



Removal of COD and surfactants from grey water by Fenton type processes

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Keywords

COD
Fenton
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Surfactant

ABSTRACT

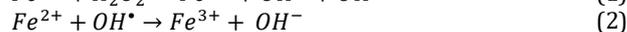
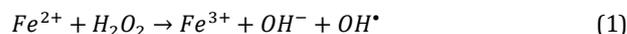
Grey water is a kind of domestic wastewater including shower, bath, lavatory and laundry waters. Grey waters without faecal waste can be considered as alternative water sources in the place where water resources are limited. In the present study, the removals of COD, anionic and non-ionic surfactants from grey water via conventional (CFP) and modified (MFP) Fenton oxidation processes was experienced. It was determined that pH adjustment to acidic values is not required in CFP. The optimum operating conditions were determined as $[Fe^{2+}] = 50$ mg/L, $[H_2O_2] = 50$ mg/L at pH 7.6 (original pH) in CFP and $[ZVI] = 50$ mg/L, $[H_2O_2] = 50$ mg/L at pH 3 in MFP, respectively. As a result, the CFP has been found to be a more efficient alternative treatment method for the treatment of grey water, compared to MFP.

1. INTRODUCTION

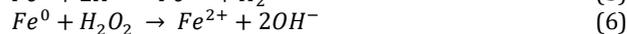
Domestic wastewater is evaluated in two streams: grey water and black water. Generally, water from the shower, bath, washbasin, washing and dishwashers is defined as grey water (Bani-Melhem et al. 2015). The remaining toilet water is defined as black water. The grey water includes 80–85% of household wastewater (Bani-Melhem et al. 2015). The re-use of this kind of wastewaters is considered as an alternative to the reduction of clean water consumption. However, there is no legal regulation in many countries for the re-use of grey waters after treatment. On the other hand, there is an increasing interest in this issue with the increasing water scarcity. The low organic matter and pathogen content of grey waters further increase this interest for reusability. The fact that grey waters can contain heavy metal and synthetic chemical structure micro pollutants such as pharmaceuticals, detergents, etc., cause us to seek alternatives other than conventional biological treatment systems. Therefore, the treatment of grey wastewaters by Fenton process and its modification has been evaluated in this study.

Conventional Fenton process (CFP) is intended to generate hydroxyl (OH^\bullet) radicals by catalyzing hydrogen peroxide (H_2O_2) with ferrous (Fe^{2+}) ions under strongly acidic conditions (Eq. (1)) (Pignatello et al. 2006). OH^\bullet radicals are very strong oxidants and can easily decompose organic matters. Oxidation of organic

substances by hydroxyl radicals (OH^\bullet) is generally achieved by the following chain reactions. (Eq. 1-4) (Vorontsov 2019; Zhu et al. 2019).



In the Fenton process, instead of ferrous iron (Fe^{2+}), iron powder (zero valent iron, ZVI, Fe^0) can also be utilized (Jaafarzadeh et al. 2017). This modification of the process is called the modified Fenton process (MFP). In order to achieve the oxidation reaction in MFP, the ZVI must first be dissolved in strongly acidic conditions in accordance with Eq. 5 (Bremner et al. 2006). The reaction will then be carried out as in the conventional Fenton process (Eq. 2). In addition, Fenton oxidation reactions can occur on the surface of ZVI (Eq. 6) (Bergendahl and Thies 2004). In this respect, the MFP is more dependent on pH than CFP.



The main advantage of the usage of ZVI in the Fenton process is that ferric ions can be converted to ferrous ions on the surface of the ZVI (Eq. 7) (Bremner et al. 2006). This conversion will cause the usage of less amount of iron than the conventional Fenton process.

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Reduction of iron consumption will reduce both the cost of treatment and the reduction of inert chemical sludge.



In the literature, there are several studies on the successful treatment of grey water with Fenton process. For example, in the study conducted by Hossain (2015), the use of grey water treated by Fenton process as toilet wash water was investigated. In the study which examined biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), turbidity and total carbon parameters, it was seen that the treated grey water provided with high efficiency through the classical Fenton process met the relevant standards in USA, Canada and Japan in order to be used as toilet wash water. In another study by Thirugnanasambandhama and Sivakumar (2015), 90% COD and 85% total suspended solid (TSS) removal was obtained by electro-Fenton process. In another study on grey water, Fenton process, starbon adsorption and a combination of the two were tested [10]. The combined use of both processes resulted in a 93% COD removal efficiency by using less Fenton reagents. However, these studies on the treatment of grey water with the Fenton process focused on COD removal with the classical Fenton process. Therefore, in the literature, there is no study comparing the classical and modified Fenton processes on the treatment of grey water and comparing them. In addition, when the studies in the literature are examined, it is observed that the common parameter for the grey waters is COD. In the studies in the literature, it has been determined that surfactant removal is not investigated and these studies are carried out via COD.

