Feasibility study of using UV/H₂O₂/O₃ advanced oxidation in phenol removal from petrochemical wastewater

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GRAPHICAL ABSTRACT
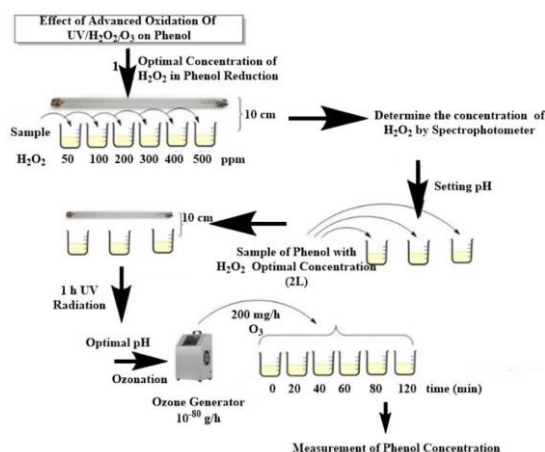
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ABSTRACT

Pollution from industrial effluents is more diverse and complex than municipal wastewater due to the use of thousands of new chemical compounds in industry every year. Subsequent introduction of small quantities of these compounds into water streams through industrial effluents has complicated water pollution problems and posed many challenges in removing contaminants from water. The purpose of the present study was to remove phenol contaminants from the effluent of petrochemical wastewater treatment plants using advanced photochemical oxidation method (ultraviolet/hydrogen peroxide/ozone) in a laboratory scale. The experiments were performed using UVC light, 30 % H₂O₂ as oxidizer and phenol (100 mg/L). The effective parameters studied in phenol removal included pH, H₂O₂ concentration, solution temperature and UVC irradiation time. The experimental results showed an increase in phenol removal efficiency with increasing H₂O₂ concentration up to 400 mg/L while decreasing with increasing oxidizer concentration to 500 mg/L, thus suggesting a concentration of 400 mg/L as the optimal value. Using a flow rate of 200 mg/L of ozone for 80 min, by optimizing other conditions, increased the phenol removal efficiency by 98 %. The phenol removal efficiency was much higher at acidic conditions than at alkaline and neutral ones. The phenol content decreased significantly with increasing contact time. In other words, prolonged contact time increased the phenol removal efficiency in the tested sample. The highest phenol removal efficiency (75.7 %) occurred at the pH value of 4 and the phenol removal efficiency in the sample decreased with increasing pH value. Prolonged contact time caused more phenol concentration to be removed from the test sample, so that 69.8 % of the phenol concentration in the sample was reduced. The results of this study showed that advanced oxidation reduced the phenol content in the analyzed sample. To conclude, the advanced oxidation methods can be useful in the process of treating petrochemical wastewater and effluent of units containing toxic aromatic compounds such as phenol.

1. Introduction

Wastewater is one of the leading sources of environmental pollution that must be collected, treated and returned to the water cycle in nature through hygienic methods (Gooran Ourimi & Nezhadnaderi. 2020: Mohammadi Aloucheh et al. 2019). Groundwater contamination due to fuels and other petroleum hydrocarbon derivatives released from oil storage tanks is a common and serious environmental concern

(Muhibbu-din and Ayodele, 2021; Nikpour et al. 2021). These compounds often contain Benzene, Phenol, Toluene, Ethylbenzene, and Xylene isomers, as well as whole petroleum hydrocarbons, which have been shown to be highly hazardous with high toxicity and bioaccumulation potential (Huntleya et al. 2002; Pinheiro et al. 2017).

The oil industry is developing rapidly and is projected to grow even faster in the coming years. Recent environmental activities and global requirements for cleaner methods have led oil refineries to use green techniques and industrial wastewater treatment. Petroleum industry effluents contain a wide variety of pollutants such as petroleum hydrocarbons, oils and greases, Phenols, Ammonia, Sulfides and other organic composites, all of which are present in petroleum industry effluents in a very complex form with harmful effects on the environment (Raza et al. 2019; Mahmoodi et al. 2022).

Phenol, or Hydroxybenzene, is a toxic aromatic compound that is resistant to biological treatment (Azizah and Widiasa. 2018; Hazrati et al., 2019). Most organic compounds are resistant to conventional chemical and biological treatments. Therefore, other alternative methods are being consideration. Several methods are available for the treatment of phenol-containing wastewater. Chemical oxidation is one of the techniques used for wastewater treatment, which can be classified into two types of conventional chemical treatment and advanced oxidation processes (AOPs) (Almomani et al. 2016; Shaykhi Mehrabadi. 2016; Habibi et al. 2017). The conventional systems for the treatment of wastewater from petroleum industries have major disadvantages such as low efficiency and high capital and operating costs. The AOP is one of the methods used for the treatment of wastewater in oil industries (Karimipour et al. 2021).

