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## TREATMENT OF THE PISTACHIO PROCESSING WASTEWATER USING FENTON'S, ULTRASOUND WITH FENTON'S, AND COAGULATION PROCESSES

Pistachio processing wastewater was characterized and the treatability of wastewater using Fenton's process, the combination of Fenton's process with ultrasonic irradiation and coagulation processes was investigated.  $[\text{Fe}^{2+}] = 27.6 \text{ mg/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 30 \text{ mg/dm}^3$  and 75 min of reaction time were determined as the optimum conditions for Fenton's process. Then, the combined treatment (ultrasound with Fenton's process, was applied to the pistachio processing wastewater and 45% of COD removal efficiency was obtained. For the coagulation process, the optimum removal efficiencies of 60% and 45% were achieved for  $\text{FeCl}_3$  dosage of  $2000 \text{ mg/dm}^3$  and  $\text{Al}_2(\text{SO}_4)_3$  dosage of  $3000 \text{ mg/dm}^3$ , respectively. The results demonstrate that higher COD removal efficiencies could be obtained from the combined ultrasound and Fenton's process with respect to Fenton's process alone. Besides, applying the coagulation process using  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  also presents high COD removal efficiencies.

### 1. INTRODUCTION

*Pistacia vera* L. is the only species of the 11 in the genus *Pistacia* that produces edible nuts. It comes from Western Asia and Asia Minor, and wild representatives are still found in hot, dry locations in these areas. The leader region of Turkey in pistachio production is the South-East Anatolia Region. However, the wastewater produced during pistachio processing has high contamination potential. This is a crucial problem that should be solved for the region as well as for the country. Pistachio processing wastewater (PPW) has high organic matter content, contains suspended solid (SS), oil and grease. This wastewater cannot be discharged to central canal systems without any pretreatment. This wastewater should be treated by physical-chemical and biological

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methods before the discharge. The treatment and disposal of the PPW are bound to legal regulatory standards. PPW associated to pistachio peeling process consists of water added to the process. Uncontrolled disposal of PPW is becoming a serious environmental problem due to its high content of phenolic compounds from live mill. Improper disposal of PPW to the environment or to domestic wastewater treatment plants is prohibited due to its toxicity to microorganisms and leads to consequent surface and groundwater potential contamination. Pistachio processing is carried out by small companies in small facilities. Management of the wastes generated during the process is an important for these companies.

Turkey is the third largest producer of pistachio with 120 000 t of annual production, (*Pistacia vera* L.) after Iran and United States [1]. An organic hull covers the harvested pistachio. According to the climatic factors and a variety of pistachio, dehulling process can either be handled using wet or dry systems [2]. Dry dehulling is the process of removing the hull in the early stages after harvesting [3]. Pistachio varieties having small nuts with hulls are not very susceptible to deterioration in Turkey. So, they can be stored for long time period without dehulling. By the time dehulling of pistachio nut is required; the already dried hull has to be removed with water flush technique called wet dehulling [2].

During dehulling of pistachio nuts after harvesting pistachio by-products containing a high level of pistachio epicarp (53.5% of dry matter) are produced. Pistachio green hull is a good source of protein, fat, mineral salts and vitamins [4, 5]. Most of the pistachio by-products are considered agricultural waste and are often mixed with soil. The chemical composition, phenolics content and digestion of pistachio hull are varied and largely dependent upon variations in pistachio cultivars, harvesting time, drying and dehulling processes [6].

Wastewater containing recalcitrant contaminants can be treated using advanced oxidation processes (AOP) as a promising technology in the past decades. In order to treat the non-degradable materials, oxidation processes such as chemical oxidation, acoustic oxidation, and advanced oxidation processes have been studied [7]. A large amount of hydroxyl radicals ( $\text{OH}^\cdot$ ) to oxidize organic pollutants can be produced during the AOPs treatment [8]. Contaminants will be degraded and converted into small inorganic molecules. One of the AOPs using  $\text{FeSO}_4$  to catalyze hydroxyl radical production is Fenton's process. In Fenton's process, the oxidation of many organic substances with  $\text{H}_2\text{O}_2$  is improved by the addition of a catalyst ( $\text{Fe}^{2+}$ ) to activate  $\text{H}_2\text{O}_2$  molecules, leading to the formation of hydroxyl radicals [9]. In particular, Fenton's process is effective in the contaminant reduction due to the degradation of recalcitrant organics even at higher initial organic content [10]. The high efficiency, simple application, the lack of residues, higher treatment capacity and short residence time are the advantages of the cost effective Fenton's process [9]. In addition, ultrasonic irradiation can enhance the treatment efficiency of Fenton's process [7]. The other popular technology of AOP is ultrasound technology for dealing with recalcitrant chemicals. In the ultrasonic process, high local temperature and pressure have been observed during transient collapse of microbubbles and  $\text{OH}^\cdot$ ,  $\text{H}^\cdot$ , and  $\text{HO}_2^\cdot$  radicals are generated. The hydroxyl radical is one of the strongest