The main aim of this study is to investigate the influences of operating parameters in the conventional and modified Fenton processes on the removals of anionic and non-ionic surfactants and COD as the main target parameters. In order to optimize the operating conditions, Fenton experiments were carried out under various pH, iron (Fe^{2+} /ZVI) and hydrogen peroxide dosages. Besides, kinetical analyses for the anionic and non-ionic surfactant and COD removals were performed in the present study.

2. MATERIALS and METHOD

Grey water was synthetically prepared within 10 L with tap water in this study as summarized in Table 1. The synthetic grey water had a pH of 7.6, COD of 590 mg/L, anionic surfactant of 9 mg/L and non-ionic surfactant of 22 mg/L.

Table 1. Content of synthetic grey water (for 10 L)

Amount in 10 L	Composition
0.64 g	Synthetic soap
8 ml	Hair shampoo
0.1 ml	Sunflower oil
24 ml	Secondary effluent

All chemicals were of analytical grade, purchased from Merck (Germany) and were used as bought without

any further purification. Ultra-pure water was utilized in the preparation of all solutions.

CFP and MFP experiments were performed with 500 mL volume using a standard jar test equipment at room temperature. These experiments were done in three steps. pH value of the grey water was first adjusted to the desired value by using 0.1 N and 6 N H_2SO_4 solutions. The second step was the addition of Fe^{2+} (as $FeSO_4 \cdot 7H_2O$) in CFP and ZVI (as solid Fe^0 dust, < 50 μm size) in MFP. Then, the final step is the addition of H_2O_2 into the grey water. After the addition of H_2O_2 into the reaction solution, it was assumed that the oxidation reaction was begun. During the 1-h oxidation period, the grey water was mixed at 90 rpm. At the end of the oxidation period, the reaction solution was neutralized and pH value was adjusted to about 7.5 using 6 N and 0.1 N NaOH solutions. After the pH adjustment, the solution was stirred for 5 min at 30 rpm to form iron (oxy)hydroxide ($Fe(OH)_3$) flocs. It was stand still to precipitate $Fe(OH)_3$ for 30 min. After the precipitation, 25 mL sample was taken from the supernatant for the analyses.

Manganese dioxide (MnO_2) can decompose H_2O_2 to H_2O and O_2 as a catalyst (Tony et al. 2016). Therefore, MnO_2 was dosed into the sample in order to quench the residual H_2O_2 to avoid the positive interference of H_2O_2 on COD analysis (Özdemir et al. 2011). The decomposition of residual H_2O_2 was tested by peroxide test strips (Macherey Nagel, Germany). Before the analyses, all samples were filtered through 0.45 μm membranes to remove $Fe(OH)_3$ and MnO_2 . The pH measurement was conducted by a multi-parameter (Hach Lange, Germany). COD analyses were conducted in accordance with Standard Methods (Clesceri et al. 1998). The concentrations of anionic and non-ionic surfactants were analyzed calorimetrically by using Hach Lange cuvette tests (Germany).

3. RESULTS and DISCUSSION

3.1. Effects of Initial pH on COD and Surfactants Removals

Since the solution pH affects both the type and the solubility of catalyst iron, pH has an important effect on the oxidation efficiency (Özdemir et al. 2011; Kwon et al. 1999). The stability of hydrogen peroxide also depends on the medium pH. For these reasons, optimization of the initial pH of the reaction medium is vital to determine the effects of the Fenton process on the $OH\cdot$ radical production efficiency. In this study, optimization of the initial pH was carried out between pH 2 and the original pH 7.6. In both experiments, catalyst iron concentration and H_2O_2 concentration were kept constant at 100 mg/L.

