[Journal of Engineering Research](https://digitalcommons.aaru.edu.jo/erjeng)

Volume 3
Issue 1 *(March)*

Article 8

2019

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Vol. 1 – 2019 Engineering Research Journal

Investigation of operational conditions for the removal of methylene blue by Fenton Reaction

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Abstract

Fenton reaction has been concerned by many researchers due to easy operation and effective degradation of bio-resistant organics. This study aims to investigate the effect of the operational conditions on the effectiveness of Fenton's process for the decolorization of methylene blue.The influence of methylene blue, pH, dose of H_2O_2 , ferrous sulfate concentration from the wastewater were studied. Experiments have shown that highly affect by the value of pH, Laboratory experiment conducted in the lab proved that pH should be between 3 - 4 to give the best results, It also proved that the increasing of the dose of both hydrogen peroxide and ferrous sulfate enhanced the removal efficiency of MB.

1- Introduction:

Dyes are used in many industries that are indispensable in Egypt and the world. They are used in the manufacture of textiles, paper, leather and plastics, which result in severe pollution of industrial wastewater due to the dyes, Scientists have observed the effect of dye toxicity on living organisms [2] , Air, water, land, humanity, plants, animals etc. get affected by industrial pollution. When industrial wastewater is discharged into the waterway, it is hazardous to aquatic life and humans [3]. As that Color is one of the most important criteria required to be controlled, because colored water bodies reduce light penetration, preventing photosynthesis of algae and submerged plants and are aesthetically undesirable [4]. Therefore, it is very difficult to break it biologically. scientists looked for an alternative

Advanced oxidation processes are one of the best alternatives to industrial wastewater treatment, which contains non-biodegradable organic pollutants. These factors include the generation of a free hydroxyl root (OH), which degrades most organic pollutants quickly. Fenton is a well-studied AOP that uses hydrogen peroxide as an oxidant in the presence of a catalyst. Interaction in the advanced oxidation processes As follow, the organic pollutants of the industrial waste water react with hydrogen peroxide in the presence of iron salts such as ferrous sulfate on acidic and better within the limits 3-4 The resulting hydroxyl radicals resulting from the interaction between iron salt (II) and H_2O_2 attack the organic aggregates methylene blue as the unsaturated pigment molecule. Therefore, both the chromophore and the chromogen of the dye molecules will be destroyed and their color removed[1] .

2. Materials and methods:

Material

Dye, $FeSO_4.7H_2O$, and H_2O_2 were purchased from El Gomhouria company. Dye solution of methylene blue was prepared with distilled deionized water. Ferrous sulfate was prepared with distilled deionized water with concentration (5gm/l). Analytical grade ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) and medical extra pure grade (35% w/w), hydrogen peroxide (30%H_2O_2), the PH adjustment and were performed with HCL to decrease pH, NaOH to increase pH.

Method

Experiments were carried out at room temperature, with 100 mL volume samples. The pH of the samples was adjusted to 3 ± 0.1 using HCL before oxidation. Under rapid mixing conditions (300 rpm) proper volumes of ferrous sulfate and hydrogen peroxide solutions were added to the reactor, respectively, Following the rapid mixing, the samples were stirred by a magnetic stirrer at for 70 minutes at 300 rpm ,The solids were allowed to settle for 10 minutes and It was centrifuged until all sediment was attached to the pipe used in the expulsion and the sample was taken for analysis. The absorbance measurements by spectrophotometer so that the wavelength of the dye used is adjusted at 660, the device is calibrated with distilled water then we take readings for each sample.

*Absorbance analysis***:**

Spectrophotometer (American German laboratory) is used to measure the concentration of dye. the light absorption of a substance is selective as a substance is excited by the radiation of the light, the light absorption effect will occur in the substance. each substance has their own special absorption spectrum. when a homogenous light passes through a solution, the light energy will be lessened, because some of the energy is absorbed by the solution. the loss of energy is in proportion to the concentration of the substance. the series of instruments can perform chemical quantitative analysis on a sample substance according to the principle of colorimetry. within the

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range of concentration, all parameter are in compliance with the Beers the range of concentration, all parameter are in compliance with the Beers low:

A = I g = I / T = KCL , T= 1/Io

Fenton's oxidation studies

Experiments were conducted on pH values ranging from 2 to 6 to find out the effect of pH on the removal efficiencies of color laboratory experiments conducted in the lab proved that maximum color removal efficiencies for dye solutions are obtained at pH = 3.0 and, When pH is increased from 4 to 6, the removal efficiency is reduced . Figure(1). These results show that increasing the dose of hydrogen peroxide enhanced the removal of color dye solutions. It appears that hydrogen peroxide plays a crucial role in the Fenton's oxidation process in the presence of sufficient ferrous ion under acidic conditions. Decolorization was also affected by temperature. The results show that the proper temperature was 40°C for the decolorization of methylene blue dye solution Figure (5). However, this effect was very limited and the change of removal efficiency between the temperatures studied was 1%. Therefore, the following experiments were performed at room temperature.

