Advanced Treatment of Pistachio Processing Industry Wastewater by Fenton Process

S. Bayar[1], T.M. Massara[2,3], R. Boncukcuoglu[4], O.T. Komesli[1], E. Katsou[2,3]

[1] Department of Environmental Engineering, Faculty of Engineering, Ataturk University, 25240, Erzurum, Turkey.

[2] Institute of Environment, Health and Societies, Brunel University London, Uxbridge Campus, Middlesex, UB8 3PH, Uxbridge, UK.

[3] Department of Mechanical, Aerospace and Civil Engineering, Brunel University London, Uxbridge Campus, Middlesex, UB8 3PH, Uxbridge, UK.

4 Department of Environmental Engineering, Faculty of Engineerig, Istanbul University, 34 320, Istanbul, Turkey.

Corresponding Author: Evina Katsou (Evina.Katsou@brunel.ac.uk; Tel.: +44 (0)1895 265721)

Abstract

In the present study, the efficiency of Fenton oxidation for the treatment of heavily loaded pistachio processing industry wastewater (PPIW) was investigated at lab-scale in terms of Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Phenol (TP) removal. Process parameters including pH, Fe^{+2} dosage, hydrogen peroxide (H_2O_2) concentration and reaction time were also examined with a view to discovering their effect on the process performance and concluding to their optimal combination. Optimum conditions for Fenton oxidation were determined to be pH=3, 1.3 gr L^{-1} Fe^{+2}; 19.2 g L^{-1} H_2O_2 and reaction time of 60 min. Under these optimal conditions, COD, TOC and TP removals were measured as equal to 80, 54 and 88.7%, respectively, thus suggesting that Fenton oxidation can be efficient in the treatment of wastewaters with high organic pollution.

Keywords: Pistachio processing industry wastewater, Fenton oxidation, pH, Fe^{+2} dosage, H_2O_2 concentration, reaction time

Nomenclature	
AOP	Advanced Oxidation Processes
COD	Chemical Oxygen Demand
PPIW	Pistachio Processing Industry Wastewater
TOC	Total Organic Carbon
TP	Total Phenol

1. Introduction

Pistachio industry is a rapidly developing industrial sector in Turkey. The estimated pistachio yield in the country was about 144 thousand tons in 2015 and Turkey is the third biggest producer of pistachio in the world. Depending on the applied processes, pistachio can constitute a great clean water consumer; approximately up to six tons of clean water can be needed to process one ton of pistachio. Pistachio processing industry wastewater (PPIW) contains components hard to degrade biologically with high chemical oxygen demand (COD), total organic carbon (TOC), total phenol (TP) and toxic organic impurities content [1]. Advanced oxidation processes (AOP) are widely used in the treatment of wastewater with high organic load. Fenton oxidation, in particular, is amongst the most commonly implemented AOP processes. According to past studies, the Fenton process has been used for the removal of organic substances [2], for reducing toxicity [3], as a preliminary treatment step before biological treatment [4], as well as in colour removal [5].

Fenton oxidation and associated reactions involve the reaction of peroxodyne (mostly hydrogen peroxide: H_2O_2) with iron ions to form active oxygen types which can oxidize organic or inorganic compounds. Production of hydroxyl radicals ($OH^\bullet$) is possible under low pH and reducing conditions, where iron ions are in soluble structures.

In Fenton application, $OH^\bullet$ are desired to react directly with organic materials. The following redox reactions can be obtained if H_2O_2 is added to an aqueous solution containing Fe^{+2} and organic matter with a pH value of 2-5 (under acidic conditions); Fe^{+2} will be formed again in the catalytic cycle. As long as H_2O_2 is present in the system, there will be a continuous recycle between Fe^{+2} and Fe^{+3}.

