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High performance degradation of phenol from aqueous media using ozonation process and zinc oxide nanoparticles as a semiconductor photo catalyst in the presence of ultraviolet radiation

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ABSTRACT

Phenol and its derivatives, which are considered to be the most important and most common pollutants in water resources, can cause severe poisonings in the form of systemic disorders, anorexia, weight loss, diarrhea, dizziness, and difficulty in swallowing, blurred urine, irritation of gastrointestinal tract, liver and blood in man. The aim of this study was to evaluate the efficiency of ozonation (O_3) and ultraviolet irradiation and ZnO nanoparticles (UV-ZnO) to remove phenol from aqueous solutions. The effect of different concentrations of phenol (10, 50 and 100 mg/L), the effect of pH (5 and 9), the effects of zinc oxide nanoparticles (0.1 and 0.2 g/l), the effect of contact time (5, 10, 20, and 30 min), and the effect of ozone initial concentration (10, 20 and 30 mg/L) were investigated on the efficiency of the phenol removal process. All experiments were performed on a laboratory scale in a cylindrical glass reactor with a volume of 2 L. The radiation source was an ultraviolet (125 W) lamp with a wavelength of 254 nm. Experiments were carried out to determine the effect of the ozonation process on phenol removal in an ozonation reactor with a production capacity of 5 g/h and an oxygenating device with production capacity of 3 L/min. The results of this study showed that the highest phenol removal efficiency in nano-photo catalytic and ozonation processes in 30 min was 94.24% (pH = 5) and 96.64% (pH = 9), respectively. Also, in nanophoto catalytic process, with the increase in the dose of zinc oxide nanoparticles from 0.1 to 0.2 g/L with contact time of 30 min, the phenol removal efficiency increased from 64.24% to 71.56%, respectively. Also, in the process of ozonation, with increasing ozone concentration, the phenol removal efficiency increased.

Keywords: Ozonation; Phenol; Zinc oxide nanoparticle; Ultraviolet radiation; Semiconductor; Photo catalyst

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1. Introduction

Among the water pollutants with organic nature, phenol and its derivatives are among the most important and most common pollutants in water resources. Phenol is an aromatic hydrocarbon with the chemical formula of C_6H_5OH, in which there is a hydroxyl (-OH) group bonded to the phenyl ring. This compound is one of the most important aromatic hydrocarbons [1–3]. Phenol is present in surface waters, underground water, drinking water, surface water and rainwater in cities, as well as in hazardous waste landfills [4]. Phenol concentration in unpolluted groundwater

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can reach over 1 ppb. Phenol concentration is very variable in various industries; including refineries (6–500 mg/L), coking (30–3900 mg/L), petrochemical manufacturing (3–1220 mg/L) and coal processing (10–6800 mg/L) [5,6].

Phenol has applications in the manufacture of resin, plastics, adhesives, rubber, paper, wood refining industry, pesticides, medical and sanitary products such as softening oils, sprays, disinfection of operating rooms, anesthetic drugs, leather production factories, electrical industry, paint and ink industries, glass fiber factories and explosives manufacturing plants [7,8]. Health effects of phenol on human health include both acute and chronic effects. Long exposure to phenol can lead to irregular breathing, muscle weakness, seizures, and coma and also causes stopping of breathing in humans at lethal doses. Inhalation and skin contact with phenol is very stimulating (irritating) to the eyes, skin and mucous membranes of the body. The chronic effects of phenol exposure include weight loss, diarrhea, dizziness, and blurred urine. Repeated exposure to phenol in animals leads to stimulation of gastrointestinal and central nervous system, liver, kidney, respiratory and cardiovascular effects [9,10]. Generally, phenol toxicity level is in concentrations between 10 and 24 mg/L for humans. The lethal concentration of phenol in the blood is about 150 mg per 100 ml. Considering the toxic nature of phenol, several monitoring devices around the world, such as the US EPA, have provided a list of phenol and phenolic compounds in the list of priority pollutants [11]. The World Health Organization (WHO) has recommended that the phenol concentration in water supplies to conventional water treatment plants be lower than 2 µg/L for human communities [12]. According to European standard, the maximum total allowed concentration of phenolic compounds except for halogenated phenols is 0.5 µg/L and single phenols (monohydric phenols) is 0.1 mg/L. According to the US EPA standard, phenol allowed in water resources of human communities and water used for fish production is 0.3 and 2.6 mg/L respectively, and the maximum permitted level in drinking water is 0.1 mg/L. The World Health Organization has reported the maximum allowed limit of 0.1 mg/L for drinking water. According to the standards of the Institute of Standards and Industrial Research of Iran, the maximum allowed concentration of phenol in drinking water is 0.5 g/L. Also, the maximum allowed at the outlet of the treatment plant if the discharge is done to surface water and irrigation costs is 1 mg/L, and if the discharge is for the intended well is insignificant [11,13].

