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Catalytic oxidation over nanostructured heterogeneous process as an effective tool for environmental remediation

Rahma H. Thabet[1], Maha A. Tony[1*], Shakinaz A. El Sherbiny[2], I. A. Ali[3], Mai K. Fouad[2]

[1]Advanced Materials/Solar Energy and Environmental Sustainability (AMSEES) Laboratory, Basic Engineering Science Department, Faculty of Engineering, Menoufia University, Shebin El-Kom, Egypt.
[2]Chemical Engineering Department, Faculty of Engineering, Cairo University, Egypt
[3]Cyclotron project, Nuclear Physics Department, Nuclear Research Center, Atomic Energy Authority, Egypt
E-mail: dr.maha.tony@gmail.com

Abstract. Industrialization has led to a severe deterioration in water quality. Textile industry is considered a huge consumer of water in Egypt; the result is generating large amounts of dye-containing wastewater that is essential to be treated before the final disposal. However, searching for efficient treatment is an important aspect for a sustainable environment. Advanced oxidation processes (AOPs) have been emerged as efficient techniques for industrial wastewater remediation. Among the AOPs, Fenton based reactions is considered a promising process for its simplicity in application and cost-efficient with high process efficiency. In this study, heterogeneous Fenton reaction using magnetite nanoparticles induced by ultraviolet radiation (UV) was applied as a green technology pathway for textile dyeing wastewater oxidation. Nanostructured magnetite was successfully obtained by co-precipitation technique that is used as the precursor of the Fenton's reaction process. The heterogeneous iron (Fe^{2+}/Fe^{3+}) supported catalyst with hydrogen peroxide (H_2O_2) was used as a coupled Fenton and Fenton-like oxidation system for methylene blue dye removal in aqueous media. The obtained results investigated that the dye oxidation rate increases with decreasing pH to 3.0. However, increasing H_2O_2 and magnetite (Fe_3O_4) nanoparticles catalyst results in an increase in the dye oxidation rate and the optimum operating values were 80 and 1600 mg/L for Fe_3O_4 and H_2O_2, respectively. By optimizing the amount of reagents, process conditions as well, the results revealed that magnetite was considered an efficient Fenton-based catalyst for dye oxidation that is reached to 94% within 3 hr of oxidation time. Finally, magnetite catalyst could be easily recovered by magnetic separation to confirm the process sustainability.

Keywords: Fenton's reagent, Methylene blue, Wastewater, Nanomaterial, Magnetite

1. Introduction
Egypt is listed as a country with a rapid population growth and is known as one of those countries that have a gap between water supply and demand [1]. In addition, a large quantity of water is consumed as a result of industrialization and a massive amount of wastewater is produced by processing and the result is a danger to the environment [2]. Therefore, the major problem affecting water scarcity and human health is wastewater generation from industrial sectors [3], domestic[4] and agricultural[5] effluents. It is also in the interests of many researchers to search for a viable solution [6].

Textile industry is considered one of the industrial sectors responsible of discharging a highly contaminated colored wastewater. Such effluents are released into the environment causing the aquatic

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system to severely deteriorate [7, 8]. Thus, the treatment of fabric effluents is important for a clean environment and also for the protection of water supplies.

Dyes could be classified according to their application to c dyes. However, according to the chemical structure they could classified into azo, triarylmethanes, diphenyl-methanes, anthraquinones, stilbenes, methines, polymethines, xanthenes, phthalocyanines, sulfurs,..etc [9]. Therefore, the presence of such chemicals decreases the transparency of the water and inhibits the penetration of solar radiation. Thus, the result is decreasing the coloured photosynthetic activity and cause disruptions in the gases solubility, causing damage to the gills of the aquatic organisms. These chemicals can remain for several decades in the aquatic environments causing severe damage to the ecosystems. Also, causing danger to human beings and other living organisms. Based on various studies by different researches, there are numerous literature cited dealing with Fenton's reagent for treating several types of wastewater that contaminated dye effluents [10]. Such as Hammami et al. [11] treated the wastewater polluted with Direct Orange 61, Wang et al. [12]studied wastewater contaminated with Acid Red 14, Ali et al. [13] removed Basic Blue 3 dye from waste effluents and Bocos et al. [14] treated Reactive Black 5 contaminated wastewater. Moreover, Gulkaya et al. [15] treated wastewater effluent with real industrial dyestuff wastewater. Methylene blue (MB) that is a cationic dye is widely used as a coloring agent in coloring, painting and wool dyeing. The wastewater effluent containing this dye is causing hazard to the surrounding environment [16-18].

