

**MINERALIZATION OF OLIVE MILL
WASTEWATER UNDER HYDROTHERMAL
CONDITIONS**

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillments of the Requirements for the Degree of
MASTER OF SCIENCE
in Chemical Engineering**

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December 2017

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ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor **Assist. Prof. Dr. Aslı YÜKSEL ÖZŞEN** for the continuous support of my M.Sc. research and study, for her motivation, enthusiasm, and immense knowledge. Her guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my M.Sc. study.

I wish to thank to **Dr. Filiz KURUCAOVALI** for TOC analysis, **Dr. Handan GAYGISIZ** for GC-MS analysis at Environmental Research and Development Center of IZTECH and also **Assist. Prof. Dr. Meral DÜKKANCI** to open her laboratory us for COD analysis with all her favor at Ege University.

I am thankful to my lab mates **Dr. Okan AKIN** and **Gökalp GÖZAYDIN** for their supports and contributions during my experiments.

I would like to express my gratitude to my dear friends **Res. Asst. Gürbüz DURSUN**, **Duygu ŞENGÜN**, **Dr. Sedef TAMBURACI** and **Sibel DEĞER** for their patience and support during writing of my thesis.

Finally, and the most important, I am really indebted to my father **Berkan ERSANLI**, my mother **Güler ERSANLI** and my brother **Çınar ERSANLI** for giving me chance to improve myself, and also their unconditional love, endless courage and precious support. If they were not my family, I could not success this M.Sc. study.

ABSTRACT

MINERALIZATION OF OLIVE MILL WASTEWATER UNDER HYDROTHERMAL CONDITIONS

The purpose of this study is to reduce the total organic carbon (TOC) and chemical oxygen demand (COD) concentrations, color, the concentration of total phenolic compounds of olive mill wastewater (OMW) by hydrothermal degradation in subcritical water medium with and without using hydrogen peroxide (H_2O_2). In addition to this, investigation of effect of reaction temperature, reaction time and H_2O_2 concentration on the reduction of TOC, COD, color and total phenolic content; and controlling the generation of secondary pollutants during the reactions are other objectives of this study. Hydrothermal degradation reactions were performed at 150-250 °C of reaction temperature, 30-120 minutes of reaction duration with 0-100 mM H_2O_2 . Experimental design and statistical analysis (ANOVA) were carried out by Minitab.

The main product of partial mineralization of OMW was acetic acid. Increase in the reaction temperature and time resulted in increasing TOC reduction rates significantly. On the other hand, presence of H_2O_2 did not affect the removal efficiency of TOC concentration significantly because of competition of hydroxyl free radicals by H_2O_2 and target molecule (OMW). The best yield (31.65%) of TOC reduction was achieved with a reaction at 250 °C, 120 min and without using H_2O_2 .

ÖZET

ZEYTİN KARASUYUNUN HİDROTERMAL KOŞULLAR ALTINDA MİNERALİZASYONU

Bu çalışmanın amacı zeytin karasuyunun toplam organik karbon (TOK) konsantrasyonunu, kimyasal oksijen ihtiyacı (KOİ) konsantrasyonunu, rengini, toplam fenolik bileşik konsantrasyonunu hidrojen peroksit (H_2O_2) kullanarak ya da kullanmadan hidrotermal koşullar ve kritik altı suyu ortamında en aza indirmektir. Buna ek olarak, reaksiyon parametresi olan reaksiyon sıcaklığı, reaksiyon süresi ve H_2O_2 miktarı değişiminin TOK ve KOİ konsantrasyonu, renk ve toplam fenolik bileşik konsantrasyonu azalması üzerindeki etkisini incelemek ve ikincil kirleticilerin oluşmasını kontrol etmektir. Hidrotermal bozunma reaksiyonları 150-250 C reaksiyon sıcaklığında, 30-120 dakika reaksiyon süresinde ve 0-100 mM H_2O_2 miktarında gerçekleştirilmiştir. Deneysel tasarım ve istatistiksel analiz (ANOVA) Minitab programında yapılmıştır.

Zeytin karasuyunun kısmi mineralizasyonun ürünü asetik asittir. Reaksiyon sıcaklığı ve süresindeki artış TOK giderim oranındaki artışa önemli oranda etken olmuştur. Öte yandan, hidrojen peroksit varlığının TOK giderimine etkisi reaksiyon sıcaklığı ve süresine oranla daha önemsiz bulunmuştur. Bunun sebebi, hidrojen peroksitli ortamda hidrojen peroksit ile hedef molekül (zeytin karasuyu) arasındaki etkileşim sonucu meydana gelen serbest hidroksil radikallerin oluşturduğu rekabetçi ortamdır. TOK giderimindeki en iyi sonuç (31.65%) 250 °C'de, H_2O_2 olmadan 120 dakika boyunca gerçekleştirilen reaksiyon ile elde edilmiştir.

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CHAPTER 1

INTRODUCTION

Olive and olive oil date back to the morning of the history. Olive trees have been grown from 8th millennium BC in Mediterranean region of the world. Thus, olive trees can only grow in warm climates.

The main three cuisines in Mediterranean countries are olive, wheat and grape. Among them, olive has a great importance in the region. Therefore, the olive oil industry has a significant role in the economy of Mediterranean countries such as Spain, Italy, Portugal, Turkey, and Greece. Main worldwide olive oil producer is Spain. Especially in the Andalusia, the south region of Spain one-third of olive oil has been produced (Sanchez et al. 2011). The worldwide production capacity of olive oil is roughly 3.17 million tons per year. The olive oil production percentages of Spain, Italy, Greece, Turkey, Tunisia, Portugal and rest of the world are approximately 45, 15, 10, 5, 4 and 5 (tons per year), respectively (Gholamzadeh et al. 2016).

There are two main process types for olive oil production. One of them is traditional method, in another words, two phase extraction and the other one is three phase extraction. Both methods have olive washing, milling, horizontal centrifugation and vertical centrifugation steps. In two phase system, horizontal centrifugation is done without addition of water. The process yields of three phase system are an oily phase, solid residue and the olive mill wastewater (OMW) as the aqueous phase. On the other hand, oil as liquid phase and very wet olive cake as a solid phase are the yields of two phase extraction process. Three phase system requires less manpower than traditional (two phase) process and also higher olive oil production rates can be obtained by using this type of extraction. On the other hand, two phase system has less water and energy requirement, higher oil quality than three phase systems. Furthermore, this process is less expensive than the traditional one (Moral et al. 2006).

The liquid waste (OMW) of olive oil industry is highly toxic and contains highly phenolic compounds. Therefore, in the case of any disposal to the environment, OMW threatens both land and aquatic environments.

1.1. Description of Olive Mill Wastewater (OMW)

OMW is dark red to black color liquid effluent of the olive oil industry that is generated while olives are pressed. It is predicted that annual production of olive oil is 2.9×10^6 tons and completion in $8.1 \times 10^6 \text{ m}^3$ OMW (Bhatnagar et al. 2014). When it is considered in the pollution effect point of view, 1 m^3 OMW is equipollent to 100-200 m^3 of domestic sewer water (Fiorentino et al. 2004).

OMW is so complicated effluent that is characterized by total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD). The value of TOC in OMW is between 15-50 g/L, COD is up to 220 g/L and COD/BOD ratio varies between 2.5 and 5. It means that OMW is hardly degradable liquid waste (Tsagaraki et al. 2007). OMW is relatively acidic with a range of 3 and 5.9 (Ün et al. 2006). High concentration of lignins and tannins included in the composition of OMW give effluent the dark color. The color value changes between 52270-180000 mg/L Pt-Co units (Niaounakis and Constantinos 2004).

The characteristics of OMW depend on the several and unpredictable factors such as (Akdemir and Ozer 2009, Mert et al. 2010):

- Quality of olives
- Climate
- Olive oil extraction type (2 or 3 phase extraction)
- Storage time

It is found that the weight composition of OMW is approximately,

- 80-85 % water
- 14-18 % organics
- 1-2 % organic salts

There are significant major organic fractions in the OMW such as sugars (18 w%), nitrogen compounds (0.524 w%), organic acids (0.515 w%), fats (0.021 w%), phenols and pectins (11.5 w%) (Hanafi et al. 2010).

The phenolic compounds exist in OMW are simple phenols or polyphenols which are products of polymerization of phenolic substances. High ratio of phenolic compounds and long chain fatty acids which are present in OMW are highly dangerous for herbs and microorganisms because of their toxic effects (Paixao et al. 1999, Rouvalis et al. 2004). The range of phenolic compounds in OMW is 0.5 to 24 gL⁻¹ (Paraskeva et al. 2006). The phenolic complex variations in OMW are related with some factors such as olive kind, extraction method and maturity step. OMW shows variability in the phenolic compound. Three major types of phenols are cinnamic acid (cinnamic acid, caffeic acid, ferrulic acid), benzoic acid (benzoic acid, protocatechuic acid) and β -3,4-dihydroxyphenylethanol (tyrosol, hydroxy tyrosol) (Lesage-Meessen et al. 2001).

1.2. Olive Mill Wastewater Treatment Technologies

Drainage of olive mill wastewater to environment is highly dangerous and forbidden because of its high organic content, acidity, and high salinity. There are no European legal regulations about OMW. It is directly sent to ponds that are placed in the field and waited there until all OMW evaporates. Generally, olives are pressed in November to February. In the summer season, these effluents are evaporated and disposed to the air. Hence, OMW should be treated because of the reasons as listed above. In this manner, there are several major types of detoxification processes such as biological, physical, physicochemical, electrocoagulation, oxidation, advanced oxidation (AOP) and membrane processes.

Microorganisms are used in biological processes to break the chemicals up that exist in OMW. Biological treatment technologies are divided into two groups as aerobic and anaerobic processes according to microorganism type. Some materials, e.g. amines, can be handled neither by chemical nor physical processes. They can just be treated by biological processes. These types of processes are significant because of environmentally friendly and safe application. On the other hand, these treatment

methods have some disadvantages. Various types of biocides show inhibition effect on the biological reactions, suppression rates are slow and high volume of storage tanks are required (Lafi et al. 2009). Anaerobic digestion occurs in the presence of such kind of microorganisms like bacteria. The digestion rate of anaerobic microorganisms is slower than aerobic microorganisms so that makes the process unfavorable.

Aerobic processes are processes that can be operated when the inlet concentration is relatively low; i.e., 1 g COD/liter. The main disadvantage of these processes is the difficulty to reach the required pollutant (e.g. polyphenols, lipids) removal efficiency. The aerobic pretreatment method can be performed at temperatures between 25 to 30 °C with the restriction of pH control (Gholamzadeh et al. 2016). Thus, aerobic processes are generally used as a pretreatment or posttreatment step in the whole process. (Tsagaraki et al. 2007)

Anaerobic digestion is a promising treatment method with the low energy requirement. Besides, less waste sludge is produced when compared with the aerobic processes. The main advantageous points of this treatment are high degree of purification and low nutrient requirement (Otles and Selek 2012). Despite the necessity of pretreatment or posttreatment step, it is the most suitable method for OMW detoxification. (Niaounakis et al. 2004, Rozzi and Malpei 1996). Anaerobic processes occur by hydrolyzation of complex organic compounds by anaerobic bacteria as a first step called “hydrolysis”. Since fermenting bacteria produces volatile fatty acids, they can be usually designated as an acidifying population (Rincon et al., 2012). Then, these molecules are converted into organic acids (acidogenesis) following by conversion of these acids into biogas (methanogenesis) by methanogenic bacteria. By this method, the final COD removals are almost up to 80% (Paraskeva et al. 2006). The dilutions of waste, sand filtration, thermal treatment are such pretreatment methods to be used in detoxification of OMW (Sabbah et al. 2004).

Another alternative technique for OMW treatment is membrane processes. Separation of the oil-water mixture does not require any solvent addition. The most common membrane separation type is ultrafiltration. Besides, microfiltration and reverse osmosis methods are also preferred. Slight amount of retentate (waste) is generated while ultrafiltration is occurring and reduction rate of lipids are high (Tsagaraki et al. 2007). The main problem of membrane processes is fouling. Fouling problem causes high operating costs and decreases the membrane efficiency. COD removal rate is inadequate with the membrane separation. COD concentrations of

retentate and permeate are still high after the process. These reasons make membrane separation processes unfavorable for OMW treatment but they may be used as pretreatment process of OMW.

