.14 eV. It contains both the Fe^{2+} and Fe^{3+} cations. So, it is expected that Magnitite will work as a photocatalyst. The possibility of using powder magnetite adsorption-Fenton oxidation as a method for removal of azo dye acid red B from water was studied by Rongcheng and Jiuhui [5]. Madrakian *et al.* [6] in their studies used magnetite nanoparticles-modified low-cost activated carbon (MMAC) as an adsorbent for the removal of the anionic and cationic dyes Congo red, reactive blue 19, thionine, janus green B, methylthymol blue and mordant Blue 29, from aqueous solutions. Utilization of magnetite nanoparticles modified with Cetyltrimethylammonium bromide (CTAB) for removal of Nyloset Yellow E-RK dye from water and waste water by magnetic force was also investigated by Dalali *et al.* [7].

The main objective of this study was to study the feasibility of Magnetite as a photocatalyst for decolorization of Methylene Blue dye. The influence of different operational parameters such as, Magnetite dosage, H_2O_2 dosage, pH, dye concentration, temperature, light source and the presence of salt which affect the efficiency of Photo-Fenton's reaction was also investigated.

II. EXPERIMENTAL

A. Methylene Blue Dye

Methylene Blue (MB) is one of the high consuming materials in the dye industry and was selected as a model organic pollutant and its degradation was studied in the presence of Magnetite under UV and solar illumination. Methylene blue (MB) is a cationic thiazine dye, basic in characteristic with the chemical name tetramethylthionine chloride. The chemical formula of MB ($C_{16}H_{18}N_3SCl$) is shown in Fig. 1. It has a characteristic deep blue colour in the oxidized state; the reduced form (leukomethylene blue-LMB) is colorless. Maximum absorbance of MB is found at 664 nm. MB has widely been used in environmental sciences to study the suitability of various materials for wastewater discoloration [8]. Several key factors such as the dye concentration, concentration of oxidizing agent (H_2O_2), light sources, pH and inorganic salts were investigated to provide a better knowledge of this photochemical reaction. Figure labels should be legible, approximately 8 to 12 point type.

B. Magnetite

Magnetite, used in our experiment was purchased from Beach Sand Materials Exploitation Centre (BSMEC). They

Manuscript received March 29, 2015; revised June 25, 2015.

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DOI: 10.7763/IJESD.2016.V7.793

seperated the sample from Cox'sbazar beach sand. XRD characteriazation of Magnetite is shown in Fig. 2.

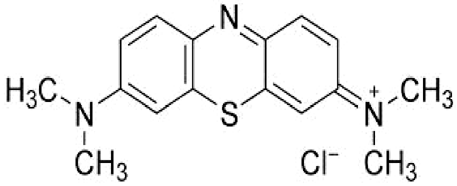

Fig. 1. Chemical formula of methylene blue.

All experiments were conducted in a thermostatic cylindrical Pyrex cell of 250 cm^3 capacity. The reaction mixture inside the cell, consisting of 100ml of organic effluent and the precise amount of Fenton reagent measured by Precision Balance (Model-PA213) purchased from Ohaus Corp. (USA), was continuously stirred with a magnetic bar with the help of Hot plates and Stirrer (HS-18) purchased from HumanLab Instrument Company, Korea. The experiments were conducted at three different temperatures 25^o C, 45^o C, 65^o C and 85^o C. UV and the Solar light were used as light source.

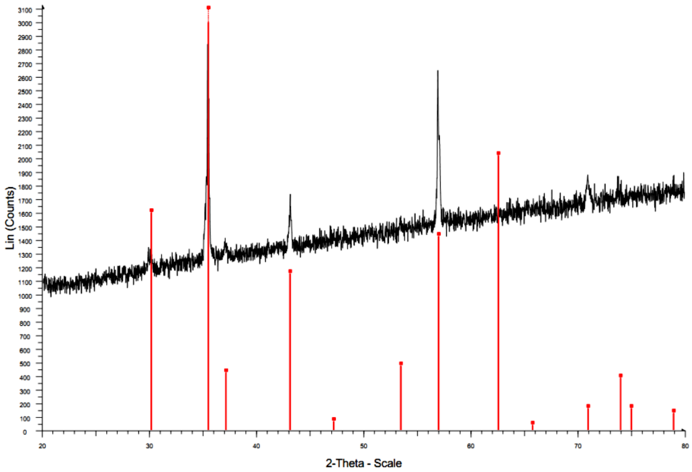

Fig. 2. XRD characterization of magnetite.