3 - Results and discussion

Effect of the Initial methylene blue Concentration:

As shown in Fig. 1, it is important to investigate how the concentration of initial dye influences color removal. Thus, Stock of methylene blue dye was 1 g / L and was replaced with distilled water. Experiments were conducted at different concentrations (20 , 25 , 40 , 50 mg/l) .

By increasing the dye concentration in the Fenton process, many intermediate compounds arose after the degradation of the basic dye that could interfere with the oxidation process. Such repression will be more pronounced in the presence of a large amount of intermediate decomposition products that occurred through increased dye concentration [5].

From the above, we note that the concentration of the dye of methylene blue and the ratio of ejaculation are inversely proportional. The less dye concentration used, the higher the percentage of removal .

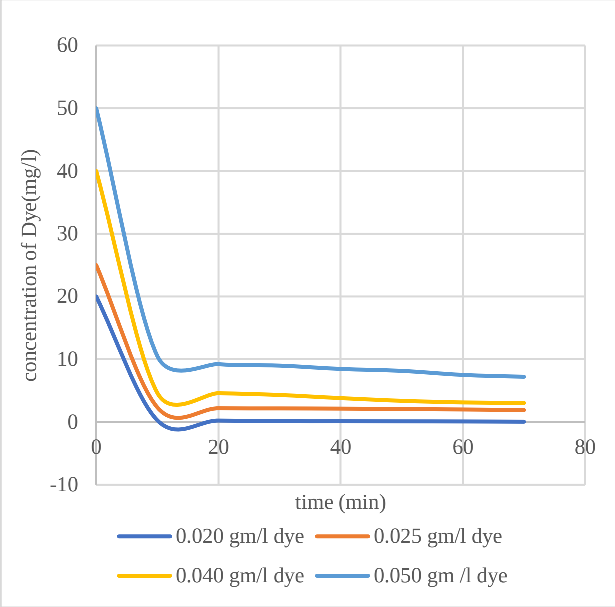
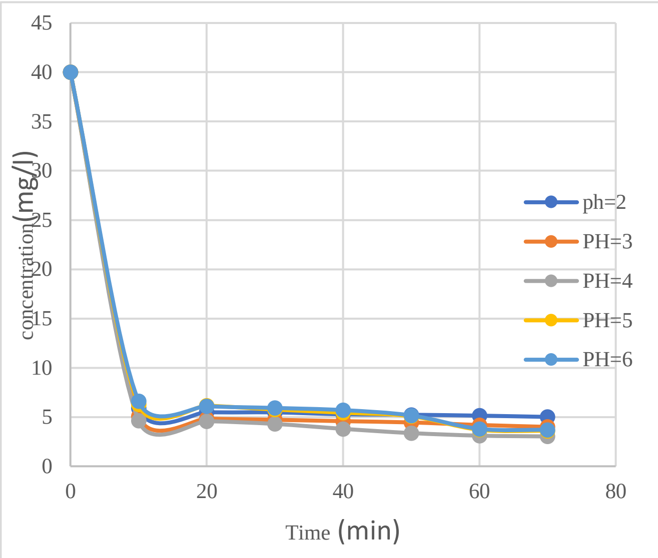


Figure (1). Effect of methylene blue concentration on degradtion methylene blue by time by time : Reaction time = 70 min .

Effect of pH on degradation of methylene blue :



Fig(2) Effect of pH on dye degradation by time ; Reaction time=70 min

In spite of the significant effect that the value of pH has on the results of the reaction, it can't alone, achieve the best results. It also affects the concentration of dye and concentration of hydrogen peroxide .to find the optimal value for pH the experiments were carried out at different pH range is from 2 – 6 by adding HCl or NaOH [6] .

Experiments have shown that the optimal value is given the best results at pH 3 – 4 [7]. AS shown in fig(2) .When the pH = 3 - 4 are formed more Fe(OH) and be more active than Fe2 this may be the reason for the disintegration of the methylene blue [8].