The produced $OH^\bullet$ attacks the organic matter and breaks down the pollutants to end products such as carbon dioxide (CO_2) and water: From an overall perspective, the Fenton process consists of four steps, which are pH adjustment, oxidation reaction, neutralization and precipitation reaction through coagulation. The mechanism that describes Fenton's reaction mainly includes the following reactions [6-8]:

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

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

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^\bullet + H^+ \quad (3)$$

$$Fe^{+3} + HO_2^\bullet \rightarrow Fe^{+2} + O_2 + H^+ \quad (4)$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \quad (5)$$

Hence, the aims of the present study were to: i) examine the efficiency of Fenton oxidation for the lab-scale treatment of wastewater resulting from the processing of red peppered pistachio nuts in terms of COD, TOC and TP removal, and ii) define optimal treatment possibilities depending on various operating conditions (e.g. pH, Fe^{+2} dosage, H_2O_2 concentration and reaction time).

2. Materials and Methods

2.1 Wastewater properties

The wastewater used in the current study originated from an industrial facility with an average daily processing capacity of 24 tonnes of peanuts per day. This industrial facility discharges the produced wastewater to the sewage system without applying any physical, biological or chemical treatment. The wastewater finally used in the experiments was obtained by mixing various volumes of sample wastewater to ensure homogeneity. Then, the wastewater was brought to the lab in containers by means of a cooling circulator and was kept untouched at 4 °C. After being allowed to settle for 6 hours, it was analyzed and characterized as follows (Table 1):

Table 1. Characteristics of the PPIW used in the current study.

Parameter	Units	Value
Conductivity	(µs cm^{-1})	4,750 – 5,750
Turbidity	(NTU)	150-250
pH	-	5-5.5
COD	(mg L^{-1})	15,000-18,000
TOC	(mg L^{-1})	5,000-5,500
TP	(mg L^{-1})	3,800-4,500
Oil-Grease	(mg L^{-1})	50-59
Cl	(mg L^{-1})	600-650

2.2 Fenton experiments

Fenton experiments were carried out in a 6-digit PHIPPS & BIRD jar mark test system. 500 ml of wastewater were used in the experiments. The steps for the experimental application of the Fenton process were performed as outlined below:

- pH adjustment was performed by using 1 M NaOH and 1 M HNO_3
- Fe^{+2} (prepared from $FeSO_47H_2O$) and H_2O_2 were added in the predetermined quantities respectively.
- The jar test unit was subjected first to 3-min rapid mixing (160 rpm) followed by 57-min slow stirring (50 rpm).
- The pH of the wastewater in 1 L beakers was adjusted to 8.5-10 using 1M NaOH at the end of the 60-min test period.
- After a 60- min sedimentation process, clear phase samples were taken and filtered through a 0.45 µm membrane. COD, TOC and TP measurements were then conducted.

- Positive interventions that the residual H_2O_2 can have on the COD measurements were considered by performing H_2O_2 analysis.

