Arabian Journal of Chemistry (2014) 7, 1116–1123

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

A comparative study for treatment of white liquor by different applications of Fenton process

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Received 12 August 2012; accepted 12 December 2012
Available online 29 December 2012

KEYWORDS

COD;
Electro-Fenton;
Fenton process;
Paper industry;
White liquor;
Zero valent iron

Abstract In this paper, the treatability of white liquor by conventional (CFP), modified (MFP) and electro-Fenton oxidation processes (EFP) was investigated depending on the COD parameter. Based on the experimental results, up to 62.4%, 58.4% and 54.9% COD removals by the CFP, MFP and EFP were achieved, respectively. It was observed that adjustment of initial pH to acidic values is not required in the CFP. The optimal operational conditions were found to be $[Fe^{2+}] = 500$ mg/L, $[H_2O_2] = 1000$ mg/L at pH 7.3 (original pH) in the CFP, $[Fe^0] = 1250$ mg/L, $[H_2O_2] = 1000$ mg/L at pH 3 in the MFP, and $I = 1.0$ A, $[H_2O_2] = 1500$ mg/L at pH 3 in the EFP, respectively. As a result, the CFP has been determined as a more efficient alternative treatment method.

1. Introduction

The pulp and paper industry is a water intensive industry and its high water consumption is one of the most important environmental concerns in this industry. The amount and characteristics of paper industry effluents depend upon the type of manufacturing process, type of the raw materials, process technology applied, management practices, internal recirculation of the effluent for recovery, and the amount of water to be used in the particular process (Pokhrel and Viraraghavan, 2004). While the wastewater originating from the pulp making process is classified as black liquor, pulp bleaching effluent is called as white liquor. White liquors may contain dissolved lignin, carbohydrate, organic and inorganic chlorine compounds such as chlorate and chlorophenols, volatile organic compounds such as chloroform and carbon disulfide and color (Pokhrel and Viraraghavan, 2004). Discharge of this kind of completely untreated wastewaters may cause scum formation, slime growth, thermal impacts, color problems, loss of esthetic beauty and toxic effects on living organisms in the environment. Therefore, the paper industry wastewaters should be treated before their discharge.

In order to treat the paper industry wastewaters, though the conventional coagulation and activated sludge processes can be applied on the pulp and paper mill effluents containing various organic and inorganic non-biodegradable materials and color; quality of the treated effluent cannot meet the environmental regulations in many cases (Amat et al., 2005). In addition, the non-biodegradable fraction of the organic compounds can be accumulated in the waste biological sludge

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2012.12.015

(Tambosi et al., 2006). Thus, for the treatment of the pulp and paper industry effluents, physico-chemical and chemical treatment processes, such as adsorption (Shawwa et al., 2001), air flotation (Gubelt et al., 2000), coagulation (Gokcay and Dilek, 1994; Tong et al., 1999), Fenton oxidation (Sevimli, 2005), foto-Fenton oxidation (Xu et al., 2007), electro-coagulation (Parama Kalyani et al., 2009; Zaied and Bellakhal, 2009), electro-Fenton oxidation (Selvabharathi and Kanmani, 2010), photo-catalytic oxidation (Amat et al., 2005), sedimentation (Thompson et al., 2001), ozonation (Sevimli, 2005) and sonication (Shaw and Lee, 2009) attracted more attention as alternative ways to be used in combination with a biological treatment process. Among all these processes, the mechanisms of adsorption, coagulation, flotation and sedimentation are based on the phase transfer from the liquid phase to solid phase and cause the problem to remain unresolved in the solid phase. Although ozonation and photo-catalytic oxidation methods are effective to remove the pollutants from the wastewater, they are not attractive owing to their high capital and operational costs. Sonication was reported as an inefficient method for COD removal from the wastewater of pulp and paper kraft mill (Shaw and Lee, 2009). But, when compared with these methods, the Fenton oxidation process is the commonly used advanced oxidation process which is utilized successfully for the treatment of various industrial wastewaters (Aydin et al., 2002; Gogate and Pandit, 2004; Mahiroglu et al., 2009; Güçlü et al., 2012), because it is cost effective, easy to handle and efficient treatment technique. The Fenton process has two distinct stages, namely Fenton's oxidation which is based on the formation of hydroxyl radicals ($OH^{\bullet}$) by the reaction of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) in the acidic medium and Fenton's coagulation which is mainly simple ferric coagulation following the oxidation stage. The Fenton oxidation process can be easily modified by using zero valent iron (ZVI) instead of Fe^{2+} as the catalyst iron source. This modified process is named as the modified Fenton process (MFP) in this study. Furthermore, the Fenton process can be combined with the electro-coagulation process, which is called as the electro-Fenton process (EFP).

