

Optimization of Combined Ozone/Fenton Process on Olive Mill Wastewater Treatment

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Abstract

The aim of this study was to investigate the applicability of Fenton process and combined ozone/Fenton process to remove color, soluble chemical oxygen demand (COD_s), phenol, and dissolved organic carbon (DOC) from real olive mill wastewater (OMW). The treatability of OMW was investigated in three different study parts. Initially, Fenton process was optimized under varying H₂O₂/Fe²⁺ molar ratios ranging between 10 and 20 at the constant H₂O₂ concentration of 0.5 mM. The H₂O₂/Fe²⁺ molar ratio of 10 was found optimum providing high color (51.6 %), COD_s (58%), DOC (27.9%) and phenol removals (93.9%). Further, combined ozone/Fenton process was applied under gradually increasing dosages of Fe²⁺ and H₂O₂ reagents at constant H₂O₂/Fe²⁺ molar ratio of 10. The high color removal efficiency (51.6% color removal for Pt-Co) was obtained at the H₂O₂ and Fe²⁺ molar ratio of 0.5/0.05. Additionally, COD_s, color, DOC and phenol removal efficiencies improved at increasing reagents concentrations. However, the color removal efficiency was adversely affected while no significant difference on COD_s and phenol removal was observed at higher concentrations of molar concentrations above 0.5/0.05. Additionally, the results indicated that combined process enhanced treatment performance of OMW by 21%, 49% and 22% in terms of color, DOC and COD_s removals, respectively, compared to only-Fenton process. In the rest of this study, combined ozone/Fenton process was optimized under varying ozonation time (60-120 min) at the optimum H₂O₂ and Fe²⁺ molar dosage of 0.5/0.05 obtained from previous parts. Ozonation time significantly affected the treatment performance, and optimum the reaction time was determined as 90 minute in terms of the high treatment productivity and low operating cost resulted from minimum ozone consumption and short reaction time.

Keywords

COD removal, Color removal, Ozone/Fenton process, Olive mill wastewater, Phenol removal

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1. INTRODUCTION

Olive oil production is one of the most important income sources for the economy of countries in the Mediterranean region and over 450.000 million-tons olive oil are produced per year [1]. Additionally, high volume fresh water with 40-120 L for per tones is consumed in olive oil production and this industry produces approximately 3.0×10^7 m³ wastewater per year [1-3]. The olive mill wastewater (OMW) is characterized by high concentrations of chemical oxygen demand (COD), biological oxygen demand (BOD), color, suspended solid (SS) and phenolic substances [4]. The discharge without treatment of this hazardous wastewater containing highly toxic phenolic compounds into environment causes adverse and dangerous effects on all living species [4, 5]. Therefore, many researchers performed the conventional treatment techniques as adsorption [6] coagulation-flocculation [7], filtration [8] and biological processes [9] for treatment of OMW. However, these treatment techniques need advanced oxidation processes (AOPs) as pre or post-treatment methods due to various disadvantage of these methods such as high membrane cost of filtration process [10], high sludge production of coagulation-flocculation [11], low color removal efficiency of biological treatment [12] and inability to meet the discharge standards [13]. Therefore, the advanced treatment technologies such as hydrogen peroxide (H₂O₂), Fenton (Fe²⁺/H₂O₂), Fenton-like (Fe³⁺/H₂O₂), ozone (O₃), UV and ultrasound has been widely applied in treatment of OMW. However recently, ozone and Fenton process are commonly used as the pre-treatment [14, 15] or post-treatment [16] to remove organic matter and color from various industrial wastewaters. Although Fenton oxidation and ozonation in wastewater treatment are effective, these processes alone are insufficient to treat OMW [17]. Therefore, combined ozone/Fenton as a new treatment process (O₃/H₂O₂/Fe²⁺) has been introduced and this process was firstly applied to stabilized solid-waste leachate. This new process offers advantages such as reduction of reaction time and increment of oxidation potential and some researchers have reported that combined ozone/Fenton process is effective in treatment of various wastewaters such as treated stabilized leachate [14], simulated amoxicillin wastewater [16], phenolic wastewater [17]. However, there are few studies [18] on treatment of olive mill wastewaters with combined ozone/Fenton process in literature. Therefore, the main aim of this study was to evaluate the effectiveness of Fenton, ozone and combined ozone/Fenton processes to remove color and COD_s from real olive mill wastewater under different operational conditions. The system performance was evaluated in terms of organic matter, color, and phenol removals with total suspended solid parameter.

