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Advanced treatment of industrial wastewater from pistachio processing by Fenton process

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ABSTRACT

This work investigated the efficiency of Fenton oxidation with respect to the removal of chemical oxygen demand (COD), total organic carbon (TOC), and phenol in the treatment of heavily loaded pistachio processing industrial wastewater (PPIW). The study was implemented at lab scale and examined the impact of a range of key process parameters on overall performance including the initial Fe^{2+} concentration, the hydrogen peroxide (H_2O_2) concentration, the PPIW pH, and the reaction time. The results revealed that the optimum conditions for Fenton oxidation on PPIW were 1.32 g L^{-1} Fe^{2+}, 19.2 g L^{-1} H_2O_2, pH = 3, and reaction time of 30 min. Given the optimal conditions, the removal efficiency of TOC, COD and phenol was 52.9%, 76.8%, and 85.3%, respectively. After optimization of the key process parameters, the Fenton process can be efficient in treating PPIW. This study confirms the hypothesis that Fenton oxidation can generally be effective in the treatment of wastewaters with high organic concentration either per se or as a pretreatment step within a larger conventional treatment scheme.

Keywords: Pistachio processing industry wastewater; Fenton oxidation; Fe^{2+} concentration; H_2O_2 concentration; pH; Reaction time

1. Introduction

Pistachios are a rich source of healthy fatty acids, metals, phytosterols, phenolic, and other compounds. Hence, their consumption has significantly increased over the past decades [1,2]. The pistachio nut tree is a native species of the Mediterranean and Middle East countries. Its cultivation, though, has now expanded around the world; pistachio is produced from Australia to the USA. Precisely, the global pistachio production rose from 348 metric kilotons (kt) in 1994 to 856 kt in 2014. In terms of annual national production, Iran comes first with the USA and Turkey ranking second and third, respectively [2–4]. Pistachio industry is growing rapidly in Turkey. In 2015 alone, the estimated pistachio

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production yield in the country was about 144,000 t. With approximately 6 m^3 of wastewater produced per ton of processed pistachio, this industrial sector is considered to be an important producer of wastewater [5,6].

Pistachio contains 5.6% of water, 19.6% of protein, 53.2% of fat, 19% of carbohydrate, and 2.6% of ash. The pistachio processing industrial wastewater (PPIW) is characterized by high chemical oxygen demand (COD), total organic carbon (TOC), and phenol concentrations. The biodegradation of the produced wastewater is therefore difficult. Moreover, phenol can inhibit the biological processes [5,6]. Treating wastewater with persistent organic pollutants is a challenging task that often requires more than the application of conventional biological wastewater treatment technologies. Alternative treatment technologies have been suggested. For instance, chemical coagulation has been implemented. Nevertheless, it can be costly due to the use of chemicals and the production of large amounts of sludge that need to be disposed. Alternatively, electrocoagulation can be an option for treatment, but its major weaknesses are the high operational and equipment costs [7–9]. Electrochemical advanced oxidation processes (AOPs) have been suggested as a promising treatment option that can provide the high level of oxidation needed for wastewater characterized by recalcitrant organic compounds [9,10]. AOPs can also degrade phenolic substances that are likely to have an inhibitory effect on bacteria. Despite having been criticized for potentially high investment and energy costs, they have been reported to achieve high organic matter removal for a wide range of resistant organic effluents including pharmaceuticals, pesticides, azo dyes, and carboxylic dyes [9,11]. The AOP treatment processes have a low-carbon footprint because they can be applied at ambient temperature and pressure with limited land requirements, with no need for auxiliary chemicals, without production of secondary waste streams, with the possibility to act as pre/posttreatment step before/after conventional wastewater treatment, and with the potential of fully automated operation [9].