The effect of initial pH on removal of COD, anionic and non-ionic surfactants is shown in Fig. 1. As can be seen from Fig. 1, the MFP process is much more dependent on ambient pH. Therefore, CFP process achieved oxidation at a much higher yield than MFP. Maximum removal efficiencies were obtained in pH 2 in MFP and in pH 5 in CFP. This advantage of the CFP process is due to the addition of catalyst iron in dissolved form to the system. In the MFP process, the iron supplied to the system in powder form must first dissolve in

solution medium. Another reason for this result is that the Fenton process causes the ambient pH to decrease. This is mainly due to the low buffering capacity of the reaction medium. The iron sulfate heptahydrate used in the CFP process was acidic in character and the introduction of hydrogen ion into the medium during the rapid Fenton process caused the pH to decrease during the 1-hour reaction. In the MFP process, the iron powder used was neutral and the dissolution time of the reaction medium caused a negligible change in pH.

Strong acidic conditions are required in the reaction medium for oxidation to occur in the Fenton process. In the literature, the optimum pH range for the Fenton process is 3 - 4. When COD and surfactant removal efficiencies were examined in Fig. 1, a decrease in yield was observed in pH 2 in CFP process. This is due to the effect of OH• radical scavenging of the excess H⁺ ions in the medium (Verma and Haritash 2019). Other causes are the iron (II) hydroxide (Fe(OH)²⁺) reacting more slowly with hydrogen peroxide and the conversion of hydrogen peroxide to the more stable H₃O₂⁺ (Kwon et al. 1999). In the CFP process, the highest yield was obtained at pH 5 and slightly decreased at higher pH. This is due to the low buffering capacity and the pH of the reaction medium to 3.5 - 4 levels. In the original pH of grey water, 7.6, the yield decreased to 74% due to the radical scavenging effect of the excess OH• radical in the environment. In the MFP process, the catalyst solid iron must first dissolve. As the solubility of the iron decreased as the pH increased, the yield decreased with increasing pH. As a result, the optimum pH for CFP was 7.6, which was the original pH, and 2 for the MFP process.

3.2. Effects of H₂O₂ Dosage on COD and Surfactants Removals

Optimization of H₂O₂ is crucial to both increasing the oxidation efficiency and reducing the cost of the Fenton process. Because the H₂O₂ used is the main source of OH• radicals produced in the system, its limited amount in the system will result in a decrease in efficiency. On the other hand, overdosing H₂O₂ into the system will also result in sweeping of the generated OH• radicals, reducing the yield and increasing the cost of treatment. In addition, the presence of residual H₂O₂ in treated water will lead to positive interference in COD analysis, leading to higher results (Şahinkaya 2013).

H₂O₂ optimizations for CFP and MFP processes were performed at a constant iron concentration of 50 mg/L. Before the experiments, the initial pH was adjusted to 7.6 in the CFP process and the initial pH to 3 in the MFP process. Doses of H₂O₂ in both processes were examined in the range of 10 - 300 mg/L. As can be seen from Fig. 2, the removal efficiency increased rapidly when the H₂O₂ dose was increased up to 50 mg / L in both processes. In doses ranging from 50 to 200 mg / L, the yield was also negligible. In the CFP process, COD removal efficiency does not change at doses above 200 mg/L, while in the MFP process there is a slight decrease in yield due to the radical scavenging effect of excess H₂O₂ in the system (Eq. 4) (Zhang et al. 2019). The oxidation of the CFP process was found to be much higher than the MFP. This is due to the fact that the type of iron supplied to the

system is in dissolved form ready to react in the CFP process. The optimum H₂O₂ dose for both CFP and MFP processes was determined to be 50 mg/L. At this optimized dose, COD, anionic and non-ionic surfactant removal efficiencies were 76, 100 and 99, respectively, for the CFP process. For the MFP process, it was measured as 61, 85 and 97% respectively.

