

Treatment and biodegradability enhancement of metalworking fluids by the Fenton and Fenton-like processes: Effect of some variables

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Abstract

The Metalworking or cutting fluids (MWCFS) used as a coolant and lubrication in by different metal working operations and machinery processes. Treatment of this kind of wastewater imposes an excessive cost on metalworking industries. The worldwide usage is estimated about 3.8–7.6 million m³ of oily wastewater results annually from the use of MWCFS. Fenton and Fenton-like processes is applied for the treatment of MWCFS characterized by high COD concentration and non-biodegradability. Affecting the processes, such as pH, dosages of Fe²⁺ (and Fe³⁺) and H₂O₂, the contact time, mixing speed were determined by Jar-test experiment, also according to dual functions of oxidation and coagulation in Fenton process, the sludge production rate and sludge settling velocity were determined in a graduated cylinder.

The results of study showed the optimum conditions, the amount of COD removal was 88.31% in Fenton Process under pH 3, 50 g/l H₂O₂, 10 g/l Fe²⁺ and 60 min settling time, and 73.97% in Fenton-like Process under pH 5, 100 g/l H₂O₂, 10 g/l FeCl₃ and 30 min settling time. Also, during the first 15 min of the Fenton's reaction, more than 92% of COD removal could be achieved. The efficiency of the Fenton-like process was less than Fenton processes. The Fenton process, when increasing the dosages of Fe²⁺ from 5 to 40 g/l, the sludge production rate increasing from 55 to 580 ml/l but also increasing sludge settling velocity.

After all processes, the biodegradability (BOD₅/COD ratio) of the treated MWCFS was increased compared to that of the raw MWCFS and the highest increase in BOD₅/COD ratio was observed in the Fenton process.

Keywords: metal cutting fluids, wastewater treatment, Fenton's reagent, Oxidation, Hydroxyl radical.

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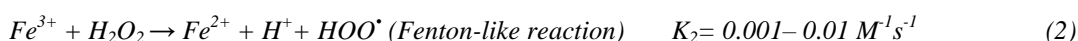
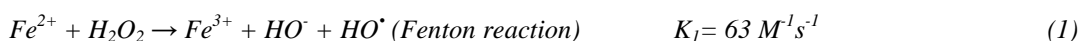
1. introduction

Metalworking or cutting fluids (MWCs) are widely used in metal industries, such as rolling mills, forge and metal workshops, because these fluids provide the combined cooling and lubrication required by different metal working operations and machining process. MWCs containing various additives like as biocides, corrosion inhibitors, lubricants, emulsifiers, extreme pressure agents, etc. Soluble oil, semi-synthetic and synthetic MWFs are generally alkaline solutions (approx. pH 9) and are diluted with water before use. The main problem with these fluids is that they become contaminated during use and, lose their properties and effectiveness. Consequently, they must be replaced by new ones and constitute waste metal working emulsions with high COD and turbidity. It is estimated that about 3.8–7.6 million m³ of oily wastewater results annually from the use of MWCs [1-4]. However, due to their nature as stable oil-in-water mixtures, MWCs create both monetary and environmental problems in their treatment and disposal [5].

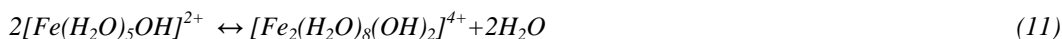
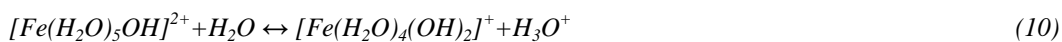
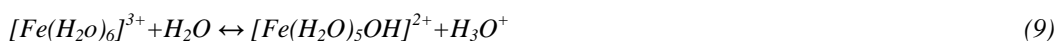
To remove part of the organic load, biological processes are usually used, because they are more economic than chemical processes [6]. Biological methods are typically applied for treatment of wastewater characterized by high 5-day biochemical oxygen demand(BOD)/chemical oxygen demand (COD) ratios (>0.4) and high concentrations of low molecular weight organics [7]. Various treatment methods are used to treat MWCs, as biological (aerobic/ anaerobic process) [8], Hydrothermal oxidation [9], Electro coagulation [10], Physical Treatment (microfiltration, ultra filtration, Evaporation and Reverse osmosis (RO) [11]. Due to their low BOD (540 mg/l)/COD (62758 mg/l) ratios (<0.1) biological processes are not effective for treatment of the MWCs. Recently, there has been considerable interest in identifying new technologies that are capable of meeting more stringent treatment standards. For this purpose, Fenton and Fenton-like processes has a more prominent role in the treatment of MWCs.