Ozone (O_3) alone is incapable of a complete oxidation of some organic compounds and has a low reaction rate (Rekhate et al. 2020). Thus, the AOPs are one or a combination of multiple processes such as O_3, hydrogen peroxide (H_2O_2), ultraviolet (UV) radiation, Titanium oxide (TiO_2) as a photocatalyst, Fenton process, as well as several other processes capable of producing hydroxyl radicals (Gottschalk et al. 2010). Shokohi et al. (2009) and Yang et al. (2009) reported that the H_2O_2 alone, as an oxidizer, has little removal efficiency. The combined use of UV radiation and a suitable oxidizer such as H_2O_2 is one of the most effective AOPs, especially in the removal of organic pollutants resistant to biodegradation (Jamshidi et al. 2009). This method is based on the oxidation of pollutants by the in situ formation of hydroxyl radical (°OH), as a strong oxidizer (E_0 = 2.8 V) (Laine et al. 2007). Various oxidants such as O_3 and H_2O_2 are able to generate hydroxyl radicals in water. These radicals are able to eliminate organic pollutants in water and wastewater (Stasinakis. 2008). The generation of hydroxyl radicals can be facilitated by UV irradiation, the addition of some metal ions, and so on. Consequently, many efforts have been made to study various combinations of oxidants and stimulants such as UV/H_2O_2, O_3/H_2O_2, O_3/UV, $O_3/H_2O_2/UV$.

In the UV/H_2O_2 advanced oxidation processes, the mechanism of action of UV is based on the introduction of energy into chemical compounds, which is absorbed by reactive molecules and is able to pass through excited sites, leading to the progression of reactions over a sufficient period of time (Bustillo-Lecompte et al. 2018). During the AOP, this photon is adsorbed by H_2O_2 and the photon absorption by the molecule separates it into two hydroxyl radicals (Movahedian & Rezaei. 2006). Hydroxyl radicals have a short life span, high oxidizing power and are prone to oxidation of organic compounds mainly through hydrogen capture. This process leads to the generation of organic radicals that react with oxygen to form peroxyl radicals (ROO°). This intermediate initiates a series of chain reactions, eventually producing CO_2 and H_2O and mineral salts. The advantages of the UV/H_2O_2 process include commercial accessibility, no sludge production and high capacity in degradation of biodegradable compounds (Lapertot et al. 2006). Borjani et al. (2010) investigated the performance of advanced oxidation in the removal of phenol from the effluents of oil depots and refineries using UV/H_2O_2 via 15-W ow pressure mercury lamp with a concentration of 20 mg/L). They showed that phenol contaminant had the highest removal efficiency, but due to the use of UV alone, the degradation and removal efficiency of the contaminant could be neglected. Poulopoulos et al. (2006) investigated the efficacy of AOPs versus alkylphenols in groundwater samples. Their results revealed that direct photolysis of phenol and its oxidation by H_2O_2 (without UV light) was negligible, but the combination of UV and H_2O_2 was very effective in phenol degradation. Azizah and Widiasa (2018) employed two methods of H_2O_2/UV and $H_2O_2/UV/O_3$ in the study of AOPs for refinery wastewater treatment containing high concentrations of phenol. Better phenol removal result was obtained using $H_2O_2/UV/O_3$ process with H_2O_2 concentration of 1000 mg/L, so that the phenol concentration was 37.5 mg/L with a Phenol degradation rate of 93.75 % after 120 min.

Sharma et al. (2015) investigated the degradation and mineralization of Bisphenol A (BPA) in aqueous solution using AOPs of UV/H_2O_2 and UV/S_2O_8-oxidation systems. The BPA at a concentration of 0.22 mM in aqueous solution using inorganic oxidants (H_2O_2 and sodium persulfate) under UV irradiation at 254 nm with a power of 40 W at the natural pH and at 29 ± 3 °C and an optimal persulfate concentration of 1.26 mM showed that the process led to the removal of about 95 % BPA after 240-min irradiation. The optimal removal of BPA was about 85 % with H_2O_2 concentration of 11.76 mM. At greater concentrations, each of the oxidants had an adverse impact due to the quenching of hydroxyl or sulfate radicals in the BPA solution.

Almasi et al. (2016) investigated the removal of phenol from aqueous solutions contaminated with phenolic compounds using H_2O_2, persulfate and periodate activated by ultrasound with a frequency of 40 kHz. Their study variables were molar concentrations of H_2O_2 (0.004-0.1 $M.L^{-1}$), persulfate (0.001-0.005 $M.L^{-1}$) and periodate (0.001-0.005 $M.L^{-1}$) in different contact times at various pH values (3, 7 and 10) and the effect of changes in the ionic strength in the contact times. They showed that increasing the concentration of oxidizer significantly elevates the removal efficiency and then a downward trend in phenol removal. The optimized concentration of H_2O_2, persulfate and periodate were selected as 0.1 $M.L^{-1}$, 0.003 M and 0.004 M respectively. Analysis of different pH values indicated that all three processes had the highest removal efficiency at the pH value of 3 and the ionic strength decreased the ultrasound/persulfate process efficiency and had no influenec on the other processes.

Shokoohi et al. (2009) compared advanced oxidation processes for phenol degradation in the laboratory scale using a 125-W UV lamp with an ozone content of 1 $g.h^{-1}$. Their results revealed that phenol could be degraded by ozonation at the pH value of 11 and UV radiation at the pH value of 5. The phenol degradation using UVC lamp after one hour of contact time was 32.4 %, while during the same period and using ozonation method reached 93.6 %.