The most traditional treatment methods of olive mill wastewater are physical treatments such as dilution, evaporation, filtration, sedimentation, and centrifugation. Physical processes are not enough for the organic content or phenolic compounds reduction of OMW to the required threshold limit value (Hanafi et al. 2010).

Dilution is a useful method for preliminary treatment of OMW before biological treatments to lower the poisonousness and to increase the activation of microorganisms. Dilution can be performed to wastewater system in two ways: First one is the addition of washing water directly to the mill and the other one is carrying it out outside of the mill with the addition of domestic wastewater (Rozzi and Malpei 1996).

Evaporation is the most common process among physical treatments. It is a cost effective method and requires less energy than other processes because of the usage of solar energy. In natural evaporation, generated OMW is directly filled to the previously opened storage ponds to take an advantage of warm climates especially in Mediterranean countries. When evaporation is completed until ponds will be totally dry, the phenolic complexes in OMW are concentrated and the contaminating sewage is turned into solid waste. The wide areas for construction of storage ponds are needed to prevent the wicked scent, decantation, and reproduction of pests (Roig et al. 2006). Because of the high organic content of solid waste, composting should be applied. Hachicha et al. (2009) turn these highly phenolic contaminants to account producing organic fertilizers. Another choice for evaporation is a vacuum evaporation that generates concentrate and distillate. Azbar et al. (2004) used sodium hydroxide for neutralization of wastewater in the distillation process. In their study, distillate was found colorless and in the 3000-4000 mg/l of COD range. This result proved that additional treatment process is required to reach the required detection limit and they suggested the biological oxidation after vacuum evaporation pretreatment. 70-75 % of COD reduction can be achieved by evaporation and sedimentation processes.

Physical processes are usually used in combination with each other to get higher organic or phenolic reduction (Paraskeva et al. 2006). Increasing conductivity and pH, removal of organic content by way of phase separation and exclusion may be obtained with centrifugation and filtration combined process. Al-Malah et al. (2000) showed that the processes including firstly sedimentation, then centrifugation and finally filtration

reduced COD by 21%. 94 % of total phenol and 83 % of TOC reduction was obtained by the combination of settling, centrifugation, filtration and adsorption of activated carbon, respectively (Azzam et al. 2004).

The other elementary and cheaper treatment ways of OMW are physicochemical treatments. These types of treatment methods include coagulation, flocculation, neutralization, precipitation and oxidation processes. To destabilize the suspended solids and colloidal materials present in the OMW, some additional chemicals are required. Suspended solids and colloidal materials can be easily detracted from OMW. Suspended solid, oil, TOC, COD and BOD reduction is observed by using this type of processes (Panizza and Cerisola 2006). Neutralization (increment or reduction of pH) and precipitation/flocculation (addition of precipitate induction matters) are used to destabilization of the colloids. The physicochemical processes are required pretreatment methods because the high organic content is still observed in treated OMW by taking a consideration of destruction of produced and precipitated matters. The other importance of requirement of pretreatment methods is causing some environmental issues of sludge (Tsagaraki et al. 2007).

In the literature, pH adjustment has been studied by some scientists. pH reduction (to the value of between 2 and 4) has an importance about contribution to the acid hydrolysis of fatty acids. This application takes an advantage for separating them easily from a waste product. Beyond reduction of pH, there are several studies about increasing the pH approximately to the value of 11 by using lime (CaO) (Mitrakas et al. 1996). Significant amount of oil, COD and TOC reduction is observed by the treatment of OMW with the addition of lime. Besides, treatment of OMW has an advantage because of production of the high amount of sludge. Aktas et al. (2001) studied lime treatment to waste samples to investigate the effects of lime treatment. They indicated that polluting reduction of OMW can be observed by using lime pretreatment and make it favorable process apply in practice.

Flocculation is the process in which transportation of destabilized particles to form collisions with flocs occurs. The flocculation process with polyelectrolytes which consists of one anionic and one cationic polyelectrolyte able to achieve high COD and phenolic compounds reduction (Sarika et al. 2005). The sludge, which is 20% of the initial feed, is generally generated during flocculation processes. Aluminum sulfate, ferric sulfate, aluminum chloride, ferric and ferrous chloride are the most important

inorganic flocculants which are used in OMW treatment. Roig et al. (2006) worked with calcium hydroxide and aluminum sulfate for OMW treatment and achieved 20-30% COD reduction. 95% of COD and 90% of phenolic content reduction was observed by flocculation with 3 g/l ferric chloride after acid cracking pretreatment. In addition, with 6 g/l dose of alum, 94% of COD and 91% of phenolic content reduction was achieved (Sarika et al. 2005).

Electrochemical processes are inviting technique for OMW because of impressive oxidation of non-biodegradable compounds present in OMW. Electrocoagulation, electrochemical oxidation with polialuminum chloride (PAC), anodic oxidation and conductive diamond electrochemical oxidation (CDEO) are the most important type of electrochemical processes. One of the preferred treatment methods for OMW is electrocoagulation. It is an electrochemical process to destabilize the particles through the chemical reaction between colloids and coagulants. Coagulants are generated in the anode (aluminum or iron) by electrolytic oxidation. Insoluble metal hydroxides are formed at convenient pH. These types of metal hydroxides can act on the removal of pollutants (Adhoum and Monser 2004). The amount of generated sludge is less than classical coagulation processes. Inan et al. (2004) reported that with 30 minutes of reaction time and at optimal pH value (pH=6), 52% and 42% of COD reduction was achieved by the use of aluminum anode and an iron anode, respectively. Besides, they showed that increased current density, directly increase the COD reduction rate. Adhoum and Monser (2004) observed that 95% of color, 91% of phenolic content and 76% of COD reduction by using aluminum anode at an optimal pH range (4-6), 75 mA of current density after 25 minutes of reaction. Un et al. (2008) practiced the electrocoagulation process with polialuminum chloride in the presence of hydrogen peroxide. Authors found out that the COD reduction range between 62-86% and also they remarked that the current density is the most important parameter for electrocoagulation techniques. In another study, conductive diamond electrochemical oxidation was applied to the fresh OMW and 98.4% COD reduction and 99% mineralization rated were obtained (Canizares et al. 2009). Complete removal of both COD and total phenolic content (TPC) was attained by the application of electrochemical oxidation with Ti/Pt anode and Ti cathode (Kul et al. 2015).

Highly pollutant reduction can be achieved by using strong oxidizing agents such as hydrogen peroxide and ozone. These agents are able to break up the organic and phenolic compounds for the treatment of wastewaters. Recently, oxidation, wet

oxidation and advanced oxidation processes (AOP) are getting attendance in the field of OMW treatment technologies. The main working principle of these processes is the formation of hydroxyl radicals (a combination of ozone with hydrogen peroxide, Fenton's reagent, photocatalysis, UV radiation) to destroy the organic content of OMW. AOPs involve the creating and acting of hydroxyl radicals that are reactive and unstable compounds. Free hydroxyl radicals are synthesized by an oxygen and energy sources. The typical oxygen source is hydrogen peroxide and ozone and energy source is solar or ultraviolet (UV) energy. Ozone and hydrogen peroxide is the most favorable oxidizing agent because they have the higher oxidizing ability and they can operate under the atmospheric conditions. Numerous organic matters may be broke up totally or partially into the smaller and non-toxic substances by the help of AOPs. Therefore, AOPs are favorable to complete mineralization of OMW.

Lafi et al. (2009) investigated the treatment efficiency of OMW by ozonation. The result found out 22% of COD was achieved by single ozonation process. Besides, the combination of ozonation and UV radiation increased the COD reduction slightly to 29%. In another study, ozonation was studied to treat the OMW that was generated after two phase olive extraction in Spain. Researchers observed that 77.2% of COD reduction and almost 68% of mineralization rate (Canizares et al., 2007).

Wet air oxidation (WAO) is a type of oxidation process, which uses oxygen under high temperature (200-250 °C) and high pressure (50-150 bar). The usage of wet air or wet hydrogen peroxide oxidation with/without catalysts such as ruthenium, platinum or zeolites is able to degrade OMW and so provides complete mineralization. Elevated number of instruments is required and because of the high operating pressures, operational costs are expensive (Levec and Pintar 2007). Minh et al. (2008) treated OMW by catalytic wet air oxidation (CWAO) with ruthenium and platinum supported on zirconium or titanium catalysts combined with anaerobic digestion. The researchers revealed that 97% of TOC and the almost complete total phenolic content reduction were achieved by using ruthenium catalysts at 190 °C operating temperature and 70 bar air pressure. Supercritical WAO was applied to OMW. At 500 °C and 25 MPa operating conditions, 79% of both COD and TOC reduction, 98% of phenolic compounds reduction was achieved (Rivas et al. 2001a). In another study, OMW treatment was done with subcritical water WAO with/without CuO/C or Pt/Al₂O₃ catalysts and hydrogen peroxide. 50% of COD reduction was observed by both catalysts after 6 hours

of reaction time at 180 °C reaction temperature and 7 MPa air pressure (Rivas et al. 2001b).

Other encouraging AOP type for OMW treatment is Fenton oxidation. Fenton oxidation is a process in combination of chemical oxidation and coagulation by using ferric or ferrous sulfate and hydrogen peroxide (Fenton's reagent). The significant parameters of Fenton oxidation reactions are concentrations of hydrogen peroxide and ferric/ferrous sulfate, reaction time and pH of the reaction solution. According to a study, after 3-4 hours of reaction, nearly 90% of COD removal was procured with 10 mM of Fe^{2+} and 1 M of H_2O_2 at 50 °C (Rivas et al. 2001c). The range of 40-60% of COD removal and complete phenolic content reduction was attained with 3 ml of H_2O_2 and 2-3 g/l of ferrous sulfate after 2 hours (Vlyssides et al. 2003, Vlyssides et al. 2004). Photo-Fenton treatment of OMW with solar irradiation provided 74% of COD and 87% of phenolic content reduction 5 mM of Fe^{2+} and 20 g/l of H_2O_2 after 19 hours of reaction. Researchers also revealed that the usage of flocculation as a pretreatment increases the reduction rate of both COD and total phenolic content to 89% and 100%, respectively.

Homogeneous or heterogeneous photocatalysis are used for the photocatalytic treatment of OMW by using either visible or solar light as an energy source. Since titanium dioxide (TiO_2) has higher mineralization and oxidizing properties than other semiconductor photocatalysts (ZnO , CdS , ZnS , Fe_2O_3), it has attracting attention with recent studies (Ochando-Pulido et al., 2017). The photocatalytic process with TiO_2 under ultraviolet light (UV) has an importance among photocatalytic treatments. Thus, TiO_2 nanoparticles have high surface/volume ratio that increases the mass transfer rate while using photocatalytic material (Chen et al. 2007, Chatterjee and Dasgupta 2005). 90% of color reduction was observed by using UV/ H_2O_2 process after 7 days (Ugurlu and Kula 2007). Photocatalytic degradation of OMW with TiO_2 was studied by Chatsizymeon et al. (2009) in laboratory scale batch reactor. Researchers revealed that contact time increase the removal of COD concentration of OMW effluent. In another study, pretreated OMW (with batch membranes) was treated with the photocatalytic process by using TiO_2 nanoparticles like studies explained previously, and 87% of COD reduction was achieved after 24 hours (Stoller and Bravi 2010). Gernjak et al. (2004) applied solar photo-Fenton process to OMW and achieved 85% of COD and total phenolic content reductions. 99% of phenolic and 90% of TOC reductions were observed with the combination of adsorption, biological and photo-Fenton processes

(Aytar et al. 2013). On the other hand, nearly 40-48% of COD removal was attained with UV/ H₂O₂ process after 30 minutes of reaction (Hodaifa and Calderon 2017).

1.3. Subcritical Water

Subcritical water (SCW) is liquid water between the temperatures of atmospheric boiling point (100 °C) and critical point (374 °C). Subcritical water has alternative terms such as pressurized hot water (PHW), hot compressed water (HCW), superheated water or near-critical water (NCW). SCW has gained significant importance from scientists and researchers over the last 10 years due to the green solvent property (Ahmadian-Kouchaksaraie et al. 2016). Pressure must be applied to the system to keep the water in the liquid state between the boiling and critical points. Phase diagram of subcritical water associated with temperature and water can be shown in Figure 1.1. Subcritical water is not a concretely described state. Hence, water above the triple point and below the critical point is in any of liquid and gaseous state (Moller et al. 2011).

