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INTERNATIONAL ADVANCED RESEARCHES and ENGINEERING JOURNAL

e-ISSN: 2618-575X

Journal homepage: www.dergipark.org.tr/en/pub/iarej

International Open Access

Volume 06
Issue 03

December, 2022

Research Article

Effects of advanced oxidation process on greywater treatment: an optimization study

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ARTICLE INFO

Article history:
Received 22 March 2022
Accepted 09 September 2022
Published 15 December 2022

Keywords:
Advanced oxidation methods
Fenton process
Fe_3O_4 magnetic nanoparticle
$KMnO_4$

ABSTRACT

Greywater is domestic wastewater from showers and sinks and has a significant potential for the protection of water resources as it is less polluted in terms of nutrients, inorganic substances and hazardous organic substances. It is aimed to treat and reuse greywater in order to meet the rapidly increasing water demand. In this research, the treatment of greywater using the Fenton Process was studied. The efficiency of the Fenton Process was optimized using the Box-Behnken Statistical Design Software. As a result of this study, 97.88 % of Chemical Oxygen Demand removal was achieved at pH = 3, Fe^{2+} dose of 3 mM, H_2O_2 dose of 2 mM, and 37 min. The effect of Potassium Permanganate on the treatability of synthetic greywater was also investigated in the study. Results showed that 84% of the Chemical Oxygen Demand removal efficiency could be achieved using 0.1 g/L Potassium Permanganate at the end of 1 hour reaction time.

1. Introduction

In recent years, fresh water resources in the world have been gradually decreasing, and new water resources are becoming more limited and expensive. For these reasons, efforts are ongoing to find new alternatives to be able to meet the water demand. Today, new sources are investigated to decrease water demand through reusing waste water. Greywater can be used as one of these sources.

Greywater is one of the alternative sources in terms of water, especially in semi-arid or arid regions [1]. Greywater is wastewater occurring due to some systems such as bathrooms, showers, handwash, sinks, dishwashers, washing machines, and kitchen sinks [2]. Soap and detergents are the most important pollutants in greywater. However, it is generally less polluted than urban wastewater because it does not contain human feces and toilet paper [3].

Greywater can be categorized as dark greywater and light greywater. While dark greywater is the source of kitchen sinks, light greywater contains water from bathrooms, toilet sinks, bathtubs, showers, washing machines and similar sources. Dark greywater contains disease-causing microorganisms and a large number of organic contaminants from nutrient residues, oil, and fat. In terms of organic pollutants, greywater is cleaner than other wastewater [4]. In addition, regarding organic matter and solids content, greywater can be categorized under two groups. Greywater from the kitchen contains surfactants such as detergents, as well as a high organic and solid content. On the other hand, greywater from bathrooms and sinks is defined as "low load" greywater that is poor in organic matter and solids. [5].

With 75% of the total volume, greywater constitutes the largest portion of the total domestic wastewater. It contains between 3% and 10% nitrogen and phosphorus but has a low pollution potential because it contains organic matter, which makes up 40% of the total. Greywater contains 23% of the total suspended solids in domestic wastewater. In terms of pathogens, there is almost no hygienic concern because greywater is not contaminated with toilet wastewater [6]. Greywater can be reused after the treatment because it is less polluted than other wastewater. Today, numerous processes are evaluated and implemented to treat greywater. Treated greywater can be used in many areas in homes and industry such as irrigation, washing of vehicles, fire

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DOI: 10.35860/iarej.1091551

response, production, toilet, and flush [7,8].

The greywater characterization and type of reuse application are crucial in order to determine the treatment process [9,10,11]. Filtration, precipitation and sedimentation, and membrane techniques are the most common physicochemical methods. Constructed wetland, rotating biological contactor (RBC), and membrane bioreactor (MBR) are the most used biological process for the treatment of greywater [10]. Although they are effective in greywater treatment, they are not successful enough in removing refractory and toxic materials. Therefore, alternative treatment methods should be investigated. Advanced oxidation processes can be suggested to solve this problem [12].

Advanced oxidation processes are one of the new applications used in water and wastewater treatment technologies and they are related to the mechanism of hydroxyl radical (OH) production emerging as a result of oxidative degradation of organics. Thanks to these processes, refractory organic compounds are converted into biodegradable compounds, and then they are mineralized into the water by giving CO_2 and inorganic anions. The dark oxidation process, homogeneous and heterogeneous photocatalytic oxidation, the Fenton and photo-Fenton processes, sonolysis, and hydrothermal and wet oxidations can be shown as examples to advanced oxidation processes [13].