oxidants that can react with organic and inorganic compounds [11]. Ultrasound with a frequency range from 20 kHz to 10 MHz has a wide range of environmental applications [12]. Due to the high energy consumption of ultrasound irradiation alone, it has no large-scale industrial application presently. Various combined ultrasound treatment systems have been proposed in order to overcome these limitations. Ultrasound treatment coupled with oxidants such as ozone, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), Fenton's reagent, photocatalysts, and other catalytic oxidation processes have been studied [11].

Coagulation and flocculation processes with  $\text{FeCl}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{FeSO}_4$ , aluminum sulfate are important processes practiced worldwide for water and wastewater treatment. [12]. Coagulation/chemical precipitation or flocculation process was conducted for the treatment of industrial wastewater to achieve maximum removal of chemical oxygen demand (COD), total phosphorus (TP) and total suspended solids (TSS). The coagulation/chemical precipitation and the flocculation of suspended particles and colloids result from different mechanisms including electrostatic attraction, sorption and bridging [13]. Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate were commonly used as coagulants.

There are a limited number of studies evaluating the treatment of pistachio wastewater in the literature. Fil et al. [14] investigated the treatment of PPW by electro-oxidation method considering effective parameters such as stirring speed, support electrolyte types, support electrolyte concentrations, wastewater initial pH, and current density by using stainless steel cathodes and graphite anodes. Optimum values of operating variables were determined at 5 h of processing time, 400 rpm of stirring speed, 3 of wastewater pH,  $30 \text{ mA/cm}^2$  of current density, and  $1.25 \text{ mol/dm}^3$  of support electrolyte ( $\text{NaCl}$ ). Removal efficiencies of 99.79, 76.55, and 100 % were obtained with optimum values for COD, TOC, and TPh, respectively.

The objective of the other study related to the PPW treatment by Bayar et al., [15] was to assess the efficiency of electrocoagulation treatment of pistachio processing industry wastewaters (PPIW) using an aluminum plate electrode. The effect of some of the parameters was examined on the removal of COD, TOC, and TPh removal efficiency. The treatment was carried out in a batch system. The evaluation of the physico-chemical parameters during the treatment by electrocoagulation showed that the best removal efficiency was obtained under the such conditions as 180 min electrolysis time, wastewater with constant pH of 6, and  $6 \text{ mA/cm}^2$  current densities. COD, TOC, and TPh removal efficiency were found to be 60.1 %, 50.2%, and 77.3 %, respectively, while energy consumption was  $39.6 \text{ kWh/m}^3$ . The results of the study show that the electrocoagulation can be applied to PPIW pre-treatment system.

In the present study, three different processes including Fenton's process, ultrasound with Fenton's process and coagulation were applied to treat PPW. Effects of various  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  concentration and reaction time were investigated and optimum

values were determined in Fenton's process. The synergistic effect of combined ultrasound and Fenton's process was also studied. In addition, ferric chloride and aluminum sulfate were used as coagulants in order to assess the treatability of PPW.

## 2. PISTACHIO (*PISTACHIA VERA* L.)

Dry and hot areas under saline conditions are suitable for the cultivation of pistachio. The main producers of pistachio nut are Iran, the USA, Turkey, Syria, Italy and Greece and the global production increases steadily [16]. Because of the nutritional components including sterols, vitamins, minerals, fatty acids and phenolic compounds and the antioxidant and antiproliferative properties, nut consumption increases [17]. Pistachio nuts are mainly dried or roasted with salt, while the kernels can also be used in cookery [18].