Movahedyan et al. (2009) compared the effect of two advanced oxidation methods of UV/H_2O_2 and microwave/H_2O_2 on the phenol removal from aqueous solution, and found that the oxidation rate depended on factors such as pH, H_2O_2 concentration and irradiation time.

Ghaly et al. (2001) found that the degradation rate of phenol was significantly accelerated by the photochemical oxidation process. They reported that the UV/H_2O_2 process had the highest degradation and photochemical removal rate of phenol compared to other advanced oxidation processes. Examination and comparison of the application of AOPs in phenol removal from wastewater clarified that the phenol removal rate depends on factors such as pH, H_2O_2 concentration and contact time. In this study, UV/H_2O_2 and US/Fenton methods were proposed as desirable processes with high efficiency in phenol removal from wastewater of chemical and petrochemical industries. In a study, the effect of using UV/H_2O_2 advanced oxidation method in phenol removal revealed that this method can remove phenol with 100 % efficiency at alkaline pH (Kidak & Ince. 2007). The findings revealed that the phenol degradation reaction is improved in alkaline environment (Yang et al. 2009). This can be attributed to the presence of more hydroxyl ions in the aqueous solution, which generate more hydroxyl radicals (Ta et al. 2006).

The Olefin Unit of Tabriz Petrochemical Company, which is located in the northwest of Iran, is the parent unit of this company. This unit is the main source of phenol introduction to petrochemical wastewater. Phenol is formed in the water sources of Olefin Unit in such a way that sour water is obtained from DLS condensation, which is used to produce DLS vapor again after the stripping stage. To prepare water vapor diluent, sour water is taken from the bottom of stripper tower 154 and sent to vessel 152. The blowdown flow (concentrated sour water) of vessel 152 of the Olefin Unit is called phenolic water, which contains phenol and other hydrocarbons. Therefore, due to the presence of high quantities of phenol in petrochemical effluents, the present study aimed to determine the optimal conditions to achieve the highest efficiency of phenol removal from petrochemical industry effluents via advanced oxidation processes using H_2O_2 and UV irradiation.

2. Materials and methods
2.1. Chemicals and equipment

The current experimental study was conducted in Winter 2022 in the Chemistry Laboratory of Islamic Azad University, Ardabil Branch, Iran. The materials used in this research as following: Phenol, HCl, NaCl and H_2O_2 30 % (all material are from Merck). Also devices and equipment used in this study to remove phenol and measure phenol content before and after removal processes are listed as following: pH meter (Metrohm), Jar test (SETA), UV lamp (125-W UV lamp by Philips,

Netherlands), Spectrophotometry (PG Instruments) and Ozonizer (Ozoneab Company). The preparation method of materials and reagents using phenol and chlorine-free distilled water was as follows: 1- Ammonium 0.5 N hydroxide: 35 mL of ammonium hydroxide was taken and reached a final volume of one liter. 2- Phosphate buffer solution: 104.5 g of K_2HPO_4 and 72.3 g of KH_2PO_4 were dissolved in distilled water and reached the final volume of one liter (pH of this solution should be 6.8). 3-4-aminoantipyrine solution: 2 g of 4-aminoantipyrine was dissolved in distilled water and reached a final volume of 100 CC. 4- Potassium Ferricyanide solution: 8 g of $K_3Fe(CN)_6$ was dissolved in distilled water and reached a final volume of 100 CC.

2.3. Experimental

This study evaluated the effect of advanced oxidation of $UV/H_2O_2/O_3$ on the concentration of phenol spiked in demineralised (DM) water (100 mg/L). The experiments were designed to reduce the phenol content by considering factors including H_2O_2 concentration, pH, contact time, UV irradiation time and ozone injection dose. First, the optimal concentration of H_2O_2 in phenol reduction was identified, so that sampling was done from different pre-prepared concentrations of H_2O_2, and then the phenol content was obtained by spectrophotometry. In the presence of the optimized concentration of H_2O_2 (as a constant variable), the levels of the other two factors (random variables) were applied to the sample in triplicate, followed by measuring different levels of pH and contact time.

The optimum H_2O_2 concentration was determined using a jar test apparatus in which a UVC lamp was used instead of a conventional lamp. Thus, the sample was poured into the beakers of the Jar test apparatus and the H_2O_2 concentrations of 50, 100, 200, 300, 400 and 500 mg/L were calculated and spiked into the beakers, followed by UV lamp irradiation for one hour. This test was repeated three times and phenol reduction values were measured.

After determining the optimal concentration of H_2O_2, two liters of the sample was poured into each of the laboratory beakers (n=9) and the optimized H_2O_2 concentration was applied to each beaker. Then, different pH values were adjusted in beakers using NaOH 1N and HCl 0.5N solutions. After adjusting the pH, the beakers were placed under a hood measuring 150 × 100 cm and a UVC lamp was positioned at a distance of 10 cm from the beakers. The hood was covered via aluminum foil to prevent the UVC rays from coming out and returning, which means optimal operation of the lamps. During the experiment, the solution inside the beakers was stirred by an electric stirrer at a uniform speed. After optimizing all the mentioned parameters, the ozone injection dose was evaluated and sampling of beakers was performed at the specified contact times.