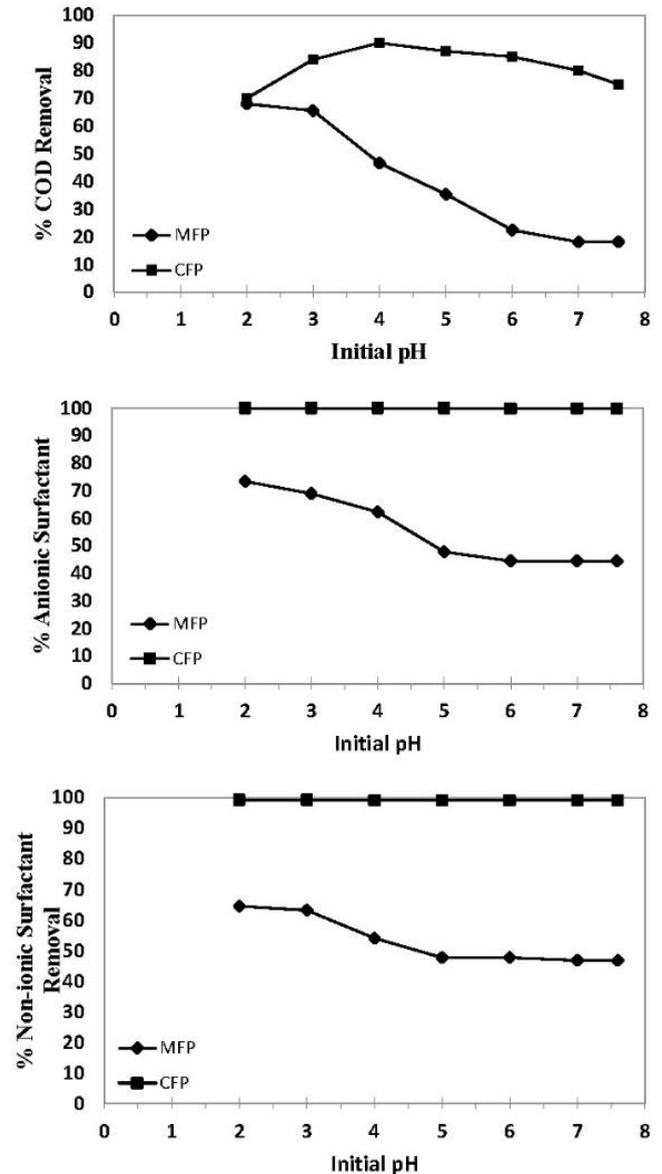


Figure 1. Effects of initial pH on COD and surfactants removals [Experimental conditions: [Fe²⁺] = 100 mg/L and [H₂O₂] = 100 mg/L in CFP; [ZVI] = 100 mg/L and [H₂O₂] = 100 mg/L in MFP]

3.3. Effects of Fe²⁺/ZVI Dosage on COD and Surfactants Removals

Excessive usage of iron in the process will increase the operating cost. In addition, excess iron in the reaction mixture will have a radical scavenging effect (Eq. (2)), resulting in reduced oxidation efficiency. On the other hand, depending on the type and amount of iron used, the amount of chemical sludge resulting from the Fenton process is also increased. The sludge management increases the total cost of the process. Therefore,

optimization of both type and amount of catalyst iron is very important for a feasible oxidation process.

In the experiments performed to optimize iron concentration in CFP and MFP processes, the dose of H_2O_2 was kept constant at 100 mg / L. Iron optimization studies were carried out at the original pH value of 7.6 and CFP process at 7.6 and MFP at pH 3. While iron sulfate heptahydrate was utilized as the catalyst iron source in the CFP process; ZVI was the catalyst iron in the MFP process. The amount of iron used in both processes was investigated in the range of 10 - 300 mg / L. Because anionic and non-ionic surfactants are readily degraded; process optimization was performed according to COD parameter. As seen from the experimental results presented in Figure 3, the increase in iron content in both processes led to a continuous improvement in COD removal. This is due to the reaction occurring in accordance with the reaction equation given in Eq. 1. In the MFP process, since the ZVI had to first dissolve in the reaction medium, the reaction yield was lower than CFP. As a result, the optimum iron dose for both processes was 50 mg/L.