Potassium Permanganate ($KMnO_4$) is a crystalline inorganic chemical substance that is found in solid form and consists of potassium and manganate ions with a molar mass of 158,034 g/mol, the density of 2,70 g/cm^3, and melting point >240^{o}C. Potassium Permanganate, a strong oxidizer, gives an intense pink-violet color when dissolved in water, and gradually turns brown when combined with oxidizable substances in the environment [14]. $KMnO_4$ is a crystalline, easy-to-use compound that dissolves up to 5% in water and is widely used to convert manganese ions to manganese dioxide (MnO_2) and is a stronger oxidant than chlorine. Unlike chlorine, the reaction of $KMnO_4$ with organic compounds does not cause Trihalomethane (THM) formation and causes a decrease in THMs [15]. Potassium Permanganate is an oxidizing agent used in water treatment. It oxidizes organic substances in the water and is thus removed from the water by filtration [14]. $KMnO_4$ is also a powerful oxidant and is used in the disinfection of water and the oxidation of toxic substances. The advantages of $KMnO_4$ compared to ozone and chlorine used as other oxidants are that it is non-toxic and safe to use [16]. Potassium Permanganate forms in the water industry are highly reactive [17]. $KMnO_4$ in water precipitates by reducing it to manganese dioxide. Reaction rates for the oxidation of its components in natural waters are relatively high and depend on temperature, pH, and concentration [14].

In the present research, the treatment of synthetic greywater by using the Fenton Process was studied. pH, Fe^{+2} dose, H_2O_2 dose, and time were determined as the parameters affecting the Fenton Process. These parameters were optimized using Box-Behnken Statistical Design Program. To the knowledge of the authors, the performance of $KMnO_4$ in greywater treatment is discussed for the first time in the literature in this study.

2. Material and Methods

2.1 Greywater Characteristics

In the present study, greywater was prepared synthetically and was used directly without any pretreatment method. The synthetic greywater was prepared according to the composition given in Table 1.

The effluent from the wastewater treatment plant was also prepared synthetically by adding some chemicals given in Table 2 into the tap water.

2.2 Greywater Treatment using the Fenton Process

2.2.1 Experimental Procedure and Box-Behnken Statistical Design

The performance of the Fenton Process on synthetic greywater treatment was investigated. To be able to optimize the parameters (pH, Fe^{2+}, and H_2O_2 doses and reaction time), the Box-Behnken Statistical Design method was utilized.

The ranges for the variables were 0.3-3 mM for Fe^{2+}, 2-20 mM for H_2O_2 and 10-60 minutes for reaction time. The Box-Behnken Statistical Design Program suggested 27 experimental runs for 4 variables. Design variables and experimental runs were given in Table 3.

Table 1. Composition of synthetic greywater [14]

Material	Quantity
Tap Water	5 L
Oil	0.05 mL
the effluent of Wastewater Treatmet Plant	12 mL
Soap	3.2 g
Shampoo	4 mL

Table 2. Wastewater Treatment Plant Effluent Characterization

Chemicals	Quantity
$CH_3COONa.3H_2O$	19.89 mg/L
Sucrose	10.6 mg/L
NH_4Cl	8.1 mg/L
KH_2PO_4	4 mg/L
K_2HPO_4	4 mg/L
$MgSO_4.7H_2O$	4 mg/L

Table 3. Design variables and experimental runs

Variables	Unit	Max Value	Min Value	
pH		3	5	
Fe^{2+}	mM	0.3	3	
H_2O_2	mM	2	20	
Time	Min	10	60	
Analysis No	**pH**	**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**Time (min)**
1	4	3	2	35
2	3	3	11	35
3	4	1.65	11	35
4	4	0.3	2	35
5	5	1.65	11	60
6	4	1.65	11	35
7	5	1.65	11	10
8	4	1.65	2	60
9	3	1.65	2	35
10	3	1.65	11	10
11	5	1.65	20	35
12	4	1.65	20	10
13	4	1.65	20	60
14	4	0.3	20	35
15	5	0.3	11	35
16	3	0.3	11	35
17	3	1.65	11	60
18	3	1.65	20	35
19	4	3	11	10
20	4	1.65	2	10
21	4	1.65	11	35
22	5	3	11	35
23	4	3	20	35
24	4	0.3	11	60
25	4	3	11	60
26	4	0.3	11	10
27	5	1.65	2	35

For each experiment, the following procedure was followed.