2. MATERIALS AND METHOD

2.1. Characteristics of Olive Mill Wastewater

Wastewater was taken from wastewater storage tank of the olive production factory located at Kahramanmaraş, Turkey. The characteristics of the raw OMW are illustrated in Table 1. The OMW were stored in a refrigerator at 4°C to avoid microbial growth before it is used in these studies.

In our previous studies, acid cracking as pre-treatment process for OMW treatment was optimized under the different operational conditions (various temperature, reaction time and pH levels). The condition where the pH of the untreated OMW was adjusted to 1.5 with concentrated HCl for 30 min was determined to be optimum in terms of the COD_s and color removals. In this way, around 10% COD_s, 37% DOC, 32% color (Pt-Co) and 18% phenol removals could be achieved (Table 1) [19]. Thus, the acid-cracked wastewater (33927 mg COD_s/L and 10120 mg DOC/L) was used through this study.

Table 1. Characteristics of olive mill wastewaters

PARAMETERS	UNIT	VALUES	
		Raw OMW	Acid cracked OMW
Soluble Chemical oxygen demand (COD _s)	(mg/L)	38000±650	33927±200
Dissolved organic carbon (DOC)	(mg/L)	16090±200	10120±
Phenol	(mg/L)	200±20	164±13
	Pt-Co	19750±300	13350±120
Color	436 nm (m ⁻¹)	575±25	366±36
	525 nm (m ⁻¹)	380±15	261±20
	620 nm (m ⁻¹)	250±15	139±12

2.2. Experimental Design

In this study, concentrated FeSO₄•7H₂O stock solution were used as the ferrous iron source. The all experiments were performed at room temperature and the treatability of real OMW was evaluated in three parts (Table 2).

In first part of lab-scale experiments, Fenton process was performed using a six-paddle programmable jar tester (VelpScientifica JLT6, Italy). Working volume of 500 mL and the mixing procedure including a rapid mix period for 5 min at 150 rpm followed by a slow-stir phase at 30 rpm for 25 min were used. In this part, the effect of various molar ratios of Fenton reagents (H₂O₂/Fe²⁺ : 10-20) was investigated at the constant H₂O₂ concentration of 0.5 M. Further, this system was connected to the ozone generator (Opal OG-400, Ankara, Turkey) and ozone gas was continuously given through a diffuser at the flow rate of 1.28 mg/min. Schematic

diagram of combined ozone/Fenton system is shown in Figure 1. The performance of the combined ozone/Fenton process was evaluated at the gradually increasing H_2O_2 and Fe^{2+} concentrations at ozonation time of 60 min and H_2O_2/Fe^{2+} molar ratio of 10 (part II). The last study part, the combined ozone/Fenton process was operated with increasing ozonation times from 60 to 120 min at the optimum H_2O_2/Fe^{2+} ratio of 10 and H_2O_2 and Fe^{2+} reagent dosages of 1/0.1 obtained from the first two parts of this study. The system performance was evaluated in terms of COD_s , DOC, color, phenol removal efficiencies.

Table 2. Operational conditions

PARTS	Reaction time (minute)	H_2O_2/Fe^{2+} molar ratio	H_2O_2 and Fe^{2+} concentrations (M:M)	Ozonation time (minute)
Part I	30	10	0.5/0.05	-
	30	12	0.5/0.041	-
	30	14	0.5/0.035	-
	30	16	0.5/0.0312	-
	30	18	0.5/0.027	-
	30	20	0.5/0.025	-
Part II	60	10	0.1/0.01	60
	60	10	0.25/0.025	60
	60	10	0.5/0.05	60
	60	10	0.75/0.075	60
	60	10	1/0.1	60
Part III	60	10	0.5/0.05	60
	90	10	0.5/0.05	90
	120	10	0.5/0.05	120