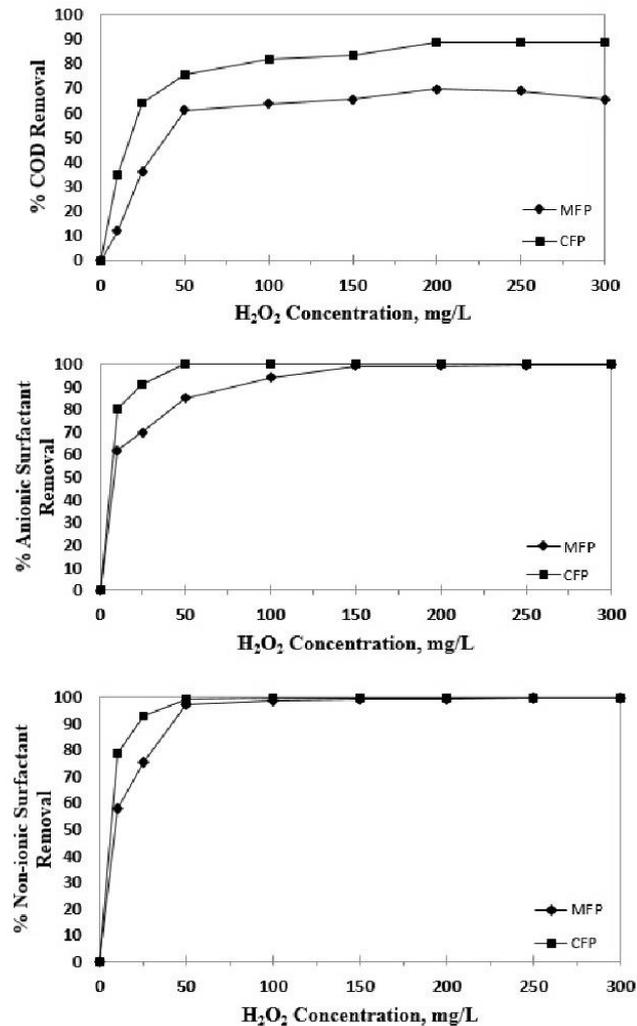


Figure 2. Effects of H_2O_2 dosage on COD and surfactants removals [Experimental conditions: pH = 7.6 and $[Fe^{2+}] = 50$ mg/L in CFP; pH = 3 and $[ZVI] = 50$ mg/L in MFP]

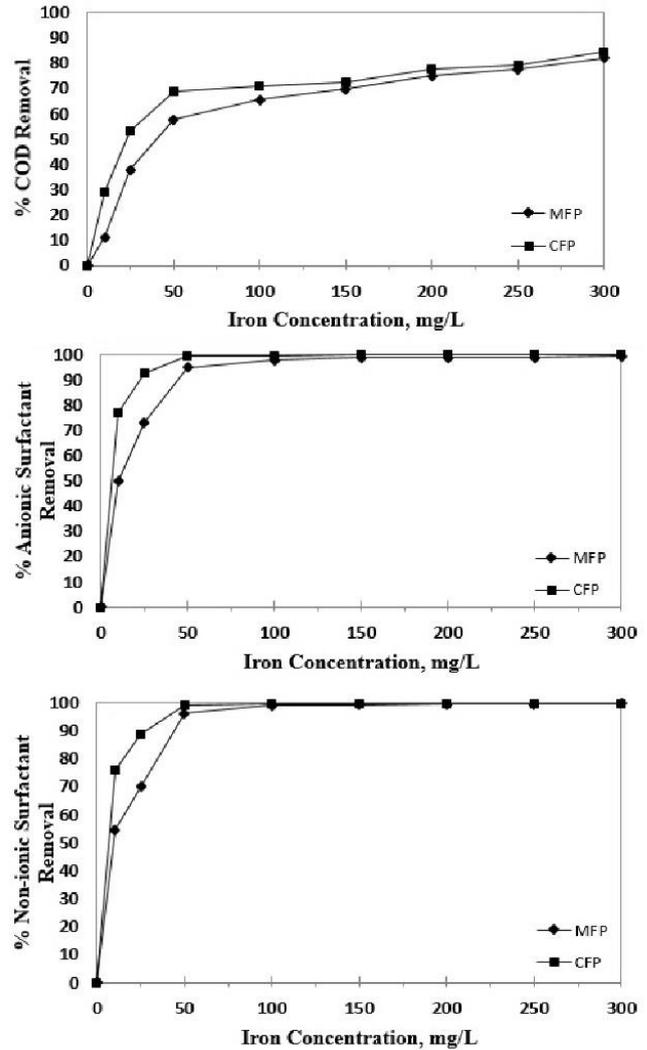


Figure 3. Effects of Fe^{2+}/ZVI dosage on COD and surfactants removals [Experimental conditions: pH = 7.6 and $[H_2O_2] = 50$ mg/L in CFP; pH = 3 and $[H_2O_2] = 50$ mg/L in MFP].

3.4. Kinetic Study

Since COD, anionic (AS) and non-ionic surfactants (NS) are the most important pollutant parameters in the grey water, kinetic study was performed separately for all these parameters under the optimized conditions (summarized in Table 2).