The Ozone generator used in this research could be operated in two modes of ambient air inlet and oxygen capsule. In this study, the ambient air inlet protocol was implemented to produce ozone so that the production rate was 10 to 80 g.h^{-1} with an inlet pressure of 1 bar. By installing a flowmeter in the ozone generator, the amount of ozone input to the analyzed sample was reduced by 200 **mg/L**. According to the mentioned operating conditions, in which the effective parameters were optimally installed, the tube related to the ozonation device was placed inside the contents of the beakers in such a way that the whole volume of material was ozonated. The ozone generator set, the relevant fittings and the test cylinder were placed under the hood with laboratory

conditions (22-25 °C) in to perform ozone depletion and emissions according to safety recommendations. Then, the ozone generator was turned on and ozonation started. The ozonation was performed for similar samples for 20, 40, 60, 80 and 120 min. At the end of the time allotted to each of the beakers, sampling was performed and the amount of phenol remaining in the samples was measured.

The method of measuring phenol reduction in spectrophotometry was that 100 mL of the sample was taken and poured into a 250-mL flask. In another flask, 100 mL of distilled water was poured as a control, and any operation performed on the sample was repeated for the control. Then, 2.5 mL of NH_4OH 0.5 N was added to the solution and the next step was performed immediately. Immediately, the pH value was adjusted to 7.9 ± 0.1 with phosphate buffer, followed by adding 1 mL of 4-Aminoantipyrine reagent and mixing thoroughly. One mL of Potassium Ferricyanide was added and stirred. After 15 min, the optical density (OD) was read by UV / Vis Spectrometer at 500 nm versus the control.

3. Results and discussion
3.1. Determining the optimal conditions for phenol removal using H_2O_2

Table 1 presents the results of the effect of different concentrations of H_2O_2 to determine the optimal conditions for phenol removal after one hour of exposure to this oxidizer. By increasing the oxidizer concentration to 400 mg/L, the reaction rate and the removal efficiency of phenol increased so that this concentration decreased the phenol content from the initial 100 mg/L to 43 mg/L. However, increasing the H_2O_2 concentration to 500 mg/L decreased the phenol removal efficiency. Therefore, the H_2O_2 concentration of 400 mg/L was considered as the optimal condition for the phenol removal.

Table 1. Mean Phenol concentration under different H_2O_2 concentrations within one hour

H_2O_2 concentrations, mg/L	Mean phenol concentration, mg/L
0	100
50	88
100	75
200	63
300	52
400	43
500	50

It seems that the increase in phenol removal efficiency with increasing H_2O_2 concentration up to 400 mg/L was due to the better effect of UV waves on the oxidizer at this concentration and the production of hydroxyl radicals, which play an important role in the oxidation of organic matter. In other words, increasing the H_2O_2 concentration to 400 mg/L had increased the production of hydroxyl radicals in the same proportion, which is itself a factor for further oxidation of organic matter. The reason for phenol removal rate deceleration at concentrations greater than 400 mg/L can be attributed to the inverse effect of the oxidizer at high concentrations on the removal rate of organic matter. In other words, H_2O_2 acts as a free radical scavenger at high concentrations and reduces the free radical concentration (Jamshidi et al. 2009). Fig.1 shows the trend of changes in phenol removal efficiency by applying different H_2O_2 concentrations.
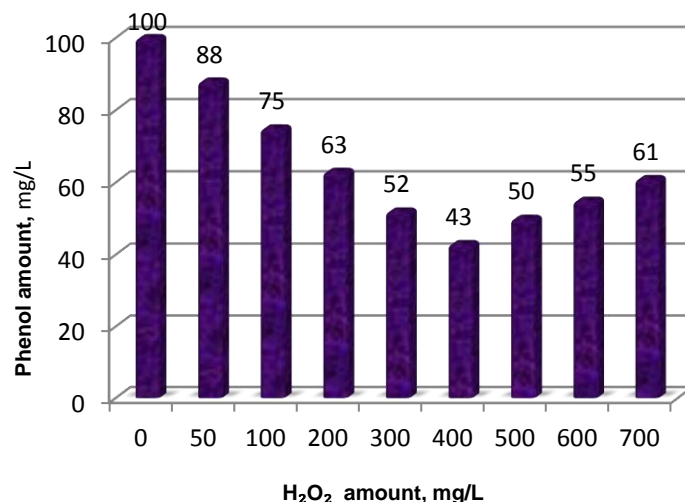

Fig. 1. Phenol removal efficiency in different H_2O_2 concentrations.

3.2. The effect of pH and contact time

The injection of 400 mg/L of H_2O_2 at different times and pH demonstrated a significant effect of pH and contact time on phenol concentration. The rate of chemical reactions depends on the pH of the environment, and pH directly and indirectly affects the oxidation of materials. In the chemical oxidation reactions, pH also influences the oxidation efficiency by affecting the production of hydroxyl radicals (Rahmani et al. 2015; Asgari et al. 2013).