*Production of pistachio in the world and in Turkey.* The leader country in the production of the pistachio (named Antep pistachio in Turkey), is Iran according to the data of the Food and Agriculture Organization (2014). USA, the second one, has become a rivalry to Iran developing production techniques. Turkey follows these countries with the fluctuating production trend (Tables 1 and 2). The ruinous price and coarse grain of Iranian pistachio lead to increasing of the demand in the worldwide.

Table 1

Pistachio production in the world [19]

Country	2012	2013	2014	
			Production	Per cent of the global value
Iran	39 0400	412000	415531	48.43
USA	275 500	213188	233146	27.17
Turkey	150 000	88600	80000	9.32
China	72 000	74.000	76943	8.96
Syrian	57 195	54516	28786	3.35
Greece	7955	6854	5700	0.66
Italy	943	3227	3555	0.41
Afghanistan	2736	2749	2761	0.32
Tunisian	1400	2.100	2500	0.29
Kyrgyzstan	800	900	900	0.1
Others	8140	8101	8056	0.93
Total	967069	866235	857878	100

Pistachio grows especially in Gaziantep, Kahramanmaraş, Adıyaman, Şanlıurfa, Mardin, Kilis, Diyarbakır and Siirt in Turkey. The professional cultivation of pistachio

began in Ceylanpınar State Farm in 1948 with the area of 114 da. Currently, this area reached 10.7 million ha. The exportation of pistachio amounted to 28.8 million \$ (2 325 t) in 2012. It reached 48 million \$ (3970 t) in 2013 (Table 2). The biggest market share is owned in Italy with 35.32 % considering exportation market in 2013. The other countries are Germany, Israel and Belgium with 11.98 % 3.728 %, 2.878 %, respectively (Table 2).

Table 2

Pistachio exportation of Turkey [19]

Country	2012		2013		
	Quantity [t]	Value [1000 \$]	Quantity [t]	Value [1000 \$]	Per cent of the global value
Italy	638	9480	1162	16961	35.326
Germany	154	2945	279	5754	11.984
Israel	468	4477	151	1790	3.728
Belgium	22	401	68	1382	2.878
USA	160	1995	86	1354	2.82
Egypt	147	1718	103	1106	2.303
Iraq	95	969	74	785	1.635
Turkmenistan	13	119	7	163	0.339
Azerbaijan	22	179	2	45	0.093
Others	606	6573	2038	18672	38.89
Total	2325	28856	3970	48012	100

*Pistachio wastewater processing.* Pistachio is first peeled with water in pistachio processing plants using peeling machines. Then the messy pistachio areas separated from the empty one are dried. Raspberries, which are found in the pistachio fruit, are soaked with water or steam. During wetting, peanuts are crushed by two horizontal and vertical millstones or using rollers after letting the red shell soften (for 3–5 h). 2–6 m<sup>3</sup> of water is used for per 1 t of pistachio. Wastewater produced during the peeling is transferred to a concrete basin for the evaporation. The operators of pistachio processing plants claimed that all wastewater was evaporated without any discharged. When this wastewater is supplied to the direct sewage system, they cause heavy burden on the urban wastewater treatment plant due to high COD, TOC and total phenol contents and decrease the efficiency of the treatment plant and prevent the discharge standards from being achieved [20]. The stages of pistachio processing are harvesting, drying, peeling, cracking and roasting.

*State of art of pistachio processing in Şanlıurfa.* The number of pistachio processing plants has been gradually increasing for the last decades. According to the knowledge

obtained from the Provincial Directorate of the Environment, there are 24 pistachio processing plants in Şanlıurfa. Beside this, nearly 40 plants are processing off the records. The plants in the Organized Industrial Zone have some processing steps such as peeling with water, drying, and selecting using machines. After the peeling, the waste is produced like sludge with a treatment difficulty. The manufacturers and the villages nearby the plants are discontented. The waste after the incineration of the pistachio branches and leaves, thickening, odorous sludge waste after the peeling and the wastewater are collected in a ditch resulting leakage contamination of the groundwater. All these problems caused by the pistachio processing have to be solved immediately because of the territorial importance.