Up to now, the treatment of black and dark brown liquors from the pulp and paper industries has been widely investigated. Sevimli (2005) carried out a comparative study for the post-treatment of corrugated board factory effluent via CFP and ozonation. In his study, the CFP was determined as a more feasible process with 83% chemical oxygen demand (COD) removal in comparison with ozonation. In the study of Kazmi and Thul (2007), only 62% COD removal was achieved by the CFP. Tambosi et al. (2006) reported a nearly 50% COD removal from the pulp and paper industry effluent by an Fenton-like process using Fe^{3+} as the catalyst iron. In another study, Selvabharathi and Kanmani (2010) reported 90% COD removal from the dark brown liquor by the EFP. In spite of those studies conducted with the black and brown liquors, the literature contains a small number of studies on the treatment of the white liquor from the paper industry with different applications of Fenton processes. Moreover, we could not meet any report related with the treatment of the white liquor via the Fenton process modified with ZVI and the electro-Fenton process using cast-iron electrodes. For this reason, the main aim of the present work is to provide more insights into the treatment of the real paper industry effluent by different modifications of the Fenton process and to determine the influences of different operating parameters on the COD removal.

2. Experimental section

2.1. The wastewater and chemicals used

The composite wastewater (white liquor) sample used in this study was obtained from the discharge point of an existing wastewater treatment plant of a paper factory in Konya, Turkey. The treatment plant has physical treatment units (equalization, pumping station, clarifier and neutralization). The wastewater sample was preserved in the dark at 4 °C in a refrigerator and used without any dilution. No significant dissolution in the wastewater sample was observed during the oxidation experiments. The wastewater had a pH of 7.3, turbidity of 434 NTU, COD of 865 mg/L, Cl^- (chloride) of 390 mg/L and SO_4^{2-} (sulfate) of 630 mg/L.

Hydrogen peroxide (H_2O_2) (35% w/w), ferrous iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), iron powder (ZVI, Fe^0), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), manganese dioxide (MnO_2), sodium chloride (NaCl) and other chemicals were all of analytical grade and purchased from Merck (Germany). All chemicals were utilized as received without further purification. Distilled water was used in the preparation of all solutions.

2.2. Experimental procedures

Classical (CFP) and modified Fenton (MFP) oxidation experiments were carried out with 500 mL working volume in Pyrex-glass beakers using a standard jar test apparatus (Velp, FC6S). The experiments were done at room temperature (24 ± 2 °C) using varying $FeSO_4{\cdot}7H_2O$–H_2O_2 (for CFP experiments) and Fe^0–H_2O_2 (for MFP experiments) dosages at different pH values in order to determine optimum dosages. The CFP and MFP experiments were conducted in three steps. The wastewater pH was first adjusted to the desired value. The second step was the addition of $FeSO_4{\cdot}7H_2O$ and Fe^0 in CFP and MFP, respectively. In the final step, H_2O_2 was added into the reaction mixture. After the additions of Fenton reagents, the wastewater was mixed at 90 rpm during the oxidation stage of the Fenton process. At the end of the oxidation stage, the solution pH was adjusted to about 7.5 using 6 N and 0.1 N NaOH solutions and the wastewater was mixed for 3 min at 30 rpm to form iron (oxy)hydroxide ($Fe(OH)_3$) flocs. After 30-min precipitation, 25 mL sample was pipetted from the supernatant for the COD analysis.

The EFP experiments were conducted with 500 mL of wastewater in a Pyrex-glass reactor. The wastewater was mixed by magnetic stirrer to homogenize the reaction solution. Cast-iron anode and cathode plates were utilized in pairs in the electro-chemical reactor. The electrodes, dimensions of which are 8.8 cm × 2.0 cm (with a thickness of 3.0 mm), were positioned approximately 7 cm apart from each other and were immersed about 5 cm into the white liquor. The electrical direct current (DC) input was supplied by a DC power supply (Good Will, Taiwan). In each experimental run, 500 mL of wastewater was pour into the reactor. The wastewater pH was adjusted to the desired value using 0.1 and 6 N H_2SO_4 solutions. H_2O_2 was added into the wastewater and the electrical current was immediately turned on. During the adjustment of the current, NaCl was dosed as the supporting electrolyte. Batch studies were performed to optimize process parameters such as pH, H_2O_2 concentration and electrical current. In the end of the reaction time, the solution pH was adjusted to about 7.5 using 0.1 and 6.0 N NaOH solutions to precipitate Fe^{2+} solved from the sacrificial anode plate as $Fe(OH)_3$. After the 30-min settling time, the sample was taken from the supernatant for the COD measurements.

2.3. Analytical methods

The residual (unreacted) Fe^{2+} and H_2O_2 can interfere with the COD measurement. In order to inhibit the interferences by removing Fe^{2+} as $Fe(OH)_3$, pH of supernatant adjusted to about 7.5 with the addition of NaOH. MnO_2 can decompose the residual H_2O_2 into water and oxygen as a catalyst (Choi et al., 2004). Thus, the 25 mL sample was poured into a beaker containing MnO_2 for quenching the residual H_2O_2 (Kiril Mert et al., 2010). The amount of catalyst MnO_2 to degrade H_2O_2 present in the sample was calculated by taking the initial H_2O_2 concentration into consideration. It was confirmed by H_2O_2 sensitive test strips (Macherey Nagel, Germany) that the residual H_2O_2 was destroyed completely (Güçlü et al., 2012). Before each analysis, samples were filtered through 0.45 μm membranes to remove $Fe(OH)_3$ and MnO_2. Turbidity was measured in NTU via a Hach Lange 2100P turbidimeter (Germany). The measurement of pH was conducted by a WTW 340i pH meter (Germany). Chloride (Cl^-), COD, sulfate (SO_4^{2-}) and turbidity analyses were performed in accordance with Standard Methods by APHA/AWWA/WEF (2005).