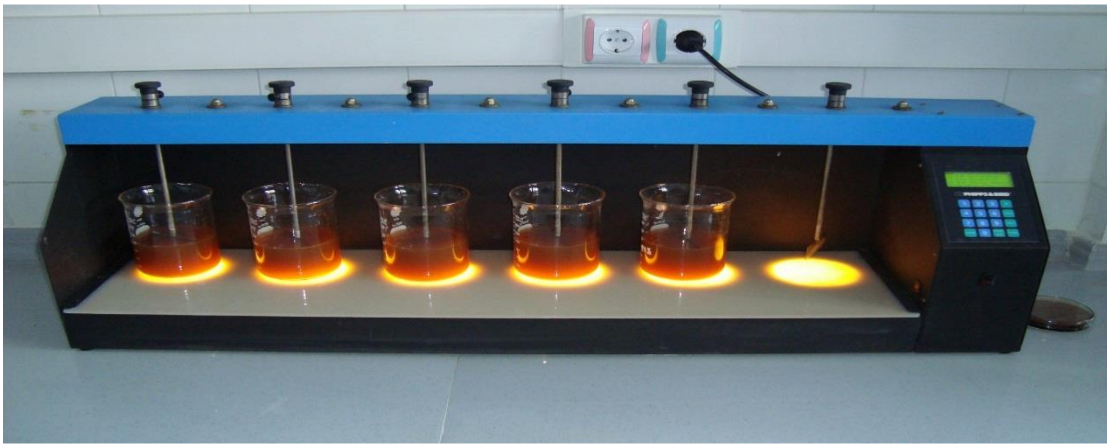

Figure 1. Schematic view of the experimental system for the lab-scale Fenton oxidation treatemnt of PPIW.

2.3 Analytical methods

COD, TOC and TP measurements were performed according to standard methods (APHA,1985). COD assays were performed according to the closed system method (reflux) defined in the standard methods. TOC analyses were performed using a T-T-A 9000 TOC-TN analyser. TP determination was realized using the Folin-Ciocalteu spectrophotometric method. Moreover, H_2O_2 analyses using the I3 method were performed, in order to determine the positive interference in the COD analyses caused by H_2O_2 during the experiments, thus allowing the determination of the quantities that interfered with the COD. The pH values of the samples were determined through a WTW pH 330i pH meter device.

3. Results and discussion

3.1. Effect of Fe^{+2} concentration on the system performance

The rate of the 1st reaction (see Eq. 1) is important for determining the efficiency and process cost of the Fenton process [9]. The effect of the Fe^{+2} concentration, used as a catalyst in the treatment of PPIW through Fenton oxidation, on the treatment performance has been investigated at the natural pH of the PPIW. Six different Fe^{+2} concentrations ranging from 0.26-1.56 gr L^{-1} were tested by keeping the theoretically calculated 19.2 gr L^{-1} H_2O_2 concentration constant. Fig. 2 shows the effect of the Fe^{+2} concentration on the COD, TOC and TP removal.