Several conventional wastewater techniques have been widely applied for wastewater treatments, such as flocculation [19], adsorption [20], ion exchange [21], filtration [22] and reverse osmosis [23]. However, those techniques may be signified by the incomplete mineralization of pollutants since they are only transferring the pollutant from one phase to another without destroying them. Therefore, a secondary treatment is needed [24, 25]. In recent two decades advanced oxidation processes (AOPs) have recognized as an effective method for treatment of wastewater. Such AOPs were first suggested for treatment of potable water in the 1980s [26, 27]. AOPs are characterized by the formation of highly reactive hydroxyl radicals (•OH) in appropriate amounts to oxidize wastewater contaminants and purify water [26]. When AOPs are introduced for the treatment of wastewater, (•OH) radicals are needed to effectively oxidize the contaminants as an efficient oxidizing agent for transformation into less and even non-toxic substances (CO_2 and H_2O). Thus, this is considered the best solution for wastewater treatment [28, 29]. The main processes of producing these radicals are including: UV [30], O_3/H_2O_2 [29], O_3/UV, [29, 30] TiO_2 photo-catalysis [31, 32], Fe^{3+}/UV [33] besides Fenton and photo-Fenton processes [34].

Fenton's reagent, i.e. Fe^{2+} and H_2O_2 is known as an efficient treatment technique as it implies high efficiency in the oxidation of organic compounds at low cost, in addition to the lack of toxicity with reagents. [35].

The photo-Fenton process is an oxidation mechanism that incorporates the Fenton reaction and ultraviolet light to oxidize ferrous ions Fe(II) to ferric ions Fe(III), as well as the decomposition of H_2O_2 into •OH radicals as in Eq. (1). Ferric ions are the source of iron in the photo-Fenton process; UV irradiation helps to regenerate the ferrous ions by equations (2-4) called Fenton-like process, which are responsible for the continuation of the Fenton reaction [36].

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

Fe^{3+} can react with H_2O_2 in the so-called Fenton-like reaction:

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad (2)$$
$$FeOOH^{2+} \rightarrow Fe^{2+} + OH^* \quad (3)$$
$$Fe^{3+} + OOH^* \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

The higher concentration of Fe^{2+} ions can improve the rate of decomposition of organic pollutants since more hydroxyl radicals are produced according to Eq. (1) [37].

Magnetite (Fe_3O_4) is a semimetal semiconductor with a band gap 0.14 eV. It contains both iron ions, i.e. Fe^{2+} and Fe^{3+} cations. Consequently, magnetite could be considered an efficient photocatalyst. Various studies have been undertaken to treat wastewater using magnetite to remove organic and inorganic pollutants [38].

Recently, nano-compounds have been introduced to the field of photocatalysis owing to its efficient removals. Nano-catalysts is applied to the Fenton systems in the form of iron nanoparticles to treat various contaminants such as emerging pollutants and in dyes oxidation [39]. Their addition to the system showed a significant enhancement to the photocatalytic oxidation reaction [40].

Magnetite, (Fe_3O_4), nanoparticles have got a great attention not only for their super paramagnetic properties, but also for their low toxicity to human body. However, based on the authors' knowledge, it is not applied so far for treating wastewater polluted with the textile effluents. Therefore, in the present investigation, magnetite (Fe_3O_4) nano-crystalline powder was synthesized using low-cost simple co-precipitation technique. Based on such nano-powder as photo-catalysis, ultraviolet illumination (UV) augmented with nano-magnetite Fenton's reagent (NMFR) was used to treat Methylene Blue dye-containing wastewater. The NMFR parameters were investigated, and the process was compared with other treatment processes.

