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Kinetic study of sonocatalytic degradation of Methylene blue by sonofenton process

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Abstract

In this work degradation of Methylene blue (MB) was studied by sonofenton process (Fenton reagent+Ultrasound irradiation). The effect of initial concentrations of H_2O_2, Fe^{2+} and MB, initial pH of solution and ultrasound power on the degradation rate were investigated. The results show that the degradation rate of MB was increased with increasing the concentration of Fe^{2+} and MB. The degradation rate was increased with increasing concentration of H_2O_2 up to 0.0001M but degradation rate was decreased by further increasing the concentration of H_2O_2. The pH effect was investigated in the range of 2.7–4.6 and the result show that degradation rate of MB was decreased by increasing the pH value. The order of reaction respect to each reactant was determined by initial rate method. The results show that the degradation efficiency of MB was increased with increasing the ultrasound power. The synergistic index was found to be 1.4 for Fenton reagent+Ultrasound irradiation, which reveals that there is a considerable synergistic effect in this coupled system.

Key word: Methylene blue, Sonocatalytic, Fenton regent, Ultrasonic degradation. Kinetic.

1. Introduction

Two major sources which dye compounds release into the environment are the textile and dyestuff industries [1]. Because of widespread use and non biodegradability for traditional aerobic wastewater treatment, the study of degradation of dyes is important [2, 3]. Because of color and high chemical oxygen demand, colored wastewaters impose serious aesthetic and environmental problems. Consequently, it is necessary to treat colored effluents prior to their discharge into receiving waters [4]. Advanced oxidation processes (AOPs) are effective to degrading a wide range of dyes [5, 6].

Fenton (Fe^{2+}/H_2O_2) and Fenton-like (Fe^{3+}/H_2O_2) processes are two examples from AOPs whose high performance relies on the great oxidation power of hydroxyl radical ($^{\cdot}OH$) formed from Fenton's reaction. For the formation of $^{\cdot}OH$ radical by Fenton's reagent a simple mechanism is given as follows [7]:

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

$$Fe^{3+} + H_2O_2 \longrightarrow Fe-O_2H^{2+} + H^{+} \qquad (2)$$

$$Fe-O_2H^{2+} \longrightarrow Fe^{2+} + HO_2^{\bullet} \qquad (3)$$

In Fenton, ferrous ion reacts with hydrogen peroxide to produce hydroxyl radical, which can then react rapidly with dye [7].

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Fenton regent is more effective than Fenton-like regent because the reaction of ferrous ion with hydrogen peroxide is very faster than ferric ion [8]. The most important disadvantage of Fenton process is that, the produced Fe^{3+} is more slowly converted to Fe^{2+} in the oxidation reaction [9, 10]. However, the conversion of Fe^{3+} to Fe^{2+} can be accelerated by ultrasonic irradiation [11, 12].

The combination of ultrasonic with other methods would speed up the rate of degradation process [13-15]. The formation of radicals during cavitation is the major potential in the sonochemical degradation of pollutants. In the collapsing gas bubbles in aqueous solution, very high temperature and pressure are generated and these conditions lead to the thermal dissociation of water molecule into H atom and hydroxyl radical [16, 17]. The generated hydroxyl radical from the sonolysis of water may react in the gas phase, gas–liquid interface and in the solution bulk to produce hydrogen peroxide and water. There are three potential sites for chemical reactions in ultrasonically irradiated liquids: the cavitation bubble itself, the interfacial sheath between the gaseous bubble and the surrounding liquid, and the solution bulk [18]. The substrate either reacts with the hydroxyl radical or undergoes pyrolysis inside the cavitation bubble. In bulk phase the reactions are occurred between the substrate and the $^{\cdot}OH$ radical or H_2O_2. Most of the hydrophobic compounds react inside the cavitation bubble whereas hydrophilic substances react at bulk phase [19]. Recently, a significant amount of researches have been conducted to the degradation of Methylene blue. For example, Fe(II)Fe(III)-Layered double hydroxides as heterogeneous Fenton catalyst [20], nanocoated RuO_2–IrO_2–TiO_2/Ti electrode plate as sonoelectrochemical catalyst [21], sonoelectrofenton [22], TiO_2 pellets as sonocatalyst [17], depositing TiO_2 particles on the surface of carbon nanotubes as photocatalyst and sonocatalyst [23] and graphitic carbon nitride as sonocatalyst [24] were used in degradation of Methylene blue. In this study, sonocatalytic degradation of Methylene blue was studied by combination Fenton with ultrasonic irradiation. The main aim of this research was studying the synergistic effect of ultrasound and Fenton regent and determining kinetics of degradation. The effects of operating conditions such as hydrogen peroxide concentration, Fe^{2+} concentration, MB concentration, initial pH and ultrasonic power on the degradation of MB were investigated. Also, the kinetic of the reaction was studied by initial rate method.