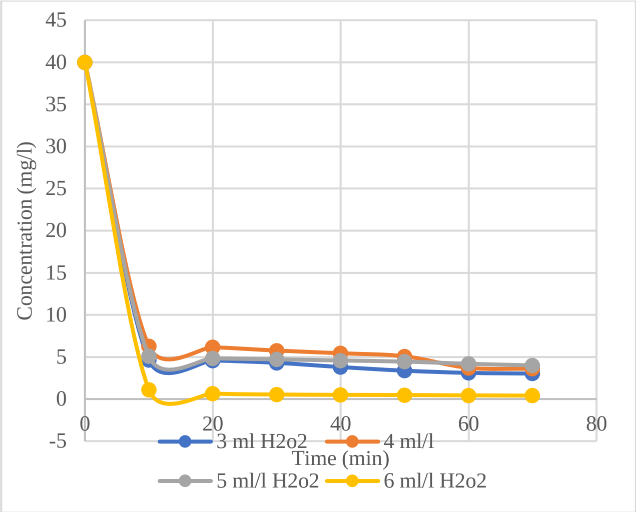


Figure (3) Effect of H_2O_2 concentration on degradation of methylene blue by time; : Reaction time = 70 min

The variation of Hydrogen peroxide during the Fenton reaction **:**

Increasing the concentration of hydrogen peroxide to accelerate the clearance of methylene blue at the beginning of the reaction, while increasing the concentration of hydrogen peroxide during the reaction, the efficiency of removal decreased. This could be because the hydroxyl radicals generated produce hydroperoxyl radicals (HO2•) in the presence of a local excess of H2O2. The hydroperoxyl radicals are much, less reactive and do not contribute to the oxidative degradation of the organic substrate which takes place only through the reaction with HO• [9].

Effect of hydrogen peroxide dose on methylene blue degradation:

Hydrogen peroxide is used in advanced processes (APs), as hydroxyl radicals source, is the best-known AP utilizing H2O2 with ferrous/ferric ion at low pH, during which hydrogen radicals are generated. When concentration of hydrogen peroxide increased, the pH decreased [10]. As shown in fig. 3, the optimum dose of hydrogen peroxide is 6 ml/l, achieved percentage removal 89.9%

Effect of FeSO4·7H2O concentration on methylene blue degradation:

The rate of degradation is dramatically increased when the ferrous sulfate concentration is increased A solution of the l ferrous sulfate was treated as a stock at a concentration of 5 g / L and used concentrations at range (0.1 gm/l : 1 gm/l). As shown in fig. 4 .Therefore, increasing the concentration of FeSO4·7H2O has stronger effect on MB degradation than increasing the concentration of hydrogen peroxide. Ferrous sulfate interacts with hydrogen peroxide to generate hydroxyl radicals which enhance degrades the dye according to the following reaction[11].

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

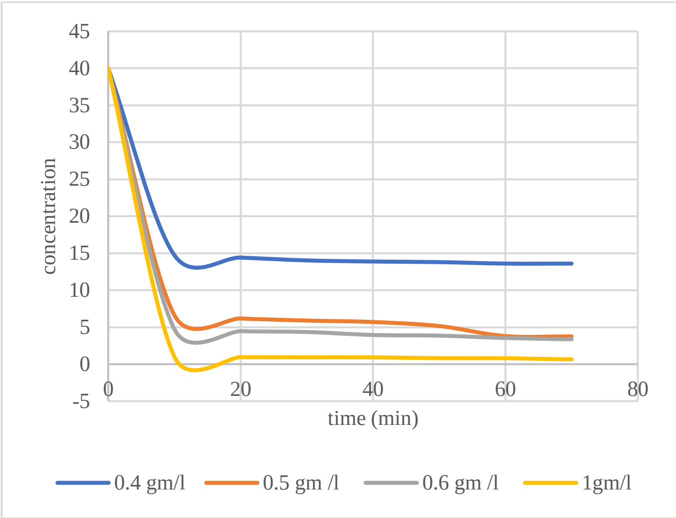


Figure (4) Effect of concentration of ferrous sulfate degradation of methylene blue by time ;Reaction time=70 min

Effect of temperature on methylene blue degradation:

The effect of temperature at room temperature, 30 ° c and 40 ° c on MB degradation was investigated. It can be seen from Fig. 5 that increasing temperature had a positive effect on the MB degradation [12] .