2. Materials and Methods

2.1. Chemicals and reagents
Methylene Blue (MB) dye was obtained from Sigma-Aldrich Co, (Germany). The nano-Magnetite was prepared from the precursors of ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and Ferric Sulfate $Fe_2(SO_4)_3$; which were all obtained from Qualikems Fine Chem Pvt. Ltd (India). Hydrogen peroxide (H_2O_2) 40% w/w. Sulfuric acid and sodium hydroxide were used for pH adjustment. All chemicals were of analytical grade and were used as received without further purification or treatment. Distilled water was used throughout this study.

2.2. Preparation of dye solution
The dye solution was prepared by dissolving 1.0 g of (MB) in 1.0 L of distilled water to produce a the stock solution of 1000 mg/L of the dye solution, which is further diluted to attain the required concentration for treatment.

2.3. Experimental procedure
2.3.1. Synthesization of Fe_3O_4 nanoparticles
The co-precipitation method has been used to synthesize Fe_3O_4 nanoparticles samples. This technique is reported elsewhere [41]. A 2 mol of $Fe_2(SO_4)_3$ and 1 mol of $Fe(SO_4)$ were mixed according their stoichiometric ratios in double-distilled water of 1.5 L volume. More than 8 mol of sodium hydroxide (NaOH) solution was then added dropwise with stirring until the pH of the solution reached 11.0. The precipitate solution was heated to 80 ^{o}C with continuous stirring. The prepared nanoparticle was washed many times afterwards with distilled water to remove the sodium hydroxide and sodium sulfate until the pH reached 7.0. Finally, the produce Fe_3O_4 was dried in an electrical oven at 60 °C and manually grounded.

2.3.2. Fe_3O_4 NPs Characterization
For the X-ray diffraction analysis, the Fe_3O_4 precipitate was dried to be a powder and analyzed using an X-ray diffractometer. The instrument used for the analysis was X-lab Shimadzu X-6000), and identified with Cu-Kα radiation.

2.3.3. Photocatalytic methodology
Methylene Blue (MB) photo-oxidation process was studied using 100 mL of 10 mg/L dye-wastewater solution. The synthesized magnetite nano-powder under UV illumination (254 nm wavelength), as

illustrated in figure 1 was subjected to the system and the reaction is initiated by the hydrogen peroxide addition.

Firstly, the pH of the solution was adjusted if needed by adding sulfuric acid and/or sodium hydroxide using a digital pH-meter (AD1030, Adwa instrument, Hungary). Adding different dosage of hydrogen peroxide H_2O_2 to the solution to initiate the Fenton reaction. Prior to the UV illumination, the desired amount of the nano-Fenton's reagent was dispersed in the MB aqueous solution using sonication for 5 min. Thereafter, the reaction is subjected to the Ultraviolet illumination using 12-W UV lamp. Then, within a specific time interval, samples are filtered using a micro filter then subjected to spectrophotometer (UV-1601, Shimadzu, Model TCC-240A, Japan) to monitor the dye concentrations remaining in solution.