Table 2. Optimum conditions and reaction efficiencies for CFP and MFP processes

	pH	Fe^{2+} / ZVI (mg/L)	H_2O_2 (mg/L)	Removal (%)		
				COD	AS	NS
CFP	7.4	50	50	75	99.9	99.4
MFP	3	50	50	69	99.8	99.3

The experimental results are presented in Figures 4 and 5. As understood from these graphs, The CFP process completed the oxidation in a much shorter time than the MFP process. In the CFP process, it is understood that the reaction is carried out rapidly in accordance with Eq. 1 and completed in 1 minute. This was due to the fact that Fenton reagents were supplied ready to the reaction medium. Figure 4 shows that the reaction in the CFP process takes place in two stages: the rapid oxidation

stage in the first 1 minute and the slow oxidation stage. In the CFP process, as the reaction was carried out rapidly in the first 1 minute and the reagents were depleted, the reaction continued for a further 59 minutes. In the MFP process, the reaction proceeded more slowly as the ZVI must first be dissolved in the reaction medium as shown in Eq. 5. On the other hand, removal within the first few minutes may have occurred on the surface of the ZVI in accordance with the reaction in Eq. 6.

$$\frac{t}{1 - \frac{C}{C_0}} = m + bt \tag{9}$$

According to Eq. 9, b, m and R² (determination coefficient) values obtained from kinetics data are summarized in Table 3. As seen in this table, high R² values demonstrated that the experimental kinetics data were in a perfect agreement with the kinetic model applied in this study. Moreover, according to this model, 1/m means the initial decay rate and the highest 1/m value is obtained in the CFP. Dimensionless constant b shows theoretical maximum removal fraction. As a result of the kinetic analyses, CFP is more rapid and effective process compared with MFP.

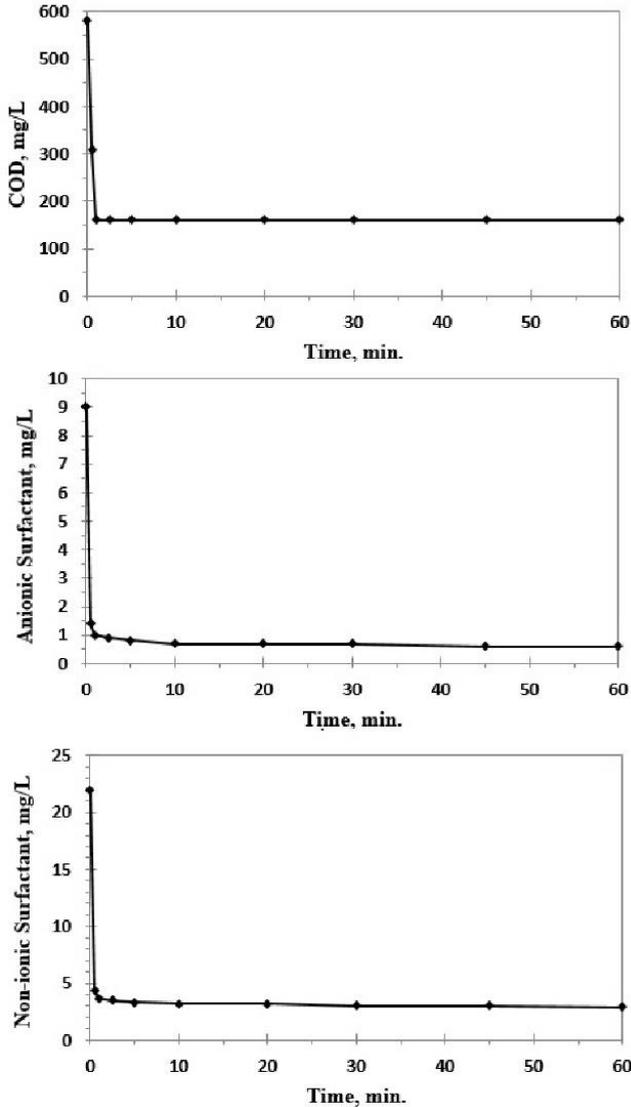


Figure 4. COD and surfactant removal curves of CFP

Experimental results presented in Eq. 4 and 5 are firstly applied to the basic kinetic models. But the results were found to be incompatible with the zero, first and second order kinetic models. Thus, a mathematical model kinetic model was used. The equation of this mathematical model is given in Eq. (8) and (9) (Behnajady et al. 2007).

$$\frac{C}{C_0} = 1 - \left(\frac{t}{m+bt} \right) \tag{8}$$

Where, C₀, is the initial concentration; C, is the concentration at time t; b and m are reaction kinetics and maximum oxidation capacity of the process, respectively. Eq. 8 is linearized to apply the model, and its linearized form is shown in Eq. 9.