3. Results and discussion

The Fenton process and its modifications can be applied for the removal of organic matters in the wastewater with high treatment efficiency at lower capital and operational costs, compared to other oxidation processes such as ozonation, sonication, UV/H_2O_2 etc. The important operational parameters, influencing the efficiency of Fenton oxidation, are oxidation time, pH, concentrations of catalyst iron (Fe^{2+}/Fe^0) and H_2O_2, and electrical current. In the preliminary Fenton oxidation experiments, the optimum oxidation times for CFP, MFP and EFP were found to be 60, 120 and 45 min, respectively. While prolonging of oxidation times negligibly improved the COD removal efficiencies of CFP and MFP, the treatment efficiency of EFP considerably decreased. Hence, the experiments were performed at the optimized oxidation times.

3.1. Conventional Fenton and modified Fenton processes

The pH of reaction solution has a great influence on the concentration of ferrous ions (Fe^{2+}) and the amount of hydroxyl radicals ($OH^\bullet$) produced. Thus, the wastewater pH manages the efficiency of the Fenton oxidation process. Although the optimum initial pH for the Fenton process has been determined as 3 in many reports (Gogate and Pandit, 2004), it has been reported that the pollutants could be removed efficiently at pH 5 and higher pH values (Güçlü et al., 2012). In this study, the pH optimizations were first executed to determine its effect on the COD removal. The effect of pH was examined by changing the pH values from 2 to 5 at constant concentrations of 1000 mg/L H_2O_2 and 500 mg/L the catalyst iron (added as Fe^{2+} in CFP and Fe^0 in MFP). As it was seen from Fig. 1, the maximum COD removals were achieved at initial pH 7.3, at which is the original pH value of the wastewater, in CFP and at solution pH 3 in MFP. The COD removal efficiencies were 60.1 and 38.1% by CTP and FTP at these pH values, respectively. In both Fenton oxidation processes, the removal of COD diminished with the decrease in the wastewater pH from 3 to 2. Because, at extremely acidic pH values (lower than 2.5), Fe^{2+} is deactivated and transformed into $(Fe(II)(H_2O))^{2+}$ complex which more slowly reacts with H_2O_2 to produce $OH^\bullet$ (Gogate and Pandit, 2004). Furthermore, the scavenging of OH by hydrogen ions (H^+) occurs and H_2O_2 is also stabilized as $H_3O_2^+$ at low pH values (Gogate and Pandit, 2004), as shown in Eqs. (1) and (2).

$$OH^\bullet + H^+ + e^- \rightarrow H_2O \tag{1}$$

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{2}$$

In the CFP experiments, the wastewater pH was continuously measured during the oxidation stage of the Fenton process. It was observed that the pH of the wastewater rapidly drops from 7.3 to around 3.5 within the first one minute after the addition of Fe^{2+} and H_2O_2. In the remaining part of the oxidation stage of CFP, the pH value slowly decreased up to around 2.9. This significant drop in pH is attributed to the fragmenting of organic material into organic acids. This change, occurred in pH, can be observed to provide that the oxidation reaction is progressing as planned. In the case of the initial pH of 2 and 2.5, the pH end value increased to 2.2 and 2.6, respectively. Similar results have been reported in the studies of Güçlü et al. (2012) and Kallel et al. (2009). Therefore, it was determined that the original pH (7.3) of the paper industry wastewater was the best for CFP due to this sharp drop in the wastewater pH. Since there is no need to adjust the initial pH to acidic values, the capital and operating costs can also be reduced with this superiority of CFP.

In the MFP experiments, it was seen that after the addition of Fe^0 and H_2O_2, the initial pH of the wastewater, adjusted to acidic pH, raised gradually during the oxidation stage due to the reaction of Fe^0 with H^+ according to Eq. (3) (Kallel et al., 2009). Since Fe^0 is first to be solved in order to catalyze the reaction with H_2O_2 in the strong acidic pH of reaction solution, keeping pH constant in the acidic range is very important for the oxidation of pollutants in the wastewater. Therefore, the wastewater pH was continuously monitored and kept fixed at the desired initial pH value during the oxidation stage of the MFP. The rise in the initial/operational pH reduced the resolution of Fe^{2+} from ZVI and thus led to a decrease in the COD removal, as seen from Fig. 1. Consequently, the optimum pH value for MFP was found to be 3.

$$Fe^0 + 2H^+ \leftrightarrow Fe^{2+} + H_2 \tag{3}$$

H_2O_2 is the main source of $OH^\bullet$ produced catalytically in the Fenton process. However, its excess usage both reduces the overall oxidation efficiency and raises the operating cost of the Fenton process. Besides, residual H_2O_2 present in the treated wastewater contributes to COD and flotation of iron sludge due to O_2 off-gassing caused by decomposition of excess H_2O_2 (Güçlü et al., 2012). Thus, optimization of H_2O_2 dosage is crucial in the environmental and economical points of view. In order to optimize the initial H_2O_2 concentration,