Absorption is measured UV spectroscopy. A sample of 3 ml in every 5 minute interval was taken to measure the absorption. In all experiments reaction mixture was stirred in dark for 20 minutes before exposed to light. Initial pH is adjusted by Oxalic acid dehydrate purified and sodium hydroxide pellets purified purchased from Merck Specialties Pvt. Ltd. (Mumbai, India).

Magnetite was purchased from BSMEC. Methylene Blue and Hydrogen Peroxide (30%) are purchased from Qualikems Fine Chemicals Pvt. Ltd. (Delhi, India) and Merck KGaA (Germany) respectively. Rest of the chemicals such as Sodium Carbonate (anhydrous pure), Sodium Sulfite, Sodium Bicarbonate are purchased from Merck Specialties Pvt. Ltd. (Mumbai, India). Lastly Sodium Nitrate and Copper Sulfate both are collected from Guangdong Guanghua Chemical Factory Co. Ltd. (China).

III. RESULTS AND DISCUSSION

Photo-decomposition of MB by Photo-Fenton reaction is controlled by several parameters. Catalyst dosage, dye concentration, amount of H_2O_2, light intensity, temperature and pH are the major parameters that affect the dye removal. It was also observed that the presence of inorganic salts also effect the degradation. To see the effects of different parameters on dye decolorization, several experiments are conducted and discussed below.

A. Effect of Magnetite Dosage

Magnetite produces the hydroxyl radical which is used to break the bond of the MB. It is expected that more the amount of magnetite catalyst more will be the hydroxyl radical and the degradation will increase as well. But in practical it is found to be different and there is an optimum value. To measure the optimum value we did several experiments varying the magnetite dosage keeping other parameter constant. In our experiment magnetite is varied from 0 gm/L to 10 gm/L.

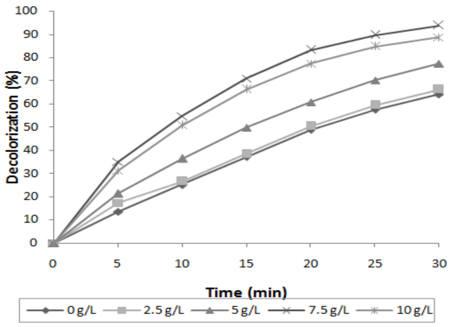

Fig. 3. Influence of catalyst concentration on the degradation of MB. Experimental conditions: [MB] = 0.05 mM; H_2O_2 = 20 ml/L; pH 4.0; temperature = (25 ±2) °C; reaction time = 30 min; UV illumination.

From the experimental results, (shown in Fig. 3) it can be seen that decolorization of MB distinctly increased with the increasing amount of magnetite. The lesser decolorization capacity of Fe^{2+} at lower concentration might be attributed due to the less hydroxyl radical production. Addition of catalyst from 2.5 gm/L to 7.5 gm/L resulted in an increase of color removal from 66.26 to 88.85% at 30 min. This is because more $OH^{\bullet}$ radicals are produced with the increase of Fe^{2+} according to Equation below [9], [10].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

The concentrations higher than 7.5 gm/L resulted in decrease in decolorization (%) of dye under study and in agreement with the work of kusic *et al*. [11] and Bouasla et al. [12].

This is because excess of Fe^{2+} ions, produced by the photo reduction of Fe^{3+} ions in the solution, compete for the hydroxyl radicals along with the dye molecules and act as hydroxyl radical scavenger [13], [14].

Fe^{2+} also has a catalytic decomposition effect on H_2O_2. When Fe^{2+} concentration is increased, the catalytic effect also increases accordingly and when its concentration was higher, a great amount of Fe^{3+} was produced.

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-}$$

Fe^{3+} has a strong absorption band causes higher absorbance, undergoes a reaction with hydroxyl ions to form $Fe\,(OH)^{2+}$, which decreases decolourization [15] according to subsequent equation:

$$Fe^{3+} + {}^{-}OH \rightarrow Fe\,(OH)^{2+}$$

Moreover, Fe^{3+} ion could react with H_2O_2 to form hydroperoxyl radicals which is signigicantly less oxidizing agent than $^{\bullet}OH$ [16].