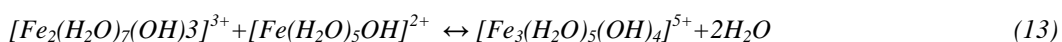
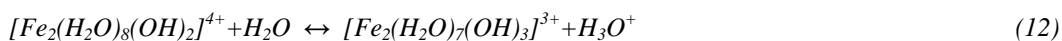
2. Fenton and Fenton-like process description

According to generation of hydroxyl free radicals, the advanced oxidation processes (AOPs) has been used to reduce the organic load or toxicity of different waters and wastewaters [12,13]. Fenton reaction (and Fenton-like reaction) is a homogeneous catalytic oxidation process using a mixture of H₂O₂ and Fe²⁺ (and Fe³⁺) in an acidic aqueous solution which effectively produces hydroxyl radical and superoxide radical. Fenton reaction has been proven promising, in terms cost effectiveness and ease of operation in the treatment of various waste waters. In the same time, the Fenton reagent is considered to be a clean reagent. Fenton reaction has a short reaction time among AOPs and is used when a high COD removal is required [6,13]. Radical mechanism can be described by the following equations (1)–(8) [14-16].



Since both ferrous and ferric ions are coagulants, the Fenton (and Fenton-like) process can therefore have a dual function of oxidation and coagulation in the treatment process. The relative importance of oxidation and coagulation depends primarily on the H₂O₂/Fe²⁺ ratio. Chemical coagulation predominates at a lower H₂O₂/Fe²⁺ ratio, whereas chemical oxidation is dominant at higher H₂O₂/Fe²⁺ ratios [17-19]. Coagulation can be described by the following equations (9)–(13) [17,20].





The efficiency of Fenton (and Fenton-like) process depends on the properties of the wastewater, the pH value, the Fe^{2+} (Fe^{3+}) and H_2O_2 dosage and the reaction time [17]. A few literature studies have been available only for the treatment of synthetic MWCFs or Emulsifying Wastewater by Fenton process.

Cheng et al. (1999) [21] reported a 90% removal of COD and more than 85% removal of TOC concentrations during a pilot study on synthetic MWCFs waste treatment using Fenton oxidation process. The study was undertaken at normal room temperature and the contaminants concentration of COD=50540 mg/l and TOC=21250 mg/l. Xiaobin et al. (2006) [22] reported a treatment trial on Metal Cutting Fluid waste using Emulsion Breaking, Coagulation and Photo catalytic Oxidation Processes. The emulsion of waste cutting fluid was broken by HNO_3 and then coagulation by Poly Ferric Sulphate and cationic Polyacrylamide (PAM) were applied. Under pH of 7.5, Poly Ferric Sulphate (PFS) dosage of 1500 mg/L, PAM dosage of 8 mg/L, the coagulation effect reported to be good and the removal rate of COD was 98.91%. Argun et al. (2010) [23] described the treatment of preliminary aerated mineral-oil recovery industry wastewater (MORIW) using Fenton process. Maximum efficiency was about 90% in COD removal and it was achieved at the conditions of 0.003 Fe^{2+} / H_2O_2 ratio, 180 min reaction period and pH = 3.

3. Materials and methods

3.1. Characteristics of MWCF

In this study, %3 volume synthetic solutions of MCF (Model Ecocool 68 CF2 Fuchs-Germany) having wide industrial applications were obtained and used to evaluate the efficiency of Fenton process in the COD removal. Ecocool 68 CF2 mixture of mineral oil (40%), anionic and no anionic agents, corrosion preventing additives in combination with stabilizers based on glycol fatty alcohols and diethanolamine or diethanolamine compounds. Characteristics of the wastewater are presented in Table 1. All solutions of H_2O_2 , Fe^{+2} , NaOH, H_2SO_4 and synthetic wastewater were Prepared with deionized water and were made on each experimental day.