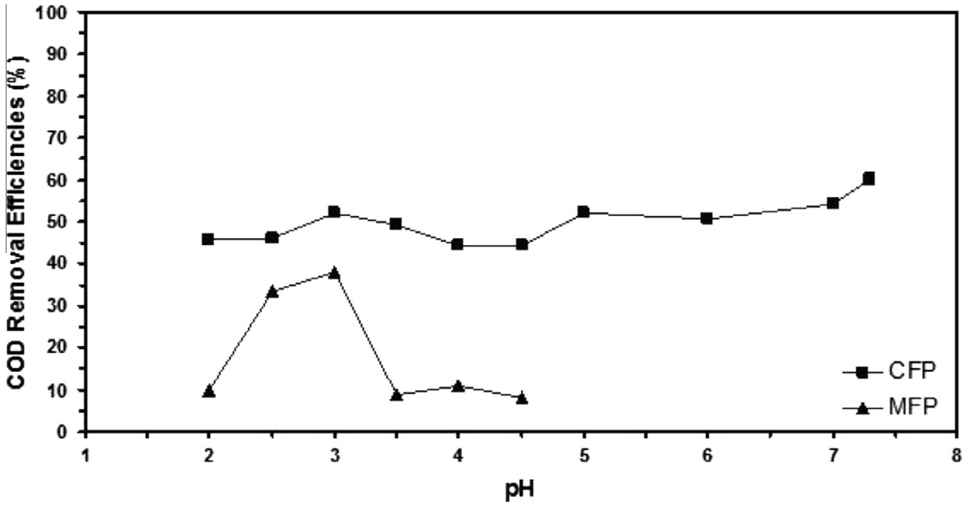

Figure 1 Effects of pH on COD removals by CFP ($[Fe^{2+}] = 500$ mg/L, $[H_2O_2] = 1000$ mg/L, time = 60 min) and MFP ($[Fe^0] = 500$ mg/L, $[H_2O_2] = 1000$ mg/L, time = 120 min).

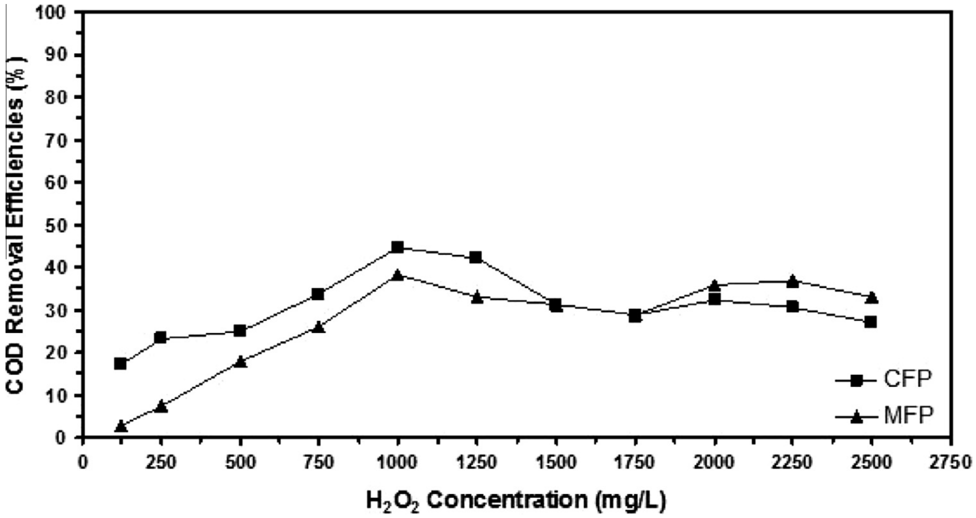

Figure 2 Effects of H_2O_2 concentrations on COD removals by CFP (pH = 7.3, $[Fe^{2+}] = 500$ mg/L, time = 60 min) and MFP (pH = 3, $[Fe^0] = 500$ mg/L, time = 120 min).

the CFP and MFP experiments were carried out at different H_2O_2 dosages in the range of 125–2500 mg/L at the optimized pH values. The catalyst iron dosages were kept fixed at 500 mg/L. COD removal efficiencies at varied H_2O_2 concentrations in both processes are represented in Fig. 2. When H_2O_2 dosage increased from 125 to 1000 mg/L, the COD removal efficiencies were raised from 17.3% to 44.3% in CFP and 2.9 to 39.2% in MFP. Up to this dosage, increment in the H_2O_2 dosage caused more $OH^{\cdot}$ production according to Eq. (4) (Neyens and Baeyens, 2003). However, further dosages led to decrease in the COD removal due to scavenging effect of excess H_2O_2 and recombination of $OH^{\cdot}$ (Eqs. (5)–(7)) (Modirshahla et al., 2007). Therefore, H_2O_2 concentration of 1000 mg/L was found to be optimum for both CFP and MFP.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \qquad (4)$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad (5)$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \qquad (6)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O \qquad (7)$$