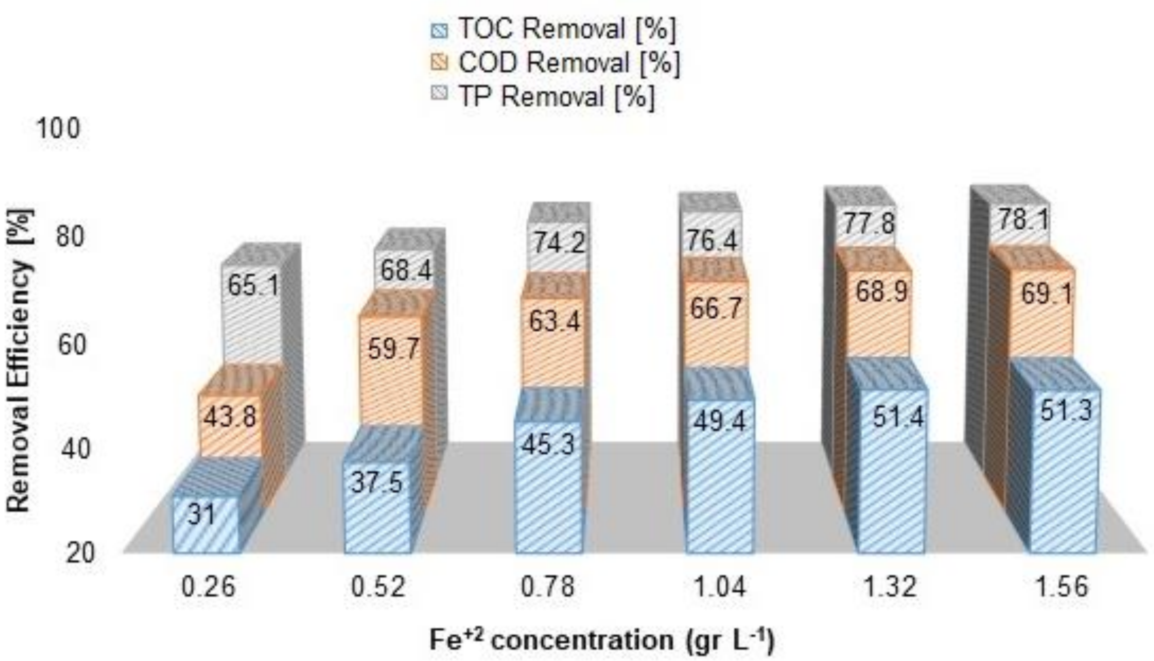

Figure 2. The effect of the Fe^{+2} concentration on the TOC, COD and TP removal.

The fact that the iron sulphate ($FeSO_4$) and H_2O_2 reagents are of acidic character is expected to affect the working pH. The pH value decreased with the $FeSO_4$ addition to the system (see Table 2). If the pH does not decrease, it can be stated that the H_2O_2 reaction is prone to inhibition.

Table 2. The effect of added Fe^{+2} concentration on the wastewater pH.

Fe^{+2} concentration (gr L^{-1})	0.26	0.52	0.78	1.04	1.3	1.56
Initial pH	5.2	5.2	5.2	5.2	5.2	5.2
Final pH	4.43	3.98	3.48	3.05	2.87	2.51

Since there is no fundamental factor to produce the $OH^{\bullet}$ in the environment in the absence of Fe^{+2}, an effective oxidation does not occur based on the fenton reaction. As the concentration of Fe^{+2} increases, the $OH^{\bullet}$ rate of production will theoretically rise.

Fig. 2 shows that increasing the Fe^{+2} concentration up to 1.3 gr L^{-1} positively affects the removal efficiencies, while the Fe^{+2} addition effect is less important above for concentrations above 1.3 gr L^{-1}. The removal efficiency for the Fe^{+2} concentrations of 0.26, 0.52 and 0.78 gr L^{-1} were 43.8%, 59.7% and 63.4% for COD, 31%, 37.5% and 45.3% for TOC, and 65.1%, 68.4% and 74.2% for TP, respectively. A Fe^{+2} dose equal to 1.3 mg L-1 provided high removals for all parameters; 51.4% TOC removal, 68.9% COD removal and 77.8% TP removal. It can be hypothesized that dosing over 1.3 gr L^{-1} adversely affected the oxidation capacity. Higher Fe^{+2} concentrations will lead to the consumption of OH$^{\bullet}$ in the medium according to with Eq. (2), thus reducing the removal efficiency [10]. Furthermore, excessive Fe^{+2} in the medium allows an additional reaction to occur, resulting in the conversion of H_2O_2 to water (see reaction 6) [11]:

$$Fe^{+2} + H_2O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O \quad 6)$$

3.2 Effect of the H_2O_2 concentration on the system performance

H_2O_2 concentration is among the most significant parameters in the Fenton process since it functions as a production source of OH$^{\bullet}$ [12]. The H_2O_2 consumption during the Fenton reactions is the most important factor limiting the efficiency of the process. In addition, the determination of the optimum value for the H_2O_2 concentration is essential to achieve both treatment efficiency and minimized cost. Any unused amount of H_2O_2 will make a positive intervention in the COD analyses, therefore excessive H_2O_2 amount is not desired.

The effect of 6 different H_2O_2 concentrations ranging from 3.2-22.4 gr L^{-1} were investigated in the experiments by keeping the optimum Fe^{+2} concentration of 1.3 gr L^{-1} as concluded in section 3.1. The experiments were carried out at the natural pH of the PPIW.