- 300 mL of the synthetic greywater sample was used.
- pH was adjusted using 1 N H_2SO_4 and 1 N NaOH.
- Fe^{2+} and H_2O_2 were added based on the experimental run using $FeSO_4.7H_2O$ and H_2O_2.
- The greywater solutions consist of Fe^{2+} and H_2O_2 doses were mixed at 150 rpm depending on the reaction time of the experimental run.
- At the end of the reaction process, the pH was adjusted to 7 and it was kept under static conditions for 1-1.5 hours to settle the formed flocs.
- The filtration of the sample was carried out using a 0.45 μm membrane filter and then 2.5 mL of the sample was used for Chemical Oxygen Demand (COD) analyses. The COD removal efficiencies were calculated by using the difference between the initial COD and COD after the Fenton Process.

2.3 Greywater Treatment Using $KMnO_4$

2.3.1 Experimental Procedure and Box-Behnken Statistical Design

Experimental studies were conducted using 100-600 g/L $KMnO_4$ to investigate the effects of $KMnO_4$ concentrations on the COD removal efficiency of greywater and to determine the concentration and time that provides maximum COD removal efficiency. pH was 7.56, the reaction time was varied as 30 minutes, 1 hour, and 2 hours. Different $KMnO_4$ doses are given in fixed times in Table 4.

300 mL of synthetic greywater sample was put in a beaker. The determined concentration of $KMnO_4$ was added to the sample, and the solution was mixed at 200 rpm for 3 minutes, then the mixing speed was decreased. At the end of the reaction process, it was waited for one hour for the floc formation via precipitation. Afterward, the centrifuge process of the treated water was performed at 3000 rpm for 5 minutes. Then, the water was filtered with a 0.45 μm membrane filter and analyzed for COD.

2.4 Analytic Methods

All COD analyzes were performed based on the standards of the Closed Reflux Method [18]. pH measurement of the samples was carried out using a Hach pH meter.

3. Results and Discussion

3.1 Greywater Characteristics

In the experiments, greywater was prepared synthetically and kept in the refrigerator. The results of the characterization studies of the synthetic greywater sample were given in Table 5.

Table 4. Different $KMnO_4$ doses at fixed times

Analysis	$KMnO_4$ (mg/L)
1	100
2	200
3	300
4	400
5	500
6	600

Table 5. Graywater characteristics

Parameters	Values
pH	7.56
Temperature ($^\circ C$)	18.5
Condcutivity (μS/cm)	398
Alkalinity ($CaCO_3$/L)	210
Turbidity (NTU)	2121.6
Total Phosphorus (TP) (mg/L)	0.046
Total Nitrogen (TN) (mg/L)	0.048

3.2 Fenton Process Results

3.2.1 Results of the Box-Behnken Statistical Design

The results of the COD analyses were adopted to Box-Behnken Statistical Design Program as given in Table 6.

ANOVA table provided by Box-Behnken Statistical Design Program was given in Table 7. The chart shows that the model was statistically "significant" according to the experiment variables and meaningful results were obtained.

In this study, p values less than 0.05 was accepted statistically significant. As seen in Table 7, Model F 24.37 shows that the model is statistically significant at 0.001 significance level ($p<0.001$). Here, B-Fe^{+2}, C-H_2O_2, B^2, and C^2 are seen as statistically significant. The "Fit F-value" of 0.63 implies that Fit Deficiency is not significant ($p>0.05$) compared to pure error. R-Squared is 0.9660. There is a 74.97% "Fit F-value" chance for this size to occur due to noise. We want the lack of meaningful fit to fit the model. "Pred R^2" (0.8332) is in a certain agreement with the "Adjusted R^2" (0.9264).