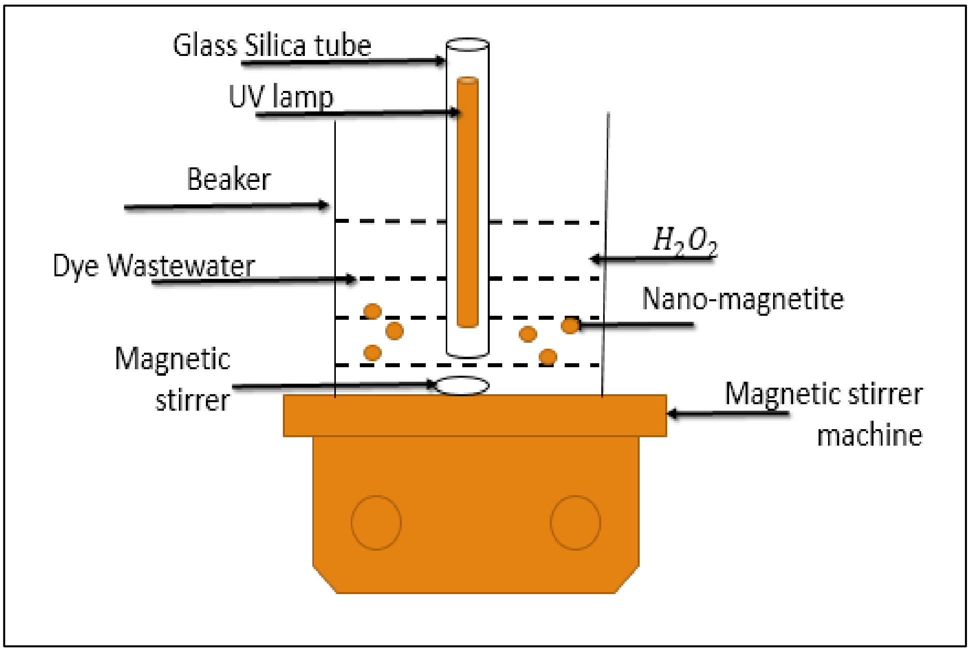

Figure 1. Schematic diagram of lab-scale photo-Fenton for MB removal

3. Results and discussions:

3.1 XRD analysis and Morphological characterization of the synthesized Fe_3O_4 nano-crystalline powder

Firstly, it is worthy to note that according to the preliminary results, the XRD pattern for the Fe_3O_4 shows diffraction peaks at 2θ (degrees) of 30.15°, 35.61°, 37.27°, 43.25°, 53.73°, 57.37°, 62.81°, 71.33°, 74.57°, 75.51° and 79.31 which correspond to the miller indices (220), (311), (222), (400), (422), (511), (440), (620), (533), (622) and (444), respectively (graph is not shown) indicate a single phase of spinel structure for nano-magnetite.

A high-resolution Transmission Electron Microscope (TEM) has been used to study the particle size of the Fe_3O_4.