The concentration and kind of the catalyst iron are important parameters influencing the amount of $OH^{\cdot}$ radical produced in the redox reactions of the Fenton process. The effects of both catalyst Fe^{2+} and Fe^0 dosages on COD removal were examined by altering the Fe^{2+} and Fe^0 dosages between 125 and 2500 mg/L, while H_2O_2 dosage was kept constant at 1000 mg/L and at optimum pH values determined previously. The experimental results are shown in Fig. 3 for both Fenton processes. As Fe^{2+} and Fe^0 dosages were increased from 125 to 1250 mg/L in CFP and 125 to 500 mg/L in MFP, COD removal efficiencies enhanced significantly from about 0.6 to 44.5% and 24.1 to 58.2% due to the production of $OH^{\cdot}$ more effectively in accordance with Eq. (4). Thus, it was seen that MFP was much more efficient at lower catalyst iron dosages

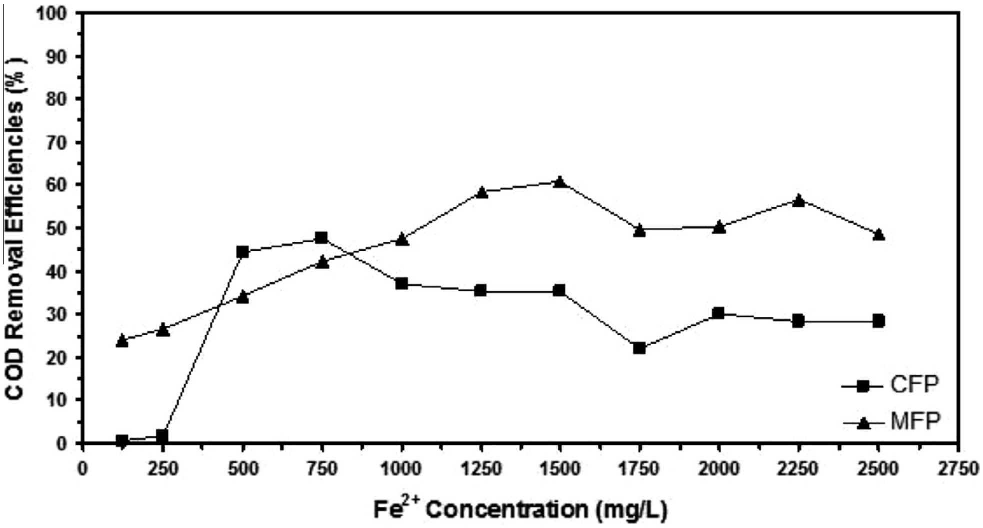

Figure 3 Effects of Fe^{2+} and Fe^0 concentrations on COD removals by CFP (pH = 7.3, $[H_2O_2]$ = 1000 mg/L, time = 60 min) and MFP (pH = 3, $[H_2O_2]$ = 1000 mg/L, time = 120 min).

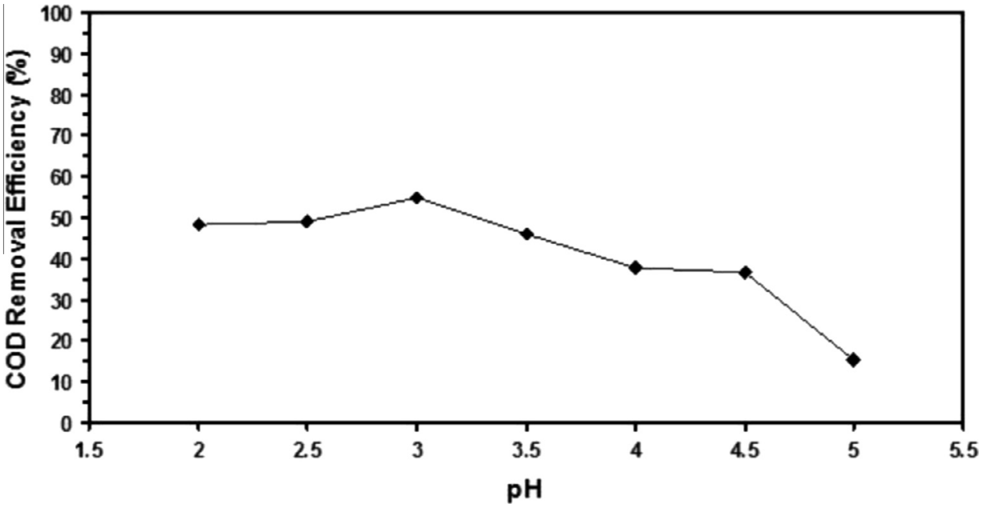

Figure 4 Effect of pH on COD removals by EFP (I = 1.0 A, $[H_2O_2]$ = 1500 mg/L, time = 45 min).

owing to the transformation of Fe^{3+} to Fe^{2+} on the metallic surface in accordance with Eqs. (3) and (8). Fe^{2+} and Fe^0 dosages were raised to 750 and 1500 mg/L, the increments in the COD removal efficiencies were negligible. However, further dosages applied in both processes resulted in a decrease in the COD removal due to the radical scavenging effect of excess iron on $OH^\bullet$ in accordance with the reaction given in Eq. (9) (Neyens and Baeyens, 2003). Therefore, while the optimal Fe^{2+} dosage in CFP was found to be 1250 mg/L, the optimal Fe^0 dosage in MFP was 500 mg/L.