### 3. MATERIALS AND METHODS

*Wastewater properties of pistachio processing plants.* Samples of pistachio wastewater were collected from a pistachio processing plant situated in Şanlıurfa, Turkey. The samples were stored in a refrigerator in order to minimize the changes in the characteristics of the wastewater sample which may vary from day to day. The samples used in the experiments were obtained after settling of raw wastewater (supernatant). pH, SS and COD were analyzed for either raw wastewater and supernatant. The other analyses were done only for supernatant. The characterization of the supernatant and raw wastewater are given in Table 3.

Table 3:

Characterization of pistachio process wastewater

Parameter	Raw wastewater	Supernatant
pH	6	6.3
Suspended solid (SS),	15350	4850
COD, mg/dm <sup>3</sup>	17550	9800
NH <sub>4</sub> -N, mg/dm <sup>3</sup>	–	8.6
NO <sub>3</sub> -N, mg/dm <sup>3</sup>	–	6.2
Cr, mg/dm <sup>3</sup>	–	3.8
Fe, mg/dm <sup>3</sup>	–	>60
Zn, mg/dm <sup>3</sup>	–	13.9
SO <sub>4</sub> <sup>2-</sup> , mg/dm <sup>3</sup>	–	921
Oil and grease, mg/dm <sup>3</sup>	–	450

*Optimization of Fenton's oxidation process.* For the optimization of Fenton's processes, the dosages of FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> as well as the reaction time were used as varia-

bles. pH is one of the most important factors related to the oxidation efficiency of Fenton's process due to its role in controlling the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, stability of hydrogen peroxide and the oxidation ability of hydroxyl radical ( $\text{OH}^{\bullet}$ ) generated in the reaction solution. The most suitable pH was found 2–4 [21]. For this reason it was adjusted to 3 throughout the Fenton's process. A solution of  $\text{Fe}^{2+}$  (prepared from ferrous chloride tetrahydrate and hydrogen peroxide (30 wt. %) was used in the experiments as Fenton's reagent for a hydroxyl radical generation.

The wastewater produced during the pistachio processing was used in Fenton's process. The samples were taken to a beaker 500  $\text{cm}^3$  in volume and pH was adjusted with HCl.  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  were added to the sample according to the applied dosage. The samples were centrifuged at 100 rpm for 1 h. After this, the solution was neutralized with  $\text{Ca}(\text{OH})_2$  and left for 1 h to settle.

*Determination of optimum  $\text{Fe}^{2+}$  concentration.* In order to determine the optimum  $\text{Fe}^{2+}$  concentration, 5 dosages were used ranging from 27.6 to 64.5  $\text{mg}/\text{dm}^3$ . In order to adjust  $\text{Fe}^{2+}$  dosage,  $\text{FeSO}_4$  was used in the range of 75–100  $\text{mg}/\text{dm}^3$ . The dosage of  $\text{H}_2\text{O}_2$  and reaction time were stable. The supernatant of PPW used in the experiments was obtained after settling the raw wastewater. The experimental runs are shown in Table 4 (No. 1–5).

Table 4

Experimental runs for the Fenton's process optimization

No.	$\text{FeSO}_4$ [ $\text{mg}/\text{dm}^3$ ]	$\text{Fe}^{2+}$ [ $\text{mg}/\text{dm}^3$ ]	$\text{H}_2\text{O}_2$ [ $\text{mg}/\text{dm}^3$ ]	Time min]	No.	$\text{FeSO}_4$ [ $\text{mg}/\text{dm}^3$ ]	$\text{Fe}^{2+}$ [ $\text{mg}/\text{dm}^3$ ]	$\text{H}_2\text{O}_2$ [ $\text{mg}/\text{dm}^3$ ]	Time [min]
1	75	27.6	30	60	11	75	27.6	30	60
2	100	36.86	30	60	12	75	27.6	30	75
3	125	46	30	60	13	75	27.6	30	90
4	150	55.3	30	60	14	75	27.6	30	105
5	175	64.5	30	60	15	75	27.6	30	120
6	75	27.6	15	60	16	75	27.6	30	10
7	75	27.6	22.5	60	17	75	27.6	30	15
8	75	27.6	30	60	18	75	27.6	30	20
9	75	27.6	37.5	60	19	75	27.6	30	25
10	75	27.6	45	60	20	75	27.6	30	30