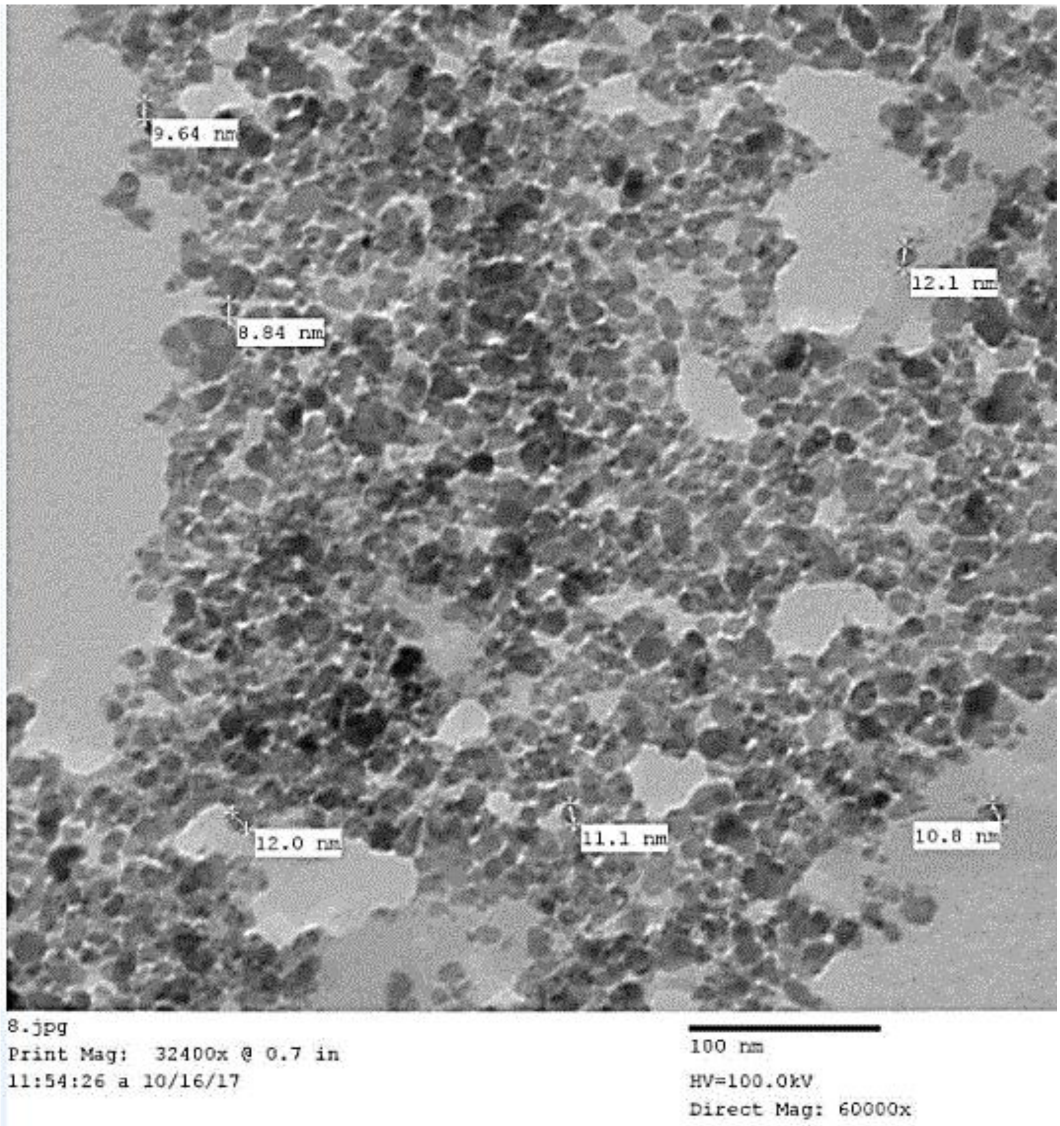

Figure 2. Tem Image of the synthesized Fe_3O_4 nanoparticles

Figure 2. shows the TEM micrographs of the synthesized Fe_3O_4 nanoparticles demonstrated that the shape of most of the nanoparticles are in spherical shape with except for small edges attached to certain nanoparticles. The average particle size estimated from the TEM images is in the range of 9-12 nm. This size gives a reasonable high surface area for the nanoparticles to perform the photocatalytic oxidation reaction.

3.2. Comparison of different oxidation systems

Firstly, three different experiments were conducted separately for eliminating dye-contaminated wastewater in order to investigate and compare the performance of the systems with the photo-Fenton system.

The results in figure 3 show the comparison of different oxidation systems with the performance of nano-magnetite Fenton reagent using the UV illumination. Analysis of the results reveals that the UV photolysis (UV-vis), for 10 ppm MB dye solution concentration and pH 3.0, removes only a 7% of MB within 60 min of reaction time. Nevertheless, the sole use of 40 mg/L of magnetite with UV radiation without H_2O_2 addition, which is called iron photo-assisted system Fe^{3+}/UV-vis achieved 68% of MB oxidation. This is due to the hydroxyl radicals which are formed via an intermolecular photo-redox process in Fe^{3+} excited hydroxy-complexes ($Fe(OH)^{2+}$) which is the most active complex in terms of $HO^{\bullet}$ formation. Such radicals are the responsible of attacking aromatic rings consisted on MB molecule . Therefore, opening the rings and creating reaction intermediates, that are ultimately converted to harmless end products, i.e. CO_2 and H_2O [2, 7]. However, when Fenton's reagent doses were used at: magnetite 60 mg/L; hydrogen peroxide 1600 mg/L at a starting pH of 3.0 under the UV illumination (photo-Fenton process), the dye removal rate reached 95.3%. This could be illustrated by the presence of UV illumination with the nanocrystals as the source of Fenton's reagent gives higher oxidation rate, since higher hydroxyl radicals were produced that are considered the main responsible of the dye oxidation [19, 34].