Table1. Characteristic of synthetic wastewater used in Fenton and Fenton-like processes

Parameter	Value
pH	9.26
COD (mg/l)	62758
BOD ₅ (mg/l)	540
Temperature (°C)	26
BOD ₅ / COD	0.0086

3.2. Fenton and Fenton-like process

The Fenton and Fenton-like process experiments were conducted by jar test method in room temperature. Every beaker was filled with 500 ml of wastewater sample, and Initial pH was adjusted on the designed value with 0.1 N sulfuric acid solutions (H_2SO_4 , 98%, Merck). The materials used in the experiments were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (in Fenton process) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (in Fenton-like process), as catalysts. In all processes H_2O_2 35% w/w (Merck) was used as oxidant. After reaction time Fenton's reagent with wastewater, 4N NaOH was added to stop the oxidation reaction (pH 8.5). To eliminate the excess H_2O_2 , the solution was heated at 50 °C for 60 min in oven. Samples were withdrawn and immediately analyzed.

3.3. Chemical analyses

For analysis COD, the supernatant was withdrawn, filtered through 0.45 μm and were diluted 100 times with distilled water. Changes in chemical oxygen demand (COD) were determined by means of the

dichromate reflux standard method methods [25]. To determine the COD in, a light scan from 600 nm was performed using a Carry50 Varian spectrophotometer.

According to a high concentration of suspended solids, the settling phenomenon, is placed in a graduated cylinder is illustrated on Fig.2 (C) settling velocity can be described by the Eq. (14).

Settling Velocity (SV) = (S/H)*100

In Eq. (14), S indicates the rate of settling inclusive hindered (zone), transition and compression settling in the various times and H indicates the height in interface [26].

4. Results and discussion (Factors affecting the performance of Fenton and Fenton-like process)

4.1. Effect of H₂O₂ and Fe²⁺(or Fe³⁺)

Many authors suggested Fe²⁺ to H₂O₂ mass ratio to be optimal at 1 to 10, but it must be optimised for particular wastewater to minimize scavenging effects. Of the two reagents, H₂O₂ is more critical because it directly affects the theoretic maximum mass of hydroxyl radical generated. Therefore, H₂O₂ dosage depends heavily on initial COD with high initial COD generally requiring more H₂O₂ [6, 27]. The theoretical mass ratio of removable COD to that of H₂O₂ is 470.6/1000; that is 1000 mg/L H₂O₂ theoretically removes 470.6 mg/L COD by oxidation. Occasionally, η as defined in Eq. (15) is used to evaluate the efficiency of H₂O₂ usage in the Fenton process [28].

$$\eta = 2.12 \text{ COD}_{\text{oxi}}/[\text{H}_2\text{O}_2] \quad \text{Eq. (15)}$$

In Eq. (11), COD_{oxi} indicates the COD removed by oxidation, and [H₂O₂] indicates the dosage of added peroxide. Thus, the H₂O₂ concentrations from 10 to 100 g/L were used. It should be mentioned that pH range for the Fenton process in different studies was 2–6 [28, 29],

Three methods have been used to optimize addition rates. First, Fe²⁺ dosage has been varied at a fixed arbitrary dosage of H₂O₂, followed by optimization of the H₂O₂ concentration at this Fe²⁺ dosage. Second, the best among several combinations of Fenton reagents' dosages has been selected as optimal in terms of COD removal over the tested range of H₂O₂ and Fe²⁺ concentrations. Third, H₂O₂ dosage has been varied at a fixed arbitrary dosage of Fe²⁺, followed by optimization of the Fe²⁺ concentration at this H₂O₂ dosage. Fourth, optimal ratio of H₂O₂ to Fe²⁺ is first found, and optimal dosages of Fenton reagents are then determined at this ratio. The success of all three methods is dependent on the extent of iteration [28].

Fig. 1(a) shows the removal of COD at different H₂O₂ dosages by Fenton and Fenton-like processes. pH, Fe²⁺(or Fe³⁺) and reaction time was fixed at 3, 10 g/l and 60 minute. When the dosage of H₂O₂ increased from 0 g/l to 50 g/l, the COD removal increased in the Fenton process. This is due to the increasing amount of ferric ion and its hydroxo complexes generated by the redox reaction. However the dosage of H₂O₂ varied over from 50 g/l to 100 g/l, the COD removal decreased from 88.31% to 66.09%. This result is attributed to the scavenging effect of peroxide on hydroxyl radicals, which presumably became stronger as the relative ratio [H₂O₂]/[Fe²⁺] rapidly increased. Also COD removal decreased the result increasing scavenging effect of Fe²⁺ on hydroxyl radicals, shown in Eq. (5). Residual H₂O₂ may inhibit downstream biological treatment. Excess H₂O₂ results in iron sludge flotation (Fig. 2(a)), also due to O₂ off-gassing caused by auto decomposition of excess H₂O₂, shown in Eq. (16) [17,28].