2. Experimental

2. 1. Materials

Methylene blue, hydrogen peroxide, sulfuric acid, sodium hydroxide and ferrous sulfate were supplied by Merck. All materials were used without further purification. Distilled water was used for preparation of solutions.

2. 2. Apparatus and procedure

All experiments were conducted in a 50 mL glass cylindrical reactor, with water cycling to keep constant the temperature of the reaction mixture. Schematic representation of experimental setup for ultrasonic degradation is shown in Figure 1. For ultrasonic degradation, MB solution sonicated by an ultrasonic generator (Dr. Hielscher UP400S ultrasonic processor) with an H3 sonotrode with diameter 3 mm. Temperature of the reaction mixture was controlled through a thermostat (Eyela, UA-10, Tokyo Rikakiai Co.). Stock solution of MB in distilled water (100 $mg \cdot L^{-1}$) was prepared gravimetrically by an analytical balance (Sartorius CP224S) with a precision of $\pm 1\times 10^{-4}$ g. Ferrous sulfate solution was prepared by dissolving desired amount of ferrous sulfate in 0.002 M sulfuric acid solution. To start each test, appropriate volume of stock MB solution, ferrous sulfate solution and hydrogen peroxide solution were placed into the reactor and then diluted with distilled water to 25 mL. Solution pH was adjusted by addition of H_2SO_4 or NaOH. The pH of solution was measured by using a Sartorius Professional Meter PP-20 pH-meter. Samples were taken out from the reactor periodically by using a syringe and were injected to the static Uv-Vis cell to measure the absorbance of the solution by the Uv/Vis spectrometer (Uv/Vis spectrometer PG Instrument Ltd T80).

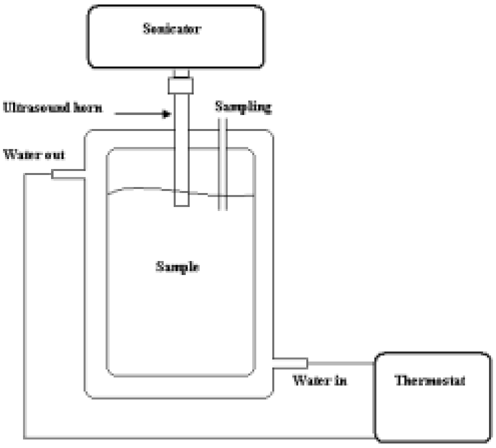

Figure 1. Schematic representation of experimental setup for ultrasonic degradation.

3. Results and discussion

3.1. Effect of H_2O_2 concentration

The degradation of MB carried out at constant dye concentration (1.56×10^{-5} M) and Fe^{2+} concentration (1×10^{-4} M) at T=296.15 K and pH=2.7 and ultrasound power 400 w while the H_2O_2 concentration was varied from 0.00001 M to 0.09 M. The absorbance of MB was measured by Uv/Vis spectrometer. The concentration of MB was calculated from the absorption in λ_{max} = 664 nm by using a calibration curve. Then unreacted fractions of MB ($\alpha = \frac{[MB]}{[MB]_0}$) were evaluated by using the concentration of MB at all times. The relationship between α and degradation time is shown in Figure 2. The results of Figure 2 indicate that the degradation extent of MB were increased by increasing H_2O_2 concentration from 0.00001M to 0.0001M but further increase in H_2O_2 concentration decreases the degradation rate. On the other word there is an optimum concentration for H_2O_2 in degradation of MB by sonofenton process. The $^{\bullet}OH$ radicals are the main oxidation agent in the solution and the amount of this agent was increased in the solution by increasing the concentration of H_2O_2. However, the degradation of MB was not improved with further increasing of the H_2O_2 concentration but dropped down. The reduction of the degradation rate of MB at high concentrations of H_2O_2 was mainly caused by the scavenging effect of excessive H_2O_2 through Equation (4):