Some of the common methods, such as chemical coagulation, solvent extraction, adsorption and biological treatment in purification of phenol containing waste have limitations. The advanced oxidation process (AOP) offers more advantages in the removal of phenolic compounds than conventional methods. Advanced oxidation processes are based on the formation of highly active species of hydroxyl radicals which are capable of rapidly decomposing a wide range of pollutants [15–18]. Among the catalytic processes, the use of heterogeneous photo catalyst processes as an alternative and new method has been considered by researchers [19]. Heterogeneous photo catalyst processes are one of the most common processes for the removal of organic matter from aqueous solutions due to low costs, catalytic separation capability, ease of use, implementation in free air temperature and pressure, and no secondary contamination. So that the heterogeneous photo catalyst process can be described as an accelerator of the optical reaction in the presence of a catalyst. In this process, two or more phases participate in the reaction.

An optical source and a semiconductor material are used to initiate an optical reaction. The catalyst can perform oxidation and reduction on the substrate simultaneously. In this process, a UV lamp with long wavelength or even sunlight can be used [20–22]. Radiation can be achieved by exciting the electrons of the substance and transferring them to a higher energy level. In returning the electrons to the base energy level, the previous obtained energy will be emitted at a certain wavelength of light. This wavelength depends on the difference between the initial energy (base) and the temporary level where the excited electrons are transmitted to. In general, material placement at temperatures up to 2500°C or more results in material activation and causes a large number of photons to be emitted by ultraviolet irradiation (UV). Such emission sources have continuous and uniform spectra. The electric discharge (discharge in the gas environment) can also be used to bring the electrons to the excited state [20–23].

In phenol oxidation, catechol, resorcinol and hydroquinone are formed in the first phase that, hydroquinone and catechol are the main products at this stage and less resorcinol is produced. With continued oxidation, hydroquinone is transformed to benzoquinone and with more process continuity, the aromatic ring of all these products is broken down and leads to the formation of carbocyclic acids and aliphatic acids, such as maleinic acid, acetic acid, fumaric acid and formic acid. In turn, these acids will eventually form the sustainable products of water and CO_2 with the progress of oxidation [21]. Fig. 1 shows the photo catalytic degradation of phenol by ultraviolet irradiation [21].

In recent years, heterogeneous metallic oxides such as ZnO have been used extensively for the removal of various organic compounds due to their high photo catalytic capability in ultraviolet reactors [22]. Zinc oxide is a member of the wurtzite family and one of the richest nano-structures. Zinc oxide has a semiconductor with Energy band-gap (E_g) = 3.2–3.7 eV (Direct) and also an excitation binding energy = 60 meV [15,16]. It also has an optical transmission = 80–95% and high electrochemical stability [23,24]. Therefore these properties make zinc oxide particles one of the richest nanostructured materials [25–27]. The quantum efficiency of ZnO particles are considerably higher than TiO_2 and high catalytic performance has been reported. The biggest advantage of ZnO compared with TiO_2 is that ZnO absorbs a larger portion of the UV spectrum up to 415 nm. This allows the use of photo catalytic processes using sunlight. When the photon energy ($h\nu$) is equal to or higher than E_g of semiconductor, an electron from the valence band (VB) is transferred to the conduction band (CB) and a positively hole h^+_{VB} and electron (e^-_{CB}) is formed on the ZnO surface [16,28]. These holes after the reaction with water can produce hydroxyl radicals (OH). These radicals can attack water molecules by taking hydrogen or increasing to a double bond, that under suitable conditions, the final products will be water and CO_2 and organic