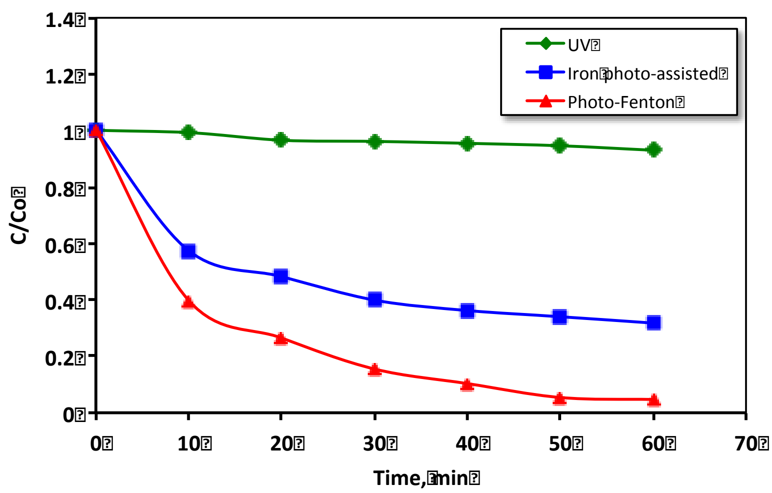

Figure 3. Comparison of different oxidation systems on the removal of MB

3.3 Effect of photo-Fenton's parameters

3.3.1. Effect of catalyst dose.

In order to investigate the role of initial concentration of iron ions on the oxidation of MB, series of experiments were conducted with different catalyst does, i.e. 40, 60, 80 and 200 mg/l and their results are observed in figure 4. The results recorded in figure4. revealed that the oxidation of MB is remarkably dependent on the iron ions concentrations at fixed initial concentration of hydrogen peroxide (1600 mg/l) and pH 3.0.

At low iron concentration (40 mg/L), the oxidation efficiency was 92% after 60 min of reaction time. Whereas, for 60 mg/L, 80 mg/L and 200 mg/L, the oxidation efficiency are 95.29, 93.97 and 95.52% during 60 min of reaction time, respectively.

The results showed that 200 mg/L of the nano powder ions gives a maximum removal of MB dye 95.52%, Furthermore, 60 mg/L reveals an almost removal rate. Therefore, considering the need to remove iron ions from the solution before discharge and with economic point of view, low catalyst consumption is preferred, the optimal iron ions concentration was selected to be 60 mg/L. This result is in accordance with, the work of Hariani et al. [40] who revealed that the high concentration of Fe_3O_4 competing the hydraoxyl radicals for attaching the dye molecules . Thus, the overall reaction rate is scavenged [42, 43] and the organics oxidation is declined. Additionally, with increasing the iron concentration, the catalytic efficiency increases. This could be attributed by the presence of Fe^{3+} in high concentration in the solution, higher amounts of UV illumination is absorbed since it has a strong absorbent band. However, higher amounts of the reagent rinders the oxidation rate since it forms $Fe(OH)^{2+}$ [44]. Furthermore, Fe^{3+} ions may react with hydrogen peroxide reagent to form hydroperoxyl radicals that has a less oxidizing efficiency than •OH radicals [33].

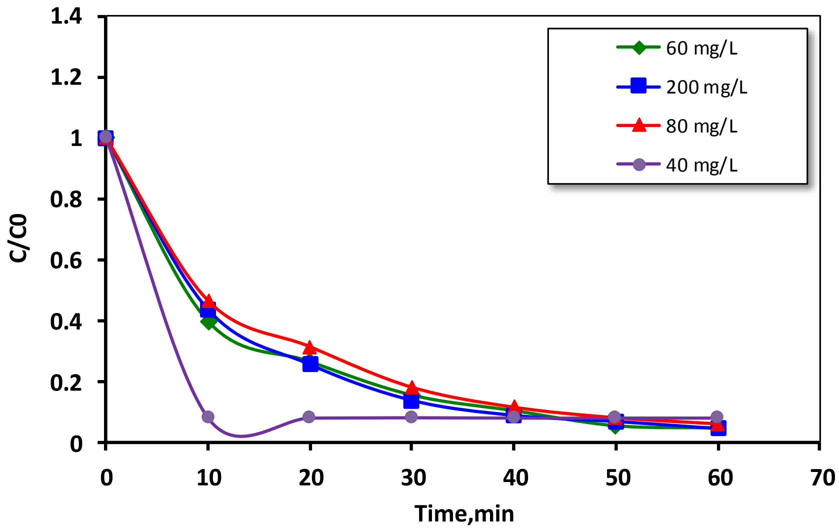

Figure 4. Effect of the concentration of Nano-magnetite on the removal of MB, [MB]o= 10 mg/L, H_2O_2= 1600 mg/L, pH 3.0.