*Determination of optimum  $\text{H}_2\text{O}_2$  concentration.*  $\text{H}_2\text{O}_2$  is the main source of  $\text{OH}^{\bullet}$  radicals produced in Fenton's process. Optimization of its concentration is crucial for Fenton's process since the treatment cost also increases upon increasing  $\text{H}_2\text{O}_2$  dosage. In addition, residual  $\text{H}_2\text{O}_2$  in the effluent increases COD in wastewater [21].  $\text{FeSO}_4$  concentration and the reaction time were kept constant while the optimization of the  $\text{H}_2\text{O}_2$  dosage varied in the range of 15–45  $\text{mg}/\text{dm}^3$ . The experimental runs were shown in Table 4 (No. 6–10). In order to find the reaction time required to reach a steady state, experiments were performed at 60–120 min and the following operating parameters:

pH = 3,  $[\text{H}_2\text{O}_2] = 30 \text{ mg/dm}^3$ ,  $[\text{Fe}^{2+}] = 27.6 \text{ mg/dm}^3$ . The COD of the wastewater was monitored continuously during the course of the reaction. (Table 4, No. 11–15).

*Treatment using combined ultrasound with Fenton's process.* The feasibility of using ultrasonication in combination with Fenton's reaction was investigated for treating supernatant of PPW. Ultrasonication was carried out using a generator Sonics VC 750 Ultrasound. The frequency was fixed at 20 kHz. The ultrasonication was performed in  $250 \text{ cm}^3$  beaker containing PPW and Fenton's reagents. 6 various reaction times were applied and the COD removal efficiencies were determined. The experimental runs are given in Table 4 (No.16–20).

*Coagulation studies and analytical methods.* A conventional jar test apparatus was used to coagulate samples of PPW by using ferric chloride and aluminum sulfate. The samples were obtained by dilution of raw wastewater using pure water and shaking vigorously. The dilution rate was 1:10. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. Stock solutions of ferric chloride and aluminum sulfate of concentrations 500, 1000, 1500, 2000, 3000 and 4000  $\text{mg FeCl}_3/\text{dm}^3$  and  $\text{Al}_2(\text{SO}_4)_3$  were prepared. pH of the solutions was controlled by adding HCl or NaOH. After the desired amount of ferric chloride and aluminum sulfate was added to the suspension, the beakers were agitated at various mixing times and speed, which consist of rapid mixing (200 rpm) for 2–3 min and slow mixing (25 rpm) for 1 h for coagulation. After the agitation, the suspension was allowed to settle for 20 min. Finally, a sample was withdrawn using a pipette from the top inch of supernatant after settling of wastewater for COD measurements. The tests were performed at 20–23°C [22]. The optimum coagulant dosage was determined by measuring COD.

The COD tests were performed by a closed reflux method [23]. The removal efficiencies were calculated from [22]:

$$\text{Removal} = \frac{C_0 - C}{C_0} \times 100\%$$

Where,  $C_0$  and  $C$  denote COD of wastewater before and after coagulation treatment, respectively. The pH was measured using a pH meter (Hach pH meter).

## 4. RESULTS AND DISCUSSION

### 4.1. FENTON'S OXIDATION PROCESS

Experiments related to the Fenton's oxidation process were carried out on PPW by varying the operating parameters ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations, operation time). The optimum values were determined according to the maximum COD removal efficiency. The effect of  $\text{Fe}^{2+}$  concentration on COD removal efficiency is illustrated in Fig.1. The