Fenton oxidation is among the most commonly implemented AOP processes. It involves the reaction of hydrogen peroxide (H_2O_2) with iron (Fe) ions to form hydroxyl radicals ($OH^\bullet$) that can oxidize organic or inorganic compounds. The $OH^\bullet$ production requires low pH and reducing conditions. In such environments, Fe ions can be found in soluble form. When H_2O_2 is added to an aqueous solution containing Fe^{2+} and organic matter within the pH range of 2–5 (i.e., under acidic conditions), the series of Fenton redox reactions will occur; Fe^{2+} will be formed again at the end of this catalytic cycle. For as long as H_2O_2 is present in the system, a continuous recycle between Fe^{2+} and Fe^{3+} will take place. The produced $OH^\bullet$ will react with the organic matter and mineralize it into carbon dioxide (CO_2) and water (H_2O) as end products. From an overall perspective, the Fenton process consists of four steps: pH adjustment, oxidation, neutralization, and precipitation through coagulation. It can be described by the following set of reactions [12–14]:

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

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

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

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

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

The Fenton process has been successfully applied for the removal of organic substances [15], for toxicity reduction [16], as a preliminary treatment step before biological treatment [17], as well as in color removal [18]. For instance, dye was removed by 75.8% from textile wastewater by applying the Fenton oxidation process [19]. Similarly, 75% of COD removal was achieved from olive mill wastewater after the Fenton implementation [20]. Moreover, TOC removal of 73.8% was noted by applying the Fenton process for coking wastewater [21]. Vergili and Gencdal [22] noted that Fenton oxidation caused 84% COD removal from pharmaceutical industrial wastewater. To the best of our knowledge though, the effectiveness of the Fenton process has been scarcely studied for PPIW effluents. For example, Bayar et al. [5] investigated PPIW treatment, but by means of electrocoagulation with aluminum electrodes; COD, TOC, and phenol removal of 60.1%, 50.2%, and 77.3%, respectively, were attained. In a similar work, PPIW was treated by applying graphite electrode electro-oxidation; COD, TOC, and phenol were removed by 99.79%, 76.55%, and 100%, respectively [6].

The objectives of this study were (i) to examine the efficiency of Fenton oxidation for the lab-scale treatment of wastewater resulting from the processing of red peppered pistachio nuts within a facility in Gaziantep (Turkey) and (ii) to define the optimal operating conditions by examining the impact of key process parameters (i.e., Fe^{2+} concentration, H_2O_2 concentration, pH, and reaction time).

2. Materials and methods

2.1. Wastewater properties

Wastewater originated from a pistachio processing industrial facility with an average daily capacity of 24 t in Gaziantep (Turkey). The wastewater from the plant is directly discharged into the local sewerage system without applying any physical, biological, or chemical treatment. The PPIW used for the purposes of this study was obtained by taking samples from various positions in the Gaziantep facility where wastewater is produced and by mixing each of them to ensure their homogeneity. Then, samples were brought to the lab in containers with the aid of a cooling circulator and stored at 4°C. After being allowed to reach room temperature, the wastewater samples were analyzed and characterized (Table 1).

2.2. Fenton experiments

Fenton experiments were conducted in a 6-digit Phipps & Bird jar mark test system (Fig. 1). 500 mL of wastewater were used in each experiment. 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 $FeSO_4{\cdot}7H_2O$) and H_2O_2 were added (specific quantities depended on the phase of the

Table 1
Characteristics of the PPIW used in this study

Parameter	Value
Conductivity, µs cm^{-1}	4,750–5,750
Turbidity, NTU	150–250
pH	5.2
COD, mg L^{-1}	15,000–18,000
TOC, mg L^{-1}	5,000–5,500
Phenol, mg L^{-1}	3,800–4,500
Oil-grease, mg L^{-1}	50–59
Cl$^-$, mg L^{-1}	600–650

experiments; optimal process performance was achieved for $Fe^{2+} = 1.32$ g L^{-1} and $H_2O_2 = 19.2$ g L^{-1} as will be detailed in section 3).

- The jar test unit was, first, subjected to a 3-min rapid mixing (160 rpm) and, then, to a 57-min slow stirring (50 rpm).
- Wastewater pH was adjusted by using 1 M NaOH in 1 L beakers at the end of the 60 min test period.
- After the 60 min sedimentation stage, clear phase samples were taken and filtered through a 0.45-µm membrane. COD, TOC, and phenol were then measured.
- The possibility of the residual H_2O_2 positively intervening in the COD measurements was considered in the H_2O_2 analysis.

2.3. Analytical methods

COD, TOC, and phenol measurements were performed according to standard methods [23]. The COD analysis was performed according to the closed system method (reflux) defined in the standard methods. TOC analysis was performed using a T-T-A 9000 TOC-TN analyzer. Phenol was determined by using the Folin–Ciocalteu spectrophotometric method, and H_2O_2 was analyzed via the I_3^- method [24]. The latter enabled the detection of the potential positive H_2O_2 intervention in the COD analysis, thus allowing the determination of the quantities that interfered with the COD. The pH values of the samples were measured with a WTW pH 330i pH meter device.

