Decolorization of Methylene Blue from Aqueous Solution Using Ultrasonic/ Fenton Like Process

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\textbf{ABSTRACT}

Decolorization of Methylene Blue was investigating using a Ultrasonic/Fenton like reactor in batch mode. The effects of pH, reaction time, initial concentration of dye, H\textsubscript{2}O\textsubscript{2} and Fe on the dye removal was studied. It was found that the increase of initial dye and H\textsubscript{2}O\textsubscript{2} concentration and the increase of initial pH, are not beneficial for improving the dye removal efficiency. Increasing the dye concentrations from 50 to 400 mg/L resulted in decreasing the rate of decolorization from 0.255 to 0.063 min\textsuperscript{-1}, respectively. Complete removal (100\%) was observed, when pH, reaction time, initial concentration of dye, H\textsubscript{2}O\textsubscript{2}, Fe and ultrasound density were found to be 3, 30 min, 100 mg/L, 200 mg/L, 25 mg/L, 40 kHz, respectively. The results showed that H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{2+} equal 8 is more effective for dye removal.


\textbf{1. INTRODUCTION}

Annually worldwide production color is more than seven hundred thousand tons that is widely used in various industries including textile, printing and paper industries, tanning, cosmetics, etc.\cite{1, 2}. Studies show that about 15\% of the colors used in the industry discharge into the environment through its effluent\cite{3}. The colors are the most dangerous groups of chemical compounds known in the industry waste, which can be cause of reducing light penetration into the water that harming photosynthesis in aquatic life\cite{4}. In addition, the colors have effect on human health, including the carcinogenic effects, and in many cases are caused by genetic mutations in living organisms\cite{5}. Studies show that colors are not easily degraded and must be removed before discharge into the environment\cite{6}. Methylene blue (MB) dye is one of the heterocyclic aromatic dyes\cite{7}. Researcher finding show that direct contact with MB can be cause of permanent eyes damages, nausea and vomiting, sweating, mental disorders and Methemoglobinemia\cite{8}.

The uncontrolled discharge of these compounds to the environment creates severe deleterious effects. Because of the low biodegradability of synthetic colors, suitable performance of biological treatment systems cannot be achieved. For this reason, usually the physical and chemical processes such as membrane filtration, electrochemical processes, irradiation, ozonation, chemical recovery, etc. are used\cite{9}. Due to several limitations such as, high cost and relatively low efficiency of aforementioned methods, research try to use new approaches, among them advanced oxidation process to treat colored wastewaters showed high ability. The advanced oxidation process produces free radicals hydroxyl with high oxidation power\cite{10}. Hydroxyl radicals have the ability to attack organic molecules and degrade them to water and carbon dioxide\cite{11}. Fenton advanced oxidation method are classified as photo-Fenton, Electro-Fenton, Fenton-like with different operating conditions, but the principal of methods are the same. Fenton-like process make possible hydroxyl radical production in two stages so...
actually increases the efficiency of the process than normal Fenton. Using this method, conventional zero-valent iron or trivalent can be used instead of divalent iron [13, 14]. Ultrasonic waves is another method of advanced oxidation that can be used to break down organic material because of many advantages such as easy setup, easy operation, no production of by-products, no need to add chemicals and lower startup costs than other methods, alone or in combination with other methods such as Fenton process [15]. When an aqueous solution under the ultrasonic process creates a lot of pressure gradient in the fluid causes an expansion and a contraction of the bubbles in the range of microns. This process resulted in areas with high temperature and pressure within the fluid environment that can pyrolysis of organic pollutants. Furthermore, in an aqueous environment, radicals (HO’ or (HO) are formed as result of cavitation that breaks the organic material inside and outside the bubble [16].

Wang and his colleagues [17] applied Fenton/Ultrasound process to remove direct blue 15. They found that process has ability to eliminate the color with 100% efficiency. Zhou Tao et al. [18] performed the Fenton/Ultrasound for removing 4-Chlorophenol. The results showed that this integrated process has high ability to remove 4-Chlorophenol. Since integration is particularly important with regard to the fact that studies show that a combination of advanced oxidation processes are efficient in pollutant removal.