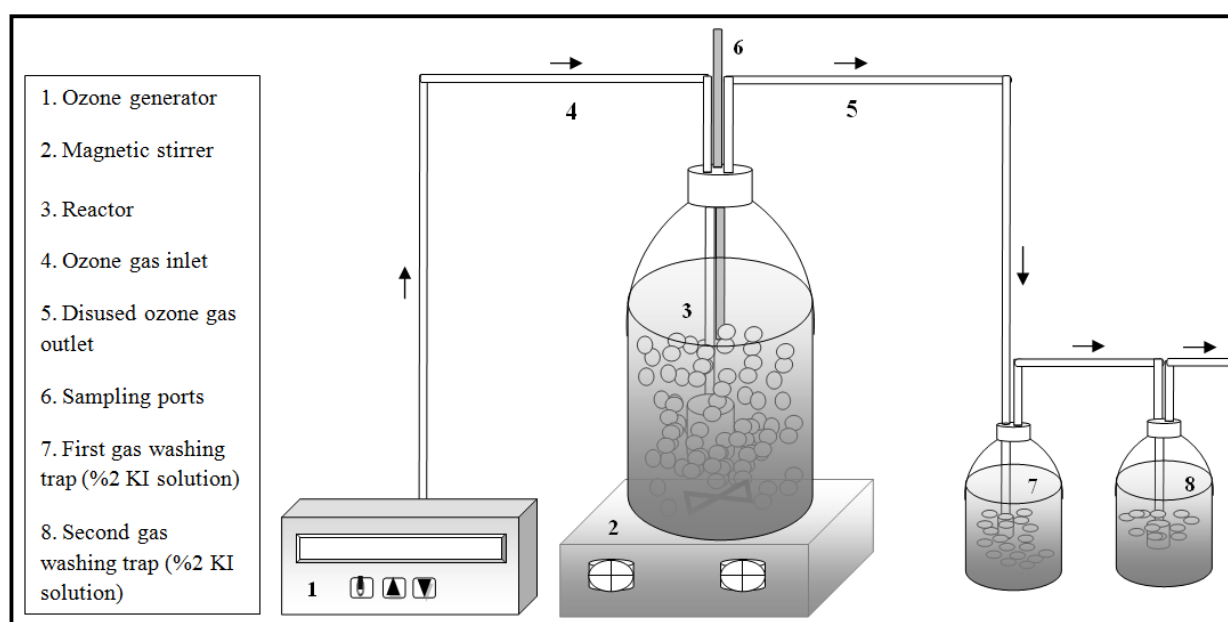


Figure 1. Schematic diagram of lab-scale combined ozone/Fenton process.

2.3. Analytical Methods

Samples centrifuged at 3000 rpm for 5 min with Eppendorf Centrifuge 514R (Hamburg, Germany) for DOC, COD_s, color and phenol measurements before samples were filtered with Sartorius NY 0.45µm filter (Sartorius AG, Gottingen, Germany). Color, COD and phenol measurements were carried out using HACH DR-5000 UV-VIS spectrophotometer (Cole Parmer Instrument, Loveland, CO., USA). COD values of samples were determined by the dichromate-closed reflux Colorimetric Method, according to Standard Methods approved by USEPA (Standard Methods, 5220 D.). Phenol measurement was carried out using colorimetric method (Standard Methods 5530 Phenol, 5530 B and D, Cleanup Method and Direct Photometric Method, 20th Edition, 1998). Color was measured in two different units as Pt-Co and number of chrominance (RES). Color as Pt-Co unit was spectrophotometrically measured at 465 nm by Hach Method No. 8025 method approved by USEPA. RES measurements were applied according to the standards of European Norm EN ISO 7887 at three different wavelengths, called 436 nm, 525 nm and 620 nm. These absorbance measurements were used to calculate the spectral adsorption coefficient (RES (λ) Eq. 1). A is the absorbance of the sample, d is the optical path length of the cell (mm) and f is the conversion factor between mm and m, which is 1000.

$$\text{RES}(\lambda) = (A/d) \times f \quad (1)$$

DOC analyses were performed in total organic carbon analyser (Shimadzu TOC-VCPN, Kyoto, Japan). pH was measured by a pH meter (Thermo, Orion 4 Star, Indonesia.). Disused ozone concentration in reactor was determined by titrating with 0.1 N Na₂S₂O₃ solution of ozone absorbed in 2% KI solution into gas washing bottles, according to Standard Methods 2350 E. Disused ozone was calculated as described by Sevimli et al [20].