The results of this experiment revealed that the highest (49.2 mg/L) and the lowest (24.3 mg/L) phenol concentrations belonged to pH values of 10 and 4, respectively, the results of which are shown in Table 2 and its schematic in Fig. 2.
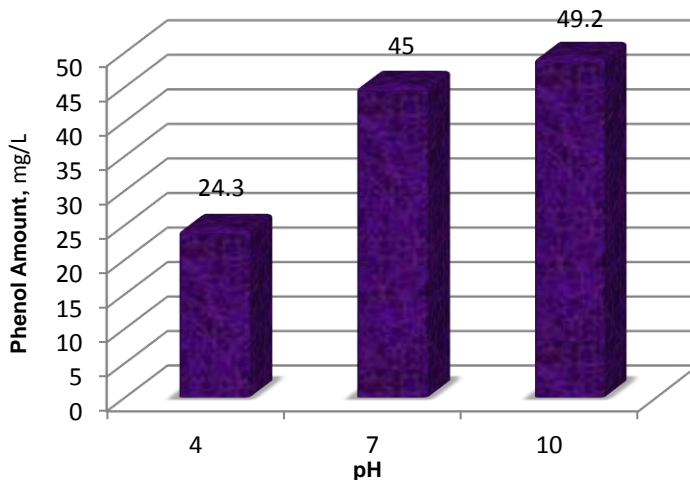

Fig. 2. Phenol removal efficiency at the H_2O_2 concentration of 400 mg/L at different pH values.

In other words, the removal efficiency of organic matter is relatively higher at acidic pHs than at alkaline and neutral ones (Yang et al. 2009; Shokohi et al. 2009). This increase in phenol removal efficiency in acidic pH medium can be attributed to the possibility of better absorption of UV waves by phenol in these conditions. The efficiency of the UV/H_2O_2 chemical oxidation process decreases under the influence of reducing compounds such as carbonates under alkaline conditions. At acidic pH, the invasive effect of H^+ on $OH°$ is much greater than OH on $OH°$. In addition, at acidic pHs, CO_2 is released as a gas from the water environment, while the formation of factors such as carbonates in an alkaline environment causes the destruction of hydroxyl radicals (Azizah and Widiasa. 2018). Appropriate reaction time is one of the effective factors in performing AOPs. Over time, the amount of intermediate products due to H_2O_2 degradation increases and eventually the production of hydroxyl radicals in the environment increases and thus the efficiency of the process increases. In this experiment, prolonging the contact time significantly reduces the phenol concentration in the effluent, the results of which are shown in Table 3 and Fig. 3, so that the lowest concentration of phenol (30.2 mg/L) belonged to two hours of contact time and the highest concentration of phenol (48.7 mg/L) was obtained under 30 min of contact time. In other words, prolonging the contact time increases the removal efficiency of phenol in the effluent. Stepnowski et al. (2002) investigated the photo-degradation of 1, 2-Dichloroethene (1,2-DCE) at concentrations of about 200 g.L^{-1} of petroleum refinery wastewater and found that a very long contact time of 3-24 h is required to remove all contaminants. Moreover, the combination of UV radiation with H_2O_2 improved the 1,2-DCE degradation compared to H_2O_2 alone.

Table 2. Effect of pH on phenol removal efficiency under H_2O_2 concentration of 400 mg/L

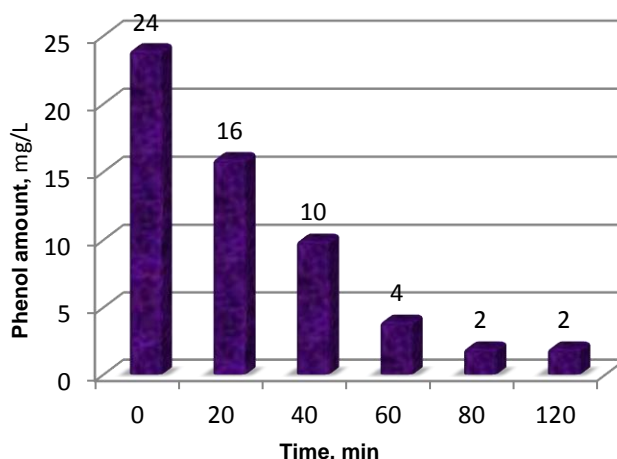| Phenol concentration (mg/L)	pH
24.3	4
45	7
49.2	10

Fig. 3. Phenol removal efficiency at the H_2O_2 concentration of 400 mg/L at different contact times.

3.3. The effect of ozone injection on phenol removal

At this stage of the experiments, since all the optimal test conditions were obtained, including pH, contact time, H_2O_2 concentration, these were adjusted in vitro to find the optimal dose of ozone injection for maximum phenol removal efficiency. Table 4 presents the optimal dose of ozone injection and Fig.4 shows the trend of changes in phenol concentration due to changes in ozone injection time. According to Table 4 and Fig. 4 which shows the maximum phenol removal efficiency using Ozonation to the test sample, it can be said that the Ozone injection dose with a flow rate of 200 mg/L for 80 min removed almost all the phenol in the sample. Based on the findings of these experiments, which reveal the optimal state of materials and tests, the advanced oxidation method of UV/H_2O_2/O_3 is the most suitable approach for removing Phenol from water and wastewater. This is because the simultaneous use of ozone and UV irradiation increases the production rate of hydroxyl radicals (Stasinakis. 2008). Zaribafan et al. (2017) investigated the effectiveness of three AOP methods including Fe^{2+}/H_2O_2/UV (Photo-Fenton), O_3/UV

and $O_3/UV/H_2O_2$ to remove alkyl phenols from groundwater sources under optimized conditions. The O_3/UV method with the removal efficiency of 84.16 % showed the best results. Miklos et al. (2018) observed that ozonation produced the best removal results against alkyl phenols in contaminated drinking water. However, it is important to note that the inherent differences between real samples require the achievement of optimization in the form of pilot studies prior to large-scale implementation (Krishnan et al. 2016).