In this study, Fenton like combined with Ultrasound was used to remove dye from aqueous solution. Oxidation parameters and appropriate removal conditions with maximum degradation of Methylene blue (MB) as a cationic dye were determined. It is necessary to investigate extensively on the relationship between oxidation efficiency and the parameters affecting it. Therefore, oxidation kinetics and effect of pH, reaction time, initial concentration of dye, H2O2 and Fe on oxidation process were investigated.

2. MATERIALS AND METHOD

The Methylene blue dye, was obtained from Merck (Germany) as Laboratory grade available dye with formula (C16H18CIN3S) with a purity degree of 98% and MW=319.86 (Figure 1). The analytical grade of Hydrogen peroxide solution (35%), Fe2SO4.7H2O, and all chemicals components were obtained from Merck, Germany. Aqueous solution containing 100mg/L MB were prepared with distilled water with low conductivity. pH adjustment has been carried out by using H2SO4 (0.1N) and NaOH (0.1N).

2. 1. Experimental Setup The Fenton-like/Ultrasound degradation experiments were carried out in a stirred batch reactor, at 20°C, as showed in Figure 2. The pH adjustment was first applied for all synthetic wastewaters by adjusting pH manually using H2SO4 (Meter Lab E537 pH Meter). In the Fenton-Like-Ultrasound experiments were applied ultrasound equipment (Model:DSA100-SK2-4.0 China with working volume 4L; with constant characteristics: 40KHz and 100w/L) to investigate the effects of different oxidant (H2O2) at various dosages between 10 and 400 mg/L on the removal of MB, when other parameters were kept constant (Reaction time 30 min, C0(dye)=100mg/L, pH=3 and C0(Fe0)=20mg/L). Optimum H2O2 was first determined and then the optimum catalyst doses (Fe0) that provide best dye removal was determined at temperature (20±2°C). The final pH was recorded in the sample taken from the supernatant phase above the precipitate; then, effluent concentrations of total MB in that sample were measured in accordance with Standard Methods by using JENWAY 6305 Spectrophotometer at 645 nm [19]. Before each analysis, samples were centrifuged and filtered on 0.45 mm millipore membranes to remove applied chemical in process. The effect of pH (2-8), reaction time (2-30 min) and MB concentration (50-400mg/L) on the decolorization of Methylene blue during Fenton-like/ultrasound treatment have been studied at a batch system.

3. RESULTS AND DISCUSSION

3. 1. Effect of H2O2 Concentration The selection of an optimum H2O2 concentration for the dye degradation by Fenton’s reagent is important from a practical point of view (due to the cost of H2O2) [20]. At the beginning of study, the effect of H2O2 on the decolorization of MB from 10 to 400 mg/L, at pH 3 and temperature 20°C with the constant Fe0 dose of 20 mg/L was investigated (Figure 3). The decolorization efficiency that increased from 38.2% to 98.5% is a consequence of increasing H2O2 dosage from 10 to 200 mg/L at 30 min reaction time. The further increase of H2O2 from 200 to 400 mg/L demonstrated a non-significant decrease in decolorization. This is a common behavior in the Fenton’s process, which might be due to the hydroxyl radical scavenging effect of H2O2 (Equation (1)) [21]. According to Gong et al., [22], decolorization rate of dye increases as the H2O2 concentration increases until H2O2 concentration reaches critical value. However, when the concentration of H2O2 was higher than the critical concentration, decolorization of dye was decreased as a result of scavenging effects (Equations (2)-(4)). The same phenomenon was also observed by [21, 23].

\[
\text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH}^+ \quad (1)
\]
\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^+ \tag{2}
\]
\[
\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{3}
\]
\[
\text{OH}^- + \text{OH}^\circ \rightarrow \text{H}_2\text{O}_2 \tag{4}
\]

Dye removal at 300 mg/L and 400 mg/L of H\text{O}_2 did not vary significantly as shown in Figure 3. The decolorization efficiency at 300 and 400 mg/L of H\text{O}_2 dose were 98% and 93%, respectively. Hence, optimum concentration of H\text{O}_2 was chosen as 200 mg/L.