3. RESULTS AND DISCUSSIONS

3.1. PART I: Effect of Different H₂O₂/Fe⁺² Molar Ratios on Fenton Process Performance

In this part of the study, Fenton process was alone applied under varying H₂O₂/Fe²⁺ molar ratios from 10 to 20 with decreasing Fe²⁺ reagent doses. The H₂O₂ concentration, initial pH level, and reaction time of Fenton process were kept constant at 0.5M, 1.5, 30 min, respectively. The performance of Fenton process in terms of the Pt-Co, RES₆₂₀, COD, phenol, RES₄₃₆, RES₆₂₅ and DOC parameters is presented in Fig. 2A, 2B, 2C, 2D, 2E, 2F and 2G, respectively.

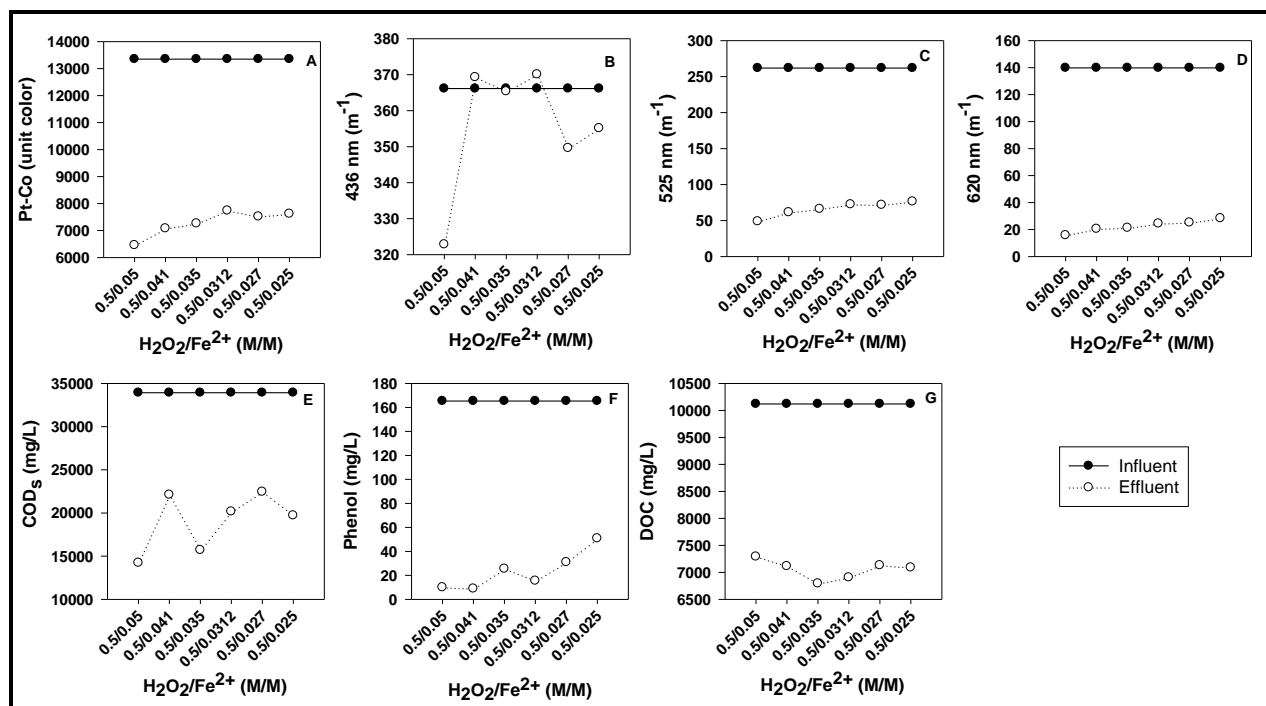


Figure 2: Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio on color removal as Pt-Co (A), $\text{Res}_{436\text{nm}}$ (B), $\text{Res}_{525\text{nm}}$ (C) and $\text{Res}_{620\text{nm}}$ (D), COD_s removal (E), Phenol removal (F), DOC removal (G).