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^{+}$$

$$Fe - OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+}$$

B. *Effect of Oxidizing Agent (H_2O_2)*

H_2O_2 plays an important role as a source of $^{\bullet}OH$ eneration in Fenton reaction. In order to investigate the effect of H_2O_2 concentration on the degradation kinetics, different quantity of H_2O_2 is added to the solution remaining other parameters constant. The results in Fig. 4 show that by increasing concentration from 0 ml to 2 ml, decolourization increased from 18.58 to 66.27% after 30 minutes. It might be due to the increasing of $^{\bullet}OH$ as the addition of H_2O_2 [17].

$$H_2O_2 + h\upsilon \rightarrow 2^{\bullet}OH$$

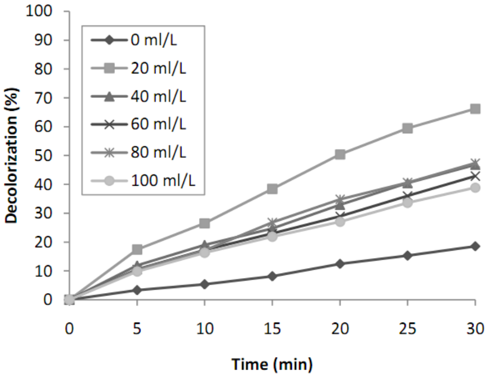

Fig. 4. Effect of the concentration of H_2O_2 on the degradation of MB. Experimental conditions: [MB] = 0.05 mM; Magnetite = 2.5 gm/L; pH 4.0; temperature = (25 ±2) °C; reaction time = 30 min; UV illumination.

Further increase in H_2O_2 concentration from 2 ml to 10 ml decreased the color removal from 66.27 to 39% after 30 minute. This phenomenon is also observed from the curve. This may be explained by the fact that the very reactive $^{\bullet}OH$ radical could be consumed by H_2O_2 and results in the generation of less reactive $^{\bullet}OOH$ radical which has much lower oxidation capabilities than $^{\bullet}OH$ and can be expressed by the following reaction [18].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$$

$^{\bullet}OOH$ also consume $HO^{\bullet}$ and produce H_2O and O_2 [12].

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$$

In addition recombination of $^{\bullet}OH$ also contributed for declining of decolourization.

$$HO^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

Adverse effect on Fenton's reaction at higher concentration of H_2O_2 is also reported by other researchers [17], [19].

C. *Effect of Dye Concentration*

Dyes may act as filters limiting the penetration of light through the solution. Therefore, the effect of the dye concentration on decolorization was studied. Fig. 5 shows the effect of different concentrations (0.01, 0.03, 0.05, 0.07 and .1 mM) of MB dye on the decolorization, remaining other parameters constant. The resultant curves show us that it follow the first order kinetics. The results indicate that while the decolorization was high at lower concentration (.01 mM), a significant decrease in the decolorization resulted at higher concentration (0.1 mM) of dye. This is in agreement with other researchers [12], [17].

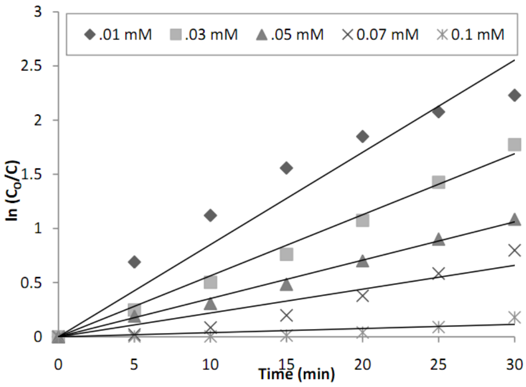

Fig. 5. The pseudo-first-order decolorization rate of MB at different dye concentration. Experimental conditions: H_2O_2 =20 ml/L; Magnetite = 2.5 g/L; pH 4.0; temperature = (25 ±2) °C; reaction time = 30 min; UV illumination.

The presumed reason is that when the initial concentration of the dye increases, the hydroxyl radical concentration remains steady for all dyes molecules and hence the removal rate fall [9], [20]. Dye molecules need to be adsorbed onto the catalyst first, and then they come in contact with active iron ion sites on the catalyst. So an increase in dye concentration resulted in competition for active sites, causing a slight decrease in the proportion of color deduction. In addition, high dye concentration also reduces the penetrability of light into dye solution, decreasing $^{\bullet}OH$ radical production.

D. *Effect of Initial pH*

pH plays an important role in the mechanism of $OH^{\bullet}$ production in the Fenton's reaction [21]. Studies confirmed that the oxidation is rapid at the pH range 2-4, and the acidification of the waste water is required [22].

In our experiment pH was varied from 1 to 10 and found that the rate increased with increasing pH up to 3 and after that it fell (Fig. 6). Several reasons are there for the rate change due to pH.

The peroxide gets solvated in the presence of high concentration of H^+ ions to form stable oxonium ions which enhanced the stability of H_2O_2 and restricted the generation of $^{\bullet}OH$ at low pH conditions [9]. In addition, the presence of excess H^+ ions, act as hydroxyl radicals scavenger [13].