Table 3. Effect of contact time on phenol removal efficiency under H_2O_2 concentration of 400 mg/L.

Phenol concentration, mg/L	Contact time, h
48.7	0.5
43	1
30.2	2

Table 4. Effect of ozone injection time on phenol removal efficiency under optimal operating conditions.

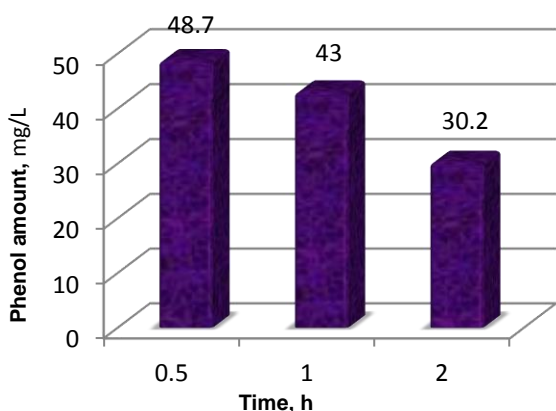| Phenol concentration, mg/L	Ozone injection time, min
16	20
10	40
4	60
2	80
2	120

Fig. 4. Phenol removal efficiency at different Ozone concentrations.

3.4. The phenol removal efficiency

Table 5. presents the effects of solution pH, contact time, H_2O_2 concentration and O_3 injection dose on phenol removal efficiency within the $UV/H_2O_2/O_3$ processes. It should be noted that the initial concentration of phenol prepared was 100 mg/L. The highest phenol removal efficiency (75.7 %) occurred at the pH value of 4 and the phenol removal efficiency in the sample decreased with increasing pH value.

Table 5. Removal efficiency of phenol tested under different experimental conditions

Experimental conditions	Test levels	Phenol removal percentage
pH	4	75.7
	7	55
	10	51.8
Contact time	0.5	51.3
	1	57
	2	69.8
H_2O_2 concentration	100	25
	300	48
	400	57
O_3 concentration	40	90
	60	96
	80	98

Prolonged contact time caused more phenol concentration to be removed from the test sample, so that 69.8 % of the phenol concentration in the sample was reduced at the contact time of 2 hours. Shokouhi et al. (2009) also found that the removal efficiency increased with prolonging the time of the advanced oxidation process using O_3 and elevating the exposure time in the UV irradiation method; in the advanced oxidation method using O_3, the best removal efficiency (93.6 %) was obtained at alkaline pH of 11, contact time of one hour and phenol concentration of 50 mg/L. In addition, the highest removal efficiency by UV irradiation method (32.4 %) was obtained under acidic

conditions (pH=5) during one hour of exposure and phenol concentration of 50 mg/L.

The highest phenol removal efficiency in the use of H_2O_2 was related to the H_2O_2 concentration of 400 mg/L, which was the most optimal condition and exhibited a removal efficiency of 57 %. The O_3 also eliminated 98 % of the phenol in the sample in the best possible case.

Mokrini et al. (1998) attempted to decompose phenol in aqueous solutions using advanced oxidation by O_3/H_2O_2 mechanism. They were able to remove 70 % of phenol by applying the contact time of 60 minutes, the pH value of 4.9, the H_2O_2 concentration of 0.319 mol.L^{-1} and the O_3 injection dose of 0.2-0.3 g.h^{-1}. Compared to the results of experiments performed in this study (98 % removal of phenol), while having a lower removal efficiency, it also used H_2O_2 simultaneously.

Splugas et al. (2002) succeeded in removing 100 % phenol in a batch reactor using advanced oxidation with O_3 mechanism and considering the flow rate of 2.5 L, the initial phenol concentration in the range of 93 to 105 mg/L, the contact time of 80 min and the pH value 9. Compared to the results obtained in the present study, their protocol is more efficient but requires more contact time. Using UV irradiation, the initial phenol concentration in the range of 93 to 105 mg/L, the contact time of 80 min and the pH value of 4, they managed to remove 24.2 % of phenol. Compared to the results obtained in this study (75.7 % phenol removal), while spending more contact time, they achieved lower removal efficiency.