concentration of  $\text{Fe}^{2+}$  was varied from 27.6 to 64.5  $\text{mg}/\text{dm}^3$  at a constant  $\text{H}_2\text{O}_2$  dosage of 30  $\text{mg}/\text{dm}^3$  and 60 min of reaction time. At the  $\text{Fe}^{2+}$  dosage of 27.6  $\text{mg}/\text{dm}^3$  and 36.86  $\text{mg}/\text{dm}^3$ , the COD removal efficiency was 22% and 20%, respectively. A negative effect on the COD removal efficiency was seen in the case of increasing  $\text{Fe}^{2+}$  concentration from 27.6 to 64.5  $\text{mg}/\text{dm}^3$ . 27.6  $\text{mg}/\text{dm}^3$  was an optimum concentration of iron in the Fenton's reaction in order to remove COD. The range of  $\text{Fe}^{2+}$  might be wider. The low concentration of  $\text{Fe}^{2+}$  could be chosen for this study. The optimum concentration can be explained by the scavenging effect of overdoses of  $\text{Fe}^{2+}$  on OH radicals. In higher dosages of  $\text{Fe}^{2+}$ , OH radicals may be scavenged by participating in reactions with  $\text{Fe}^{2+}$  and the COD removal could decrease [24]. Therefore, as the optimum COD removal (22%) occurs at doses of 27.6  $\text{mg}/\text{dm}^3$  and no increase in COD removal was obtained by increasing the iron concentration. The optimum  $\text{Fe}^{2+}$  concentration was found to be 27.6  $\text{mg}/\text{dm}^3$  which resulted in 22% of COD removal after approximately 1 hour reaction time.

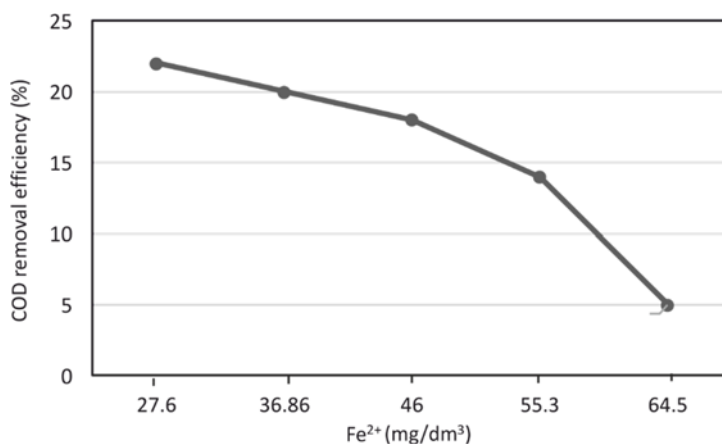


Fig. 1. Effect of  $\text{Fe}^{2+}$  concentration on COD removal efficiency at pH 3, 30  $\text{mg}/\text{dm}^3$  of  $\text{H}_2\text{O}_2$  and 60 min process time

In the study by Alver et al. [9] recalcitrant total phenol (TPH) and organic matter removal were investigated at an olive mill wastewater in sequential coagulation and Fenton's system. This study focused on various operational parameters such as pH,  $\text{H}_2\text{O}_2$ , and  $\text{Fe}^{2+}$  dosages and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratios. The optimum conditions were determined at pH 3,  $\text{Fe}^{2+}$  concentration 2.5  $\text{g}/\text{dm}^3$ , and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio 2.5. In the present study, the optimum concentration of  $\text{Fe}^{2+}$  0.0276  $\text{g}/\text{dm}^3$  was lower than that in the study by Alver et al., [9] but the COD removal efficiency was also lower than that in the study. The difference can be attributed to different types of the wastewater .

Bianco et al. [10] applied chemical Fenton's oxidation in various industrial wastewater treatments. The authors determined COD % removal for various initial conditions, with  $R^2 = 0.85$  and they observed that optimal quantities of Fenton's reagents

depend on the initial COD of the treated wastewater. The maximum COD elimination yield was found to be 80%. The initial COD concentration, COD/H<sub>2</sub>O<sub>2</sub> ratio and H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> ratio were selected in the optimization study.

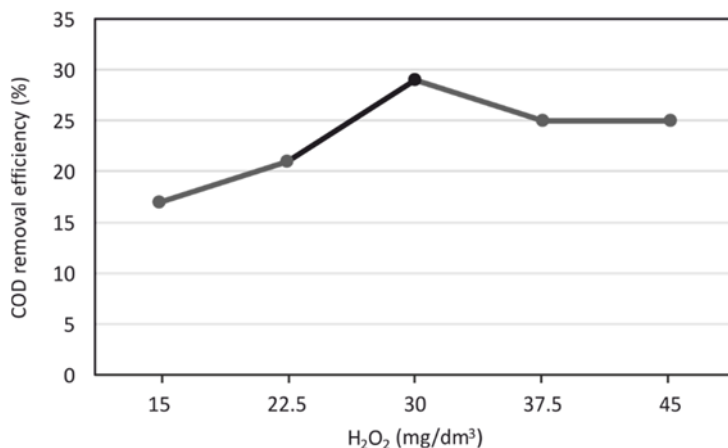


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> concentration on COD removal efficiency at pH 3, 27.6 mg/dm<sup>3</sup> of Fe<sup>2+</sup> and 60 min process time