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + {}^{\bullet}O_2H \qquad (4)$$

On the other word H_2O_2 consumes the oxidant agent in high concentration thus the available amount of $^{\bullet}OH$ radicals for degradation of MB decreases in the solution. Similar results were reported in literatures and this behavior was mainly explained by radical scavenging property of H_2O_2 [8, 25]. In order to study the kinetic of the degradation of MB by sonofenton process the initial rate method was employed. The general rate equation can be written as:

$$R_0 = \left(\frac{-d[MB]}{dt}\right)_0 = \left(\frac{-d\alpha}{dt}\right)_0 [MB]_0 \qquad (5)$$

The values of α were fitted to a meaningful equation to obtain the initial rate of degradation. The value of initial rate, R_0, was obtained from initial slope of α versus time. The values of initial rate, R_0, for $[H_2O_2]$=0.0001, 0.02, 0.03, 0.06 and 0.09 M were obtained 1.90×10^{-7}, 4.52×10^{-8}, 3.72×10^{-8}, 2.54×10^{-8} and 2.39×10^{-8} $mol\cdot L^{-1}\cdot s^{-1}$ respectively. The rate equation for degradation reaction can be written as:

$$R_0 = k[MB]_0^n [H_2O_2]_0^m [Fe^{2+}]_0^p \qquad (6)$$

where n, p and m are the orders respect to MB, Fe^{2+} and H_2O_2 respectively and k is the rate constant. With constant initial concentration of MB and Fe^{2+}, the plot of $\ln R_0$ against $\ln[H_2O_2]_0$ was found to be linear, whence the slope of the line is the order (m) with respect to the H_2O_2 (Figure 3). The order of degradation reaction respect to H_2O_2 was obtained -0.3. It should be mentioned that this order is for the concentration range of 0.0001 M to 0.09 M.

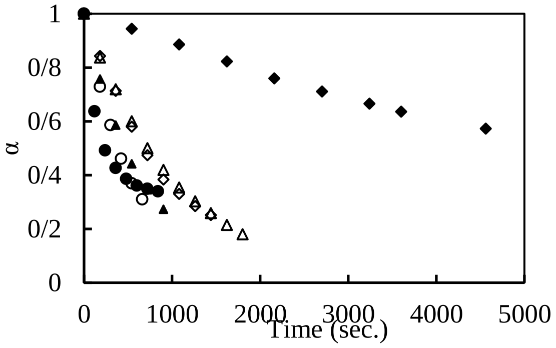

Figure 2. Effect of hydrogen peroxide concentration on the degradation extent of MB, $[MB]=1.56\times10^{-5}$M, $[Fe^{2+}]=1\times10^{-4}$M and P=400W. ♦, $[H_2O_2]$=0.00001 M; ●, $[H_2O_2]$=0.0001 M; ○, $[H_2O_2]$=0.02 M; ▲, $[H_2O_2]$=0.03 M; ◊, $[H_2O_2]$=0.06 M; Δ, $[H_2O_2]$=0.09M

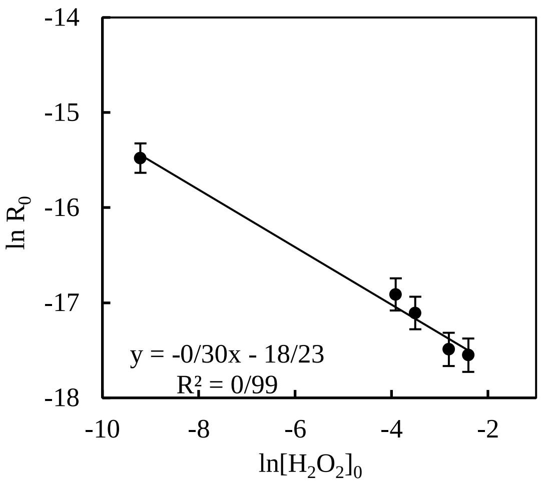

Figure 3. Plot of $\ln R_0$ versus $\ln[H_2O_2]_0$ for degradation of MB in aqueous solution.