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (8)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \quad (9)$$

3.2. Electro-Fenton process

The pH of the reaction solution affects the dissolution of iron from the sacrificial anode plate into the solution, the regeneration of Fe^{2+} from Fe^{3+} on the cathode plate and the amount of $OH^\bullet$ produced during the Fenton's reaction in the EFP, as well (Sahinkaya, 2012). Its effect on the COD removal was investigated in the pH range of 2–5 at constant electrical current (I) of 1.0 A, H_2O_2 dosages of 1500 mg/L and a reaction time of 45 min. As shown in Fig. 4, a remarkable influence was observed for the COD removal by the EFP. With rising pH from 2 to 3, the COD removal efficiency increased from 48.5% to 54.9%. Because Fe^{2+} is formed and stabilized as $(Fe(II)(H_2O))^{2+}$ at extremely low pH values (<2.5) (Gogate and Pandit, 2004). Besides, the oxidation performance of EFP decreases due to the radical scavenger effect of H^+ ions and the stabilization of H_2O_2 as $H_3O_2^+$ (Gogate and Pandit, 2004), as given in Eqs. (1) and (2). Furthermore, the COD removal efficiency decreased at higher pH values than 3 because of the decrements in the amount of Fe^{2+} solved in the solution and the production of $OH^\bullet$ with rising pH. Thus, the optimum pH value was determined to be 3 for the EFP.

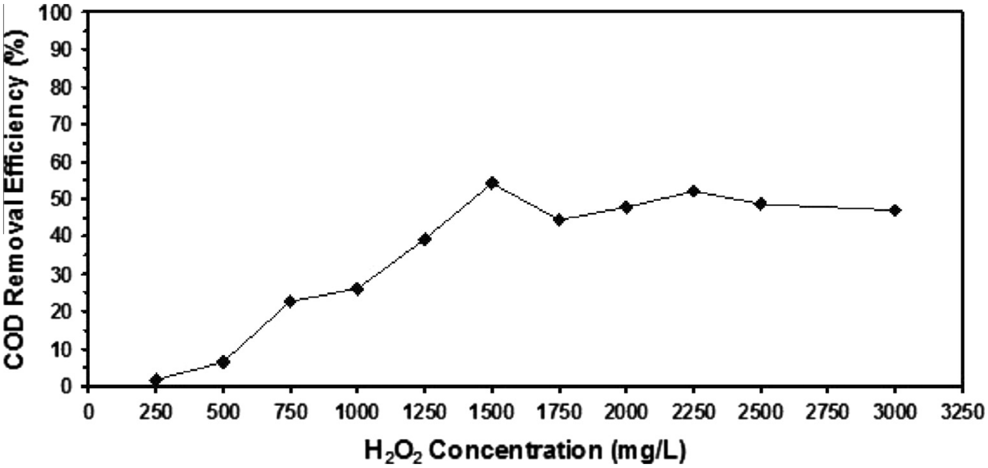

Figure 5 Effect of pH on COD removals by EFP (pH = 3, I = 1.0 A, time = 45 min).

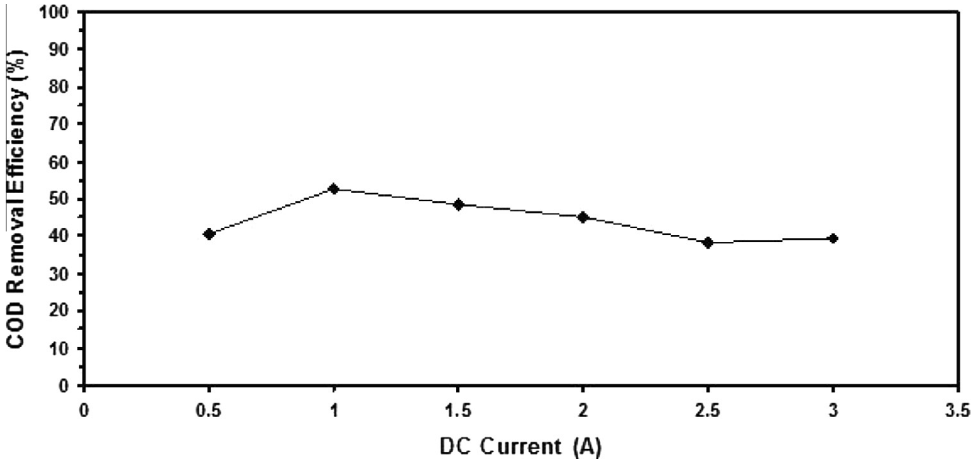

Figure 6 Effect of constant electrical DC current (A) on COD removals by EFP (pH = 3, $[H_2O_2]$ = 1500 mg/L, time = 45 min).