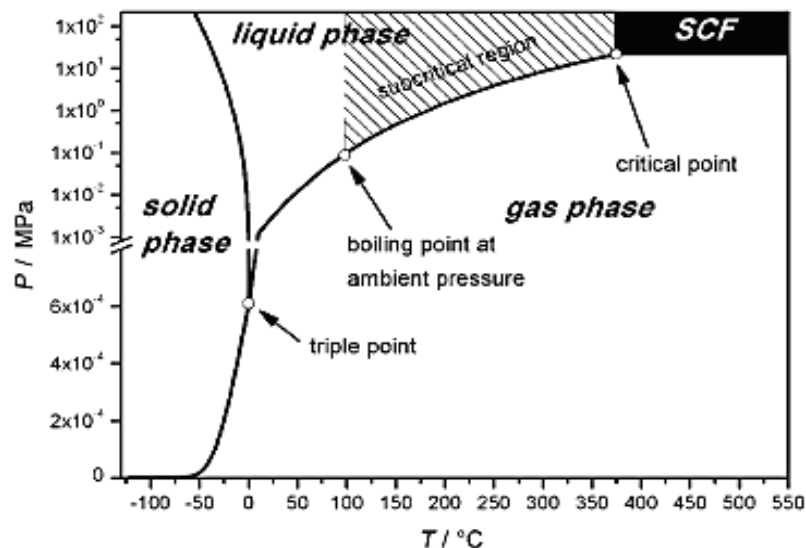


Figure 1.1. Subcritical water phase diagram

(Source: Moller et al. 2011)

Physicochemical properties of subcritical water at 250 °C are given in Table 1.1. Density, viscosity, dielectric constant and pK value of water are decreased with

increasing temperature, in order words, this can be described as a transition from ambient condition to subcritical condition. The specifications of subcritical water such as dielectric constant, ionic product are altered by changing the parameters of temperature and pressure. The dielectric constant of ambient water is higher than subcritical water because of stronger hydrogen bonds. Solvent properties of water change with a decrease in dielectric constant (Guo et al. 2010). The density and dielectric constant of water are high at elevated temperatures. This means that stabilization and solution ability of ionic compounds decreases at these temperatures. Ionic product of the water also increases with increasing temperature because of the endothermic reaction of self-dissociation of water (Kruse and Dinjus 2006). In the subcritical region, water is an excellent acid or base catalyst due to the presence of a dominant concentration of H_3O^+ OH^- ions. Water becomes non-polar while the temperature is increasing and leads to solubilization of organic matters (Lee 2012, Kruse and Dinjus 2006). Additionally, the viscosity of the water drastically decreases with increasing temperature. A low viscosity will be the effect of the high diffusion coefficient and increase in the reaction rate of mass transfer limited chemical reactions (Moller et al. 2011, Tekin et al. 2014). Graphical representation of the change in density, ionic product, dielectric constant and viscosity of the water with respect to temperature is given in Figure 1.2.

Table 1.1 Comparisons of physicochemical properties of ambient water and subcritical water

	Ambient water	Subcritical water
Temperature (°C)	25	250
Pressure (MPa)	0.1	5
Density (g/cm³)	0.997	0.80
Viscosity(mPas)	0.89	0.11
Dielectric constant	78.5	27.1
pK_{water}	14.0	11.2
Heat capacity (kJ/kgK)	4.22	4.86
Thermal conductivity (mW/mK)	608	620

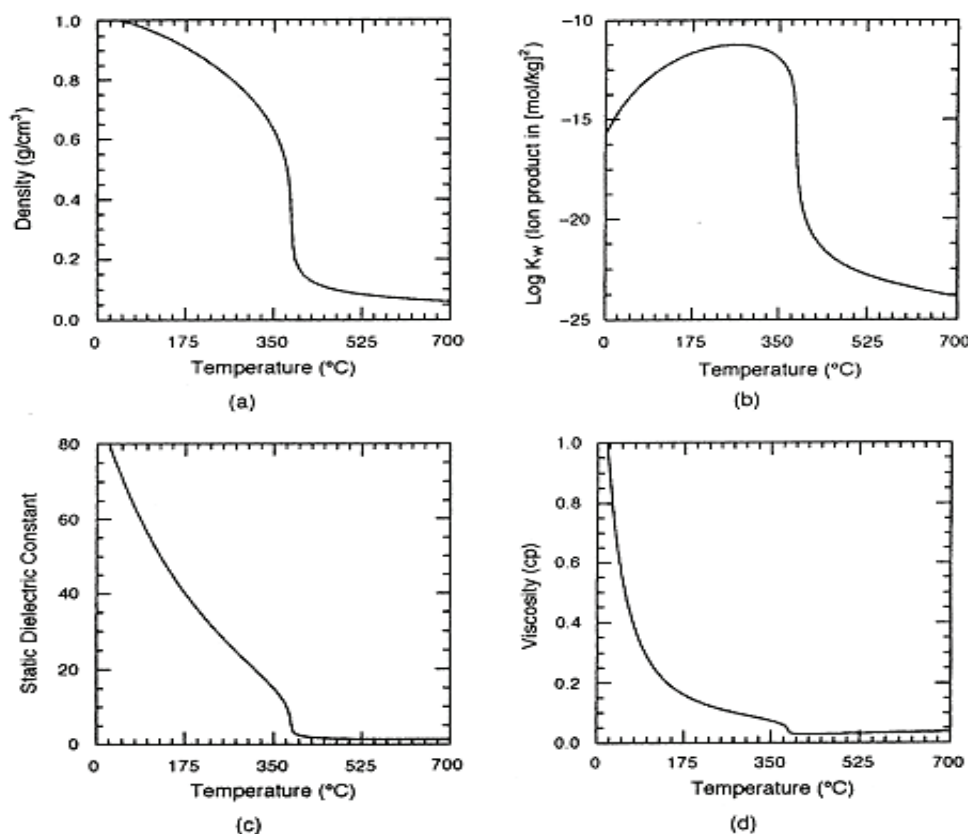


Figure 1.2. The change of a) density, b) ionic product, c) dielectric constant and d) viscosity of water along with temperature

(Source: Akiya and Savage 2002)

1.4. Aim and Importance of the Study

In the present study, the main goal was mineralization of olive mill wastewater in subcritical reaction medium. The treatment of OMW has significance due to its high organic and phenolic content, high salinity, and acidity. Turkey is one of the biggest producers of olive oil and concordantly high amount of olive mill wastes (OMW) are generated. We also aimed to investigate the effects of temperature (150-250 °C), reaction time (30-120 min) and external oxidizer, hydrogen peroxide, (0-100 mM) on the hydrothermal reaction of OMW in subcritical water. TOC and COD analyses were done to understand the mineralization degree; color measurement was completed to observe the effects of reaction parameters on color change; Folin Ciocalteu method was examined to find out total phenolic content; and gas chromatography-mass

spectrophotometer (GC-MS) analyses were prepared to control and understand the generated secondary pollutants during the reaction. Besides, the results were statistically analyzed by ANOVA in Minitab (licensed by IZTECH).

As listed above, there are several treatment technologies about OMW such as advanced oxidation processes, electrochemical oxidation, wet air oxidation, electrocoagulation, photocatalytic study, etc. However, to our best knowledge, in literature, there is no study in which subcritical water plays a key role in the degradation of OMW. The originality of this study is to mineralize OMW by using subcritical water as a reaction medium in the absence and presence of the external oxidant.

CHAPTER 2

EXPERIMENTAL

2.1. Materials and Instruments

Materials and chemicals used in this study are as follows: Folin Ciocalteu reagent (Merck-1090010500), gallic acid (Merck-842649), sodium carbonate (Sigma Aldrich-S2127), hydrogen peroxide (30% purity, Sigma Aldrich-18312), de-ionized water (by using Millipore-TANKPE060) and COD kits (Lovibond-2420722). Used equipments in analyses are given in Figure 2.2. Olive mill wastewater was taken from ‘Köyüm Olive Oil Factory’ in Foça/İzmir. De-ionized water was used for preparing the slurry as reaction medium and analyses.

Table 2.1. Instruments that were used in analyses

Analysis	The producer company	Equipment
pH	Thermo Scientific	Orion Star A111 pH Meter
TOC	Shimadzu	TOC-Vcph Analyzer
COD	Lovibond	ET 108 mini reactor
GC-MS	Agilent Technologies	6890 N - 5973 N Network

2.2. Experimental Equipment

Hydrothermal reactions in the subcritical medium were carried out in a batch reactor (Parr 5500 High-Pressure Compact Reactor). The reactor made of stainless steel (T-316) consists of the magnetically driven stirrer, gas inlet and outlet valves, a safety disk, a thermocouple, a pressure gage and a u-tube heat exchanger. The reactor has a volume of 300 mL and the reaction solution was prepared as 100 mL for each

experiment. The maximum temperature and pressure of the reactor are 350 °C and 3000 psi, respectively. The image of the reactor and schematic diagram of the reactor are given in Figure 2.1 and Figure 2.2, respectively.



Figure 2.1. Image of the batch reactor

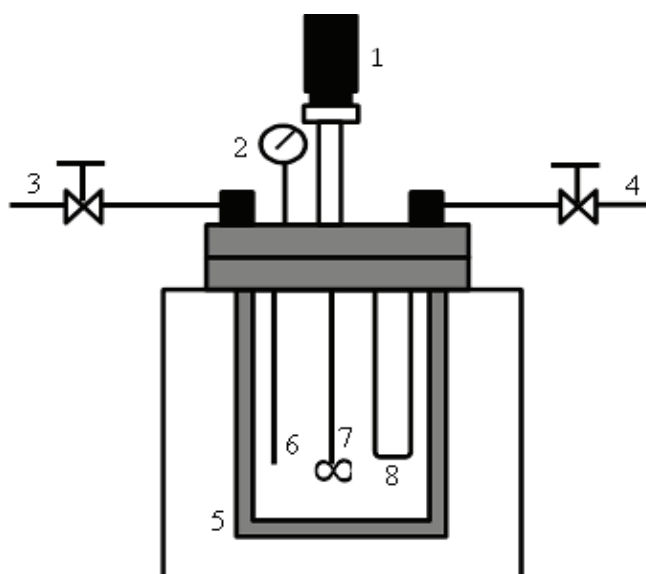


Figure 2.2. Schematic diagram of high pressure batch reactor: 1) magnetic stirrer driver, 2) pressure gage, 3) gas outlet valve, 4) gas inlet valve, 5) stainless steel beaker, 6) thermocouple, 7) stirring impeller, 8) U-tube heat exchanger

2.3. Experimental Procedure

As a reaction solution, 100 ml of OMW was placed into the reaction vessel. For the experiments with an external oxidizer, 50 or 100 mM of hydrogen peroxide (H_2O_2) was used. Then reaction vessel was placed in the reactor and all the pins were tightened to prevent any pressure loss. Afterward, the reactor was purged with an inert gas (nitrogen) for 5 minutes to remove oxygen remained in the reactor. Next, the temperature was set to desired reaction temperature (150, 200 or 250 °C) and magnetic stirrer was set to 200-250 rpm. The reaction temperature and pressure values were recorded in every 5 minutes during both heating and reaction steps. The typical temperature-pressure profile for 200 °C and a reaction time of 60 minutes is given in Figure 2.3.