When increasing the H₂O₂ dosages from 50g/l to 100g/l, the COD removal remained in the range of 61.59–64.58%. Due to Fig. 1(a) optimal ratio of Fe²⁺ to H₂O₂ is 1/5 by Fenton and Fenton-like processes. Fig.1 (b) shows the removal of COD at Different dosages of H₂O₂ and Fe²⁺(or Fe³⁺) in optimal ratio Fe²⁺(or Fe³⁺) to H₂O₂ (0.2) by Fenton and Fenton-like processes. The Fenton-like process, 67.33% COD could be maximum removed under pH 3, 100 g/l H₂O₂, 20 g/l FeCl₃ and 60 min settling time.

Fig. 3(a) shows the effect of ferrous dosage on the COD removal with a amount of 50 g/l H₂O₂ by Fenton process. The maximum COD removal efficiency of 88.87% occurred at in the FeSO₄ dosage from 20g/l. As the dosage of Fe²⁺ increased from 2 g/l to 10 g/l, the COD removal increased from 25.16% to 88.31%. This was due to the increasing amount of HO[•] generated and ferric hydroxo complexes by the redox reaction with the increasing dosage of Fe²⁺. When increasing the FeSO₄ dosage from 10g/l to 40g/l, the COD removal remained in the range of 83.82–88.87%. Excess iron salt contributes to an increase in the amount of iron sludge and TDS, turbidity and electrical conductivity in the effluent Fig. 2(b) [30]. Also Fig. 3(b) Show the effect of ferric dosage on the COD removal with a amount of 100 g/l H₂O₂ by Fenton-like process.

In Fenton treatment of wastewaters, oxidation and coagulation by generated iron sludge both contribute to removal of organic constituents, though the effect of coagulation has not been well recognized [28]. Fig. 4

Show the effect of H_2O_2 and ferrous dosage on sludge production rate in Fenton process, when increasing the dosages of Fe^{2+} from 5 to 40 g/l, the sludge production rate increasing from 55 to 580 ml/l and also increasing sludge settling velocity. Therefore, the dosage of $FeSO_4$ was fixed at 10 g/l for Fenton process experiment.

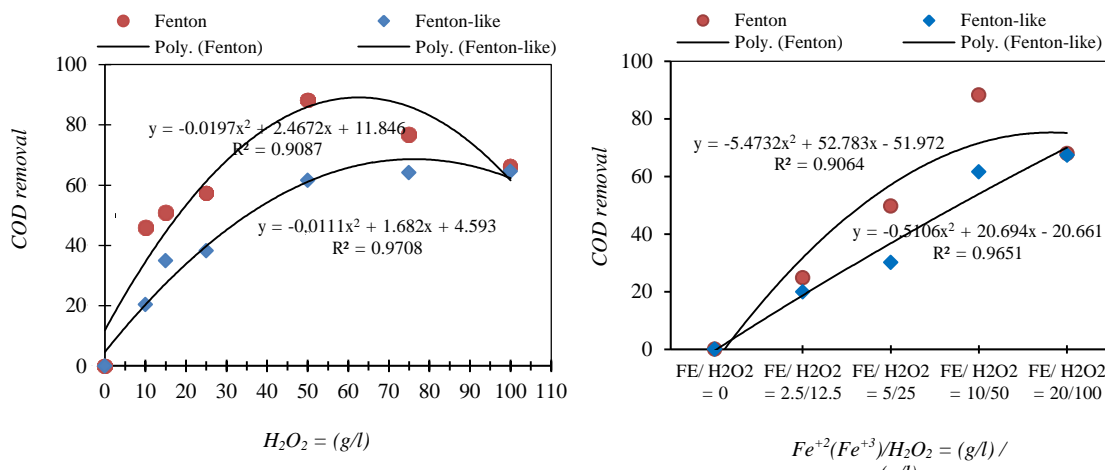


Fig.1. (a) Effect of H_2O_2 dosage on the COD removal efficiency (%) by Fenton and Fenton-like processes (Fe^{2+} (or Fe^{3+})=10 g/l, pH= 3, time=60 min); (b) Effect Different dosage of H_2O_2 and Fe^{2+} in optimal ratio (Fe^{2+} (or Fe^{3+}) to H_2O_2 at on the COD removal efficiency (%) by Fenton and Fenton-like processes (pH= 3, time=60 min)