Table 6. Experiment sets and results

Analysis No	pH	Fe^{2+} (mM)	H_2O_2 (mM)	Time (min)	Effluent CODs (mg/L)	COD Removal (%)
1	4	3	2	35	49.92	93
2	3	3	11	35	30.72	95
3	4	1.65	11	35	74.24	89
4	4	0.3	2	35	125.44	82
5	5	1.65	11	60	107.52	85
6	4	1.65	11	35	80.64	89
7	5	1.65	11	10	116.48	85
8	4	1.65	2	60	57.6	92
9	3	1.65	2	35	38.4	94
10	3	1.65	11	10	112.64	87
11	5	1.65	20	35	145.92	80
12	4	1.65	20	10	153.6	81
13	4	1.65	20	60	168.96	78
14	4	0.3	20	35	234.24	68
15	5	0.3	11	35	157.44	78
16	3	0.3	11	35	156.16	78
17	3	1.65	11	60	110.08	86
18	3	1.65	20	35	160	80
19	4	3	11	10	55.04	93
20	4	1.65	2	10	55.04	93
21	4	1.65	11	35	115.2	85
22	5	3	11	35	58.88	92
23	4	3	20	35	134.4	83
24	4	0.3	11	60	179.2	75
25	4	3	11	60	52.48	93
26	4	0.3	11	10	180.48	77
27	5	1.65	2	35	65.28	92

Table 7. ANOVA Table

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	1253.55	14	89.54	24.37	<0.0001	significant
A-pH	5.33	1	5.33	1.45	0.2515	
B-Fe^{+2}	690.08	1	690.08	187.85	<0.0001	
C-H_2O_2	481.33	1	481.33	131.02	<0.0001	
D- Time	4.08	1	4.08	1.11	0.3125	
AB	2.25	1	2.25	0.61	0.4490	
AC	1.00	1	1.00	0.27	0.6113	
AD	0.25	1	0.25	0.068	0.7986	
BC	4.00	1	4.00	1.09	0.3173	
BD	1.00	1	1.00	0.27	0.6113	
CD	1.00	1	1.00	0.27	0.6113	
A^2	0.15	1	0.15	0.040	0.8442	
B^2	46.68	1	46.68	12.71	0.0039	
C^2	17.93	1	17.93	4.88	0.0474	
D^2	2.68	1	2.68	0.73	0.4101	
Residual	44.08	12	3.67			
Lack of Fit	33.42	10	3.34	0.63	0.7497	not significant
Pure Error	10.67	2	5.33			
Cor Total	1297.63	26				

Std. Dev.	1.92	R^2	**0.9660**
Mean	85.30	Adj R^2	0.9264
C.V.%	2.25	Pred R^2	0.8332
PRESS	216.48	Adeq Precision	19.483

Core Total: It expresses the variation amount in the the observations' means. **Adj (Adjusted) R-^{2}:** Shows variation that is explained by the studied model around the mean. **Pred R^2**: It refers to the variation explained by the model in the new data. **Adeq Precision**: presents the comparison of the predicted value ranges at the design points with the average estimation error.

The coefficients of the Box-Behnken Statistical Design Program were given in Table 8. By putting these coefficients on their places in Equation (1), the real experimental results and predicted results were obtained and presented in Table 9. As can be seen from Table 8, actual test results and predicted values were close to each other.

Equation for Box-Behnken Statistical Design program for 4 variables are given below.

$$y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{11}{X_1}^2 + b_{22}{X_2}^2 + b_{33}{X_3}^2 + b_{44}{X_4}^2 \quad (1)$$

3.3 Optimization Results

3.3.1 Effects of Fe^{2+} and H_2O_2 doses

The graphics provided by the Box-Behnken Statistical Design Program can be utilized for the determination of the optimum Fe^{2+} and H_2O_2 doses and reaction times in terms of the highest values of COD removal efficiency.

Table 8. Equation coefficients

bo	+ 85.41424
b1	- 2.04444
b2	+ 11.77229
b3	- 0.48601
b4	+ 0.016000
b12	- 0.55556
b13	+ 0.55556
b14	+ 1.00000E-002
b23	+ 0.082305
b24	- 2.22222E-003
b11	+ 0.16667
b22	- 1.62323
b33	- 0.022634
b44	- 1.13333E-003