In order to determine the optimum H<sub>2</sub>O<sub>2</sub> concentration, the H<sub>2</sub>O<sub>2</sub> doses were varied from 15 to 45 mg/dm<sup>3</sup>. Experiments were conducted with constant 60 min reaction time and the Fe<sup>2+</sup> dosage of 27.6 mg/dm<sup>3</sup>. COD removal efficiencies are presented in Fig. 2. They increased from 21% to 29% as H<sub>2</sub>O<sub>2</sub> concentration increased from 22.5 to 30 mg/dm<sup>3</sup>. An increase in the concentration of H<sub>2</sub>O<sub>2</sub> up to 37.5 mg/dm<sup>3</sup> did not affect the removal of COD and there was a little decrease between the dosages of 30 and 37.5 mg/dm<sup>3</sup>.

H<sub>2</sub>O<sub>2</sub> acts as a scavenger of the OH<sup>•</sup> radicals to produce the perhydroxyl radical (HO<sup>•</sup>) in the case of excessive amounts of H<sub>2</sub>O<sub>2</sub>. Increasing of H<sub>2</sub>O<sub>2</sub> concentration from 30 to 37.5 mg/dm<sup>3</sup> resulted in a decrease in COD removal efficiency from 29 to 25%. Therefore, the H<sub>2</sub>O<sub>2</sub> dosage of 30 mg/dm<sup>3</sup> was chosen as the optimum dosage. Arslan-Alaton et al. [25] used Fenton's-like advanced oxidation for the COD removal of penicillin wastewater. They determined the optimum H<sub>2</sub>O<sub>2</sub> amount for the COD removal of penicillin wastewater as 25 mM. The high amount of H<sub>2</sub>O<sub>2</sub> needed can be explained by the fact that they did not use any pretreatment processes before the Fenton's process [25].

In order to find the reaction time required to reach a steady state, experiments were performed for the 60–120 min period. Fenton's reagent was used at the following operating parameters: pH 3, H<sub>2</sub>O<sub>2</sub> concentration 30 mg/dm<sup>3</sup>, Fe<sup>2+</sup> concentration 27.6 mg/dm<sup>3</sup>. The COD of the wastewater was monitored continuously during the course of the reaction. COD removal efficiency increased with increasing reaction time as illustrated in Fig. 3, after about 75 minutes, the rate of COD removal became stable.

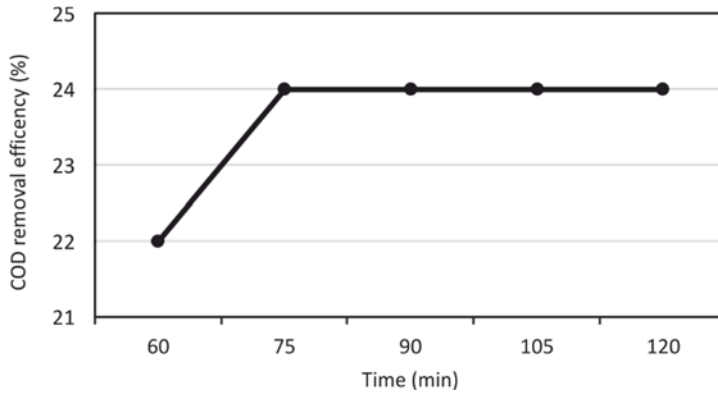


Fig. 3. Effect of reaction time on COD removal efficiency at pH 3, 30 mg/dm<sup>3</sup> mg of H<sub>2</sub>O<sub>2</sub> and 27.6 mg/dm<sup>3</sup> of Fe<sup>2+</sup>

The experiments were conducted for 10–30 min sonication. Fenton's reagent was used for the following operating parameters: pH 3, H<sub>2</sub>O<sub>2</sub> concentration 30 mg/dm<sup>3</sup>, Fe<sup>2+</sup> concentration 27.6 mg/dm<sup>3</sup> and sonication for 20 min gave the maximum COD removal efficiency of 45% (Fig. 4). The results showed that COD removal efficiency first increased then decreased since Fe<sup>2+</sup> is a known radical scavenger, which could react with hydroxyl radicals.