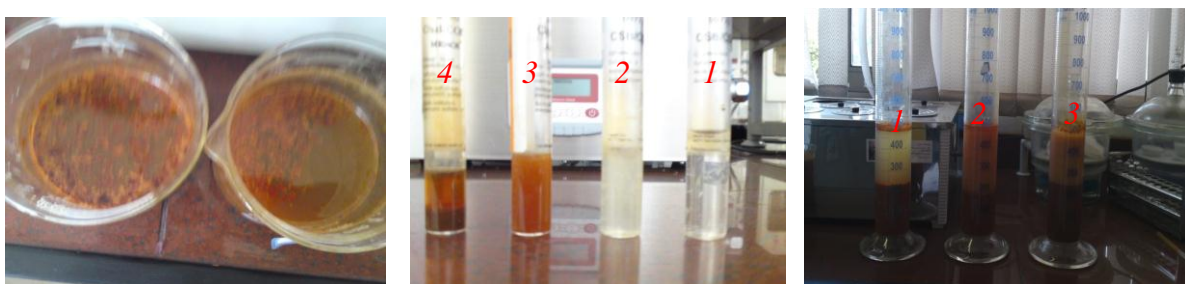


Fig.2. (a) iron sludge flotation by Fenton process (H_2O_2 =(75 - 100) g/l, Fe^{2+} = 10 g/l, pH= 3, time=60 min); (b) turbidity by Fenton process(1- Fe^{2+} = 5 g/l, 2- Fe^{2+} = 10 g/l, 3- Fe^{2+} = 20 g/l, 4- Fe^{2+} = 40 g/l), (H_2O_2 =50 g/l, pH= 3, time=60 min); (C) amount of iron sludge(1- H_2O_2 = 50 g/l, 2- H_2O_2 = 75 g/l, 3- H_2O_2 = 100 g/l)

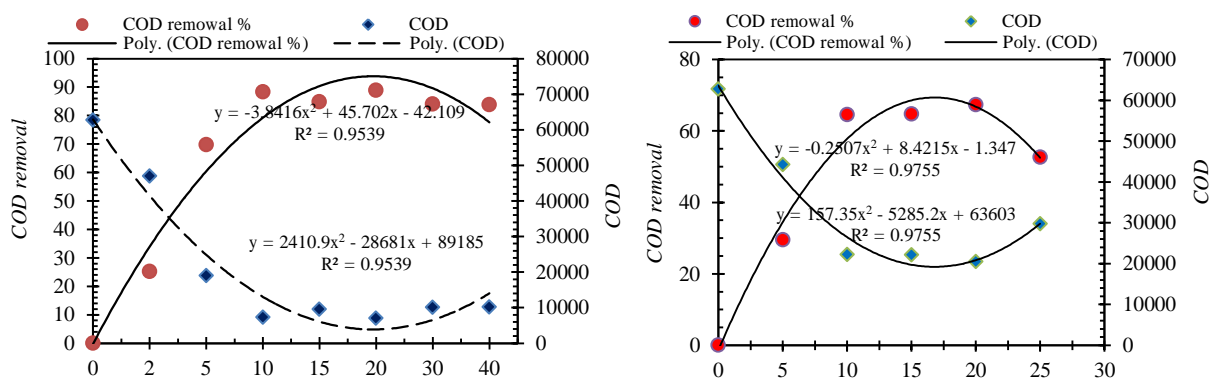


Fig.3. (a) Effect of Fe^{2+} on the effluent COD and COD removal efficiency (%) by Fenton process (H_2O_2 = 50 g/l, pH= 3, time=60 min). (b) Effect of Fe^{3+} on the effluent COD and COD removal efficiency (%) by Fenton-like process (H_2O_2 = 100 g/l, pH= 3, time=60 min)