3.3.2. Effect of hydrogen peroxide dose.

According to the literature cited [4, 5], hydrogen peroxide is described as an important parameter in the Fenton's reaction system. figure 5 shows the effect of increasing hydrogen peroxide reagent on the MB removal rate while keeping the other parameters fixed (pH 3.0 and iron dose of 40 mg/L). Various initial H_2O_2 concentrations ranged from 100 to 3000 mg/L was studied. The results show that by increasing the hydrogen peroxide concentration from 100 to 1600 mg/L, MB removal increased from 40.3 to 91.9% after 60 minutes of illumination time. It might be due to the increasing of •OH with the addition of hydrogen peroxide. The effect of high dose of H_2O_2 on Fenton's reaction is previously reported by several authors [45, 46].

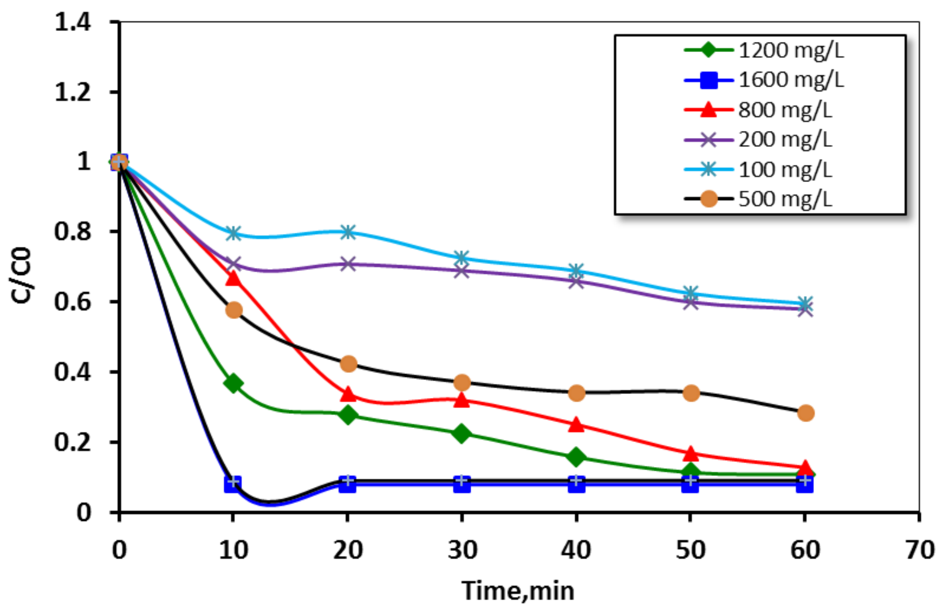

Figure 5. Effect of the concentration of H_2O_2 on the removal of MB, [MB] = 10 mg/L, iron = 40 mg/L, pH 3.0

Additionally, further increase in H_2O_2 concentration (3000 mg/L) rather than the optimal value (1600 mg/L), the oxidation rate is decreased. This may be attributed by the excess hydrogen peroxide reagent will react with •OH radicals instead of generating them equation 6, Also perhydroxyl radicals (•OOH) are produced in the solution. This radicals have much less potential for oxidation than •OH. Additionally •OH radical was consumed to H_2O and O_2 according to Equations (7, 8). Thus, the overall reaction rate is declined according to the excess initial hydrogen peroxide concentration rather than the optimal dose that is called hydrogen peroxide scavenging effect [4, 19, 21].

$$H_2O_2 + h\upsilon \rightarrow 2OH^* \quad (5)$$
$$OH^* + OH^* \rightarrow H_2O_2 \quad (6)$$
$$H_2O_2 + OH^* \rightarrow H_2O + OOH^* \quad (7)$$
$$OOH^* + OH^* \rightarrow H_2O + O_2 \quad (8)$$

3.3.3. Effect of pH

The pH of solutions is a primary parameter of the treatment efficiency of Fenton's reagent, since it influences the production rate of hydroxyl radical and the concentration of Fe^{2+} [47]. The effect of initial pH value of solutions on the degradation of MB was obtained in the pH range of 3.0- 8.0 and the results are shown in figure 6.