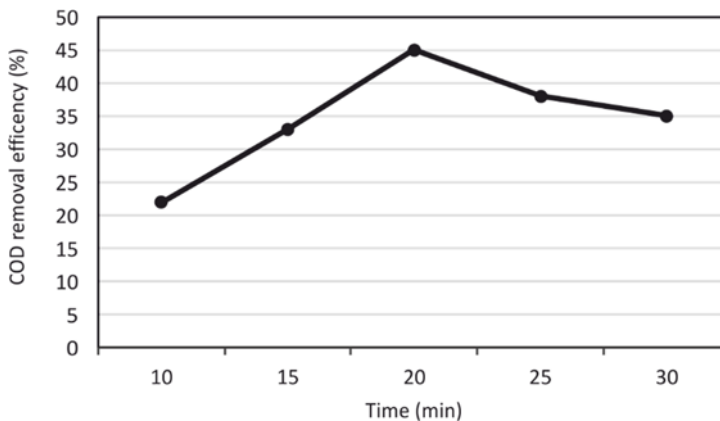


Fig. 4. COD removal efficiency for combined ultrasound with Fenton's oxidation at pH of 3, 30 mg/dm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> and 27.6 mg/dm<sup>3</sup> of Fe<sup>2+</sup>

#### 4.2. TREATMENT USING COAGULATION

To evaluate of coagulant dosage effect on COD removal of PPW, six different coagulant doses were used. The results are presented in Fig. 5 which showed the effects

of coagulant dosage on COD level and the percentage of COD level reduction by using ferric chloride and aluminum sulfate.

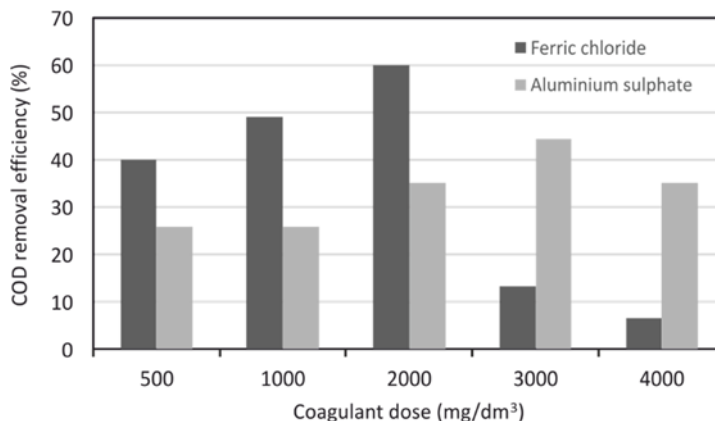


Fig. 5. Effect of coagulant dose on COD removal efficiency

The highest efficiency of COD removal of such wastewater was achieved using 2000 mg  $\text{FeCl}_3/\text{dm}^3$  (60%) and 3000 mg  $\text{Al}_2(\text{SO}_4)_3/\text{dm}^3$  (45%). The results showed that ferric chloride and aluminum sulfate had successfully flocculated the suspended particles and reduce the levels of COD in the PPW.

## 5. CONCLUSION

The focus of this paper was to investigate the potential use of Fenton's, ultrasound with Fenton's processes and coagulation for the treatment of pistachio processing wastewater. Due to the extra generation of oxidizing agents in ultrasound with Fenton's process, its efficiency was higher with respect to Fenton's process. The results showed that ferric chloride and aluminum sulfate successfully flocculated anionic suspended particles and reduced the levels of COD in the PPW. The optimal conditions for the Fenton's process were determined. 45% COD removal was obtained from the combined system. The coagulation process showed under selected conditions 60% and 45% COD removal for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , respectively. Finally, it became clear that the combined processes ultrasound and Fenton's process demonstrate higher efficiency in COD removal than the Fenton's process, besides, the coagulation process using  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  presents high COD removal efficiencies.

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