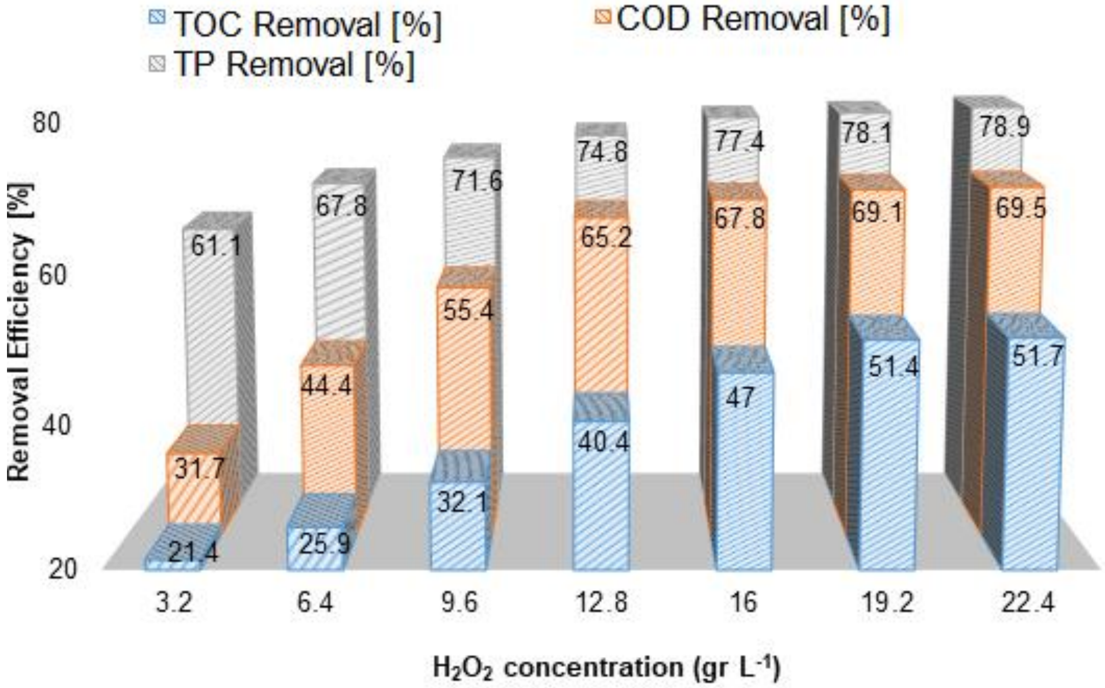

Figure 3. The effect of the H_2O_2 concentration on the TOC, COD and TP removal.

Fig. 3 shows the effect of H_2O_2 concentration on the COD, TOC and TP removal during Fenton oxidation. COD, TOC and TP removals increased with the H_2O_2 concentration increase. However, it was observed that the removal yield did not significantly change when the H_2O_2 concentration was increased above 19.2 gr L^{-1}. Theoretically, H_2O_2 is the production source of $OH^{\bullet}$, and as the H_2O_2 concentration increases, more $OH^{\bullet}$ radicals will be produced. However, it is known that H_2O_2 acts as a radical scavenger at higher concentrations in accordance with the reactions 7-9. It forms $HO_2^{\bullet}$ with lower oxidation capacity by reacting with the $OH^{\bullet}$ radicals in the medium, consumes $OH^{\bullet}$ radicals and, thus, reduces the removal efficiency [10].

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (7)$$

$$OH^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (8)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H^{+} \quad (9)$$

The optimum H_2O_2 dose was determined to be 19.2 gr L^{-1} in the Fenton processes according to the reactions given above and the COD, TOC and TP removal efficiencies obtained at this dose (69.5%, 51.7% and 78.4%, respectively).

3.3 Effect of initial PPIW pH on system variables

Fenton processes are strongly pH dependent due to the interaction between Fe^{+2} and H_2O_2. In the Fenton process, the interrelation between the pH value and the oxidation potential explains the decisive Ph influence on the $OH^{\bullet}$ [13]. The majority of studies performed applying the Fenton process have shown that the best removal, regardless of the target pollutant, are obtained in a pH range of 2 to 5 (mostly at pH=3). Studies focusing on PPIW treatment through Fenton oxidation have been mostly performed in a pH range of 2 to 6. Higher pH values are not recommended due to the precipitation ability of Fe^{+2}. The removal efficiencies of COD, TOC and TP at different pH values with the Fenton process are given in Fig 4.