3. Results and discussion

3.1. The effect of the initial Fe^{2+} concentration

The rate of Eq. (1) given in section 1 is important to determine the efficiency and cost of the Fenton process [25]. The effect of different initial Fe^{2+} concentrations on the treatment performance was investigated at the influent PPIW pH (i.e., 5.2; Table 1).

Fe^{2+} functions as a catalyst during the Fenton oxidation process. Six different Fe^{2+} concentrations (i.e., 0.26, 0.52, 0.78, 1.04, 1.32, and 1.56 g L^{-1}) were tested by applying the theoretically calculated 19.2 g L^{-1} H_2O_2 initial concentration. Fig. 2 shows the effect of the different Fe^{2+} concentrations on the COD, TOC, and phenol removal efficiency.

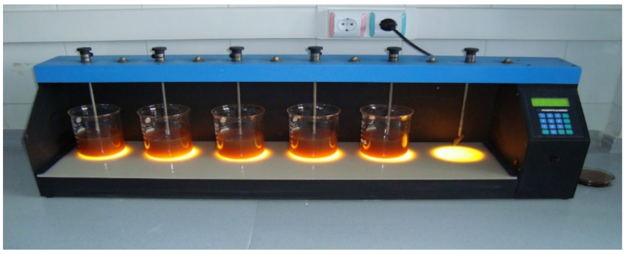

Fig. 1. Schematic view of the experimental system for the lab-scale Fenton oxidation treatment of PPIW.

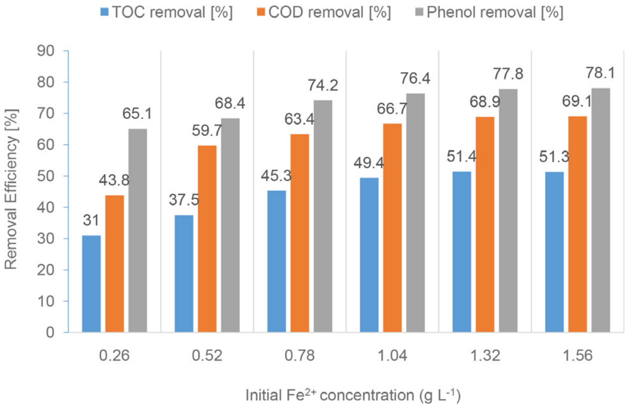

Fig. 2. Effect of different initial Fe^{2+} concentrations on the TOC, COD, and phenol removal (19.2 g L^{-1} H_2O_2, initial PPIW pH = 5.2, and reaction time = 60 min).

The iron sulfate ($FeSO_4$) and H_2O_2 reagents are of acidic character and are expected to affect the working pH. It was observed that the pH value decreased with the $FeSO_4$ addition to the system in all cases (Table 2). If the pH does not decrease, it can be hypothesized that the H_2O_2 reaction was inhibited.

Fig. 2 shows that increasing the initial Fe^{2+} concentration up to 1.32 g L^{-1} positively affects the removal (TOC, COD, and phenol), while the Fe^{2+} addition effect was less important for concentrations above 1.32 g L^{-1}. The pollutant removal for Fe^{2+} concentrations of 0.26, 0.52, and 0.78 g 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 phenol, respectively. Before the Fe^{2+} addition, there was no fundamental factor to produce $OH^\bullet$. Thus, effective Fenton oxidation did not occur. When Fe^{2+} was added, the $OH^\bullet$ production started and was expected to increase with the Fe^{2+} concentration increase. Fe^{2+} concentration equal to 1.32 g L^{-1} provided high removal for all parameters; 51.4% for TOC, 68.9% for COD, and 77.8% for phenol. Further addition of Fe^{2+} (1.56 g L^{-1}) did not significantly improve the organic matter removal process (Fig. 2). Dosing over a certain Fe^{2+} quantity (i.e., 1.32 g L^{-1} for this study) can gradually start affecting the oxidation capacity in a negative way. Higher Fe^{2+} concentrations will lead to the $OH^\bullet$ consumption in the medium according to Eq. (2), thus reducing the removal efficiency [26]. Furthermore, excessive Fe^{2+} in the medium allows for Fe^{2+} to be oxidized into Fe^{3+}, resulting in the conversion of H_2O_2 to water (Eq. (6)) [27]:

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

Table 2
The effect of different initial Fe^{2+} concentrations on the wastewater pH

Initial Fe^{2+} concentration (g L^{-1})	Initial pH	Final pH
0.26	5.2	4.43
0.52	5.2	3.98
0.78	5.2	3.48
1.04	5.2	3.05
1.32	5.2	2.87
1.56	5.2	2.51

Sharma et al. [28] attempted the optimization of the Fenton process for simulated textile wastewater. They posit that COD removal increased from 50.5% to 71% as the Fe^{2+} concentration rose from 450 to 600 mg L^{-1}. Under a slightly higher Fe^{2+} concentration (i.e., 650 mg L^{-1}), COD removal decreased to 67.8%. The applied H_2O_2 dose was 5,538 mg L^{-1}. Similarly, the removal of residuals of organic pollutants present in cosmetic wastewater using the Fenton technology was enhanced by increasing the Fe^{2+} concentration from 0.25 to 0.75 g L^{-1} under a H_2O_2 dose of 1 mL L^{-1}; COD removal improved remarkably from 55% to 95.5%. The further addition of Fe^{2+} to 1.25 g L^{-1} had a negative effect on COD removal, causing it to drop to 85% [29]. While optimizing the Fenton process, different initial Fe^{2+} concentrations are tested. The Fe^{2+} concentration can be minimized to the one that ensures satisfying organic matter removal without unreasonable process costs associated with potentially excessive Fe^{2+} use. The optimum Fe^{2+} concentration was found to be equal to 1.32 g L^{-1} in this study.

3.2. The effect of the initial H_2O_2 concentration

H_2O_2 concentration is among the most significant parameters in the Fenton process since it functions as an $OH^•$ production source. H_2O_2 consumption during the Fenton reactions is the most important factor limiting the efficiency of the process. Any unused H_2O_2 amount will interfere in the COD analysis; therefore, excessive H_2O_2 amount is not desired [30]. The effect of different initial H_2O_2 concentrations, which are lower, equal, and higher than the theoretically calculated one of 19.2 g L^{-1} (i.e., 3.2, 6.4, 9.6, 12.8, 16, 19.2, and 22.4 g L^{-1}) was investigated by maintaining the optimum initial Fe^{2+} concentration of 1.32 g L^{-1} as detailed in section 3.1. The experiments were carried out at the influent PPIW pH (i.e., 5.2).

Fig. 3 shows the effect of applying different initial H_2O_2 concentrations on the COD, TOC, and phenol removal during Fenton oxidation. COD, TOC, and phenol removal generally increased with the H_2O_2 concentration increase. However, it was observed that the removal yield was not significantly affected when the H_2O_2 concentration increased above 19.2 g L^{-1}. Theoretically, H_2O_2 is the production source of $OH^•$, and as the H_2O_2 concentration increases, more $OH^•$ radicals will be produced. H_2O_2 at higher concentrations acts as a radical scavenger in accordance with Eqs. (7)–(9). It reacts with the $OH^•$ radicals in the medium to form $HO_2^•$. $HO_2^•$ has lower oxidation capacity; thus, $OH^•$ radicals are consumed, and the overall removal efficiency is reduced [26].

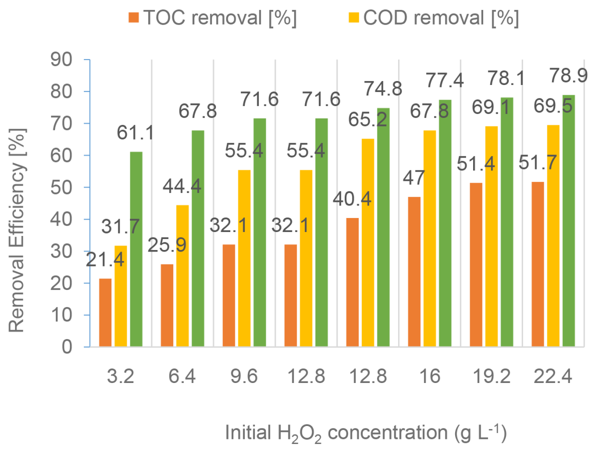

Fig. 3. The effect of different initial H_2O_2 concentrations on the TOC, COD, and P removal (1.32 g L^{-1} Fe^{2+}, initial PPIW pH = 5.2, and reaction time = 60 min).