Table 9. Actual test results and predicted test results

No	pH	Fe^{2+} (mM)	H_2O_2 (mM)	Time (min)	Effluent CODs (mg/L)	COD Removal (%)	Predicted COD Removal (%)
1	4	3	2	35	49.92	93	95.79
2	3	3	11	35	30.72	95	93.87
3	4	1.65	11	35	74.24	89	87.66
4	4	0.3	2	35	125.44	82	82.62
5	5	1.65	11	60	107.52	85	86.12
6	4	1.65	11	35	80.64	89	87.66
7	5	1.65	11	10	116.48	85	86.79
8	4	1.65	2	60	57.6	92	91.54
9	3	1.65	2	35	38.4	94	93.5
10	3	1.65	11	10	112.64	87	88.62
11	5	1.65	20	35	145.92	80	79.5
12	4	1.65	20	10	153.6	81	79.87
13	4	1.65	20	60	168.96	78	77.7
14	4	0.3	20	35	234.24	68	67.95
15	5	0.3	11	35	157.44	78	77.37
16	3	0.3	11	35	156.16	78	77.2
17	3	1.65	11	60	110.08	86	86.95
18	3	1.65	20	35	160	80	79.83
19	4	3	11	10	55.04	93	91.66
20	4	1.65	2	10	55.04	93	91.54
21	4	1.65	11	35	115.2	85	87.66
22	5	3	11	35	58.88	92	91.04
23	4	3	20	35	134.4	83	85.12
24	4	0.3	11	60	179.2	75	75.33
25	4	3	11	60	52.48	93	91.5
26	4	0.3	11	10	180.48	77	77.5
27	5	1.65	2	35	65.28	92	91.16

The graph of Fe^{2+} versus H_2O_2 is given in Figure 1. In this figure, time was fixed as 30 min and pH was 4. The highest COD removal efficiency was achieved with 95.68% at the dose of 2 mM H2O2 and 3 mM Fe^{2+}.

Considering the changes in H_2O_2 versus Fe^{2+} at a fixed time of 30 minutes and pH = 3, it was observed that the highest COD removal (97.81%) was at the dose of 2 mM H_2O_2 and 3 mM Fe^{2+} (Figure 2).

3.3.2 Effects of Time

Considering the time versus H_2O_2 dose at 2 mM fixed Fe^{2+} dose and pH = 3 (Figure 3), the highest COD removal efficiency (95.21 %) was achieved with 2 mM of H_2O_2 dose at a time of 30 minutes.

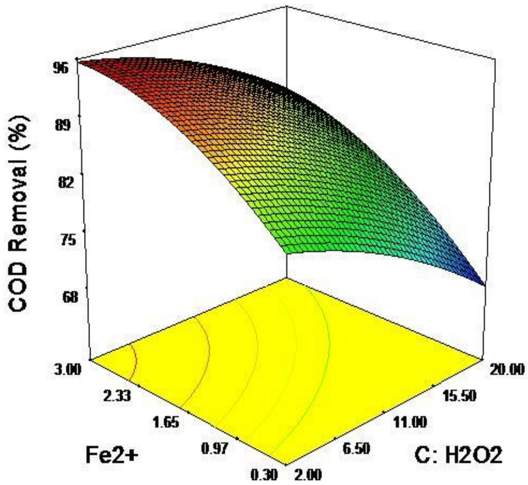

Figure 1. Fe $^{2+}$ versus H_2O_2 at pH = 4, time= 30 min

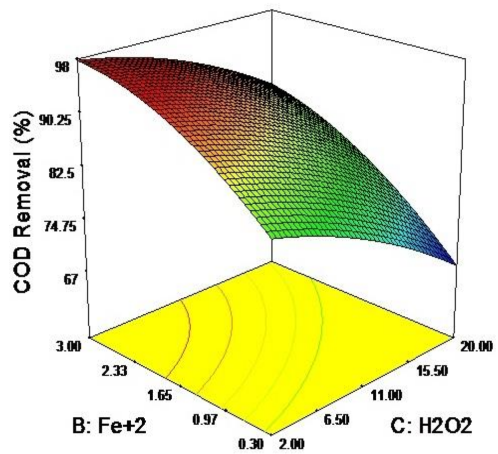

Figure 2. Fe^{2+} versus H_2O_2 at pH = 3, time= 30 min

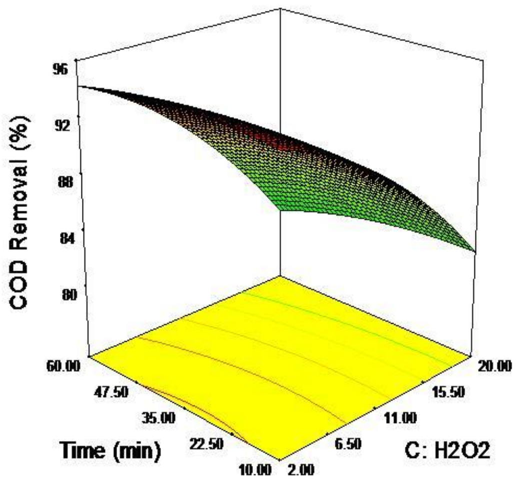

Figure 3. Time versus H_2O_2 at pH = 3, Fe^{2+}=2 mM

For the 2 mM fixed H_2O_2 dose and pH = 3, time and Fe^{2+} dose changes are given in Figure 4. The highest COD removal efficiency (97.88 %) was achieved in the experiment conducted with 3 mM Fe^{+2} dose and at 37 minutes.