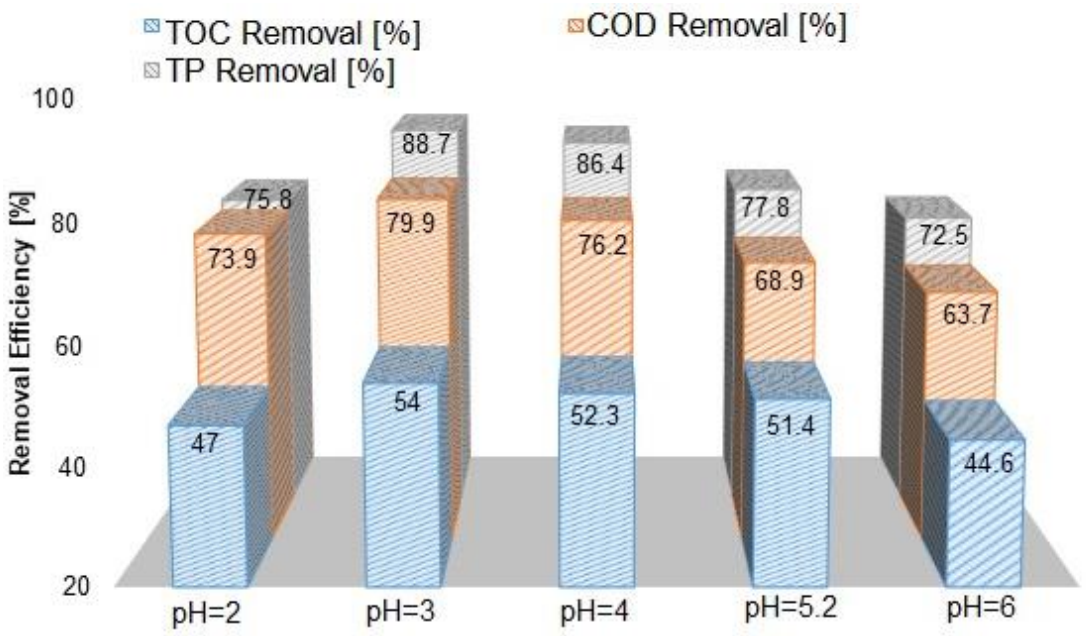

Figure 4. The effect of initial PPIW pH on TOC, COD and TP removal.

It can be seen in Fig. 4 that the highest removals were obtained with a baseline PPIW pH value of 3; 79.9% for COD, 54% for TOC and 88.7% for TP. At higher pH values, H_2O_2 forms oxygen and water and loses its oxidation activity. There is also the conversion of the aqueous Fe^{+2} ion into Fe^{+3} which means that it loses its catalytic activity. At pH<3, the $OH^{\bullet}$ production decreases and H^+ ions act like a $OH^{\bullet}$ radical scavenger (see reaction 10). The latter is thought to be due to the reduction in the amount of Fe^{+3} in the soluble form due to the formation of $Fe(OH)^{+2}$ and $Fe(OH)_2^+$, which leads to the continuation of oxidation [14]. Therefore, removal is expected to decrease at very low pH values [15].

$$OH^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \, (10)$$

At low pH conditions in the experiments, the pH values at the end of the experiments decreased very little, but the pH change rapidly decreased at the end of experiments with near neutral pH values. This is thought to be due to the formation of acids such as carboxylic acid, acetic acid and formic acid during phenol decomposition

3.4 Reaction time effect

The reaction time can vary depending on the nature of the pollutant load and the type of organic matter in the wastewater. Under optimum conditions determined as described in sections 3.1-3.3 (Fe^{+2}:1.3 gr L^{-1}, H_2O_2: 19.2 gr L^{-1}, initial PPIW pH=3), changes in COD, TOC and TP removal were investigated over time by taking samples at 15, 30, 60 and 90 min. The results are presented in Fig. 5. They increased continuously over time with the maximum being reached at 90 min; 80.1% for COD, 89% for TP and 53.9% for TOC. Once again, after 30 min of reaction time, no significant changes were observed in the removal efficiencies. According to the analyses performed, 99% of the H_2O_2 added had been already consumed after 30 min of reaction.