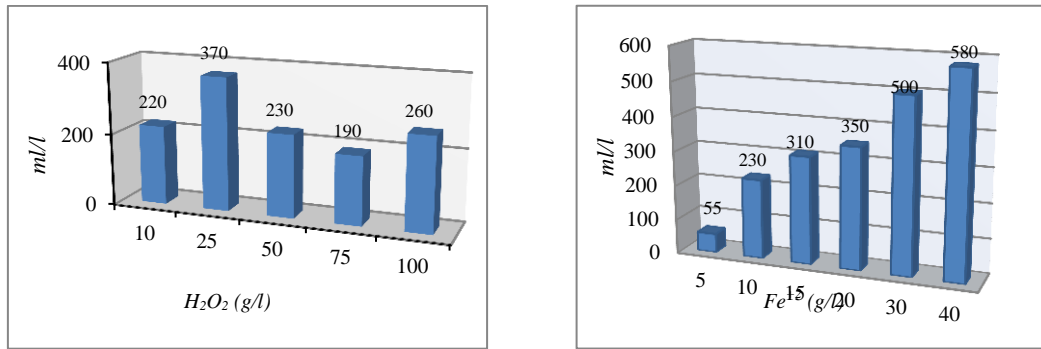


Fig.4. (a) Effect of H_2O_2 on the sludge production rate by Fenton process ($Fe^{2+} = 10$ g/l, pH= 3, time=60 min). (b) Effect of Fe^{2+} on the sludge production rate by Fenton process ($H_2O_2 = 50$ g/l, pH= 3, time=60 min).

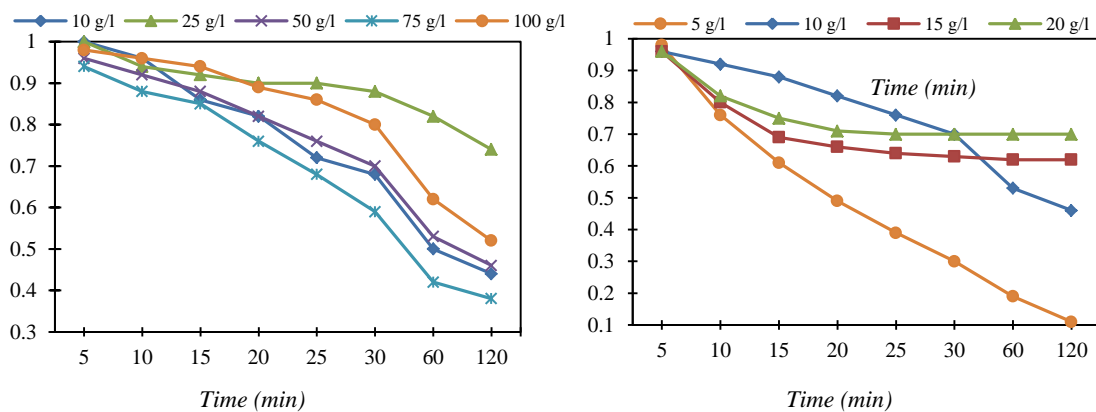


Fig.5. (a) Effect of H_2O_2 on the rate of settling (sludge settling velocity) by Fenton process ($Fe^{2+} = 10$ g/l, pH= 3, time=60 min) (b). Effect of Fe^{2+} on the sludge rate of settling (sludge settling velocity) by Fenton process ($H_2O_2 = 50$ g/l, pH= 3, time=60 min)

4.2. Initial pH

The pH has been observed to be a highly important factor for the effective Fenton and Fenton-like processes [8]. According to a previous researcher's report, pH value should be in the range of 2 to 6 [28, 31]. The effect of initial pH on COD removal efficiency is shown in Fig. 6(a). At a Fe^{2+} (or Fe^{3+}) concentration of 10 g/l and reaction time 60 minute, maximum COD removal efficiencies (88.31%) by Fenton process occurred at pH 3 and (73.97%) by Fenton-like process occurred at pH 5 and 100 g/l of H_2O_2 .

The Fenton process when the initial pH decreased to 2, the COD removal efficiencies decreased from 88.31% to 84.17%. A pH below optimal can inhibit oxidation in three ways. First, at extremely low pH values, the $[Fe(H_2O)]^{2+}$ formed reacts relatively slowly with H_2O_2 , producing less hydroxyl radicals. Second, exceptionally low pH can inhibit reaction between Fe^{3+} and H_2O_2 Third increased scavenging of hydroxyl radicals by H^+ . On the other hand, a pH above optimal (3) the COD removal efficiencies decreased, due to the increasing rate of auto decomposition of H_2O_2 , deactivation of iron ions into iron oxy-hydroxides, and the decreased oxidation potential of hydroxyl radicals[7,28].

Fig.6. (b) shows the pH changes for indicator for Fenton reaction monitoring progress. As the reaction proceeds, the pH declines, first at the point where the iron sulfate is added, and then a more-pronounced decline at the point where hydrogen peroxide is added. This occurs partly due to the fragmenting of organic materials into organic acids. This pH change indicates that the reaction is proceeding as desired, and it is monitored as a sign of such progress [32].