Finally, considering the graphic of Fe^{2+} versus H_2O_2 at pH = 3 and 37 min, the maximum removal efficiency (97.88%) was observed at 2 mM of H_2O_2 dose and 3 mM of Fe^{2+} dose (Figure 5).

In a study conducted by Blanco et al. [19], Fenton oxidation and its combination with aerobic Sequencing Batch Reactor (SBR) were examined in terms of reusing textile wastewater. They optimized H_2O_2, temperature, and Fe (II) concentrations as independent variables. Results showed that >99 % *E.coli* removal efficiency and 64% TOC reduction were achieved by Fenton oxidation at condition where Y=25 ºC, H_2O_2 = 1650 mg/L, pH = 3, and Fe (II) = 216 mg/L. In condition where SBR was used for 1 day, TOC reduction and *E.coli* removal efficiency were determined as 92% and >99% at H_2O_2=1582 m/L and Fe(II) = 66.5 mg/L, respectively [19].

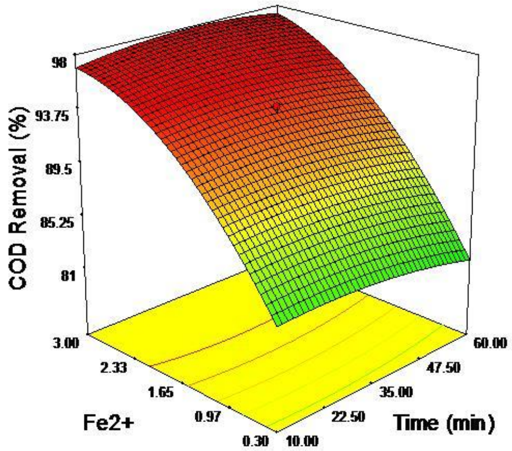

Figure 4. Time versus Fe^{2+} at pH = 3, H_2O_2=2 mM

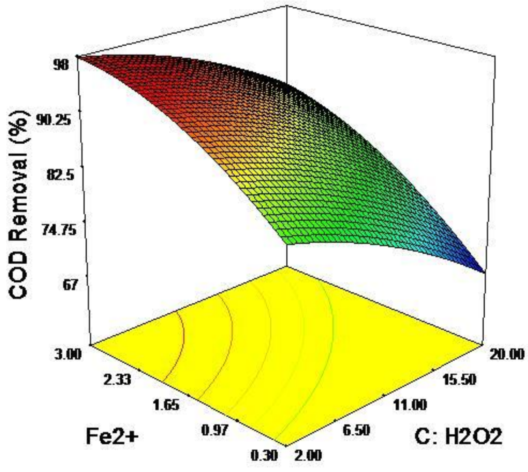

Figure 5. Fe^{2+} versus H_2O_2 at pH = 3, time=37 min

In the study carried out by Öztürk [10], the recovery of greywater from UV-assisted electrocoagulation was achieved. In the first study, the optimum operating conditions of the electrocoagulation process were determined as the raw water pH value 7.4 ± 0.2, 1 g Na_2SO_4 /L electrolyte addition, 3 mA/cm^2 current density, and 40 minutes process time. Under these optimum conditions, 88.1% COD and 97.2% turbidity removal efficiencies were achieved using Al electrodes, while 79.3% COD and 99.4% turbidity removal efficiencies were obtained using Fe (iron) electrodes. TS (Suspended Solids), TN, TP, and BOD_5 parameters were 62.3%, 44%, 98%, and 88.5%, respectively. In the presence of iron electrode, 80.6%, 8.5%, 98.4%, and 78.46% removal efficiencies were obtained, respectively. Tony et al. [20] achieved maximum COD removal efficiency (95%) using the Fenton process for the treatment of greywater under condition where pH = 3, H_2O_2= 200 mg/L, and Fe^{3+}= 40 mg/L. Thirugnanasambandham and Sivakumar investigated the treatability of greywater using Electro Fenton Process [21]. In their study, under conditions where current density was 10 mA/ cm^2, treatment time was 14 min, H_2O_2/Fe^{2+} molar ratio was 0.70, and pH was 4, COD and TSS removal efficiencies were achieved 90% and 85%, respectively. In the study conducted by Özgüroğlu [22], the removal of COD, anionic and non-ionic surfactant parameters of greywater by the classical Fenton application was investigated. Under the optimum conditions (Fe^{+2} = 50mg/L, pH = 7.4, and H_2O_2= 50mg/L) determined through the classical Fenton application, the removal efficiencies of 99.9%, 99.45%, and 75% were achieved for anionic surfactants, non-ionic surfactants, and COD, respectively [22]. Hassanshahi and Karimi-jahsni studied the comparison and optimization of greywater treatment performance using the processes called photocatalysis, photo-Fenton, and ozone / H_2O_2 / UV. In these three processes, the highest COD removal efficiencies were achieved as 55%, 90%, and 92%, respectively. The ozone / H_2O_2 / UV process was suggested for greywater treatment with 92% and 93% removal efficiencies for COD and turbidity, respectively [23]. In another study conducted by Faggiano et al., [24], the treatment of greywater using the