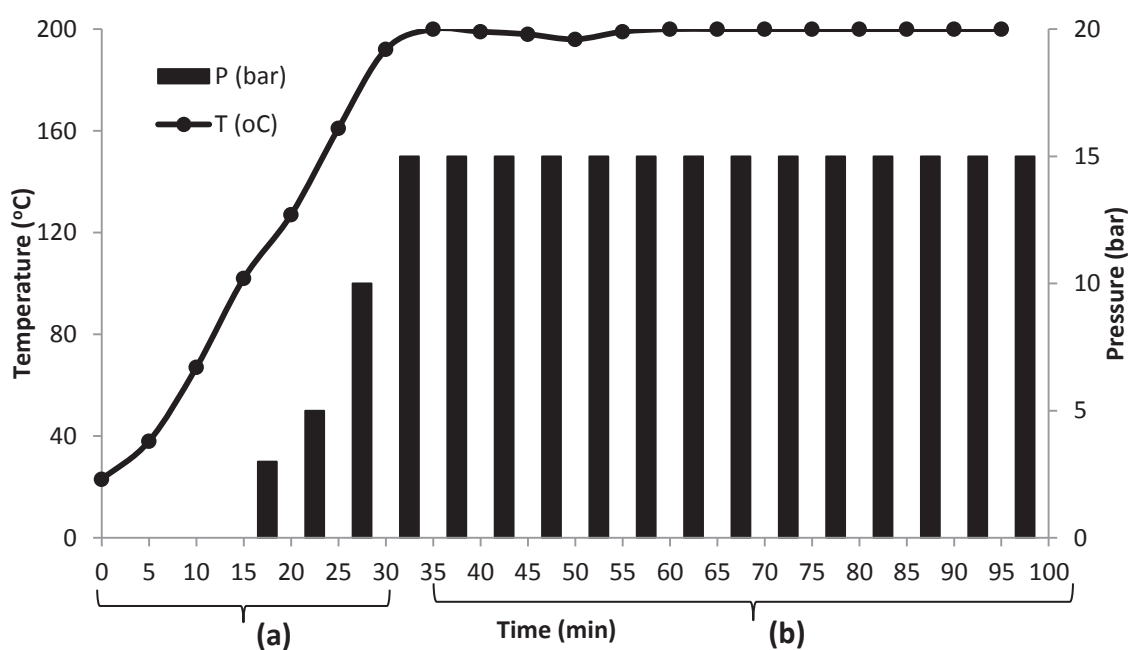


Figure 2.3. Temperature-pressure profile (200 °C, 60 min): a) heating step, b) reaction

The reaction was carried out for a certain reaction time (30, 60, 75, 90 and 120 mins). When the reaction was completed, the reactor was cooled by an internal cooler until 40-50 °C and then the pins were opened to collect the liquid product. The liquid product solution was filtered through a filter paper to remove solid particles. Almost no solid particles were observed after experiments. After that, pH of the solution was measured and pictures of the liquid product solutions were taken to compare the color change visibly. Finally, the liquid product was analyzed by Total Organic Carbon

(TOC), Chemical Oxygen Demand (COD), Gas Chromatography-Mass Spectrophotometer (GC-MS), total phenolic content (TPC) and color analyses. The mineralization rate of olive mill wastewater was calculated in terms of TOC reduction. The related equation is given below:

$$TOC\ Reduction\ (\%) = \frac{TOC(0) - TOC(t)}{TOC(0)} \times 100 \quad (2.1)$$

where TOC (0) is the initial TOC value and TOC (t) is the TOC value of the product solution.

An experimental design was performed by Analysis of Variance (ANOVA). Designed reactions are given in Table 2.2.

Table 2.2. Experimental design of hydrothermal treatment of OMW

Run Order	Reaction Time (min)	Temperature (°C)	H₂O₂ Content (mM)
1	120	150	0
2	30	150	100
3	30	150	0
4	30	150	0
5	120	150	0
6	75	200	50
7	120	250	0
8	30	250	0
9	75	200	50
10	30	250	0
11	30	250	100
12	30	250	100
13	120	250	100
14	30	150	100
15	120	150	100
16	120	250	0
17	120	150	100
18	120	250	100

2.4. Product Analysis

TOC analyses were carried out to evaluate the mineralization rate of OMW. The TOC Analyzer (Shimadzu) was placed in Environmental Development Application and Research Center at IZTECH. First of all, samples are introduced into the TC combustion tube, which is filled with an oxidation catalyst and heated to 720 °C. Generally, samples are burned at 680 °C for TOC analysis but in these analyses, they are heated to 720 °C, which is the suitable temperature for TOC analysis. Then, samples are burned in the combustion tube and, as a result, the total carbon (TC) components in the sample are converted to carbon dioxide. A carrier gas (dry air) flowing at a rate of 150 ml/min to the combustion tube, carries the sample combustion products from the combustion tube to an electronic dehumidifier, where the gas is cooled and dehydrated. Finally, the carrier gas delivers the sample combustion products to the cell of a non-dispersive infrared (NDIR) gas analyzer, where the carbon dioxide is detected. The NDIR outputs an analog detection signal that forms a peak; the TOC-Control V Software measures the peak area.

COD analyses were performed to understand the chemical oxygen demand. COD analyses were carried out by COD reactor (Lovibond ET 108) as shown in Figure 2.4.

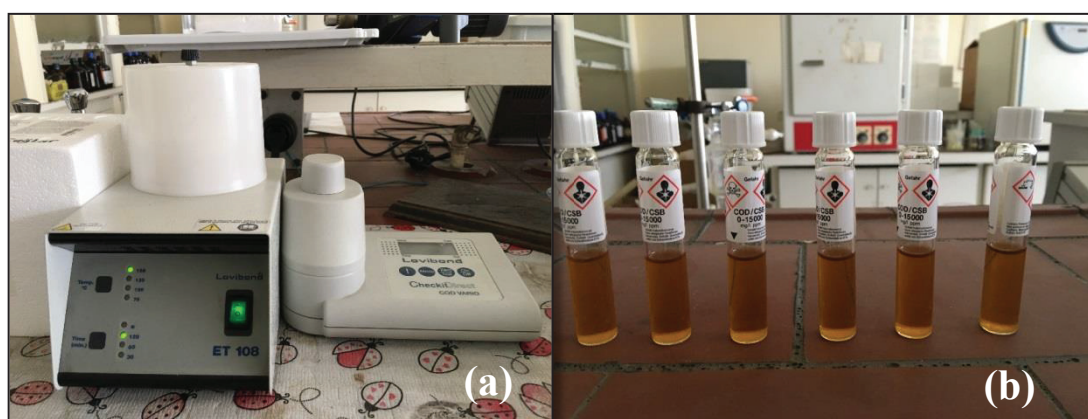


Figure 2.4. (a) COD reactor, (b) COD kits

In order to understand possible secondary pollutants, which might be formed during the hydrothermal reactions, and to identify the mineralization products, GC-MS (Agilent Technologies 6890 N - 5973 N Network) analysis was performed. The analysis method is as follows: oven program is 140 °C (5 minutes with an increment of 8

°C/min), 230 °C (15 minutes with an increment of 10 °C/min) and 240 °C (5 minutes with an increment of 0.5 °C). Analyses run by using capillary column (30 m of nominal length and 320 µm of nominal diameter) with Front Inlet Split mode. Split ratio is 10 and splits flow is 13.1 ml/min. Eluent gas (helium) with a flow rate of 1.3 ml/min was used at an operating temperature of 240 °C and an operating pressure of 0.04 bar. Analyses were done in Environmental Development Application and Research Center at IZTECH.

The color change was examined qualitatively by taking photographs of raw material and products.

Folin Ciocalteu method was used to evaluate the total phenolic content of liquid products. To obtain a calibration curve, the stock solution was prepared with 50 mg of Gallic acid and 100 ml of distilled water. Then samples with different concentrations were prepared. Folin Ciocalteu reagent was diluted by 10-fold with distilled water and 7.5% of sodium carbonate solution was prepared for the analyses. After that, 0.5 ml of Folin Ciocalteu solution, 1 ml of sodium carbonate solution, 8 ml of distilled water and 0.5 ml of samples were mixed, covered with aluminum foil and waited in the dark room at room temperature for 45 mins. Finally, prepared solutions were analyzed by UV analyzer at 725 nm. The calibration curve obtained for the total phenolic content is given in Figure 2.6.

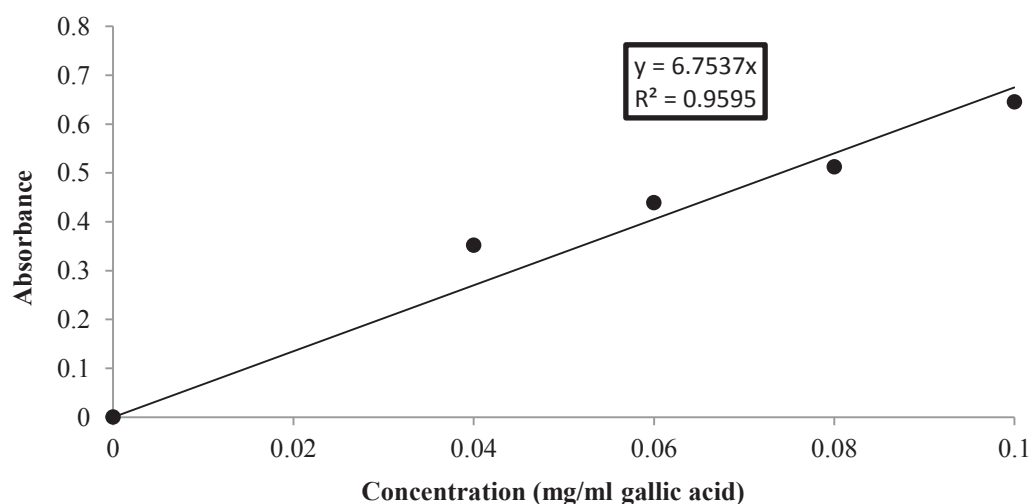


Figure 2.5. The calibration curve of Folin Ciocalteu method (at 725 nm)

CHAPTER 3

RESULTS AND DISCUSSION

Mineralization of olive mill wastewater was performed at several reaction temperatures (150, 200, 250 °C), reaction times (30, 60, 90, 120 min) and with an external oxidizer (H_2O_2) with varying concentrations (0, 50, 100 mM) in subcritical water medium.

The reaction temperature is one of the most significant parameters that affect the efficiency of subcritical water treatment, since rising reaction temperature influences the physicochemical properties of water (Wiboonsirikul and Adachi 2008). In subcritical region, increasing temperature is strikingly decreased the viscosity, dielectric constant and surface tension of water. This situation utilizes the reactions and dissolution of organic molecules in high temperature water (Yang et al., 1998). At the temperature range of 200-300 °C, the dissociation constant of water is three orders of magnitude larger than ambient water which is able to make a great contribution to subcritical water reactivity with organic compounds (Yang et al., 2006). Furthermore, mass transfer rate of reaction increases in the presence of subcritical water medium (Wiboonsirikul and Adachi 2008).

Another effective parameter on subcritical water treatment efficiency is the reaction duration. In literature, mineralization rate almost always rises with the increasing reaction time (Daskalavi et al. 2011, Daneshvar et al. 2014).

Generally, lower pH values increase the degradation rate of complex molecules into the smaller intermediates with acidic properties (Fernandez et al. 2004). However, in this study, pH adjustment was not required because OMW is highly acidic sewage with a pH value of 4-5.

Mineralization of complex molecules can be described with three different paths that are represented in Figure 3.1 (Gomes et al. 2007). Complex organic molecules in OMW can be directly converted to complete mineralization products of CO_2 and H_2O (Path I). In another way, complex molecules firstly break into smaller molecules and then carboxylic acid derivatives and finally these intermediates converted to CO_2 and

H₂O (Path II). Furthermore, the third path is that complex substances are transformed into carboxylic acid derivatives; especially acetic acid (Path III). Paths I and II describe the ways of complete mineralization and also path III describes the partial mineralization.

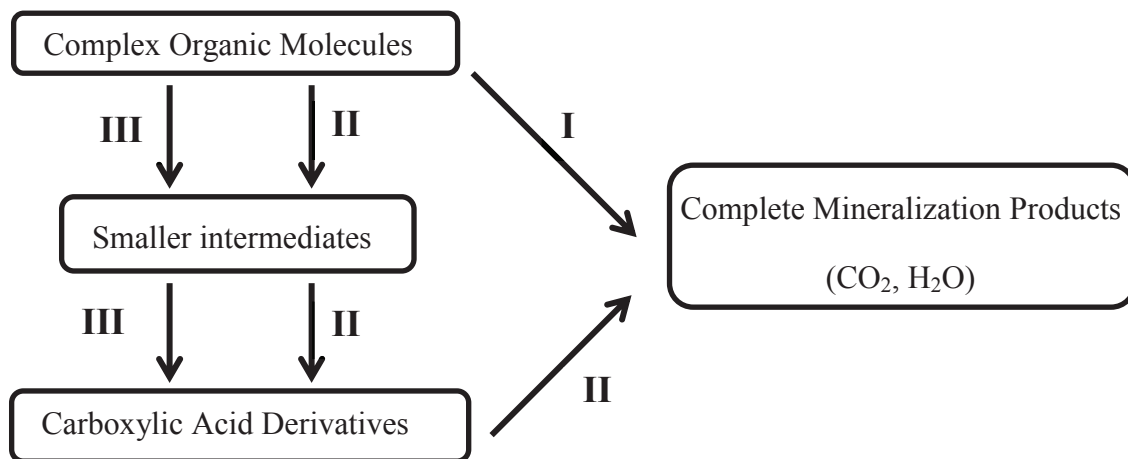


Figure 3.1. Scheme of mineralization paths

(Source: Gomes et al. 2007)

A GC-MS analysis of raw OMW was performed in order to understand the chemicals exist in OMW before and after the treatment. GC-MS spectrum of raw OMW and list of chemicals for this spectrum are given in Figure 3.2 and Table 3.1, respectively. Acetic acid and butanoic acid are common chemicals found in OMW.