3.2. Effect of Fe^{2+} concentration

The effect of initial concentration of Fe^{2+} on the degradation of MB was examined. The Fe^{2+} concentration were adjusted between 8×10^{-6} M and 3×10^{-5} M, while keeping constant the other parameters ($[H_2O_2]_0 = 3\times10^{-4}$ M, $[MB]_0 = 1.56\times10^{-5}$ M, T=296.15 K and pH=2.7). The effect of Fe^{2+} concentration on the degradation rate of MB is shown in Figure 4. The results of Figure 4 indicate that the degradation extent was increased with increasing the Fe^{2+} concentration. The amount of generated $^{\cdot}OH$ radicals were increased with increasing concentration of Fe^{2+}. Fe^{2+} is the catalyst of sonofenton reaction thus the $^{\cdot}OH$ radical production increase by increasing the catalyst amount. R_0 values for $[Fe^{2+}]=8\times10^{-6}$, 9×10^{-6}, 2×10^{-5} and 3×10^{-5} M were obtained 6.60×10^{-9}, 7.69×10^{-9}, 1.18×10^{-7} and 2.75×10^{-7} $mol\cdot L^{-1}\cdot s^{-1}$ respectively. The order of reaction respect to Fe^{2+} was obtained similarly to those of H_2O_2. The plot of $\ln R_0$ against $\ln[Fe^{2+}]_0$ was found to be linear, whence the slope of the line is the order (p) with respect to the Fe^{2+} (Figure 5). The order of degradation reaction respect to Fe^{2+} was obtained 2.97.

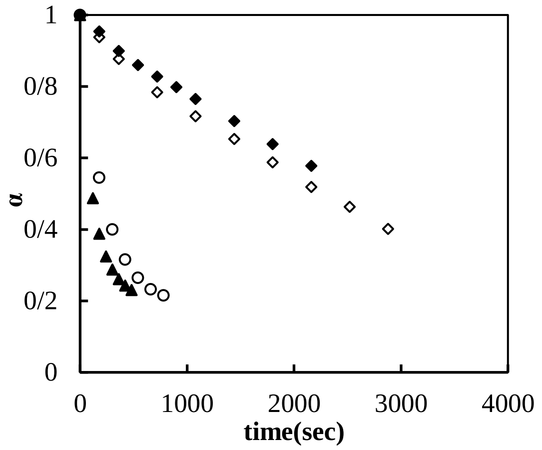

Figure 4. Effect of Fe^{2+} concentration on the degradation extent of MB, $[MB]=1.56\times10^{-5}$ M, $[H_2O_2]= 3\times10^{-4}$ M and P=400W. ♦, $[Fe^{2+}]=8\times10^{-6}$ M; ◊, $[Fe^{2+}]=9\times10^{-6}$ M; ○, $[Fe^{2+}]=2\times10^{-5}$ M; ▲, $[Fe^{2+}]=3\times10^{-5}$ M

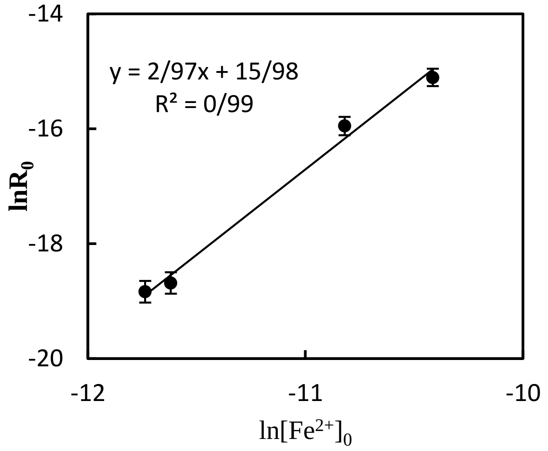

Figure 5. Plot of $\ln R_0$ versus $\ln[Fe^{2+}]_0$ for degradation of MB in aqueous solution.