combination of photo-driven advanced oxidation (P-AOP) and physical foam fractionation was examined. As a result of the study, COD removal efficiencies of 63.8% and 30.2% were achieved through photo-Fenton and P-AOPs, respectively. On the other hand, in the foam fractionation processes, the removal of COD was 95.3%. When the UV-C light source was replaced with sunlight, it was observed that there was a decrease from 95.3% to 89.5% in the COD removal efficiency [24]. By using *Pseudomonas aeruginosa*, which is an indicator microorganism, Teodoro et al. [25] investigated the performance of the photo-Fenton and some other advanced oxidation processes in terms of the treatment of greywater. The H_2O_2 concentration was vary from 25 to 150 mg/L at 10 mg/L of the Fe^{2+} concentration and the pH=3. There was no difference in treatment at high H_2O_2 concentrations. Besides, the results obtained in the H_2O_2/UV process with the concentration of 150 mg/L H_2O_2 were similar to the results obtained in the pH-adjusted system.

3.4 $KMnO_4$ Oxidation

3.4.1 Effect of $KMnO_4$ Concentration

At this stage of the study, the effect of $KMnO_4$ on the treatability of greywater was investigated. The experimental studies were carried out with a variety of $KMnO_4$ concentrations on COD removal efficiency. Effects of different $KMnO_4$ doses on COD removal efficiency in 30 minutes fixed time were summarized in table 10.

The raw greywater COD of 1376 mg/L was subjected to a reaction time of 3 minutes at 200 rpm first, and then 30 minutes at 50 rpm in a jar test. And during the experiments, a color in eggplant purple tones was observed as a result of adding $KMnO_4$ into greywater. As a result of the COD analysis performed after the period was completed, the highest removal efficiency was obtained as 71% at the concentration of 0.1 g/L.

Under experimental conditions, raw greywater COD of 1203.2 mg/L was subjected to a reaction time of 3 minutes at 200 rpm, then 1 hour at 50 rpm in a jar test. The highest COD removal efficiency (83%) was obtained at a concentration of 0.1 g/L. The effects of different $KMnO_4$ doses on COD removal efficiency in 1 hour fixed time were summarized in Table 11.

The raw greywater of COD 1459.2 mg/L was subjected to a reaction time of 3 minutes at 200 rpm and then 2 hours at 50 rpm in a jar test. The highest COD efficiency was determined as 84% at 0.1 g/L concentration. The effects of different $KMnO_4$ doses on COD removal efficiency in 2 hours fixed time were summarized in Table 12.

COD removal efficiencies achieved as a result of the treatment with the $KMnO_4$ addition at different reaction times, 0.1-0.6 g/L range, and pH value 7.48 are shown in Figure 6. Based on the figure, it can be concluded that the highest COD removal efficiency of synthetic greywater (84%) was achieved with 0.1 g/L $KMnO_4$ concentration at the end of 2 hours of reaction time. However, at a concentration of 0.1 g/L $KMnO_4$, as a result of the 1-hour treatment, a yield (83%) very close to the highest COD removal efficiency was achieved. Therefore, the optimum concentration is considered 0.1 g/L $KMnO_4$ and the most appropriate time can be accepted as 1 hour.

In addition, by using 0.1 g/L of $KMnO_4$, the maximum COD removal efficiency (83 %) was obtained at 60 min of reaction time.