$$OH^• + H_2O_2 \rightarrow H_2O + HO_2^• \tag{7}$$

$$OH^• + HO_2^• \rightarrow H_2O + O_2 \tag{8}$$

$$OH^• + H_2O_2 \rightarrow HO_2^• + H^+ \tag{9}$$

The determination of the optimum value for the initial H_2O_2 concentration is essential to achieve high treatment efficiency, without using excessive amounts of chemicals. In this concept, the optimum H_2O_2 concentration was 19.2 g L^{-1} for the Fenton process implemented in this study; precisely, the COD, TOC, and phenol removal obtained at this concentration were 69.5%, 51.7%, and 78.4%, respectively. Similar trends have been reported in previous works. For instance, raising the initial H_2O_2 concentration from 0 to 3 g L^{-1} increased the COD removal from 50% to 99%, when treating cosmetic industry wastewater. A further increase of H_2O_2 to 5 g L^{-1} aggravated the system's performance since COD removal decreased to 80% [29]. In the work of Sharma et al. [28], COD removal increased from 50% up to 62% with the H_2O_2 concentration increase from 4.4 to 6.6 g L^{-1} for the treatment of synthetic textile wastewater. Providing a higher H_2O_2 concentration equal to 8.8 g L^{-1} resulted in decreasing the COD removal to 56.9%.

3.3. The effect of the initial PPIW pH

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 $OH^•$. Most of the studies performed by applying the Fenton process have shown that the optimal removal, regardless of the target pollutant, can be obtained in a pH range of 2–5 (mostly at pH = 3). Higher pH values are not recommended due to precipitation of Fe^{2+} [31]. Five different pH values lower, equal, and higher than the natural influent PPIW pH of 5.2 (i.e., 2, 3, 4, 5.2, and 6) were tested to examine the pH effect on the system's performance. The COD, TOC, and phenol removal for different PPIW initial pH values after the Fenton process implementation are shown in Fig. 4.

The highest pollutant removal was obtained for a PPIW initial pH value of 3; 79.9% for COD, 54% for TOC, and 88.7% for phenol (Fig. 5). At higher pH values, H_2O_2 forms oxygen and water, thus losing part of its oxidation activity. Furthermore, the oxidation of Fe^{2+} into Fe^{3+} means that it loses its catalytic potential. At pH < 3, the $OH^{\bullet}$ production decreases and H^+ cations act like an $OH^{\bullet}$ radical scavenger (Eq. (10)) [32]. Therefore, the removal of organics is expected to decrease at very low pH values (e.g., <3) [33].

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \tag{10}$$

Moreover, as seen in Table 1 the PPIW used in this study contains a 600–650 mg L^{-1} of chloride ions (Cl^-). At pH < 3 and under the Cl^- presence, iron chloride ($FeCl_2$) is formed (Eq. (12)) which competes with the $Fe(OH)^{2+}$. Thus, the rate of $OH^{\bullet}$ production (Eq. (1)) decreases. Under such conditions, Cl^- acts as a strong free $OH^{\bullet}$ radical scavenger (Eq. (11)) [34–37]. As seen in Fig. 4, the decrease of the pH from 3 to 2 results in lower removal of TOC, COD, and phenol.

$$Cl^- + OH^{\bullet} \rightarrow ClOH^{\bullet -} \tag{11}$$

$$ClOH^{\bullet -} + Fe^{2+} \rightarrow Cl^- + OH^- + Fe^{3+} \tag{12}$$

The experimental results shown in Fig. 4 show that the initial PPIW pH = 3 can be considered as the optimal pH for the purposes of this work. Similar trends have been observed in the past. For instance, Torrades et al. [38] achieved the highest COD removal (around 80%) from an effluent originating from the pulp and paper industry at an initial pH of 2.75; COD removal was significantly lower both at lower and higher pH values (i.e., 52% for pH = 2 and 51% for pH = 4). Meriç et al. [39] tested various pH values from 2.5 to 4, while applying the Fenton oxidation process for the treatment of wastewater containing reactive black 5. COD removal was only 44% at pH = 2.5, significantly improved at pH = 3.5 (87%) and, finally, slightly reduced at 84% for a pH equal to 4.