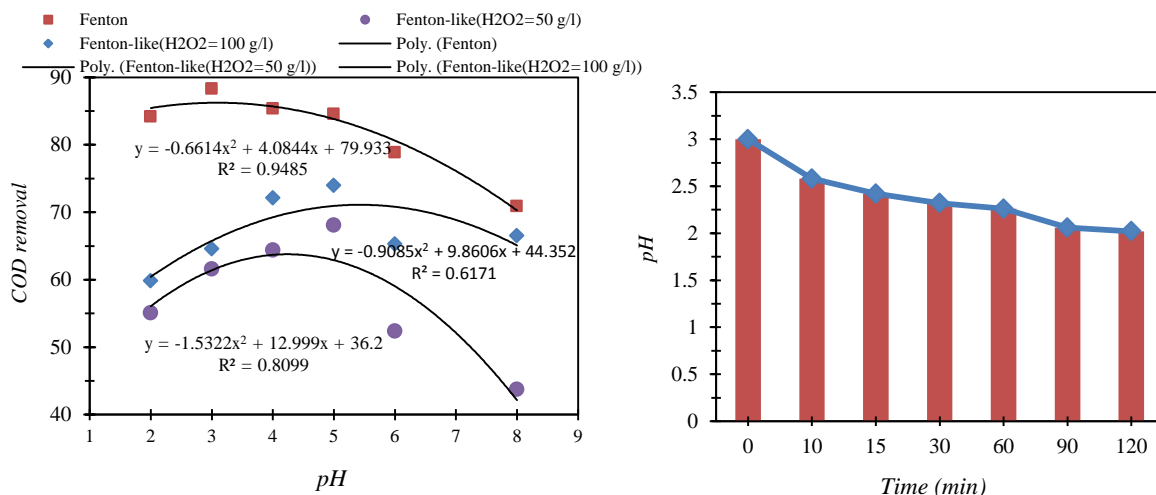


Fig.6. (a) Effect pH on COD removal efficiency (%) by Fenton and Fenton-like processes (Fe^{+2} or $Fe^{+3} = 10$ g/l, time=60 min). (b). pH changes by Fenton process ($Fe^{+2} = 10$ g/l, $H_2O_2 = 50$ g/l, time=60 min).

4. 3. Effect of contact time and mixing speed

Fig. 7 shows the effect of reaction time and different mixing speeds on COD removal in the Fenton and Fenton-like processes. As shown in this Figure, the optimum reaction time for Fenton and Fenton-like processes were 60 and 30 minutes, respectively. More than 92% of COD removal was achieved in the first 15 min of reaction in the Fenton process. There appears to be no difference in COD removal under the mixing speeds studied. Such observation is different from those reported by others, who indicated simultaneous removal of color and COD [19].

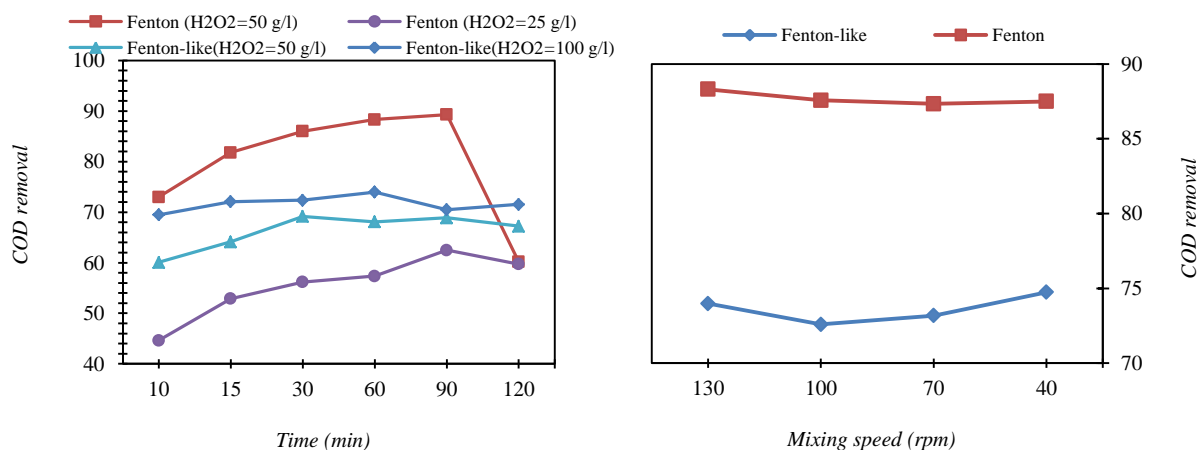


Fig.7. (a) Effect of contact time on the COD removal efficiency by Fenton and Fenton-like processes (Fe^{+2} or $Fe^{+3} = 10$ g/l, $H_2O_2 = 50$ g/l, pH= 3). (b). Effect of mixing speeds on the COD removal efficiency by Fenton process ($Fe^{+2} = 10$ g/l, $H_2O_2 = 50$ g/l, pH= 3) and Fenton-like process ($Fe^{+3} = 10$ g/l, $H_2O_2 = 100$ g/l, pH= 5).