The effect of H_2O_2 dosage on the COD removal was shown in Fig. 5. In order to investigate the influence of H_2O_2 dosage on the oxidation performance, a series of experiments was carried out at the varying dosages of H_2O_2 in the range of 1000–5000 mg/L at the initial pH of 3 and a constant current of 1.0 A for the reaction time of 45 min. As seen from Figure 5, the increment in H_2O_2 dosage from 250 mg/L to 1500 mg/L improved the COD removal efficiency from about 1.7% to 54.3% as a result of the more effective production of oxidizing $OH^{\bullet}$ radical in accordance with Eq. (3). However, at higher dosages, excess H_2O_2 led to a decrease in the oxidation potential of the EFP owing to the radical scavenging effect of H_2O_2 according to Eqs. (5)–(7). Therefore, 1500 mg/L was found to be the optimum H_2O_2 dosage for the EFP (see Fig. 6).

The electrical current manages the dissolution and regeneration of Fe^{2+} and the electro-chemical production of H_2O_2. Thus, its effect on electro-Fenton oxidation of the paper industry wastewater was examined in the current range of 0.5–3.0 A. As shown in Fig. 3, the COD removal enhanced with the rise of current to 1.0 A. The improvement in treatment efficiency can be associated with a greater production of more oxidizing $OH^{\bullet}$ with increasing amounts of Fe^{2+} and H_2O_2 in the wastewater in accordance with Eq. (4). However, the oxidation efficiency diminished at higher electrical currents. This decrease can be attributed to extreme increases in Fe^{2+} and H_2O_2 concentrations in the reactor. The dissolution of iron from the anode plate was gradually increased from about 440 mg to 2440 mg as the current raised from 0.5 to 3.0 A. Recent studies show that an increment of the Fe^{2+} concentration lessens the degradation of the organics due to the radical scavenging effect of excess Fe^{2+}, as given in Eq. (9). Besides, electro-chemical production of H_2O_2 (Eq. (10)) leads to the scavenging of $OH^{\bullet}$ (Eqs. (5)–(7)) (Modirshahla et al., 2007). Therefore, by taking the operating cost and treatment efficiency into account, 1.0 A current was found to be optimum for the electro-chemical treatment of the paper industry wastewater.

$$O_2 + 2H^+ + e^- \rightarrow 2H_2O_2 \qquad (10)$$

3.3. Degradation performances

Optimum operating conditions were determined as $[Fe^{2+}]$ = 500 mg/L, $[H_2O_2]$ = 1000 mg/L at pH 7.3 that is the original pH value of the wastewater in the CFP, $[Fe^0]$ = 1250 mg/L, $[H_2O_2]$ = 1000 mg/L at pH 3 in the MFP, and I = 1.0 A, $[H_2O_2]$ = 1500 mg/L at pH 3 in the EFP. The comparative

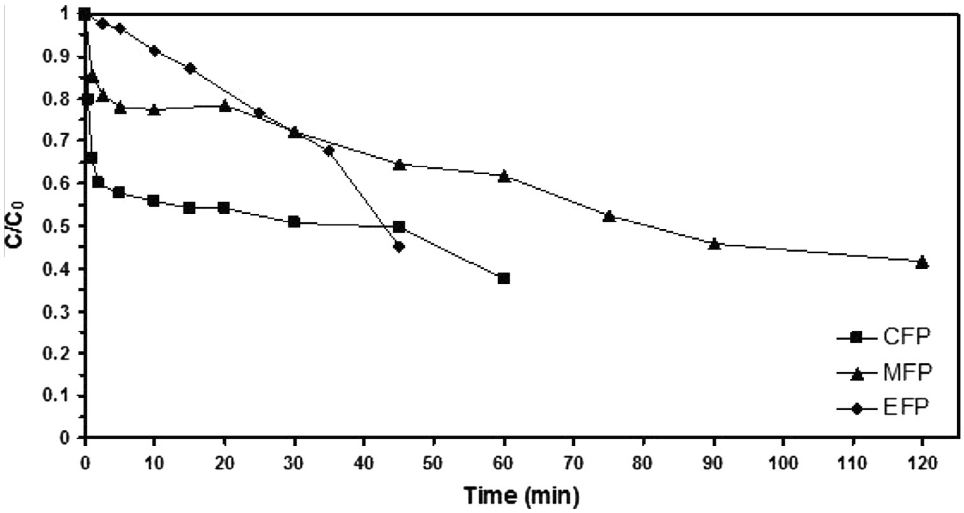

Figure 7 Dimensionless experimental data for the removal of COD by CFP (pH = 7.3, [Fe^{2+}] = 1250 mg/L, [H_2O_2] = 1000 mg/L, time = 60 min), MFP (pH = 3, [Fe^0] = 500 mg/L, [H_2O_2] = 1000 mg/L, time = 120 min) and EFP (pH = 3, I = 1.0 A, [H_2O_2] = 1500 mg/L, time = 45 min).

experimental results for the processes performed under the optimum conditions were shown in Figure 7 in terms of percent COD removal. As seen from this figure, the COD concentrations are rapidly decreased in the first 2.5 min of oxidation stage in the CFP and MFP. Then, the oxidation rates were slowed down in the remaining part of oxidation time of the both processes. Therefore, it was determined that the COD removal occurred in two stages in CFP and MFP. While the rapid oxidation stage is based on the initial concentrations of Fe^{2+}/Fe^0 and H_2O_2 in accordance with Eq. (3), the oxidation rate was slowed down owing to the rapid decrements of Fe^{2+} and H_2O_2 concentrations. Contrast to the CFP and MFP, the oxidation rate gradually increased in the EFP. As a result, it was determined that the COD removal from the paper industry wastewater happened more rapidly in the CFP owing to the addition of catalyst iron in the solved form (Fe^{2+}), compared to other two applications of the Fenton process. On the other hand, although the Fenton process is very efficient for the removal of pollutants from various wastewaters (Gogate and Pandit, 2004), it was determined that the Fenton process and its modifications were not very effective for the COD removal from the white liquor in our study. This outcome was resulted from a high inorganic content of the white liquor (such as Cl$^-$ and SO_4^{2-}).