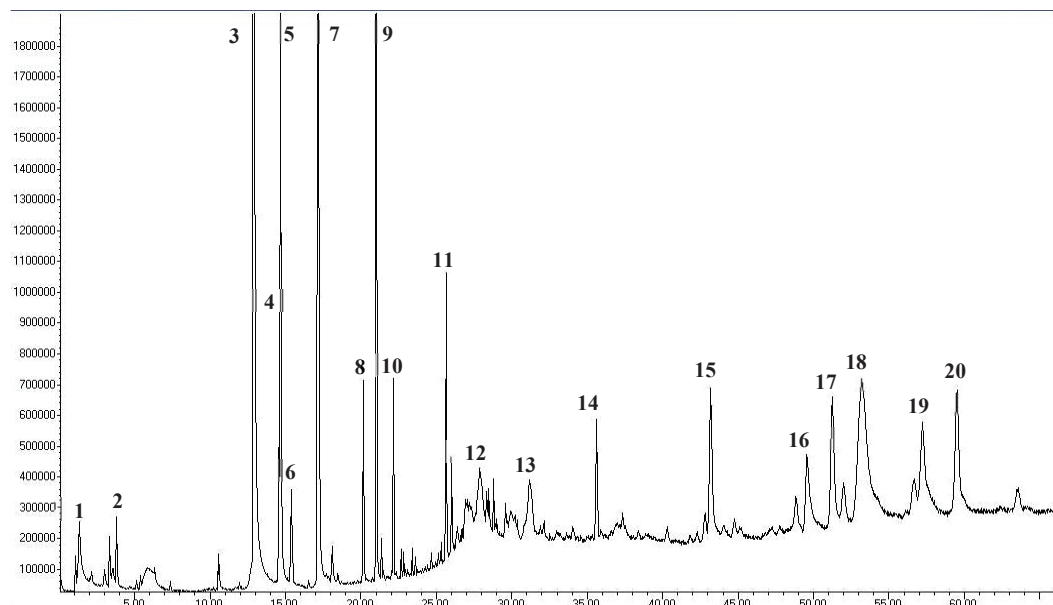


Figure 3.2. GC-MS spectrum of raw OMW

Table 3.1. List of main compounds in GC-MS spectrum of raw OMW

Peak number	Retention time (min)	Chemical formula	Molecular weight (g/mol)	Common name
1	1.33	C ₂ H ₄ O	44.05	Ethylene oxide
2	3.80	C ₂ H ₆ O	46.07	Ethanol
3	12.85	CH ₃ COOH	60.05	Acetic acid
4	14.58	C ₄ H ₁₀ O ₂	90.12	2,3-Butanediol
5	14.66	C ₃ H ₆ O ₂	74.08	Propanoic acid
6	15.37	C ₄ H ₈ O ₂	88.11	Isobutyric acid
7	17.15	C ₄ H ₈ O ₂	88.11	Butanoic acid
8	20.16	C ₅ H ₁₀ O ₂	102.13	Pentanoic acid
9	21.02	C ₃ H ₆ O	58.08	Propylene oxide
10	22.16	C ₆ H ₁₂ O ₂	116.16	Hexanoic acid
11	25.64	C ₇ H ₁₂ O ₂	128.17	Cyclohexanecarboxylic acid
12	27.89	C ₂₀ H ₃₆ O ₂	308.51	Ethyl linoleate
13	31.18	C ₁₂ H ₂₄	168.32	Cyclododecane
14	35.62	C ₁₉ H ₃₀ O ₂	290.45	5-dodecyl-2-hydroxybenzaldehyde
15	43.18	C ₇ H ₁₀ O ₂	126.16	1,3-Cyclohexanedione, 2-methyl-
16	49.59	C ₇ H ₁₄ O ₃	146.18	Pentanoic acid, 5-methoxy-, methyl ester
17	51.26	C ₈ H ₁₂ O ₂	140.18	Benzeneethanol
18	53.21	C ₈ H ₁₆ NO ₅ P	237.19	Dicrotophos
19	57.23	C ₁₀ H ₂₀ O ₅	220.27	15-crown-5
20	59.52	C ₁₈ H ₃₄ O ₂	282.47	Oleic acid

3.1. Reactions without External Oxidizer

The reaction temperature and time are one of the major parameters of this study as can be seen in Figure 3.3. Hydrothermal degradation reactions of OMW were carried out at reaction temperatures of 150, 200 and 250 °C and reaction durations of 30, 60, 90 and 120 minutes. The importance of these reaction parameters on TOC removal efficiency was examined by statistical analysis (ANOVA).

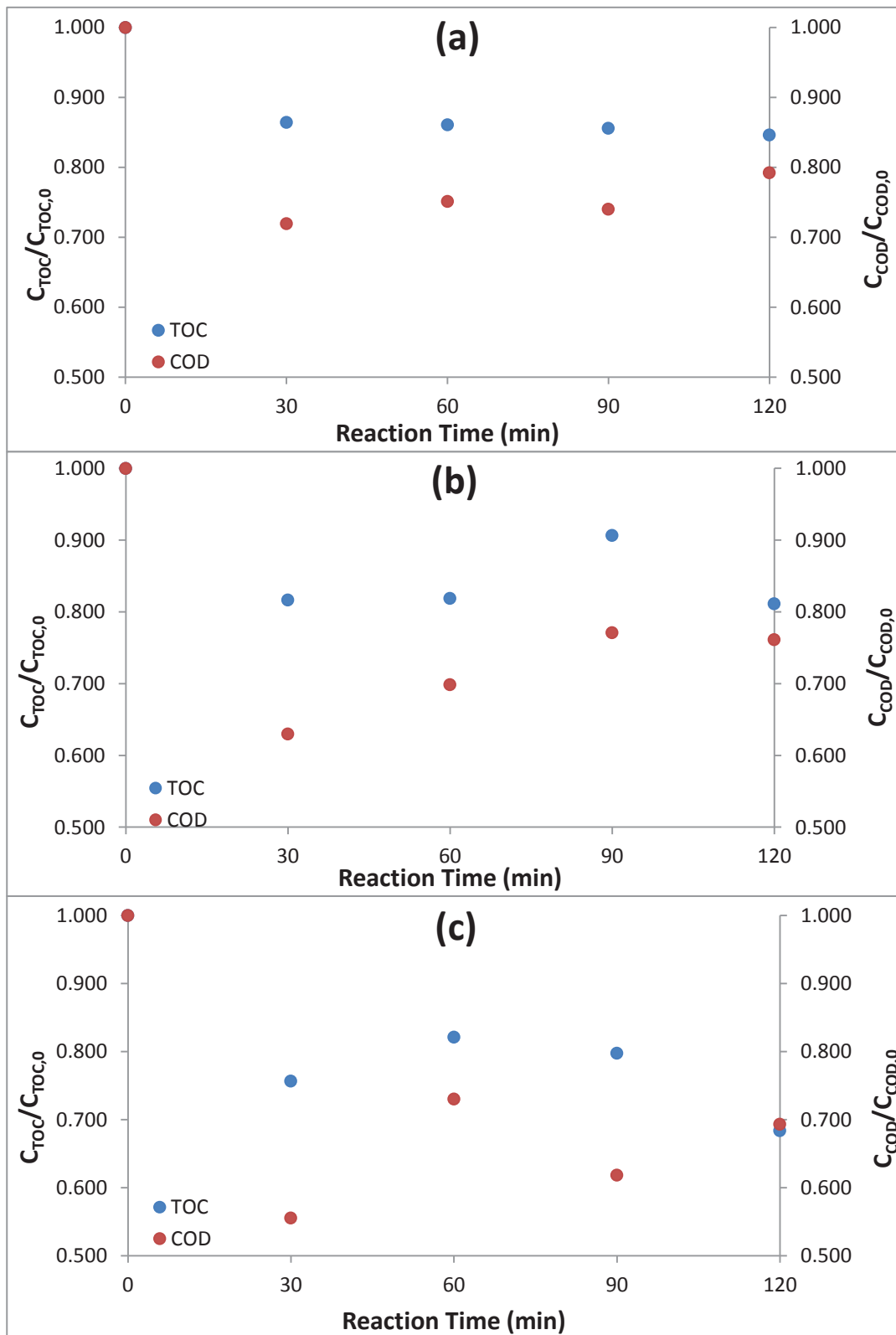


Figure 3.3. The variations of TOC and COD concentrations with respect to reaction time for reactions at (a) 150 °C, (b) 200 °C, (c) 250 °C

Higher reaction temperatures generally lead to higher reduction rate of both COD and TOC. When reactions were carried out at 250 °C, final to initial ratio of TOC concentration was 0.757 for 30 min and 0.683 for 120 min of reaction times. Besides, similar trend was observed in change of COD concentration during 30 and 120 mins. At the end of 120 min, final to initial concentration ratio of COD were 0.792 and 0.693 at 150 °C and 250 °C, respectively. Furthermore, according to this study, it can be said that shorter reaction times resulted in higher COD reductions. The highest TOC removal rate, 31.65%, was achieved at 250 °C after 120 min. In the case of COD removal, highest efficiency was obtained at 250 °C and 30 min reaction conditions.

In literature, researchers demonstrated that TOC removal rate increased with the reaction temperature and reaction time as observed in this study. Daneshvar et al. (2014) revealed that TOC removal percentage of textile dye (acid orange 7) increased with increasing reaction temperature and reaction time in subcritical water medium without using any external oxidizer. They observed that higher amount of TOC reduction was achieved at temperatures equal or higher than 120 °C. At 170 °C, 20% of TOC removal was achieved. In another study, it was shown that temperature has a significant role for the degradation of Reactive Red 120 dye and TOC removal in subcritical water medium with H₂O₂ was studied (Daskalavi et al. 2011). Authors indicated that after 70 min of reaction time, TOC reduction was 18% and 33 % at 150 and 200 °C, respectively. Minh et al. (2008) studied with platinum and ruthenium supported zirconia or titanium nanoparticles for wet air oxidation of OMW and concluded that increase in the time up to 80 hours lowered the TOC concentration of raw OMW. Ruthenium catalysts were found to be more efficient than platinum catalyst in terms of TOC reduction. For example, after 24 h, 96% of TOC reduction was achieved with ruthenium catalyst but 76% of TOC reduction was observed with platinum catalysts under same conditions.

Lucas and Peres (2009) studied the treatment of OMW by Fenton's reaction with H₂O₂ and showed that the percentages of COD removal increased with increasing reaction time at all H₂O₂/COD ratios. Besides, they observed that COD concentration reduced when the temperature of Fenton's reaction was higher than 30 °C. The COD removal rate was approximately 70% and 65 % at 30 °C and 50 °C, respectively. Furthermore, Nogueira et al., (2015) indicated that with the biological treatment of OMW with fungi (*P. chrysosporium* and *P. sajor caju*) pretreated by photocatalytic oxidation, COD reduction rate increased with treatment time. In this study, they achieved COD removal rate between 10% and 50%.

TOC and COD abatements of OMW with respect to hydrothermal reaction temperatures and durations showed similar orientation with several studies in literature. Despite we obtained similar trend with studies in literature, in some cases we observed less COD removal even for longer reaction times. This might be arised from high dilution rates during COD analysis with high range COD kits. For each analysis, minimum 10 times of dilution was needed to remain within the range.

Observation of color change has an importance for wastewater treatment studies to visualize the degree of decolorization. In this content, photographs of raw material and all products were taken to analyze the color change of OMW, qualitatively. Representation of the effect of the reaction temperature and time on the removal of color is given in Figure 3.4, respectively.