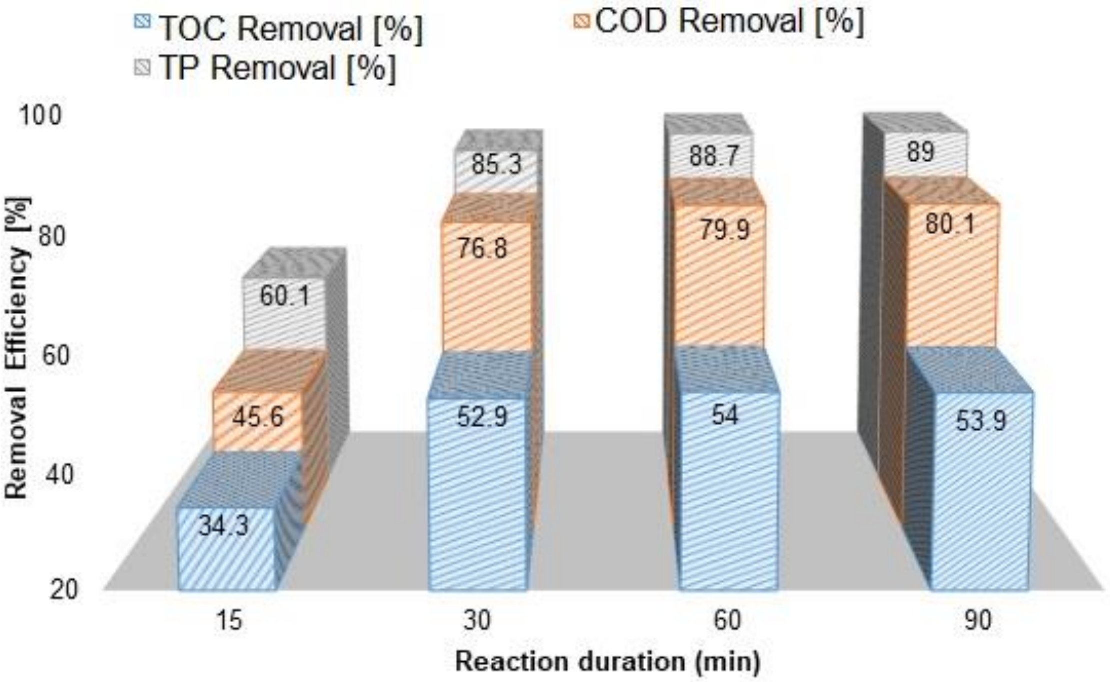

Figure 5. The effect of reaction duration on the TOC, COD and TP removal.

The absence of H_2O_2 which reacts with the Fe^{+2} as well as the inhibition by the produced $OH^{\bullet}$, which oxidize the organic substances, are likely to be the reasons why the removal efficiency did not change with the extension of operation.

4. Results

In this study, the efficiency of Fenton oxidation for the lab-scale treatment of wastewater resulting from the processing of red peppered pistachio nuts was evaluated in terms of COD, TOC and TP removal. During the different tests, Fe^{+2} dosage ranged from 0.26 to 1.56 gL^{-1}, H_2O_2 dosage from 3.2 to 22.4 gr L^{-1} and the baseline PPIW pH from 2 to 6. Different reaction times were also examined within the range of 15 to 90 min. Optimum conditions in the study were determined to be as follows: pH=3, 1.3 gr L^{-1} Fe^{+2}, 19.2 gr L^{-1} H_2O_2 and 60 min of reaction time. Under these conditions, COD, TOC and TP removal efficiencies were 79.9, 54 and 88.7%, respectively.