4.4. Biodegradability changes of MWCFs

Initially, the biodegradability of the MWCFs was evaluated through the evolution of the BOD₅/COD ratio. The BOD₅/COD ratio was 0.0086 in raw MWCF. The BOD₅/COD ratio of the treated MWCF after the studied Fenton process is illustrated in Figure 6. As shown in this figure, the BOD₅/COD ratio increased in

the treated MWCF. The highest increase in BOD_5/COD ratio was observed in the Fenton process. Also, Kim et al. (2001) found that Fenton reaction achieved a higher COD removal and a higher BOD_5/COD than Fenton-like reaction in the leachate treatment. And the optimal pH 3.0 for Fenton oxidation was below the optimal pH 4.5 for Fenton-like reaction.

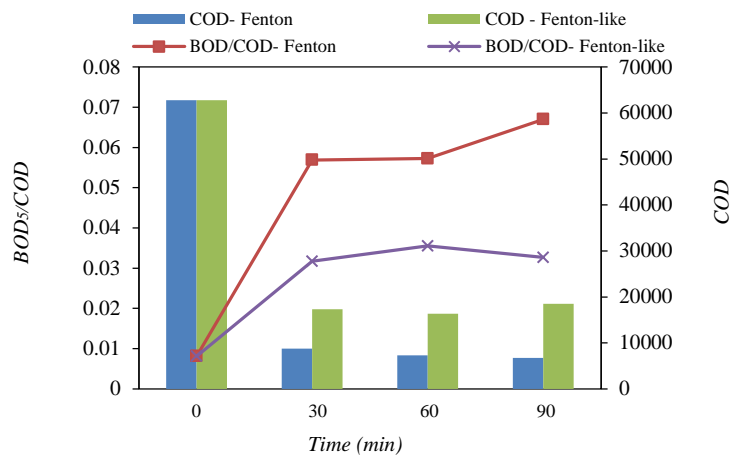


Fig.8. Variations of BOD_5/COD ratio of the treated MWCF based by Fenton process (Fe^{+2} or $Fe^{+3} = 10$ g/l, $H_2O_2 = 50$ g/l, pH= 3) and Fenton-like process ($Fe^{+3} = 10$ g/l, $H_2O_2 = 100$ g/l, pH= 5).

5. Conclusions

According to the results above described, it could be concluded that:

1. Due to their low BOD_5 (540 mg/l)/COD (62758 mg/l) ratios (0.0086) biological processes are not effective enough for treatment of the MWCF. The results here presented can be considered as an effective treatment of this type of wastewaters, when direct biological treatments are not effective.
2. The results of study showed, the efficiency of the Fenton-like process was less than Fenton process. A great difference in practice is that a greatly quick generation of hydroxyl radicals may occur at the beginning of Fenton process, whereas Fenton-like process has a slow generation rate of hydroxyl radicals. The reason is that the rate constant in Eq. (1) (the main reaction at the initial stage of Fenton oxidation) is much higher than that in Eq. (2) (the main reaction at the initial stage of Fenton-like oxidation).
3. At the optimum conditions, the efficiency of COD removal was 88.31% in Fenton Process under pH 3, 50 g/l H_2O_2 , 10 g/l Fe^{2+} and 60 min settling time, and 73.97% in Fenton-like Process under pH 5, 100 g/l H_2O_2 , 10 g/l $FeCl_3$ and 30 min settling time.
4. During the first 15 min of the Fenton's reaction, more than 92% of COD removal can be achieved. This finding is of special interest in the industrial application of Fenton's reagent, because it permits a significant COD reduction in a very short period of time.
5. By increasing the dosages of Fe^{2+} from 5 to 40 g/l, the sludge production rate increasing from 55 to 580 ml/l.
6. The BOD_5/COD ratio increased in the MWCF treated. The highest increase in BOD_5/COD ratio was observed in the Fenton process.

6. References

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