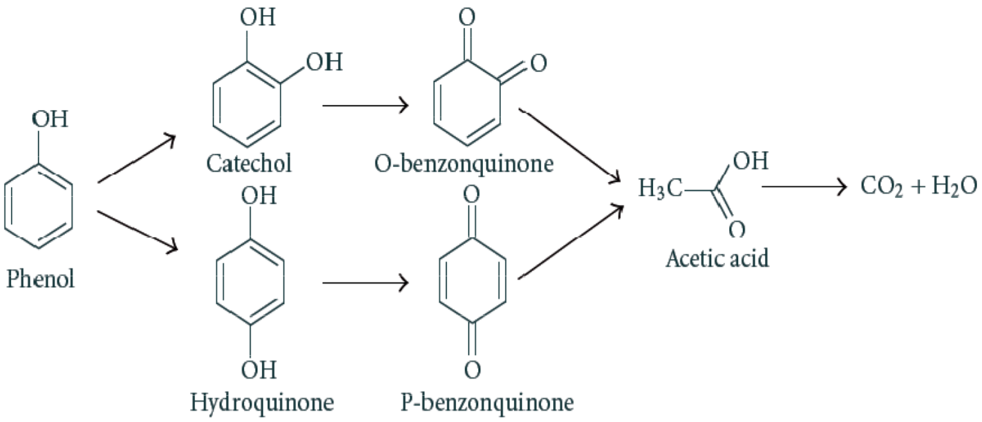

Fig. 1. Proposed photo catalytic degradation pathways of phenol under the UV irradiation [21].

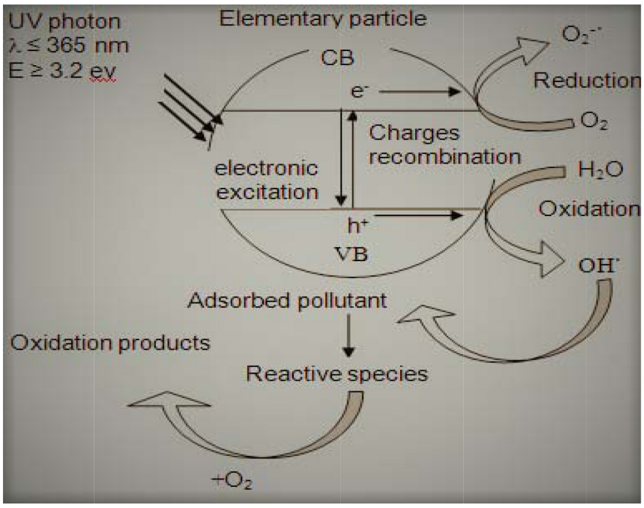

Fig. 2. General mechanism of the photo catalysis. Adapted with kind permission from Laoufi [30].

acids [15,16,19,21,29]. The general photo catalytic process is shown in Fig. 2 [30].

Ozone is a pale and unstable blue gas which is decomposed rapidly into oxygen under normal conditions, if the temperature rises above 35°C. The formation of ozone is accompanied by the adsorption of heat, so its molecule is unstable and degrades itself. Ozone gas has the boiling point of –112°C, melting point of –251°C and density of 1.5 times that of oxygen (2.14 g/L at 0°C) under standard conditions. It is colorless a room temperature and is dark blue is liquid state [31]. With the highest oxidation potential ($E° = 2.07$ V), the ozone is the strongest oxidizing agent and disinfectant used in the process of water and wastewater treatment. Phenols are quickly and easily oxidized by ozone [32]. Initial interstitial products have more toxicity than starting products. For the appearance of finished products, sufficient ozone and time should be provided, which can be easily obtained at ozone treatment plants [31,32]. Phenolic products are identified and characterized by the presence of the electron donor group of OH on aromatic nuclei. These compounds are strongly reactive with ozone and have been extensively studied due to their importance in drinking water treatment and sewage management [31–33].