As the result of this study, it can be suggested that Fenton oxidation is an effective treatment alternative for PPIW. It can even be integrated into biological treatment units as a pre-treatment step for wastewaters with high organic content, thus contributing to the increase of the overall removal efficiency of such treatment schemes.

Acknowledgements

This study was supported by Ataturk University, Scientific Research Projects (BAP) unit under the project 2011/147. T.M. Massara is grateful to the Natural Environment Research Council (NERC) of the UK for the 4-year full PhD studentship.

References

[1] Bayar, S., Boncukcuoğlu, R., Yilmaz, A.E., Fil, B.A.: Pre-Treatment of Pistachio Processing Industry Wastewaters (PPIW) by Electrocoagulation using Al Plate Electrode. Separ. Sci. Technol. 49, 1008-1018 (2014)

[2] Fan, C., Horng, C.Y., Li, S.J.: Structural characterization of natural organic matter and its impact on methomyl removal efficiency in Fenton process. Chemosphere 93 (1), 178-183 (2013)

[3] Zhang, J., Chen, S., Zhang, Y., Quan, X., Zhao, H., Zhang Y.: Reduction of acute toxicity and genotoxicity of dye effluent using Fenton-coagulation process. J. Hazard. Mater. 274, 198-204 (2014)

[4] Lopez, A., Pagano, M., Volpe, A., Di Pinto, A.C.: Fenton’s pre-treatment of mature landfill leachate. Chemosphere 54 (7), 1005-1010 (2004)

[5] Santana, C.S., Aguiar, A.: Effect of biological mediator, 3-hydroxyanthranilic acid, in dye decolorization by Fenton processes. Int. Biodeterior. Biodegrad. 104, 1-7 (2015)

[6] Neyens, E., Baeyens, J.: A review of classic Fenton’s peroxidation as an advanced oxidation technique. J. Hazard. Mater. 98, 33-50 (2003)

[7] Pera-Titus, M., Garcıa-Molina, V., Banos, M.A, Gimenez, J., Esplugas, S.: Degradation of chlorophenols by means of advanced oxidation processes: a general review. Appl. Catal. B: Environ. 47, 219-256 (2004)

[8] Walling, C.: Fenton’s reagent revisited. Acc. Chem. Res. 8, 125-131 (1975)

[9] Özdemir, C., Öden, M.K., Şahinkaya, S., Güçlü, D.: The sonochemical decolorisation of textile azo dye CI Reactive Orange 127. Color. Technol. 127 (4), 268- 273 (2011)

[10] Pérez-Moya, M., Graells, M., del Valle, L.J., Centelles, E., Mansilla, H.D.: Fenton and photo-Fenton degradation of 2-chlorophenol: Multivariate analysis and toxicity monitoring. Catal. Today, 124 (3-4), 163-171 (2007)

[11] Tarr, M.A.: Chemical degradation methods for wastes and pollutants: Environmental and industrial applications. New York, NY: Marcel Dekker (2003)

[12] Sun, S.P., Li, C.J., Sun, J.H., Shi, S.H., Fan, M.H., Zhou, Q.: Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study. J. Hazard. Mater. 161 (2-3), 1052-1057 (2009)

[13] Li, J., Luan, Z., Yu, L., Ji, Z.: Pretreatment of acrylic fiber manufacturing wastewater by the Fenton process. Desalination 284, 62-65 (2012)

[14] Lucas, M.S., Peres, J.A.: Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. Dyes and Pigm. 71 (3), 236-244 (2006)

[15] Muruganandham, M., Swaminathan, M.: Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. Dyes and Pigm. 63 (3), 315-321 (2004)