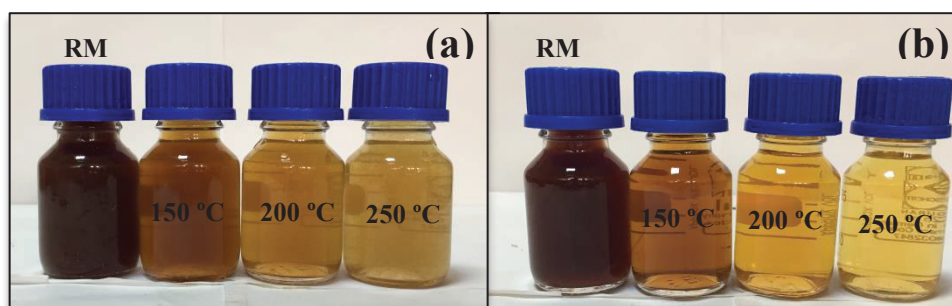


Figure 3.4. Pictures of raw material (RM) and products after treatment at 150, 200 and 250 °C at different reaction times of (a) 30 min (b) 120 min

In literature, researchers revealed that decolorization rate increased with increasing reaction temperature and time. For instance, azo-reactive dye was mineralized by ultraviolet irradiation in the presence of hydrogen peroxide and higher than 50% of color reduction was observed after a short reaction time of 10 min. Almost complete mineralization of azo dye was achieved after 20-30 min of irradiation with hydrogen peroxide (Georgiou et al. 2002). After 1 and 10 h of electrolysis by using Ti/Pt type anode and stainless steel 304 type cathode, 70 and 99.4% of color of non-cyanide strippers wastes was reduced, respectively (Vlyssides et al. 1999). On the other hand, Wu and Yu (2009) showed that color of C.I. Reactive Red 2 dye was reduced with increasing reaction temperature by both ultraviolet/TiO₂ and ultrasound/TiO₂ systems. Gomes et al. (2007) obtained complete color removal of OMW with the Pt/C catalyst after 8 h of catalytic wet air oxidation reaction.

The color reduction was changed linearly with both reaction temperature and time as expected. The lighter colors can be easily observed from Figure 3.4 while reaction temperature and/or reaction time were increasing. The reason of this linear trend was related to the physicochemical properties of water in subcritical reaction medium at different temperatures. The highest decolorization was observed at 250 °C and 120 min of reaction time.

Phenolate anions are formed as a result of dissociation of phenolic proton during the reaction of Folin Coicalteu reagent (yellow color) and phenolic substances exist in OMW. Then, formation of blue-colored compounds starts as a consequence of reversible one or two electron reduction reactions of Folin Coicalteu reagent and OMW (Roudsari 2009). Total phenolic content in OMW was measured with UV spectrophotometer at 725 nm wavelength and results were evaluated in Gallic acid equivalent (GAE). The effect of reaction temperature and reaction time is represented in Figure 3.6.

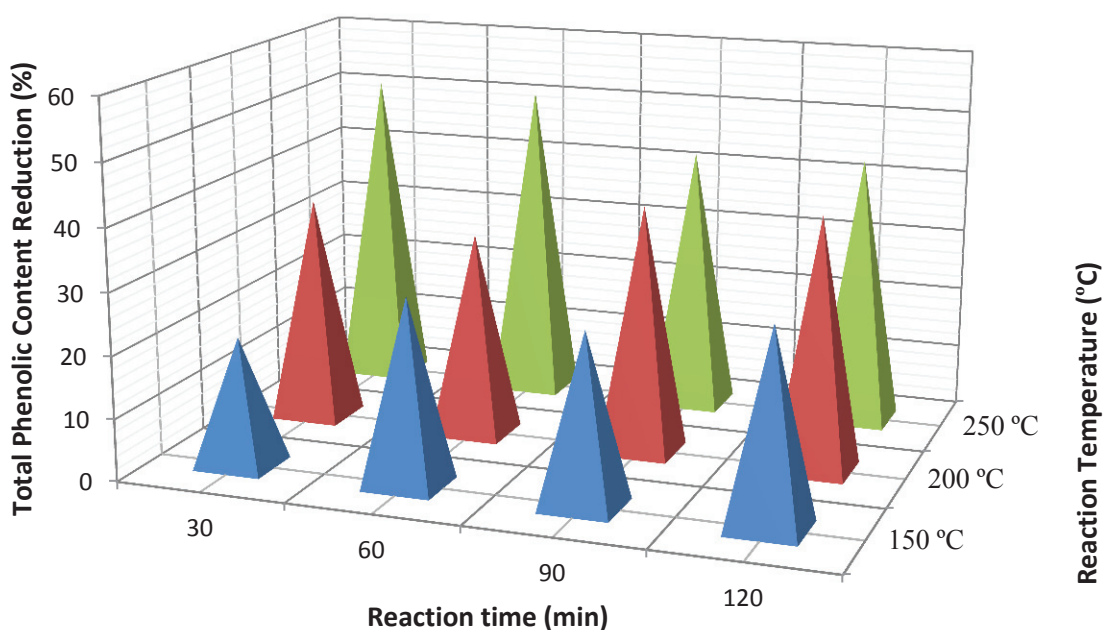


Figure 3.5. Total phenolic content reduction of OMW at various reaction temperatures (150-250 °C) and reaction times (30-120 min) without using H₂O₂

Katsoni et al. (2008) showed that the single effect of reaction temperature or reaction time was significant on the reduction of phenols in the study of wet oxidation of OMW. In our study, results showed the same trend with both reaction temperature and reaction time. In Figure 3.6, it was found that the TPC removal efficiencies in the OMW increased from 36.31% up to 40.66% as the reaction time was increased from 30

to 120 min at 200 °C. OMW includes high amount of phenolic compounds as mentioned before. Normally, the phenolic content of raw OMW is 58.45 mg GAE/L. However, at 30 min and 150 °C, the least reduction rate of phenolic content was observed. This reduction rate was about 20.69% which means that phenolic content decreased to 46.35 mg GAE/L from 58.45 mg GAE/L.

On the other side, the highest TPC reduction percentage of OMW in this study was 51.24% that was obtained after 30 and 60 min treatment at 250 °C. Results clearly showed that, removal rate of TPC were affected in direct proportion to reaction time. Higher reaction time was needed to obtain higher phenolic reduction of OMW. Besides, lower reaction temperatures led to higher TPC removal for longer reaction times.

The partial mineralization also can be observed by investigating the spectrum given below. As can be seen from Figure 3.7, the main compound was acetic acid. Acetic acid is derivative of carboxylic acid. As explained before, complex substances are transferred into these derivatives, if partial mineralization is observed (Path II). Therefore, existence of acetic acid peak in the spectrum, another way to understand occurrence of partial mineralization in the reactions.

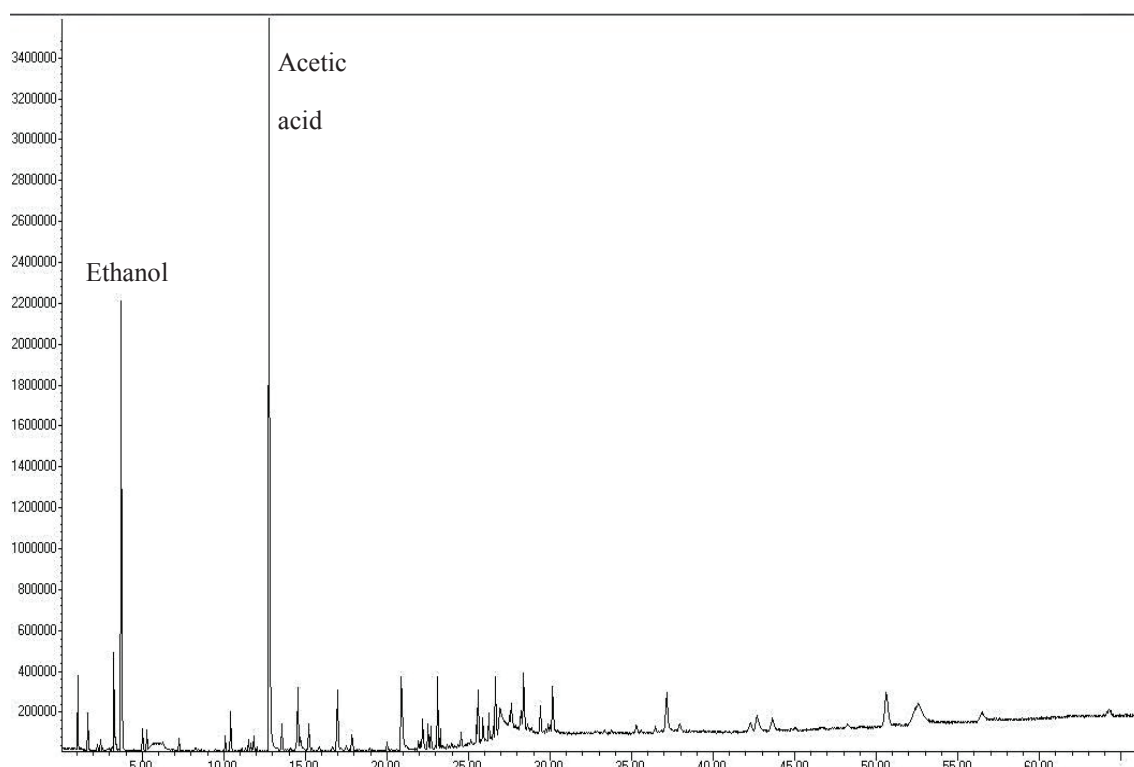


Figure 3.6. GC-MS spectrum of treated OMW with 120 min reaction time at 250 °C without using H₂O₂

When the products were analyzed by GC-MS, we did not observe any major peaks, except ethanol and acetic acid. Therefore, we can conclude that no secondary pollutants were generated during reactions of OMW in subcritical water medium.

3.2. Reactions with External Oxidizer

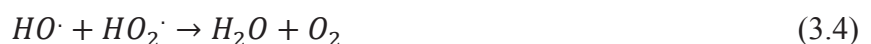
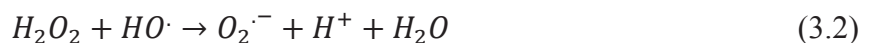
Hydrogen peroxide (0, 50, 100 mM) was used as an external oxidizer to investigate the effects of external oxidizer on the color removal efficiency in subcritical water medium.

It is clear that H_2O_2 decomposes to H_2O and $\frac{1}{2}O_2$ at room temperature and pressure. Both H_2O and $\frac{1}{2}O_2$ have not any degrading effect for wastewater treatment systems (Onwudili and Williams 2007).

Removal rate of TOC increases with temperature till optimum degree of reaction temperature is gained. Kayan and Gozmen (2012) were observed the increasing TOC reduction of Acid Red 274 with increasing temperature by using H_2O_2 in subcritical water medium until temperature was reached its definite grade. For instance, the researchers obtained 11.3 % and 54.60 % of TOC reduction with 100 °C reaction with 50 mM H_2O_2 , and 175 °C reaction with 150 mM H_2O_2 , respectively.

The lowest TOC and color reduction rates were observed at lowest reaction temperature and also at lowest reaction times that can be seen in Figure 3.8 and Figure 3.9. Otherwise, the effect of the H_2O_2 content on color removal of OMW was analyzed qualitatively and given in Figure 3.10.

While hydrogen peroxide is decomposing, highly reactive hydroxyl radicals ($OH\cdot$) are generated and then these reactive radicals attack the H_2O_2 molecules rapidly. After this attack, less reactive hydroperoxide ($HO_2\cdot$) radicals are produced as reactions given below (Kasiri and Khataee 2011, Behnajady et al. 2006, Gemeay et al. 2003, Aleboyyeh et al. 2003).



In a study of degradation of reactive red 120 dye by H_2O_2 in subcritical water medium by Daskalavi et al. (2011) as mentioned before, initially slow degradation was achieved because of the slow degradation of H_2O_2 . When their reaction systems were reached to experimental temperature, the degradation rate of azo dye was dramatically increased. Thus, H_2O_2 reached the activation energy barrier which it suddenly decomposed to hydroxyl free radicals.