4. Conclusions

Biological wastewater treatment systems may be disrupted for a variety of reasons such as toxic compounds, hydraulic activity, organic shock loads, operational interruptions and holidays, in which case achieving proper efficiency is time consuming and will result in economic losses. In biological treatment ponds, phenol acts as a toxin for microorganisms, which imposes shock and disrupts the biological treatment of wastewater. Due to the destructive and toxic effects of phenol on the activity of microorganisms in biological ponds and inhibiting their growth and spread, it is necessary to provide a suitable method to reduce the concentration of phenol and total hydrocarbons, indeed a preliminary pretreatment in wastewater treatment, one of the best of these methods is advanced oxidation processes. The use of ultraviolet (UV) irradiation and a suitable oxidizer such as hydrogen peroxide (H_2O_2) and ozone (O_3) can be an effective approach to the removal of persistent organic pollutants (POPs) such as phenol. Therefore, the present study tried to remove phenol from petroleum refinery wastewater of Tabriz Petrochemical Company (Iran) through advanced oxidation process using $UV/H_2O_2/O_3$. The research results confirmed the high efficiency of using this advanced oxidation process in removing phenol from laboratory scale samples. The advanced oxidation using ozone was more efficient than ultraviolet irradiation in phenol degradation. The use of ozone increased the phenol removal efficiency by 98 %. However, phenol removal efficiency increased in both methods by prolonging the contact time. Therefore, the results of this research can be performed as a pilot experiment in petrochemical refineries.

References

Almasi H., Asgari G., Leili M., Sharifi Z., Seid-Mohammadi A., The Study of Phenol Removal from Aqueous Solutions Using Oxidizing Agents of Peroxide Hydrogen, Persulfate and Periodate Activated by Ultrasound, Journal of Rafsanjan University of Medical Sciences 15 (2017) 835-848.

Almomani F.A., Shawaqfah M., Bhosale R.R., Kumar A., Removal of emerging pharmaceuticals from wastewater by ozone-based advanced oxidation processes, Environmental Progress and Sustainable Energy 35 (2016) 982–995.

Asgari G., Chavoshani A., Seid-mohammadi A., Removal of Pentachlorophenol Using Microwave Assisted Persulfate from Synthetic Wastewater, Water and Wastewater (In Persian) 25 (2013) 1-10.

Azizah A.N., Widiasa I.N., Advanced oxidation processes (AOPs) for refinery wastewater treatment contains high phenol concentration, MATEC Web of Conferences 156 (2018) 03012.

Borjani S., Olya M.A., Marandi R., Monkchian Sharifabad K., Evaluation of the performance of UV/H_2O_2 advanced oxidation method in the phenol removal from wastewater storage and oil refineries, The First National Conference on Wastewater Management in the Oil and Energy Industries, Tehran, (2010).

Bustillo-Lecompte C.F., Kakar D., Mehrvar M., Photochemical treatment of benzene, toluene, ethylbenzene, and xylenes (BTEX) in aqueous solutions using advanced oxidation processes: Towards a cleaner production in the petroleum refining and petrochemical industries, Journal of Cleaner Production 186 (2018) 609-617.

Elmobarak W.F., Hameed B.H., Almomani F., Abdullah A.Z., A review on the treatment of petroleum refinery wastewater using advanced oxidation processes, Catalysts 11 (2021) 1-29.

Ghaly M.Y., Härtel G., Mayer R., Haseneder R., Photochemical Oxidation of P-Chlorophenol by UV/H_2O2 and Photo-Fenton Process. A Comparative Study, Waste Management 21 (2001) 41-47.

Gooran Ourimi H., Nezhadnaderi M., Comparison of the application of Heavy metals adsorption methods from aqueous solutions for development of sustainable environment, Anthropogenic Pollution 4 (2020) 15-27.

Gottschalk C., Libra J.A., Saupe A., Ozonation of water and waste water: a practical guide to understanding ozone and its applications, John Wiley & Sons Edn. 2(2010).

Habibi M., Zinatizadeh A.K., Akia M., Advanced oxidation processes treating of Tire Cord production plant effluent: A comparative study , Journal of Applied Research in Water and Wastewater 4 (2017) 319-330.

Hazrati H., Sadat Sajadian Z., Jahanbakhshi N., Rostamizadeh M., Reduction of membrane fouling in MBR by ZSM-5 nano adsorbent in various sludge retention times for phenol removal, Journal of Applied Research in Water and Wastewater 6 (2019) 62-66.

Huntleya D., Beckettb G.D. Persistence of LNAPL sources: Relationship between risk reduction and LNAPL recovery, Journal of Contaminant Hydrology 59 (2002) 23-26.

Jamshidi N., Torabian A., Azimi A.A., Nabi Bidhendi Gh.R., Jafarzadeh M.T., Investigation of Phenol Removal in Aqueous Solutions using Advanced Photochemical Oxidation (Apo). Water and Wastewater 20 (2010) 24-29.

Karimipour Z., Jalilzadeh Yengejeh R., Haghighatzadeh A., Mohammadi M.K., Mohammadi Rouzbehani M., UV-Induced Photodegradation of 2, 4, 6-Trichlorophenol Using Ag–Fe2O3–CeO2 Photocatalysts, Journal of Inorganic and Organometallic Polymers and Materials 31 (2021)1143-52.

Krishnan S., Chandran K., Sinnathambi C.M., Wastewater treatment technologies used for the removal of different surfactants: A comparative review, International Journal of Applied Chemistry 12 (2016) 727-739.

Laine D.F., Cheng I.F., The destruction of organic pollutants under mild reaction conditions: A review, Microchemical Journal 85 (2007) 185-193.

Lapertot M., Pulgarín C., Fernández-Ibañez P., Maldonado M.I., Pérez-Estrada L., Oller I., Advanced Oxidation Processes (AOPs) for Refinery Wastewater treatment, Water Research 40 (2006) 1086–1094.