3.4. The effect of the reaction time

The reaction time can vary depending on the nature of the pollutant and the type of organic matter contained in wastewater. Under optimum conditions determined as described in sections 3.1–3.3 (i.e., Fe^{2+}: 1.32 g L^{-1}, H_2O_2: 19.2 g L^{-1}, and initial PPIW pH = 3), changes in COD, TOC, and phenol removal were investigated over time by collecting samples at 15, 30, 60, and 90 min. The results are presented in Fig. 5. The removal efficiency of all the tested parameters continuously increased over time with the maximum removal efficiency being reached after 90 min; 53.9% for TOC, 80.1% for COD, and 89% for phenol. After 30 min of reaction time, no significant changes were observed in the removal efficiency of the system. According to the experimental results, 99% of the H_2O_2 added had already been consumed after 30 min of operation.

The absence of H_2O_2 (which reacts with the Fe^{2+}) combined with the inhibition by the produced $OH^{\bullet}$ (which oxidize the organic substances) can possibly explain why the removal efficiency did not change significantly beyond 30 min. Hence, 30 min can be considered as the optimal reaction time with respect to the conditions under investigation. The results are comparable with the available literature. The Fenton process duration of 30 min was enough to attain almost 90% of COD removal from wheat straw black liquor; COD removal was practically stable after 60 or 90 min of operation (91% and 92%, respectively) [38]. Finally, COD removal of organic compounds from cosmetic industry wastewater was similar for 30, 40, and 50 min of operation; 94%, 95%, and 97%, respectively [29].

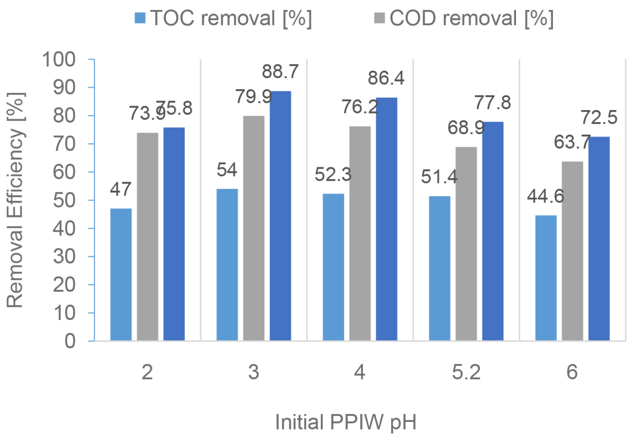

Fig. 4. The effect of different PPIW initial pH on TOC, COD, and phenol removal (1.32 g L^{-1} Fe^{2+}, 19.2 g L^{-1} H_2O_2, and reaction time = 60 min).

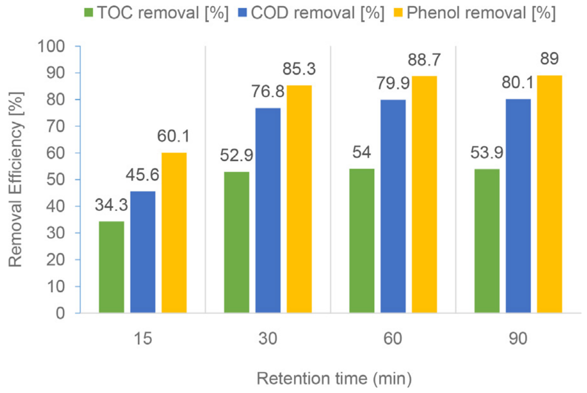

Fig. 5. The effect of the reaction time on the TOC, COD, and phenol removal (1.32 g L^{-1} Fe^{2+}, 19.2 g L^{-1} H_2O_2, and initial PPIW pH = 3).

4. Conclusions

- Fenton oxidation is an effective process in terms of COD, TOC, and phenol removal from wastewater originating from the processing of red peppered pistachio nuts.
- Optimum conditions in the study were determined as follows: 1.32 g L^{-1} Fe^{2+}, 19.2 g L^{-1} H_2O_2, pH = 3, and 30 min of reaction time. Under the combination of these conditions, COD, TOC, and phenol removal was 79.9%, 54%, and 88.7%, respectively.
- Fenton oxidation can be integrated into biological treatment units as a pre/posttreatment step for wastewaters

having high organic content, thus contributing to the improvement of the overall performance of such treatment schemes.

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