In photo catalyst degradation process using UV rays, in accordance with Eqs. (2)–(10), by UV irradiation on the catalyst surface, by stimulating the capacity layer, the pair of electrons produced reacts with water and produces hydroxyl radicals which leads to further degradation of phenol [15,16,21,29].

$$ZnO + hv \rightarrow ZnO\left(e^{-}_{CB} + h^{+}_{VB}\right) \tag{1}$$

$$e^{-}_{CB} + h^{+}_{VB} \rightarrow heat \tag{2}$$

$$e^{-}_{CB} + O_2 \rightarrow .O_2 \tag{3}$$

$$h^{+}_{VB} + OH^{-} \rightarrow .OH \tag{4}$$

$$.OH + R - H \rightarrow R.' + H_2O \tag{5}$$

$$h^{+}_{VB} + R \rightarrow R^{+.} \rightarrow Intermediates \tag{6}$$

$$e^{-}_{CB} + O_2 \rightarrow .O^{-}_{2} + H^{+} \rightarrow HOO. + .O^{-}_{2} \rightarrow HOO. + O^{-} \tag{7}$$

$$HOO. \rightarrow H_2O_2 + O_2 \tag{8}$$

$$H_2O_2 + .O^{-}_{2} \rightarrow .OH + OH^{-} + O_2 \tag{9}$$

The mechanism of ozone reaction with organic compounds in aqueous media occurs in two steps [according to Eqs. (11)–(16)].

$$O_3 + OH^{-} \rightarrow O_2 + HO_2^{-} \tag{10}$$

$$O_3 + HO_2 \rightarrow HO_2^{\circ} + O_3^{\circ} \tag{11}$$

$$HO_2 \rightarrow O_2^{-} + H^{+} \tag{12}$$

$$O_3 + O_2^{\circ -} \rightarrow O_3^{\circ -} + O_2 \tag{13}$$

$$O_3{}^{\circ-} + H^+ \rightarrow HO_3{}^{\circ} \tag{14}$$

$$HO_3{}^{\circ} \rightarrow O_2 + OH^{\circ} \tag{15}$$

In the first step, the direct reaction of organic compounds occurs with ozone, the reaction speed at this stage is low. In the second step, the indirect reaction of ozone molecules with organic compounds occurs after ozone degradation and the formation of secondary oxidants, especially radical hydroxyl species. At this point, the reaction happens quickly.

The main objective of this study was to evaluate and compare the (UV/ZnO) process efficiency and the ozonation for removing phenol from aqueous solutions under different test conditions such as pH, contact time, initial phenol concentration, ozone concentration, and zinc oxide nanoparticles content.

2. Materials and methods

The following materials were prepared for testing in the laboratory:

Phenol (99%), NaOH, (K_3 $(Fe(CN)_6)$), (PO_4HK_2), ($PO_4H_2K{\cdot}xH_2O$), (NH_4OH), (H_2SO_4), (HNO_3), (HCl), KI, $Na_2S_2O_3$. The method presented in the standard methods for the examination of water and wastewater [37] was used for measuring phenol concentration. For this purpose, the necessary reagents and solutions were prepared as follows:

- Ammonium hydroxide 0.5 N
  35 mL of ammonia solution was reached to 1 L in distilled water.
- Buffered phosphate solution
  104.5 g of di-potassium hydrogen phosphate and 72.3 g of potassium dihydrogen phosphate was dissolved in distilled water and then the solution volume was diluted to 1 L. The pH of the solution should be 6.8.
- Reagent of 4-amino-anti-pyrene
  2 g of the above chemical material was dissolved in distilled water and reached to 100 ml volume by distilled water (this solution was prepared daily according to the instructions).
- Reagent of potassium ferrocyanide
  8 g of the above reagent was dissolved in distilled water and diluted to 100 mL with distilled water (this solution was prepared weekly and kept away from light).

2.1. Phenol measurement method

Take 5 mL of the sample with pipettes and bring it up to the volume in a 100 mL volumetric flask with distilled water. Take 10 mL from the solution again and poured it into the 100 mL volumetric flask. Add diluted solution to Erlenmeyer flask or Beakers, add 2.5 mL of ammonium hydroxide and the pH of 7.9 ± 0.1 was obtained with the aid of phosphate buffer. Then mL 1 of the 4-amino-anti-pyrene reagent was added to it and well stirred and again 1 mL of potassium Ferro-cyanide was added to the solution. All of the above operations were performed on the control sample of distilled water. After 15 min, the absorbance of the light was measured in samples using a spectrometer apparatus at 500 nm wavelength. Adding the Ferro-cyanide reagent to the specimens caused a yellow to dark red color depending on the phenol concentration in the solution. For example, in the control solution, which was distilled water, yellow was created and in other solutions, with the increase in the phenol concentration, the color was developed to the red. Before the specimens were read, the apparatus was calibrated with the control sample.