3.3. Effect of MB concentration

Degradation of MB was carried out in the presence of $[Fe^{2+}]=1\times10^{-4}$M and $[H_2O_2]=0.09$ M with various concentrations of MB (in the range of 0.63×10^{-5} M to 2.23×10^{-5} M) in order to study the effect of MB concentration on the degradation rate. The effect of MB concentration on the degradation extent is shown in Figure 6. The results of Figure 6 indicate that rate of degradation are increased by increasing MB concentration. Since the rate of hydroxyl radicals formation is constant at a given condition, increasing dye concentration would increase the probability of hydroxyl radicals attack on dye molecules [25]; therefore rate of degradation are increased by increasing MB concentration. R_0 values for $[MB]=0.63\times10^{-5}$, 1.12×10^{-5}, 1.56×10^{-5} and 2.23×10^{-5} M were obtained 5.23×10^{-9}, 1.24×10^{-8}, 2.39×10^{-8} and 3.46×10^{-8} $mol\cdot L^{-1}\cdot s^{-1}$, respectively. The plot of $\ln R_0$ against $\ln[MB]_0$ was found to be linear, whence the slope of the line is the order (*n*) with respect to the MB (Figure 7). The order of degradation reaction respect to MB was obtained 1.54.

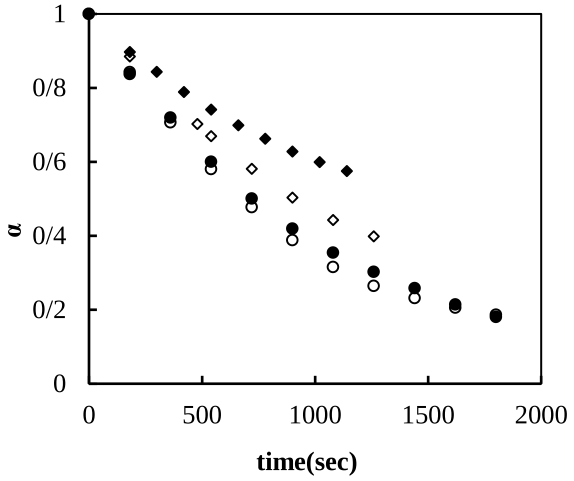

Figure 6. Effect of MB concentration on the degradation extent of MB, $[H_2O_2]$=0.09 M, $[Fe^{2+}]=1\times10^{-4}$ M and P=400W.♦, [MB]=0.63×10^{-5} M; ◊, [MB]=1.12×10^{-5} M; ●, [MB]=1.56×10^{-5} M; ○, [MB]=2.23×10^{-5} M.

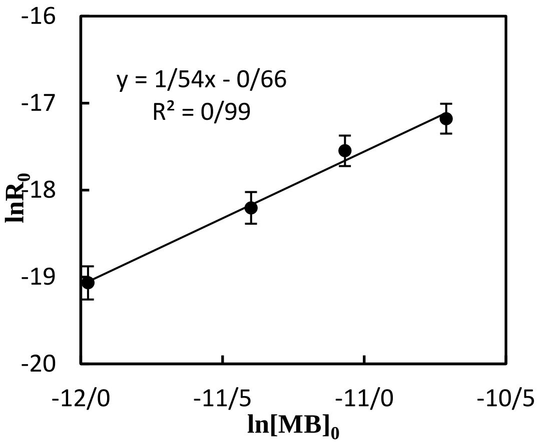

Figure 7. Plot of $\ln R_0$ versus $\ln[MB]_0$ for degradation of MB in aqueous solution.