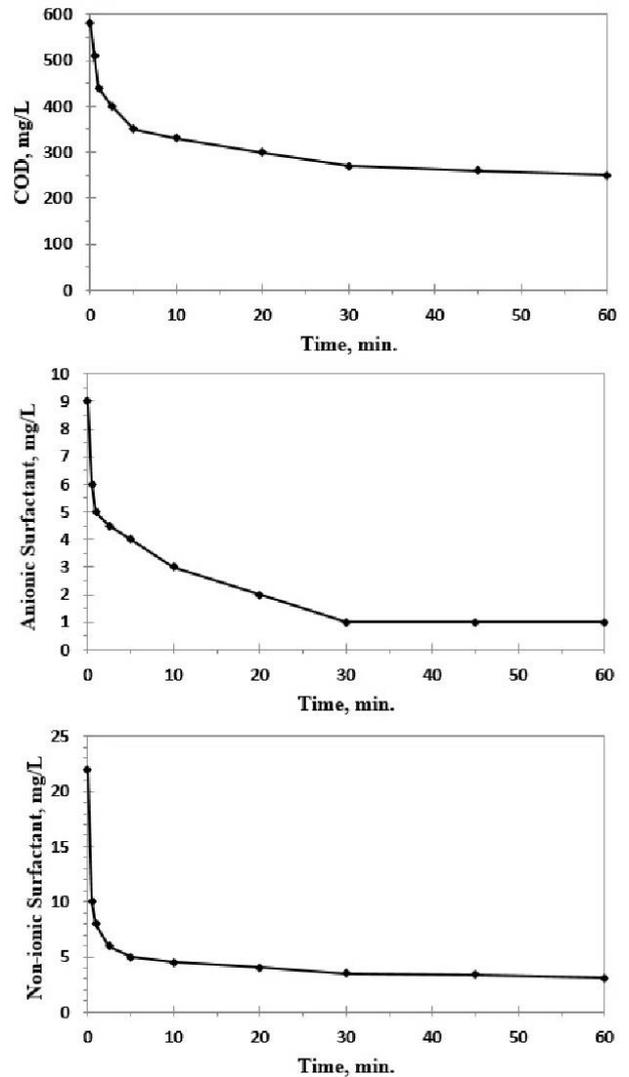


Figure 5. COD and surfactant removal curves of MFP

Table 3. Kinetic constants and R² values of the mathematical model

Process	b	m	R ²
COD Removal			
CFP	0.7252	0.058	1
MFP	0.5833	2.4885	0.998
Anionic Surfactant Removal			
CFP	0.999	0.0015	1
MFP	0.9985	0.0161	1
Nonionic Surfactant Removal			
CFP	0.995	0.0031	1
MFP	0.9946	0.0136	1

4. CONCLUSIONS

In this study, both CFP and MFP were experienced for the removal of COD, anionic and non-ionic surfactants from grey water. The main conclusions are obtained in the following;

- The influences of important operational conditions were experienced in both processes. Operating parameters were optimized as $[Fe^{2+}] = 50 \text{ mg/L}$, $[H_2O_2] = 50 \text{ mg/L}$ and pH 7.6 that is the original pH value of the grey water in CFP, $[ZVI] = 50 \text{ mg/L}$, $[H_2O_2] = 50 \text{ mg/L}$ and pH 3 in MFP.
- pH adjustment is not required in CFP because of the rapid drop in the grey water pH after additions of the Fenton's reagents. On the other hand, since the modified Fenton process uses metallic iron powder in solid form, the pH adjustment to the acidic values is needed in order to solve the solid iron. The pH adjustment to the acidic values is required for the best yield in the modified Fenton process.
- It was seen that less the chemical treatment sludge was produced in MFP.
- The experimental data were fitted perfectly to the applied mathematical model. According to both the kinetic analyses and the applied model, CFP was more rapid and efficient process for the treatment of grey water because of the usage of ferrous ion as the catalyst, compared to the MFP.
- Both Fenton type processes can be used for the treatment of grey water in order to re-use in the water scarce regions.

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