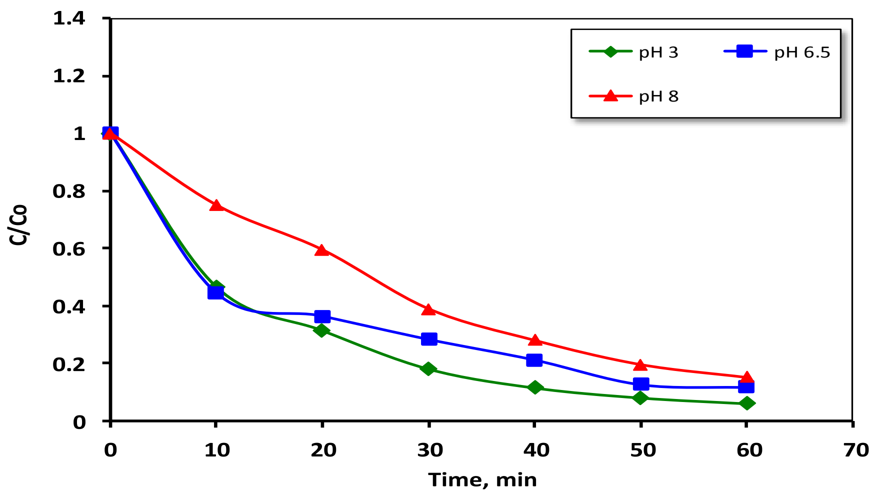

Figure 6. Effect of pH on the removal of MB, $[MB]_o$= 10 mg/L, iron= 60 mg/L, $[H_2O_2]$=1600 mg /L

The results in figure 6 showed that the dye oxidation was significantly influenced by the solution pH. The optimal pH-value is 3.0. At this pH value and within 60 minutes of reaction time, there is a 93.9% removal of MB compared to the removal rate of 84.8%, which obtained at pH 8.0. This could be illustrated by, at low pH (2.0-4.0), the oxidation reaction may be reduced because hydrogen peroxide will remain stable, potentially by dissolving a proton in the presence of a high concentration of H^+ forming an ion of oxonium (H_3O^+). An oxonium (H_3O^+) ion makes H_2O_2 electrophilic to be stable and likely greatly to reduce the reactivity of Fe (II) ion. The results reported in literature [49-50], displayed that low activity of Fenton's reagent is attained at high pH values since undesired radicals are produced rather highly reactive •OH radicals. Thus, the reaction rate is scavenged.

Moreover, Fe^{3+} complexes are formed in the reaction media, which decrease the dissolved iron and also declines the oxidation process.

4. Conclusion

Nano-Magnetite powder can be efficiently prepared using co-precipitation method and it is attained a good photo reactivity as a Fenton's reagent Photo-Fenton catalyst for the oxidizing Methylene Blue dye (MB) dye in aqueous media. MB oxidation via Fenton process was investigated in the current work and the results revealed that the solution pH, initial H_2O_2 concentration and initial iron concentration are the main influencing parameters in the dye oxidation through the Fenton system. The optimal operating parameters for the Fenton oxidation of MB are 1600 mg/L and 60 mg/L for H_2O_2 and iron nanoparticles, respectively, at an initial pH of 3.0. Under such conditions, 95.3% oxidation of the MB dye in the aqueous solution is attained within 3 hrs. of reaction time. Hence, this study is recommending the use of nano-magnetite for its low toxicity effect and simplicity in removal from aqueous media. The study suggests that the catalyst could be reused for successive cycles; however, further research is needed to signify this investigation.

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