Decreasing Fe^{2+} concentration caused a decline in color removal efficiency and color removal as Pt-Co decreased from 51.6% to 42.9% at Fe^{2+} reagent dose of 0.05 and 0.025, respectively (Fig. 2A). Similar results were also obtained with RES parameters and maximum color removal as RES_{436} , RES_{525} and RES_{620} was 11.8%, 81.3% and 88.7%, respectively, at the Fe^{2+} reagent dose of 0.05, corresponding to $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratios from 10. In the conventional Fenton process, the Fe^{2+} reacts with H_2O_2 and hydroxyl radicals that degrade organic matters form [21]. Additionally, the reaction of ozone with H_2O_2 generates hydroxyl radicals. However, H_2O_2 dissociates into the hydroperoxide ion, which rapidly reacts with ozone when H_2O_2 dissolved in water [14]. Thus, low treatment performance obtained in this study probably originated from formation of hydroxyl, which further increased ozone destruction. Similarly, Amr and Aziz [14] indicated that the removal efficiency of the contaminant parameters generally decreased with increasing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio.

The increasing molar ratio from 10 to 20 adversely affected COD removal performance of system and the COD removal efficiency decreased from 58% to 41.8%, respectively (Fig. 2E). Similarly, the maximum phenol and DOC removals were observed as 93.9%, 27.9% at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 10 respectively (Fig. 2F and 2G). These results indicated that low $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio was found favorable for OMW treatment in Fenton process and thus, the subsequent study parts were continued at this ratio.

3.2. PART II: Effect of Different Chemical Dosages on Combined Ozone/Fenton Process Performance

In this part of present study, the effect of combined ozone/Fenton process on the treatability of OMW was investigated under different H_2O_2 and Fe^{2+} concentrations at constant ozonation time of 60 min and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 10. The performance of combined ozone/Fenton with color, DOC, TOC, phenol and ozone profiles is shown in Fig. 3.