3. 2. Effect of Fe Concentration  

The effect of adding Fe\textsuperscript{3+} on the decolorization of MB has been studied at optimum (pH=3) and optimum \text{H}_2\text{O}_2 dose through varying the concentration of Fe\textsuperscript{3+} in the range of 10 to 30 mg/L (Figure 4). It was observed that the amount of ferrous ion is one of the main parameters influencing the Fenton process. The decolorization was increased from 71.1% to 100% as the concentration of ferrous ion increased from 10 to 25mg/L at 30 min. The decrease in the decolorization can be explained by the redox reaction since HO\textsuperscript{2+} radicals are scavenged by the reaction or with another Fe\textsuperscript{3+} molecule (Equation (5) and (6)).

\[
\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \tag{5}
\]
\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^\circ + \text{OH}^- \tag{6}
\]

The Fe\textsuperscript{3+} formed can react with H\text{O}_2 as well as with hydroperoxy radicals that regenerate Fe\textsuperscript{2+} in the solution resulting in decrease in dye removal by Equations (7) and (8) [21].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} - \text{OOH}^{2+} + \text{H}^+ \tag{7}
\]
\[
\text{Fe} - \text{OOH}^{2+} + \text{H}^+ \tag{8}
\]

It was seen during the studies that maximum dye removal were reached at ferrous ion concentration of 25mg/L. Considering the weak distinction in the decolorization efficiency at ferrous ion concentration from 20 to 30 mg/L, as seen in Figure 4, 25mg/L of Fe\textsuperscript{3+} dosage was selected as an optimum dosage for decolorization of MB by Fenton like/Ultrasonic. Sun et al. [24] studied degradation of azo dye Acid black 1 using low concentration of iron in Fenton process facilitated by ultrasonic irradiation. The results show that by increasing Fe ion concentrations from 0.01mM to 0.5mM, the decolorization was increased.

3. 3. Effect of the pH  

The effect of the initial pH on the decolorization of MB using Fenton like/ Ultrasonic process was investigated and the results are demonstrated in Figure 5. The previous studies showed that the pH would influence on the amount of OH\textsuperscript{\circ} generation, and the preferable condition for OH\textsuperscript{\circ} generation was under acidic conditions [21, 25].

Therefore, the experiments were carried out at different pH values ranging from 2 to 8 by adding 0.1N H\text{SO}_4 or NaOH to adjust the pH value. The reaction was carried out for 30 min using 25mg/L Fe\textsuperscript{3+} and 200mg/L H\text{O}_2 under controlled pH conditions.

It is apparent from the Figure 5 that the extent of decolorization decreased with increasing the pH and removal efficiency at pH 3 was 100%, whereas it reduced to 80% at pH 8. These results also are similar to results obtained from previous studies. Decreasing the oxidation potential of OH\textsuperscript{\circ} in the high pH condition might be the reason for the decrease in the decolorization rate. In addition, under high alkaline conditions (pH>4), the precipitation of hydroxide ions Fe(OH)\textsubscript{3} occurs, decreasing the concentration of dissolved Fe\textsuperscript{3+}. Besides, in such conditions, hydrogen peroxide is less stable, therefore, less hydroxyl radicals are formed, reducing the efficiency of process [21]. On the other hand, for pH condition below 3, the OH\textsuperscript{\circ} can be consumed via scanning hydroxyl radicals with H\textsuperscript{+} ions (Equation (9)). Subsequently, hydrogen peroxide can capture a proton to form an H\text{O}_2\textsuperscript{2+} ion (Equation (10)) and H\text{O}_2\textsuperscript{2+} will make hydrogen peroxide to be electrophilic presumably reducing the reactivity of the reaction between hydrogen peroxide and ferrous ion [21, 25].

\[
\text{OH}^\circ + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} \tag{9}
\]
\[
\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2^2+ \tag{10}
\]

Inhabitation of °OH radical formation at pH below 3 seems to be due to decrease of the soluble amount of Fe\textsuperscript{3+} (responsible for the continuity of the oxidation process) that is in equilibrium with other iron species Fe(OH)\textsubscript{3} and Fe(OH)\textsuperscript{2+} under such conditions by Equation (7) [21].