Table 10. Effects of different $KMnO_4$ doses on COD removal efficiency in 30 minutes fixed time

Analysis	$KMnO_4$ (g/L)	Time(min)	Remained COD (mg/L)	COD Removal (%)
1	0.1	30	396.8	71
2	0.2	30	504.32	63
3	0.3	30	550.4	59
4	0.4	30	532.48	61
5	0.5	30	524.8	61
6	0.6	30	519.68	62

Table 11. Effects of different $KMnO_4$ doses on COD removal efficiency in 1 hour fixed time

Analysis	$KMnO_4$ (g/L)	Time (hour)	Remained COD (mg/L)	COD Removal (%)
1	0.1	1	199.68	83
2	0.2	1	299.52	75
3	0.3	1	216.32	82
4	0.4	1	209.92	82
5	0.5	1	215.04	82
6	0.6	1	254.72	78

Table 12. Effects of different $KMnO_4$ doses on COD removal efficiency in 2 hours of fixed time

Analysis	$KMnO_4$ (g/L)	Time (hour)	Remained COD (mg/L)	COD Removal (%)
1	0.1	2	230.4	84
2	0.2	2	364.8	75
3	0.3	2	748.8	48
4	0.4	2	684.8	53
5	0.5	2	646.4	55
6	0.6	2	608	58

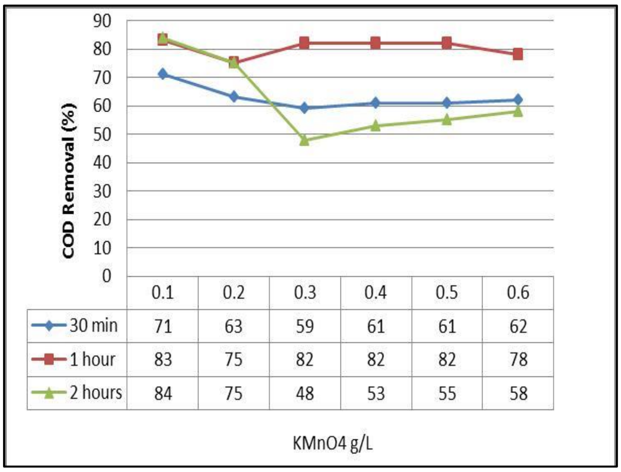

Figure 6. The effect of $KMnO_4$ on COD removal efficiency

4. Conclusion

In this study, firstly, the treatment performance of greywater using the Fenton Process, which has become attractive due to the advantages such as high efficiency, easy availability of the chemicals used, low investment cost and short hydraulic retention time, was investigated. The Box-Behnken Statistical Design Program was applied to Fenton Process for greywater treatment to be able to reduce the number of experiments and provide an estimation of the untested experimental conditions in the light of the coefficients provided by the program. During this application, variable parameters affecting the process, pH, Fe^{2+} and H_2O_2 dose, and the effect of time were evaluated.

As a result of the study, the optimum value of pH was chosen as 3. Then, the optimum dose of Fe^{+2} was determined as 3 mM. 2Mm and time of 37 min were determined as the optimum dose of H_2O_2 and reaction time, respectively.

In addition, as a strong oxidant, $KMnO_4$ was used to investigate its effect on the greywater treatability. $KMnO_4$ concentration range was determined as 0.1-0.6 g/L and time variation was determined as 30 minutes, 1 hour, and 2 hours. At the end of the 60 min reaction time, the highest COD removal efficiency was achieved as 83% at 0.1 g/L $KMnO_4$ concentration. The pH of 7.48, 60 min reaction time, and 0.1 g/L $KMnO_4$ were accepted as optimum conditions.

As a result of the study, it can be concluded that $KMnO_4$ oxidation can be used as an advanced oxidation process to achieve high COD removal efficiencies in greywater treatment. However, the optimal dose of oxidant should be determined from an economical perspective. Further studies are required to better understand the effect of $KMnO_4$ oxidation on greywater treatment.

Declaration

The authors declared no potential conflicts of interest to the research, authorship, and/or publication of this article. The authors also declared that this article is original and was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

Author Contributions

Ö. Demir developed the methodology. E.S. Aktaş performed the analysis. Ö. Demir supervised and improved the study. Ö Demir and E. S. Aktaş wrote the manuscript together.

Acknowledgement

The authors would like to thank the management and staff of the GAP Renewable Energy and Energy Efficiency Center Biomass laboratory of Harran University for their support.

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