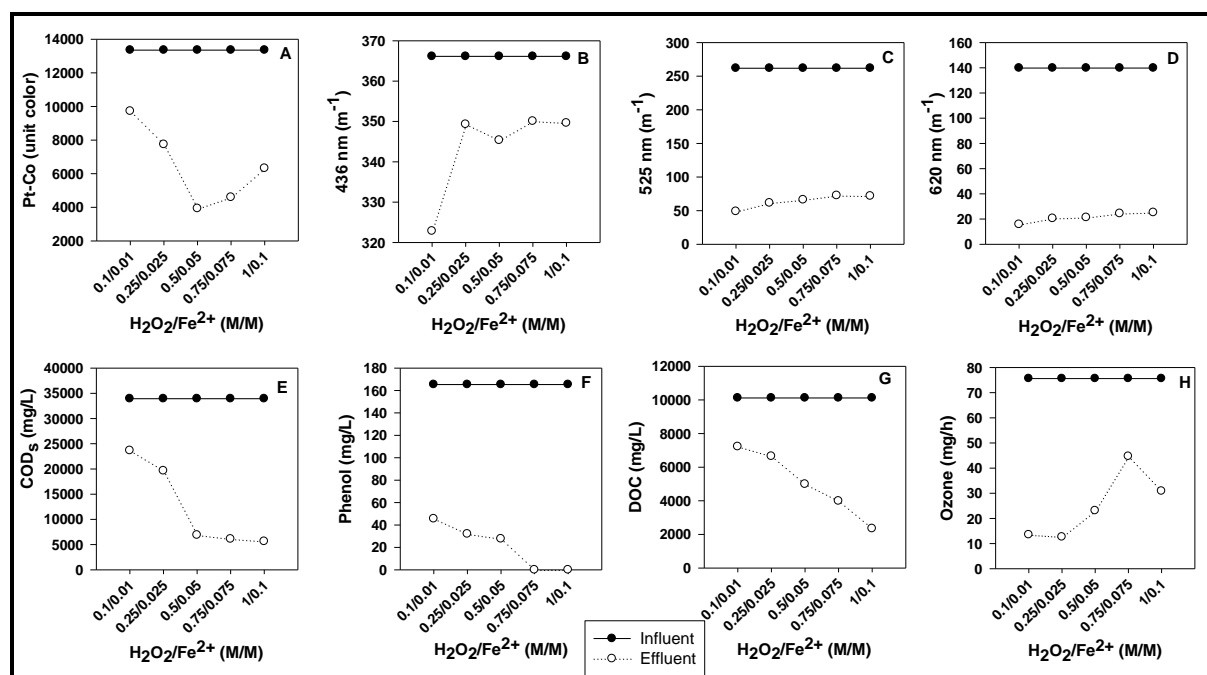


Figure 3: Effect of different chemical dosages on color removal as Pt-Co (A), $\text{RES}_{436\text{nm}}$ (B), $\text{RES}_{525\text{nm}}$ (C) and $\text{RES}_{620\text{nm}}$ (D), COD_s removal (E), phenol removal (F), DOC removal (G), ozone consumption (H).

The color removal efficiency was relatively low at H_2O_2 and Fe^{2+} reagent molar concentrations of 0.1/0.01 and 0.25/0.025, corresponding to 27.2 % and 42% removal efficiency as Pt-Co, respectively. The color removal efficiency as Pt-Co reached to 70.5% at increasing Fe^{2+} and H_2O_2 molar concentrations, corresponding to maximum color removal efficiency (Fig. 3A). In this operational condition similarly, the best color removal efficiency as RES_{436} , RES_{525} and RES_{620} were 24.7%, 92.4%, 96%, respectively. However, it was observed that color removal efficiency decreased at molar concentrations of both reagents above 0.5/0.05. Additionally, COD removal efficiency improved in the increasing reagents concentration however, no significant difference on COD removal was observed at higher concentration of 0.75/0.075 and 1/0.1, corresponding to around 80% removal efficiency and 6700 mg COD/L effluent value. The increased reagents concentrations had an improving effect on phenol and DOC removal in the combined ozone/Fenton process and all of the phenol present in the wastewater was consumed at the H_2O_2 and Fe^{2+} molar concentrations of 0.75/0.075 and 1/0.1 (Fig. 3F).

Additionally, DOC removal efficiency reached to 76.8%, corresponding to 2344 mg DOC/L effluent concentration (Fig. 3G). The amount of ozone applied to the system was 75.6 mg/h. High ozone consumption efficiencies were observed at low Fenton reagents molar concentrations of 0.1/0.01 and 0.25/0.025, corresponding to average 82% consumption yield. Increasing Fenton reagents molar concentrations caused a decrease in ozone depletion and achieved high treatment productivity based on all pollution parameters with lower ozone consumption dosages. The results were similar to that of literature study carried out by Van Aken et al. [22].

This study indicated that the combined process of ozone and Fenton was more effective for the treatment of OMW compared to only-Fenton process. Additionally, the color, DOC and COD_s removals improved 21%, 49% and 22% at the same Fenton reagent concentrations with combine process. Kılıç et al. [23] investigated the effect of the advanced oxidation processes containing ozone/UV, H₂O₂/UV, and ozone/H₂O₂/UV on olive oil mill wastewater at a pilot plant. They stated that the ozone/H₂O₂/UV process combination showed highest treatment performance among all treatment methods, corresponding to COD_s, phenol and organic carbon removals of 99%. However, they were also indicated that this was not an economic selection for treatability of olive oil mill wastewater.

3.2. PART III: Effect of Ozonation Times on Combined Ozone/Fenton Process Performance

In this last part of study, the effect of gradually increasing ozonation times from 60 to 120min was evaluated on combined ozone/Fenton process at the optimum H₂O₂/Fe²⁺ reagents molar dosage of 0.5/0.05 determined in the previous part of the study. The Fig. 4 shows color, DOC, COD_s, phenol and ozone profiles that are changing with increasing ozonation times.