The low activity at high pH has been reported in the literature [21], [23]. The reason behind is the formation of Fe^{3+} complexes which decrease the dissolved iron.

The complexes would further form [Fe $(OH)_4$] when the pH value is higher than 9.0 [24].

Furthermore, the concentration of hydroperoxy anions (conjugate base of H_2O_2) increases at higher pH. These anions reduced the concentration of H_2O_2 and $^{\bullet}OH$ radicals.

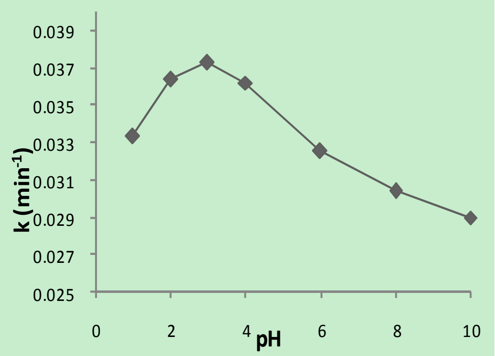

Fig. 6. Photocatalytic decolorization rate constants of MB at different pH. Experimental conditions: [MB] = .05 mM; Magnetite = 2.5 g/L; H_2O_2 =20 ml/L; temperature = (25 ±2) °C; reaction time = 30 min; UV illumination. Effect of the concentration of H_2O_2 on the degradation of MB. Experimental conditions: [MB] = 0.05 mM; Magnetite = 2.5 gm/L; pH 4.0; temperature = (25 ±2) °C; reaction time = 30 min; UV illumination.

Additionally, the oxidation potential of hydroxyl radicals was known to decrease with increasing pH. The decolorization rates become significantly slower with decreasing pH while a similar behavior is also found in highly alkaline solutions [24]. The results show that the optimum pH for photo-phenton was found to be pH 3, a result found to be similar to others research [22].

E. Effect of Light

Photocatalytic degradation processes based on the generation of hydroxyl radicals from H_2O_2 in the presence of Fe ions have been shown to be enhanced by light. Not only that, Intensity of light has also effect on the rate of photo degradation of pollutants.

To examine the effect of light intensity, four experiments were conducted. First, the experiment was performed in dark and then under solar irradiation. Lastly UV is applied with one and then two UV light sources. It was found that in dark decolorization was almost absent and the number of the UV sources has no effect on the decolorization. Solar light has no impact on the decolorization.

The reason behind the result (Fig. 7) is that in Photo-Fenton process $^{\bullet}OH$ radicals are produced from the reaction of ferrous ions and hydrogen peroxide and also from direct photolysis of H_2O_2.

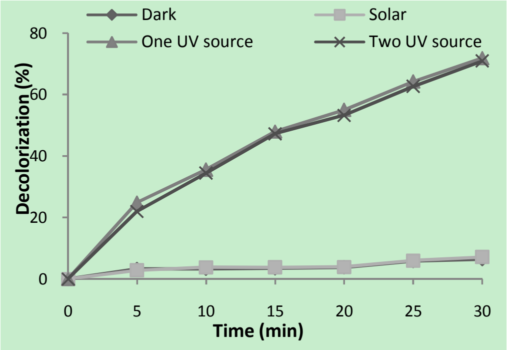

Fig. 7. Effect of light source on the decolorization of MB. Experimental conditions: [MB] = .05 mM; Magnetite = 2.5 g/L; H2O2 =20 ml/L; pH=4; temperature = (25 ±2) °C; reaction time = 30 min.

Decolorization is also accelerated due to photo-reduction of Fe $(III)_{aq}$ or $Fe(OH)^{2+}$, formed as a consequence of oxidative processes in Fenton's system, to Fe^{2+} ions with the production of reactive $^{\bullet}OH$ radicals [21].

IV. CONCLUSION

Magnetite was found to be a good photocatalyst for the decolorization of dye. The following conclusions can be drawn from the experiments:

- The combination of Magnetite, H_2O_2 and light illumination is essential for the photodecomposition of MB.
- There is an optimum Magnetite dosage for which Photo-decomposition is found to be highest.
- Addition of H_2O_2 increases the decolorization rate, as it enhance the generation of $^{\bullet}OH$. But beyond a limit it has negative impact on the reaction rate.
- As the hydroxyl radical concentration remained steady for a certain operational condition, addition of dye concentration will degrade the rate. $^{\bullet}OH$ generation should be augmented for higher dye concentration. Reduction in penetration of light due to higher concentration of dye is also responsible for the drop of the rate.

ACKNOWLEDGMENT

The authors are grateful to Bangladesh University of Engineering and Technology for providing facilities to carry out this research work.

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