4. Conclusions

In this comparative study, the conventional, modified and electro-Fenton oxidation processes were investigated for the COD removal from the white liquor from a paper industry. The effects of some operational conditions were experienced comprehensively. Optimum operating parameters were determined as [Fe^{2+}] = 500 mg/L, [H_2O_2] = 1000 mg/L at pH 7.3 that is the original pH value of the paper industry wastewater in the conventional Fenton process, [Fe^0] = 1250 mg/L, [H_2O_2] = 1000 mg/L at pH 3 in the modified Fenton process, and I = 1.0 A, [H_2O_2] = 1500 mg/L at pH 3 in the electro-Fenton process. Due to the rapid drop in the wastewater pH in the conventional Fenton process after additions of the Fenton's reagents, pH adjustment at the beginning of the oxidation stage is not required. Since the inorganic content of the white liquor is very high compared to its organic content, the COD removal efficiencies of the conventional, modified and electro-Fenton oxidation processes were not effective and were found to be 62.4%, 58.4% and 54.9%.

Acknowledgement

The authors are grateful for kindly financial support provided by the Selçuk University Scientific Research Project Funds (S.U. BAP).

References

Amat, A.M., Arques, A., Lopez, F., Miranda, M.A., 2005. Sol. Energy 79, 393–401.

APHA/AWWA/WEF, 2005. In: Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (Eds.), Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC.

Aydin, A.F., Altinbas, M., Sevimli, M.F., Ozturk, I., Sarikaya, H.Z., 2002. Water Sci. Technol. 46, 323–330.

Choi, Y.H., Son, S.U., Lee, S.S., 2004. Sensor Actuat. A: Phys. 111, 8–13.

Gogate, P.R., Pandit, A.B., 2004. Adv. Environ. Res. 8, 501–551.

Gokcay, F.C., Dilek, F.B., 1994. Water Sci. Technol. 29, 165–168.

Gubelt, G., Lumpe, C., Joore, L., 2000. Pap. Technol. 41, 41–48.

Güçlü, D., Şirin, N., Şahinkaya, S., Sevimli, M.F., 2012. Environ. Prog. Sustain.. http://dx.doi.org/10.1002/ep. 10626.

Kallel, M., Belaid, C., Mechichi, T., Ksibi, M., Elleuch, B., 2009. Chem. Eng. J. 150, 391–395.

Kazmi, A.A., Thul, R., 2007. J. Environ. Sci. Eng. 49, 189–194.

Kiril Mert, B., Yonar, T., Kılıç, M.Y., Kestioglu, K., 2010. J. Hazard. Mater. 174, 122–128.

Neyens, E., Baeyens, J., 2003. J. Hazard. Mater. 98, 33–50.

Modirshahla, N., Behnajady, M.A., Ghanbary, F., 2007. Dyes Pigments 73, 305–310.

Mahiroglu, A., Tarlan-Yel, E., Sevimli, M.F., 2009. J. Hazard. Mater. 166, 782–787.

Parama Kalyani, K.S., Balasubramanian, N., Srinivasakannan, C., 2009. Chem. Eng. J. 151, 97–104.

Pokhrel, D., Viraraghavan, T., 2004. Sci. Total Environ. 333, 37–58.

Selvabharathi, G., Kanmani, S., 2010. J. Environ. Sci. Eng. 52, 103–106.

Sevimli, M.F., 2005. Ozone Sci. Eng. 27, 37–43.

Shaw, L.E., Lee, D., 2009. Ultrason. Sonochem. 16, 321–324.

Shawwa, A.R., Smith, D.W., Sego, D.C., 2001. Water Res. 35, 745–749.

Şahinkaya, S., 2012. J. Ind. Eng. Chem.. http://dx.doi.org/10.1016/j.jiec.2012.09.023.

Tambosi, J., Domenico, M., Schirmer, W.N., José, H.J., Moreira, R.F.P.M., 2006. J. Chem. Technol. Biot. 81, 1426–1432.

Thompson, G., Swain, J., Kay, M., Forster, C.F., 2001. Bioresource Technol. 77, 275–286.

Tong, Z., Wada, S., Takao, Y., Yamagishi, T., Hiroyasu, I., Tatsumi, K., Qingxiang, Z., 1999. J. Environ. Sci. 11, 480–484.

Xu, M., Wang, Q., Hao, Y., 2007. J. Hazard. Mater. 148, 103–109.

Zaied, M., Bellakhal, N., 2009. J. Hazar. Mater. 163, 995–1000.