3.4. Effect of initial pH

The pH of the solution is an important parameter in the sonofenton process which it controls the concentration of ferrous ions (Fe^{2+}) and the production of $^{\cdot}OH$ in the solution. To investigate the effect of this parameter on the degradation rate of MB, a series of experiments were conducted by changing this parameter while keeping constant the others parameters ($[H_2O_2]_0$ = 3×10^{-4} M, $[MB]_0$ = 1.56×10^{-5} M and us power 400 w). The pH values of solutions were adjusted to 2.7, 3, 3.6, 4.1 and 4.6. The effect of pH on the degradation rate of MB is shown in Figure 8. It was found that the rate of degradation of MB decreases with increasing the pH of the solution. The efficiency of Fenton processes was improved in acidic conditions in general. At high pH values, Fe^{3+} is contributed in two competitive reaction to formation two ferric complexes $Fe\text{-}O_2H^{2+}$ and $Fe(OH)_3$ as follows:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe - O_2H^{2+} + H^{+} \qquad (7)$$

$$Fe^{3+} + 3OH^{-} \longrightarrow Fe(OH)_3 \qquad (8)$$

Ultrasound reacts with former complex to accelerate regeneration of Fe^{2+} as follows [11, 12, 26]:

$$Fe - O_2H^{2+} \xrightarrow{)))} Fe^{2+} + HO_2^{\bullet} \qquad (9)$$

Whereas later complex ($Fe(OH)_3$) is stable. Through the formation of this complex, the regeneration of Fe^{2+} slows down. Therefore, the maximum degradation efficiency was achieved at lower pH. A similar behavior was reported in literature [27].

3.5. Effect of ultrasound power

Figure 9 shows the effect of ultrasound power on the degradation rate of MB by sonofenton process. The results of Figure 9 indicate that the degradation extent of MB was increased by increasing the ultrasound power. As power increases, the number of collapsing bubbles increases. Also the generation of $^{\cdot}OH$ radical was increased with increasing the ultrasound power. Therefore the degradation extent of MB was increased by increasing the ultrasound power.

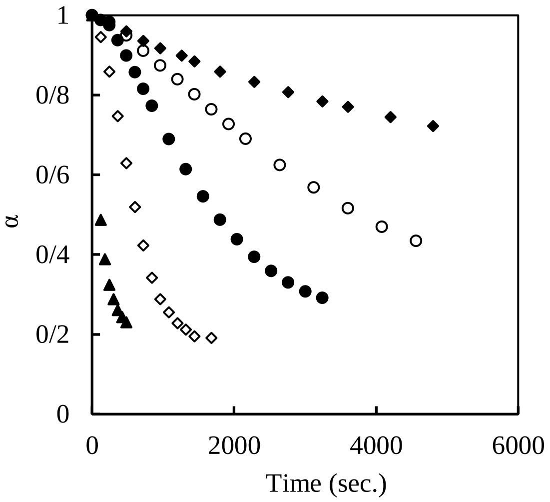

Figure 8. Effect of pH on the degradation extent of MB. [MB] = 1.56×10^{-5}M, $[H_2O_2]$ = 3×10^{-4}M, $[Fe^{2+}]$ = 5×10^{-5}M and P = 400W. ▲, pH = 2.7; ◊, pH = 3; ●, pH = 3.6; ○, pH = 4.1; ♦,pH = 4.6.

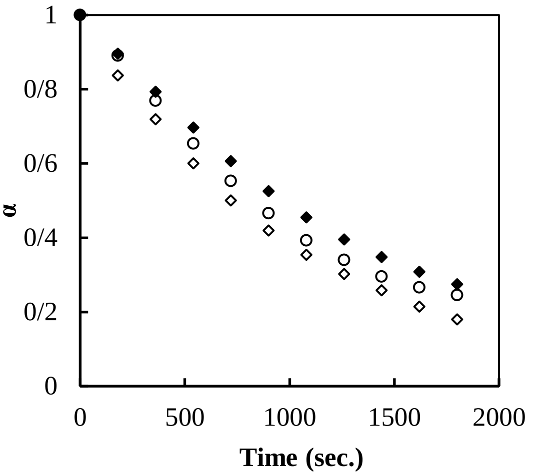

Figure 9. Effect of ultrasound power on the degradation extent of MB. [MB] = 1.56×10^{-5} M, [H_2O_2] = 0.09 M, [Fe^{2+}] = 1×10^{-4} M, pH = 2.7. ♦, P = 160W; ○, P = 320W; ◊, P = 400W.