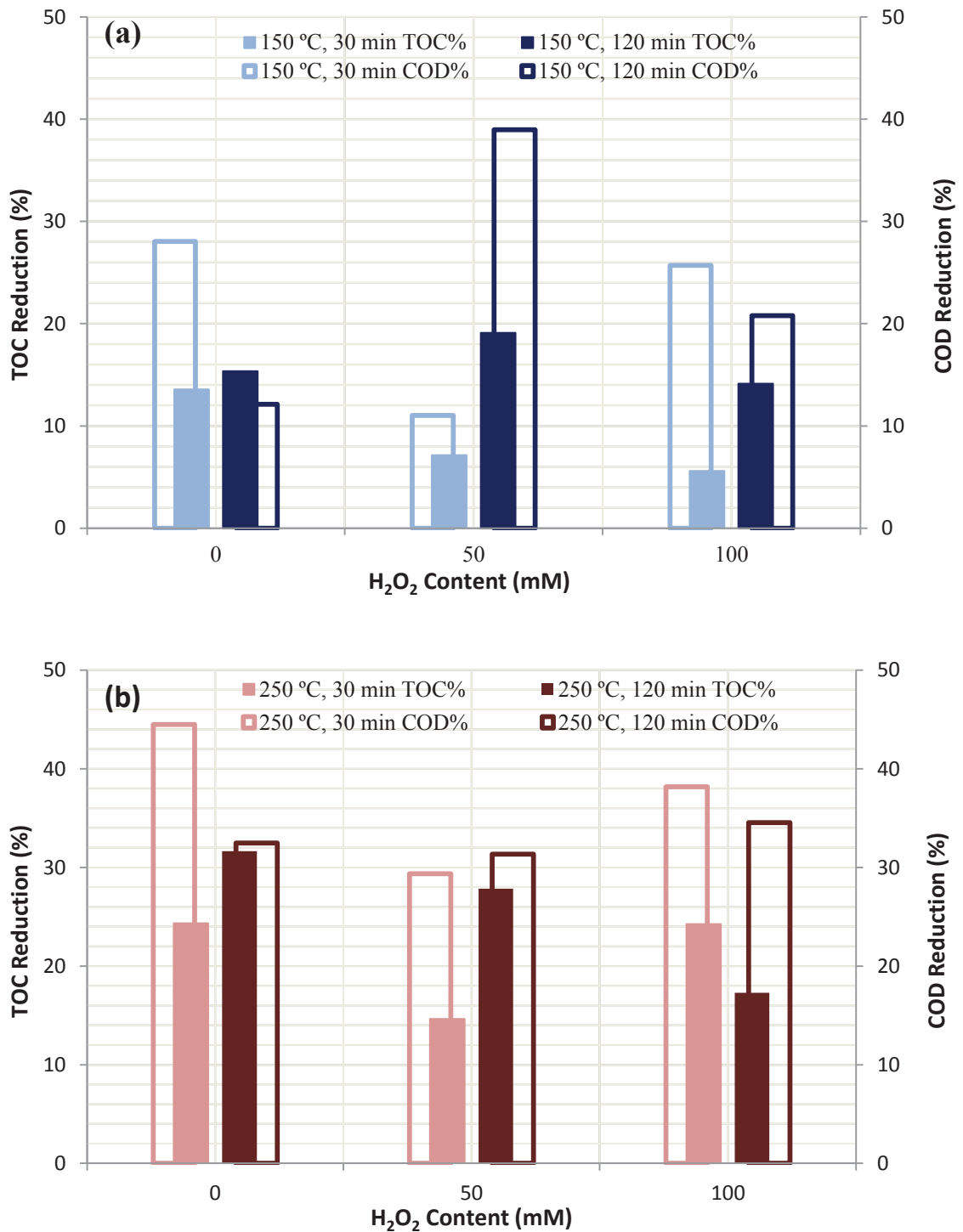


Figure 3.7. Effect of H₂O₂ concentration on TOC and COD removal rates at 30 and 120 min reaction times; (a) at 150 °C, (b) at 250 °C

Increment of the concentration of H₂O₂ benefits the generation of more OH· radicals, which are highly reactive and able to attack the complex substances. Therefore, degradation rate of processes increases. Unfortunately, hydroxyl radicals have a quite limited lifetime and they quickly reach equilibrium with H₂O₂. In this situation, H₂O₂ is

rather used more and $\text{OH}\cdot$ radicals react with H_2O_2 , and also generation of less reactive $\text{HO}_2\cdot$ radicals was observed. The reason for nonlinear trend of TOC, COD and color reduction of OMW in the presence of H_2O_2 can be explained by this situation (Kayan and Gozmen 2012).

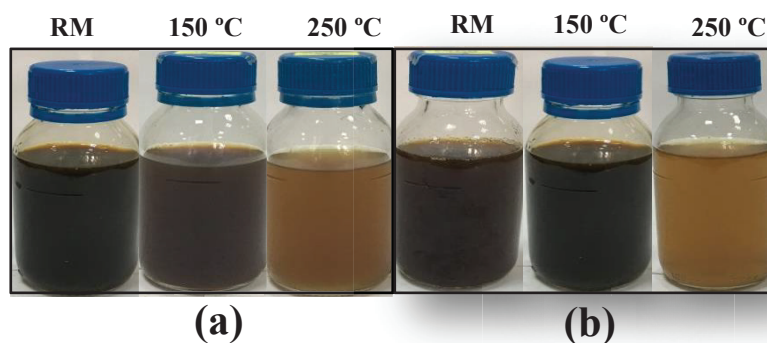


Figure 3.8. Qualitative analysis of raw material and products of 120 min reactions at 150 and 250 °C and with; (a) 50 mM H_2O_2 , (b) 100 mM H_2O_2

In this study, shorter reaction times lead to lowest degradation rates of OMW. At a reaction temperature of 150 °C and by using 50 mM H_2O_2 , the TOC reductions were 7.14% and 19.1% after 30 and 120 min, respectively. Besides, at 250 °C, color removal percentages of OMW by using 50 mM H_2O_2 were 79.61% and 97.95% for 30 and 120 min reactions, respectively. This situation can be explained by there was no required time to attack of highly reactive hydroxyl radicals ($\text{OH}\cdot$) to complex organic substances exist in OMW.

On the other hand, H_2O_2 decomposes to free radicals with increasing temperature, and higher temperatures can activate $\text{OH}\cdot$ radicals without using any activator by an unknown path as given below.



At 250 °C, both TOC and color removals were higher than that were at 150 °C. With the addition of 100 mM H_2O_2 , TOC rate were recorded as 5.6% for 30 min reaction time at 150 °C. When temperature was increased to 250 °C while keeping the other conditions same, the percentage of TOC removal increased to 24.25%.

The competition of hydroxyl free radicals by H_2O_2 and target molecules such as dye molecules has been revealed in literature (Rezaee et al. 2008, Laszlo 1994). According to studies, higher H_2O_2 concentrations than optimal H_2O_2 concentrations may result in lower removal rates. In this study, it can be understood that optimal H_2O_2 content was around 50 mM. For instance, TOC reduction rate of OMW after 120 min at

250 °C was 27.84% with 50 mM H₂O₂. However, when the concentration of external oxidant rose to 100 mM, the value was decreased to 17.3% at same reaction temperature and pressure. Furthermore, similar trend was observed for color removal efficiencies. Color of OMW for 120 min reactions at 250 °C was darker by using 100 mM H₂O₂ than reactions with 50 mM H₂O₂.

In the point of view of COD concentration removal, it can be said that lowest reaction time (30 min) leads to higher COD removal percentages. For example, with 50 mM H₂O₂ at 150 °C, the percentages of COD removal were 11.02% and 38.96% for 30 and 120 min reaction times, respectively. In other respects, higher degrees of COD removals were observed at reactions with higher temperature. With 100 mM H₂O₂, COD removal rate was 25.72% at a reaction temperature of 150 °C but it was 38.18% at 250 °C.

Table 3.2. Concentration of phenolic compounds in OMW at 150 and 250 °C reaction temperatures, 30 and 120 min reaction times, and with using various amount of H₂O₂ (0, 50 and 100 mM)

Reaction Temperature (°C)	Reaction Time (min)	H ₂ O ₂ Concentration (mM)	Total Phenolic Content (mg GAE/L)
150	30	0	46.36
		50	53.18
		100	40.00
	120	0	51.47
		50	41.55
		100	39.38
250	30	0	36.43
		50	39.53
		100	41.40
	120	0	42.17
		50	41.71
		100	40.93

Total phenolic content in OMW was not strongly affected by H₂O₂ addition as shown in Table 3.2. The total phenolic content of OMW before reaction was 74.73 mg GAE/L. After the treatment of OMW under different reaction conditions, TPC was

recorded between 36.43 mg GAE/L and 51.24% (30 min reaction, without using H₂O₂ at 250 °C). At same reaction temperature and duration, concentrations of phenolic compounds were 39.53 and 41.40 mg GAE/L with using 50 and 100 mM H₂O₂, respectively.

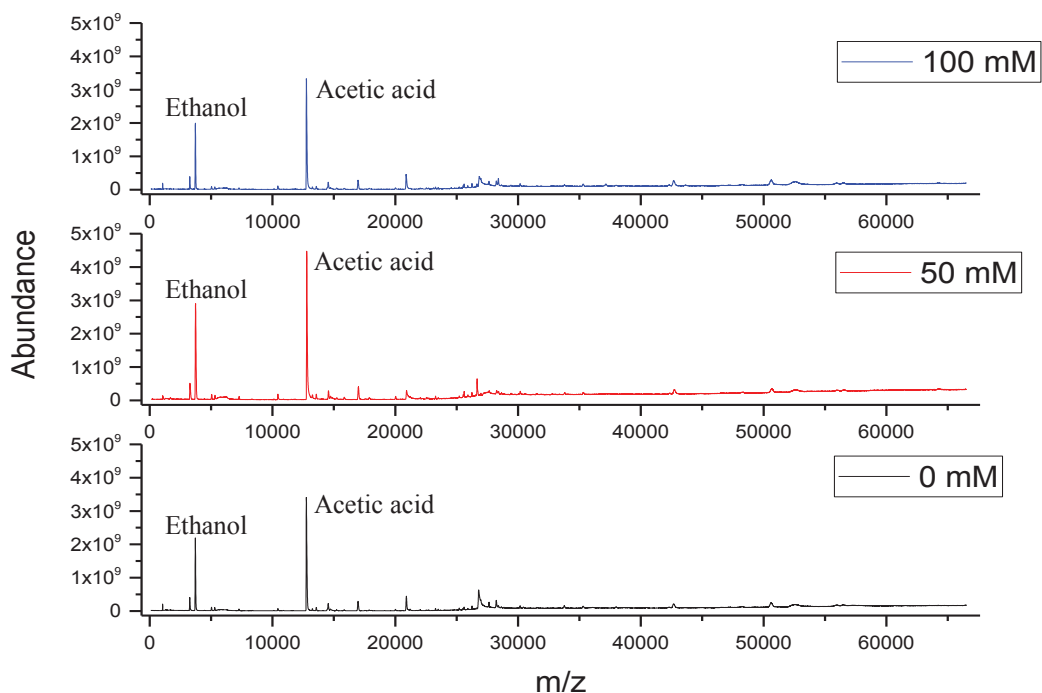


Figure 3.9. GC-MS spectrum of treated OMW at 150 °C and 120 min with 0 mM, 50 mM and 100 mM H₂O₂

Presence of hydrogen peroxide in the hydrothermal degradation of OMW did not generate any secondary pollutants and contributed the degradation of complex molecules. On the other hand, peak areas of acetic acid increased with using H₂O₂ in the reaction. Hence, the competition reactions could be occurred in reactions by using H₂O₂. Figure 3.11 shows the GC-MS spectrum of treated OMW with 120 min at 150 °C and in the absence of H₂O₂ and with the addition of 50 mM H₂O₂ and 100 mM H₂O₂. The percentage of peak area of acetic acid (second peak) increased from 48% to 59% when H₂O₂ content was increased from 0 to 100 mM, respectively. Furthermore, hydrogen peroxide content was not significantly affected the concentration of other substances. For instance, at 150 °C, the percentage of ethanol (first peak) was 5.72% and 4.43% with 50 mM and 100 mM H₂O₂, respectively.

3.3. Statistical Analysis

Significance of reaction parameters of reaction temperature, reaction duration and hydrogen peroxide content on the reduction of TOC was evaluated by Analysis of Variance (ANOVA) in Minitab. Experimental design was created in view of the fact that each experiment was repeated twice to provide accuracy of the study. Acceptable deviation is 95% in this study. Therefore, acceptable p values are nearly 0.05 or less than 0.05.

The p values of individual effects of reaction temperature, reaction duration and H₂O₂ content for percentages of TOC removal are 0.00, 0.07 and 0.001, respectively. According to results, it can be said that all reaction parameters affect TOC reduction rate significantly. Reaction temperature is the most significant reaction parameter on TOC removal in this study. It has been revealed previously in this chapter. The p value of reaction duration is a little higher than 0.05, but still it can be said that reaction duration affects the TOC removal. All these observations were shown graphically in Figure 3.10.