4. 3. Effect of Initial Dye Concentration  

The effect of initial dye concentration on the decolorization of MB by Fenton like/ Ultrasonic process was investigated and the results obtained are shown in Figure 6. The results show that increasing initial concentration from 50 to 400 mg/L decreased the decolorization from 100% to 90% in 30 min. This is because when the number of dye molecules increases, the concentration of OH\textsuperscript{\circ} radicals does not increase correspondingly and hence the removal rate decreases [21]. Ozdemir et al. [26] investigated dye removal from synthetic textile wastewater by Sono-Fenton Process. The results pointed out that the efficiency of process decreased from 95% to 71% by increasing of initial dye concentration form 50 to 250 mg/L, respectively.

5. 3. Effect of Reaction Time  

From the results shown in Figures 7, it is possible to observe that reaction time at 30 min is a sufficient time to obtain 100% dye removal when pH, \text{H}_2\text{O}_2 and Fe were 3, 200 mg/L, and 25 mg/L, respectively. The result is in
agreement with previous investigation on the effect of reaction time. Mousavi et al. [27] confirmed that in low dosage of Fenton's reagent, degrading of LAS was very low but with increase of reaction time from 20 to 80 minutes, the LAS removal improved to 80%. Further increase of reaction time had not showed more effect on the process efficiency. Lin and Lo [28] investigated the effect of reaction time on treatment of desiring wastewater by Fenton process. The result shows that after 120 minutes reaction time degradation did not improve and after this reaction time H₂O₂ remained in solution. Lin et al. [29] studied the decoloration and mineralization of azo dye C.I. Acid Red 14 by Sonolysis. The rate improved via Fenton’s reactions and the result confirmed that by increasing reaction time, the percentage removal of dye increased.

The effect of initial dye concentration of aqueous solution of MB on Fenton-like/Ultrasound process was investigated since pollutant concentration is important parameter in wastewater treatment. This study showed that the concentration of MB in aqueous solutions decrease with reaction time in all experiments, and the degradation rate can be explained by Equation (11).

$$\ln \frac{C}{C_0} = -kt$$

Figure 8 showed that the decrease in dye concentration as a function of time was dependent on the dye concentration. Increases of dye concentrations from 50 to 400 mg/l decreases the rate constant of decolorization from 0.255 to 0.063 min⁻¹.

4. CONCLUDING REMARKS

The present study clearly demonstrated the removal of MB using Ultrasonic/Fenton like process. The effect of five operating variables of process including initial pH, reaction time, initial dye, Fe and H₂O₂ concentration were studied. The results showed that operating parameters efficiently control the MB degradation using Ultrasonic/Fenton like, which under optimal values of process parameters, complete removal (100%) was achieved.

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6. REFERENCES

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Dr. یوسفی تاکنون، دانشگاه آمریکا در کرمانشاه بحث و بررسی در مورد استفاده از فرتون به سوی فراوانی در هیدروفون برای کمک به کاهش کیفیت آب در کاراکتر شرکت مورد بررسی قرار گرفت. الکتریکی pH رسانه های. غلظت اولیه رنگ، غلظت هیدروفون پراکسید و آهن بر روی حذف رنگ بررسی شد. بدست آمد که افزایش غلظت رنگ به میزان تا 200 ضریب pH به میزان 0.63 min⁻¹ کاهش یافته و قابل اندازه گیری می‌باشد. درصد حذف رنگ رسانه که رمان تیمی که هیدروفون پراکسید، آهن و فلزات به ترتیب با اندازه 3800 تا 400 می‌باشد. pH به میزان 200 می‌باشد. رنگ به میزان 50 کیلوهمت بودن. نتایج نشان داد که رمان را افزایش دهند. 