Effect of interaction time on methylene blue degradation :

As shown in Fig(6) time enhanced the decomposition of methylene blue, MB was found to be almost decomposed at all in 30 minutes, if only hydrogen peroxide or iron ions were added. Therefore, it can be confirmed from the figure that MB is heavily oxidized by the Fenton detector. The complete decomposition. It is possible to say that the reaction time can be divided into two phases. Interaction in the first minute of the reaction is the fastest reaction. Approximately 70% of the pigmentation can occur at the first minute [8]. The second part of the decomposition of the dye is slow taking about 30 minutes to deteriorate approximately 97%. The main reason for the reaction in two phases is hydrogen. The phase name Fe 2 + / H2O2. Ferric ions can react with hydrogen peroxide to detect hydroxyl (HO2 +) iron wafers, and iron ions react with hydrogen peroxide to produce hydroxyl radicals, Hydroxyl roots are formed [8].

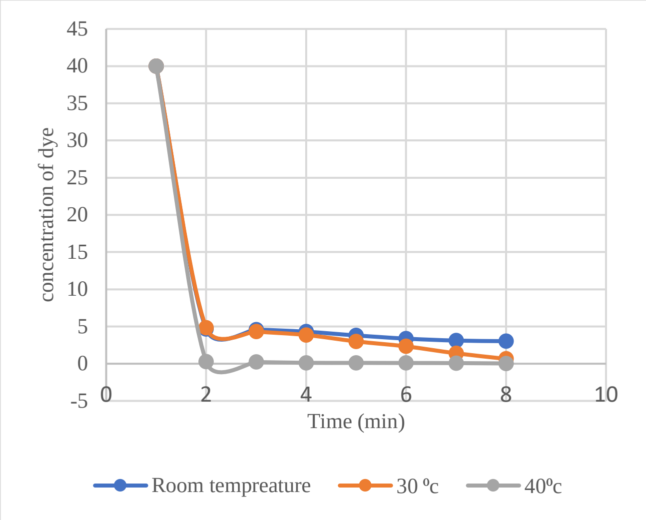


Figure (5) Effect of temperature on degradation of methylene blue by time ;Reaction time=70 min

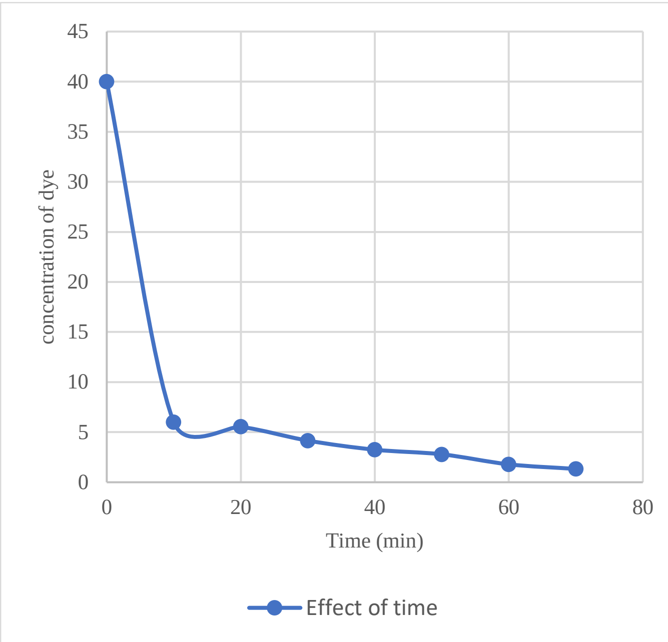


Figure (6) Effect of Time on degradation of methylene blue by time ; Reaction time=70 min .

Conclusion

From the results of this study.

- The degradation of MB efficiency by oxidation was greatly affected by the pH reaction. The most effective pH range was observed at 4.0 and below. The degradation of MB it is also affected by the dose of hydrogen peroxide. The most effective H2O2 dose is 6 ml/l.
- The highest color removal efficiency of 99.85% was achieved for an external addition of 60 ml/L hydrogen peroxide with 1.0 g/L methylene blue and 0.5 g/L Ferrous sulfate at 40ºc, pH 4 after 70 min.
- Without temperature effect, the highest color removal efficiency of 98.33% was achieved for an external addition of 6 ml/L hydrogen peroxide with1.0 g/L methylene blue and 0.5 g/L Ferrous sulfate, pH 4 after 70 min. From laboratory experiments, we can determine the optimal dose that gave the best removal rate 5 gm/l ferrous sulfate, 6 ml/l H2o2.

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