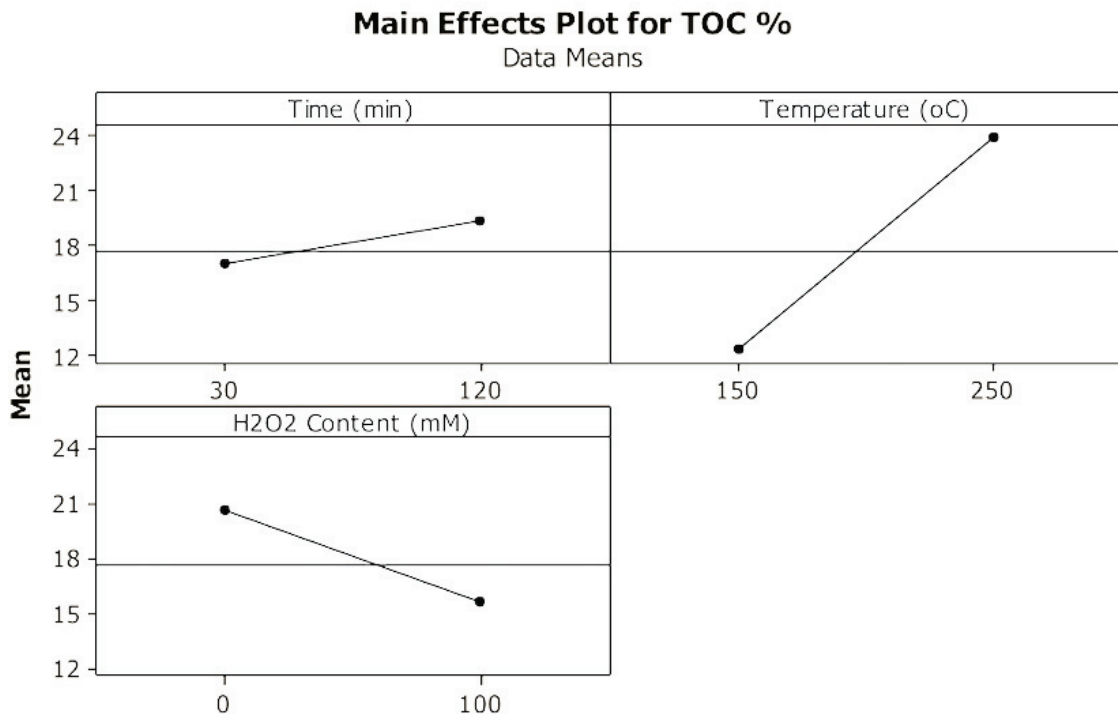


Figure 3.10. Main effects of reaction temperature, reaction duration and H₂O₂ content on TOC reduction

On the other hand, two way and three way interactions of reaction parameters on TOC removal were performed. Two way interactions of temperature-time and time- H_2O_2 content were found significant on TOC removal rate and p values are 0.027 and 0.0112, respectively. In contrast, multiple effect of temperature- H_2O_2 content was insignificant and p value of this interaction is 0.517. Interaction plots of reaction parameters and surface plots are given in Figure 3.11 and Figure 3.12, respectively. In interaction plots, parallel lines symbolize weak interactions while intersecting lines symbolize strong interactions. In the shade of this situation, it is easily said that two way interactions of temperature - time and time - H_2O_2 content were much stronger than two way interaction of temperature - H_2O_2 content.

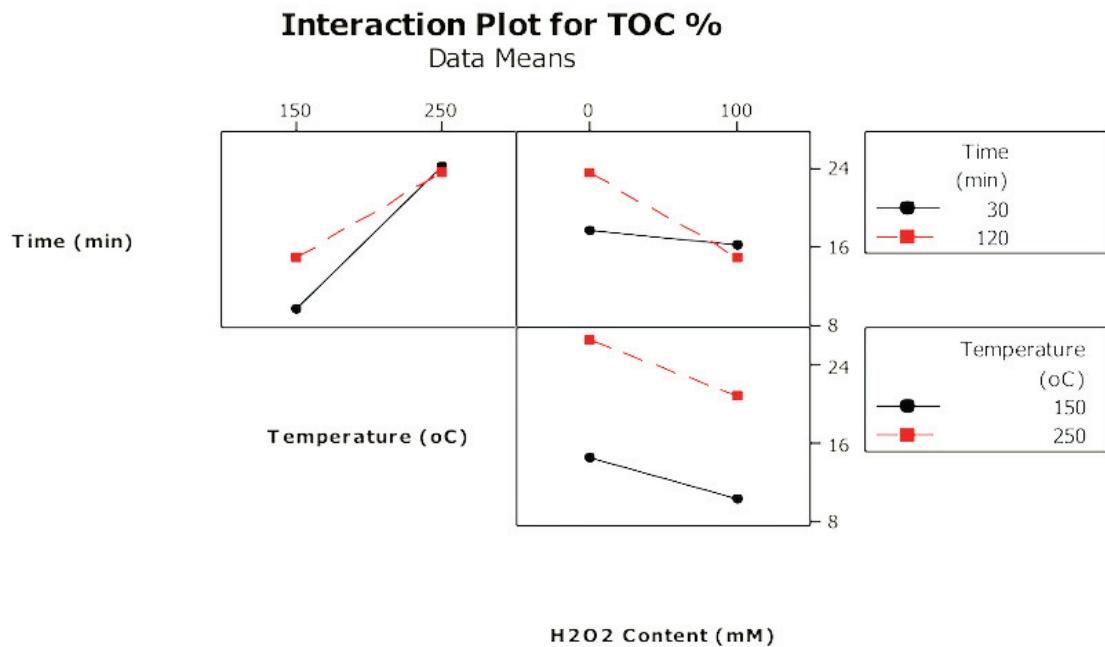


Figure 3.11. Interaction plots of reaction parameters on TOC reduction

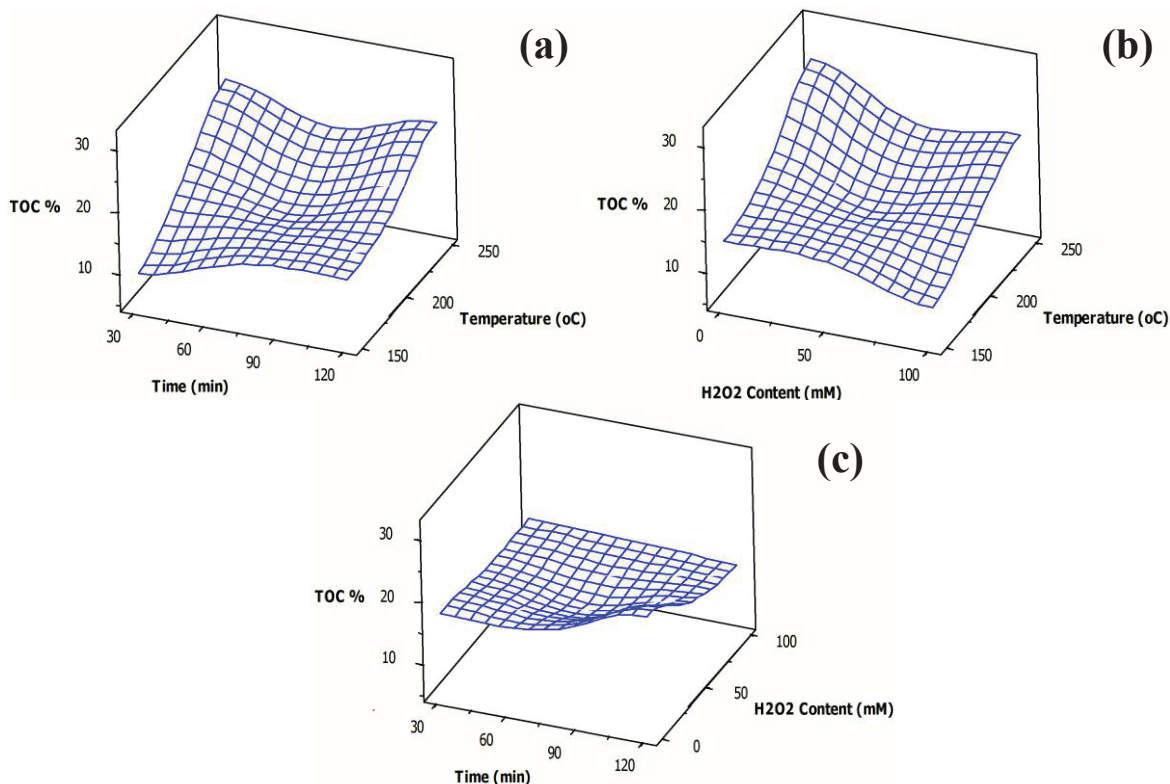


Figure 3.12. Surface plot of TOC reduction rate versus (a) temperature and time, (b) temperature and H₂O₂ content, (c) H₂O₂ content and time

Residual plots for normal probability and versus fits for the percentages of TOC reduction are given in Figure 3.13 and according to these plots it can be said that experimental data was normally distributed. In other respects, experimental and adjusted R² values were 94.21% and 90.17%, respectively. Also, predicted R² value was high and 86.87%. This means that, experimental data fit to the model equation.

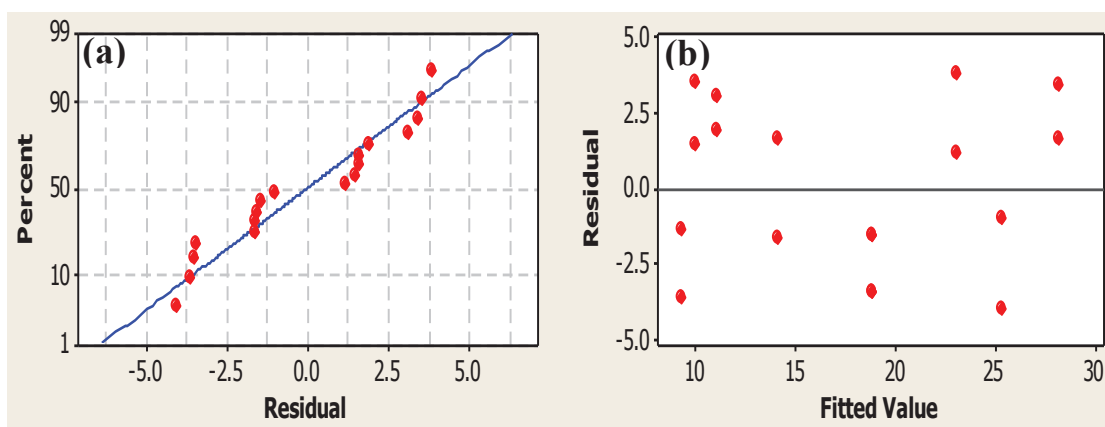


Figure 3.13. Residual plots for TOC reduction percentage (a) normal probability plot; (b) versus fits plot

CHAPTER 4

CONCLUSION

Hydrothermal degradation of OMW was performed under subcritical water by using batch type of reactor that consists of a magnetically driven stirrer, a pressure gage, a thermocouple, a safety disk, gas inlet and outlet valves and a U-tube heat exchanger. Reactions were carried out at different reaction temperatures (150, 200 and 250 °C), reaction durations (30, 60, 75, 90 and 120 minutes) and H₂O₂ concentration (0, 50 and 100 mM). Higher TOC, color and TPC reductions were observed by increasing reaction temperature and pressure. However, it was observed that presence of H₂O₂ was less effective on TOC reduction than the other parameters such as reaction temperature and time. This could be explained by the competition reaction medium among free radicals. On the other hand, coupled effects of reaction temperature - reaction duration and reaction time - H₂O₂ content were also found significant by performing of ANOVA analysis. The best yield in TOC removal (31.65%) was observed with 120 min reaction at 250 °C and without using H₂O₂.

The proposed study has advantages such as easy performing, no need to pH adjustment and any activator like metal ions and ozone, easy setup of batch reactor. In addition to them, in this study subcritical water was used as a reaction environment, which is a green solvent, and by this technique, almost complete decolorization was achieved. In contrast, partial mineralization was observed by this study so any alternative catalyst or higher reaction temperatures (up to 374 °C) and reaction durations could be preferred to increase the mineralization rate of OMW.

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