3.6. Synergistic effect of ultrasound and Fenton

The degradation of MB was carried out in the presence Ultrasound (just sonication with P = 400W), Fenton and sonofenton (with P = 400W). The experiments conditions in the cases Fenton and sonofenton were $[MB]_0 = 1.56\times10^{-5}$ M, $[Fe^{2+}]_0 = 1\times10^{-4}$ M, $[H_2O_2]_0 = 0.09$ M, T = 296.15 K and pH = 2.7. Time evolution of MB in the presence ultrasound, Fenton and sonofenton was shown in Figure 10. For a coupled process, synergistic index (f) expressed as follows [26]:

$$f = \frac{R_{US/Fe^{2+}+H_2O_2}}{R_{US} + R_{Fe^{2+}+H_2O_2}} \qquad (10)$$

where R_{US} , $R_{Fe^{2+}+H_2O_2}$ and $R_{US/Fe^{2+}+H_2O_2}$ are the rate of degradation in sonication, Fenton and sonofenton process, respectively. The initial rates of degradation were obtained as 0.31×10^{-8}, 1.38×10^{-8} and 2.39×10^{-8} mol $L^{-1}s^{-1}$ for sonication, Fenton and sonofenton process, respectively. The obtained rate of degradation in the presence of ultrasound is in good agreement with literature [28]. The synergistic index for studied reaction was found to be 1.4, which indicates a considerable synergistic effect in this coupled system. Therefore the efficiency of sonofenton process was higher than Fenton and sonication process. During the reaction between Fe^{3+} and H_2O_2, Fe-OOH^{2+} complex produced. The regeneration of Fe^{2+} from this complex by ultrasound irradiation increases the Fe^{2+} concentration in the solution (Equation 9). Also according to Equation 11 water sonolysis produce excessive $^{\cdot}OH$ in the solution. Thus the degradation of MB by sonofenton process was more efficient [12].

$$H_2O \xrightarrow{)))} {}^{\bullet}OH + {}^{\bullet}H \qquad (11)$$

Sonocatalytic degradation of MB has been investigated by many researchers [23, 24]. The reported results in the literatures indicate that degradation efficiency of MB in the presence of graphitic carbon nitride and TiO_2-CNT along with sonication as sonocatalyst reach to 10% during 10 minutes [23, 24]. Whereas, our results indicate that degradation efficiency of MB in the presence of sonofenton reaches to 80% during 10 minutes. Therefore the efficiency of sonofenton is greater than other sonocatalyst.

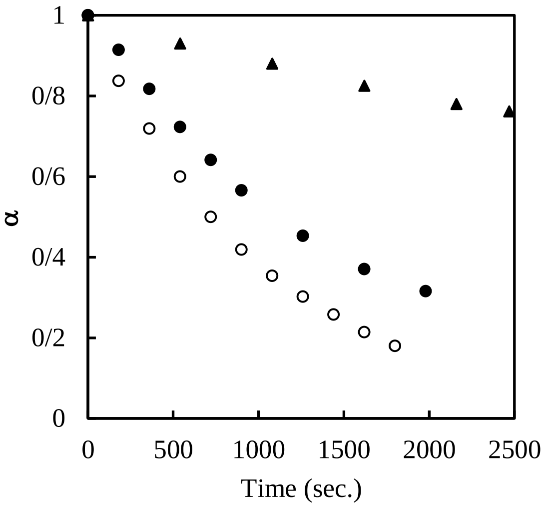

Figure 10. Comparison of Fenton and Sonofenton on degradation extent of MB. [MB]=1.56×10^{-5} M, [H_2O_2]=0.09 M, [Fe^{2+}]=1×10^{-4} M. ●, Fenton; ○, Sonofenton with P=400W; ▲, Just sonication with P=400W.

4. Conclusion

The degradation of MB was studied by sonofenton process. The effect of concentration reactants on the rate of degradation was investigated. An optimum concentration was obtained for H_2O_2. The concentration of Fe^{2+} and MB showed a straight relationship with rate of degradation. The degradation rate was strongly affected by the pH value and it was found that sonofenton process is more effective in acidic conditions. The ultrasound power leads to enhancement degradation efficiency. The order of reaction respect to each reactant was obtained by initial rate method. Also the degradation efficiency of sonofenton and Fenton reactions were comprised. This study demonstrates that sonofenton process is more effective than Fenton process for degradation of MB.

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