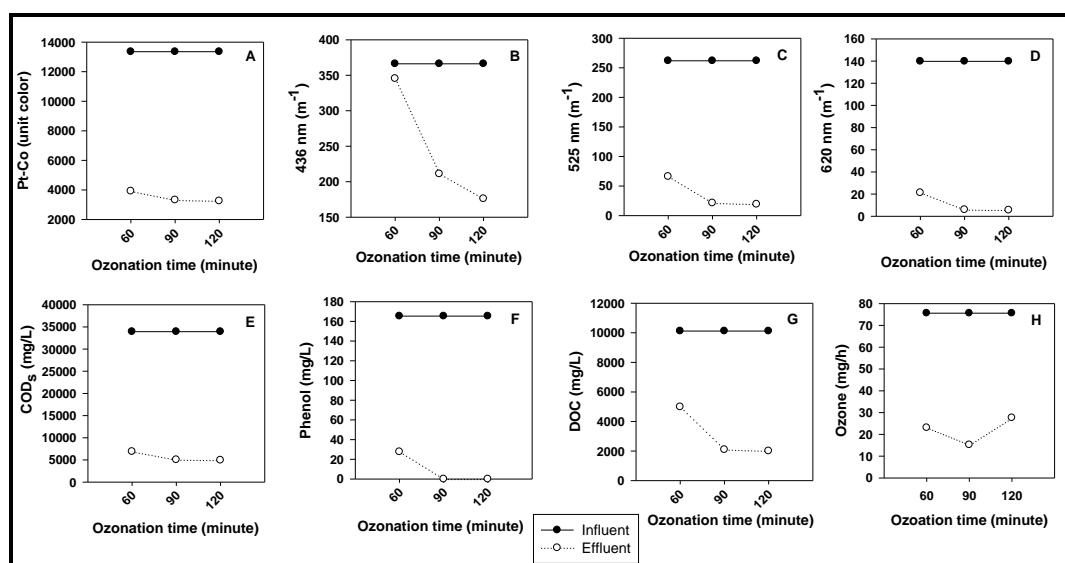


Figure 4: Effect of ozonation times on color removal as Pt-Co (A), Res_{436nm} (B), Res_{525nm} (C) and Res_{620nm} (D), COD_s removal (E), phenol removal (F), DOC removal (G), ozone consumption (H).

In ozonation time of 60 min, the color removal efficiencies as Pt-Co, RES₄₃₆, RES₅₂₅ and RES₆₂₀ were 70.5%, 5.6%, 74.7% and 84.7%, respectively. The color removal efficiency increased distinctly at the increasing ozonation time to 90 min, corresponding to 75.1%, 42.3%, 91.8% and 95.7% removal efficiencies as Pt-Co, RES₄₃₆, RES₅₂₅ and RES₆₂₀, respectively (Fig 4A-D). However, ozonation time over 90 min did not significantly affect the performance of color removal and efficiency reached to 76% as Pt-Co. The COD, phenol and DOC profiles showed similar behavior to the color profile and high COD, phenol and DOC removal efficiencies were observed at the reaction time of 90 minute. In this operational condition, consumed ozone amount was also 52.6 mg/h (Fig. 4H). The reaction time was optimized as 90 min when considering low operating cost and high reaction performance with minimum reaction time. In a study performed by Amr and Aziz [14] was reported the effectiveness the combine ozone/Fenton process for the treatment of mature landfill leachate. Similar to the optimum ozonation time determined from this study, ozonation time of 90 minute was found optimum and COD_s, color, and NH₃-N removals were 65%, 98%, and 12%, respectively, at H₂O₂ and Fe²⁺ concentrations of 0.05/ 0.05.

4. CONCLUSION

The aim of this study was to evaluate chemical treatability of raw OMW by alone Fenton and combined ozone/Fenton process under different operational conditions. In the alone Fenton process, the maximum treatment performance was achieved in the operational condition containing H₂O₂/Fe²⁺ molar ratio of 10 at constant influent H₂O₂ concentration of 0.5 M. This system was converted to a combined ozone/Fenton process by applying ozone gas for 60 min and combined process resulted in 21%, 49% and 22% improvement of treatment yield in terms of color, DOC and COD_s removals, respectively, compared to only-Fenton process. Ozonation time significantly affected the treatment performance, and the reaction time of 90 minute was found optimum in terms of the high treatment productivity and low operating cost resulted from minimum ozone consumption and short reaction time. However, effluent color and COD_s values are still not compliant with the discharge standards of 280 Pt-Co and 250 mg COD/L in the Water Pollution Control Regulation of Turkey that was created in 2011[24]. Therefore, this combined process can be used as post or pre-treatment process of the biological treatment processes to achieve the desired water quality.

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