Mahmoodi F., Jalilzadeh yengejeh R., Tirgir, F., Sadeghi M., 'Removal of 1-naphthol from Water via Photocatalytic Degradation Over N,S-TiO2/ Silica Sulfuric Acid under visible Light, Journal of Advances in Environmental Health Research 10 (2022) doi: 10.32598/JAEHR.10.1.1242.

Miklos D.B., Remy C., Jekel M., Linden K.G., Drewes J.E., Hübner U., Evaluation of advanced oxidation processes for water and wastewater treatment-A critical review, Water Research 139 (2018) 118-131.

Mokrini A., Oussi G., Chamarro E., Estlugas S., Photoxidation of phenol in aqueous solution, Water Science and Technology (1998) 95-102.

Mohammadi Aloucheh R., baris O., Asadi A., Gholam zadeh S., kharat sadeghi M., Characterization of Aquatic Beetles Shells (Hydraenidae family) derived chitosan and its application in order to eliminate the environmental pollutant bacterial, Anthropogenic Pollution 3 (2019) 43-48.

Movahedian Atar H., Rezaei R., Investigating the Efficiency of Advanced Photochemical Oxidation (Apo) Technology in Degradation of Direct Azo Dye by UV/H_2O_2 Process. Water and Wastewater 17 (2006) 75-83.

Movahedyan H., Seid Mohammadi A.M., Assadi A., Comparison of Different Advanced Oxidation Processes Degrading P-Chlorophenol in Aqueous Solution, Iranian Journal of Environmental Health Science and Engineering, 6 (2009)153-160.

Muhibbu-din I., Ayodele I., Application of Steam Enhanced Extraction method on BTEX contaminated soil in a Nigerian petroleum depot and Automobile workshop sites in Ilorin metropolis, Nigeria. Anthropogenic Pollution, 5 (2021) 30-38.

Nikpour B., Jalilzadeh Yengejeh R., Takdastan A., Hassani AH., Zazouli MA., Effluent quality of enhanced Modified Ludzack Ettinger-Oxic Settling Anaerobic Process (E-MLE-OSA) for treating real municipal wastewater, Journal of Advances in Environmental Health Research 9 (2021) 345-360.

Pinheiro C., Pereira R., Vieira M., Endocrine disrupting compounds in lotic ecosystems: A review on its occurrence, sources and effects on Chironomus riparius, Environment Pollution and Climate Change 1 (2017) 2-7.

Poulopoulos S.G., Arvanitakis F., Philippopoulos C.J., Photochemical treatment of phenol aqueous solutions using ultraviolet radiation and hydrogen peroxide, Journal of Hazardous Materials 129 (2006) 64-68.

Rahmani A.R., Shabanloo A., Mehralipour J., Fazlzadeh M., Poureshgh Y., Degradation of Phenol in Aqueous Solutions Using Electro-Fenton Process, Research Journal of Environmental Sciences 9 (2015) 332-341.

Raza W., Lee J., Raza N., Luo Y., Kim K.H., Yang J., Removal of phenolic compounds from industrial waste water based on membrane-based technologies, Journal of Industrial and Engineering Chemistry 71 (2019) 1-18.

Sharma J., Mishra I.M., Kumar V., Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H_2O_2 and UV/$S_2O_2^-$ oxidation system, Journal of Environmental Management 156 (2015) 266-275.

Shaykhi Mehrabadi Z., Performance of advanced oxidation process (UV/O_3/H_2O_2) degrading amoxicillin wastewater: A comparative study, Journal of Applied Research in Water and Wastewater 3 (2016) 222-231.

Shokouhi R., Ebrahimzadeh L., Rahmani A.R., Ebrahimi SJAD., Samarghandi MR., Comparison of the Advanced Oxidation Processes in Phenol Degradation in Laboratory Scale, Water and Wastewater 20 (2010) 30-35.

Shokohi R., Mahvi A.H., Bonyadi Z., Comparison efficiency of both sonochemical and sonochemical/hydrogen peroxide processes for cyanide removal from aqueous solutions, Journal of Mazandaran University of Medical Sciences (In Persian) 19 (2009) 59-67.

Splugas, S.E., Gimenes, G., Contreras, S., and et al. (2002). Comparison advanced oxidation processes for phenol degradation, Water Research 36, 1034-1042.

Stasinakis A.S., Use of selected advanced oxidation processes (AOPs) for wastewater treatment: A mini review. Global NEST Journal 10 (2008) 376-385.

Stepnowski P., Siedlecka E.M., Enhanced photo-degradation of contaminants in petroleum Refinery wastewater, Water Research 36 (2002) 2167-2172.

Ta N., Hong J., Liu T., Sun Ch., Degradation of Atrazine by Microwave-Assisted Electrodeless Discharge Mercury Lamp in Aqueous Solution, Journal of Hazardous Materials 138 (2006) 187-194.

Yang Y., Wang P., Shi S., Liu Y., Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, Hazardous Materials 168 (2009) 238-245.

Zaribafan A., Baharlouie Yancheshmeh M., Fathi T., Ahmadkhani R., Haghbeen K., Advanced oxidation processes against alkyl phenols in groundwater samples, Caspian Journal of Environmental Sciences 15 (2017) 343-355.