2.2. Preparation of the standard curve

To prepare the standard curve, 5 concentrations of 1, 2, 3, 4 and 5 mg/L of phenol were used [34]. For example, to prepare the standard of 1 mg/L of phenol, using the $C_1V_1 = C_2V_2$ equation, the sample volume of the storage solution was 0.34 mL that, it was brought up in 1000 volumetric flask. The other standard concentrations were prepared in this way and, after adding the necessary reagents and creating a color at a wavelength of 500 nm, they were read in the spectrophotometer.

2.3. ZnO characterizations

ZnO (99.8%) used in the research was supplied by Iran-Isfahan-Spadana Company. The surface area, as determined by the BET method is 40–150 m^2/g, Specific surface is 40–150 m^2/g, Density is 105 kg/m^2. The consistency of the physicochemical characteristics of nanoparticle was confirmed by using X-ray diffractogram (XRD) and scanning electron microscopy (SEM) measurements (Figs. 3a, b.)

2.4. Reactor

All experiments were performed on a laboratory scale in a cylindrical glass reactor with the volume of 2 L. The schematic of the photo catalyst reactor is shown in Fig. 4. The irradiation source was a UV lamp (125 W) at the wavelength of 254 nm. Specifications regarding the ultraviolet lamp used in the study included the type of lamp: 125 W, length: 65 mm, diameter: 10 mm, voltage: 15 + 130 V, current: 3.25 Amp, life time: 10000 h, Intensity of radiation: 1020 $\mu W/cm^2$. For the samples to be better irradiated, the lamp was immersed in the center of the vessel in the solution.

Experiments to determine the effect of the ozonation process on phenol removal were also carried out in the ozonation reactor. This reactor is made up of an ozone generator with a production capacity of 5 g/h, as well as an oxygenating machine with a production capacity of 3 L/min.

In this study, a special reservoir was used for the contact of solution with ozone. A one-way steel valve was installed in the path of outlet ozone from the ozonation reactor in order to prevent the possible introduction of water into the reactor and its failure. To measure the actual amount of ozone produced by reactor, KI solution (10%) was prepared and produced ozone was allowed to enter this solution. The generated ozone was then measured by Iodometry method. In other words, to determine the concentration of ozone, the solution sample is mixed with KI solution. I

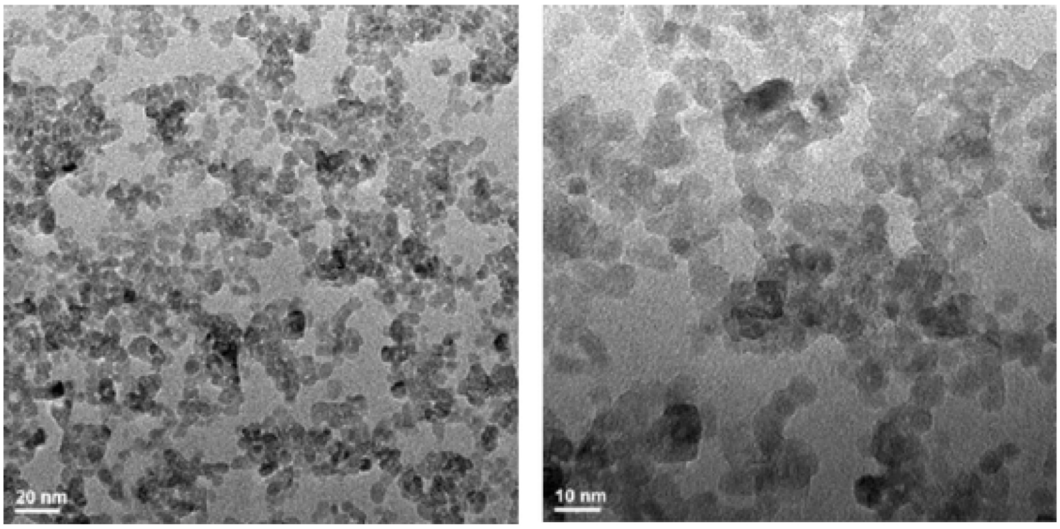

Fig. 3. (a) TEM images of the ZnO nanoparticle.

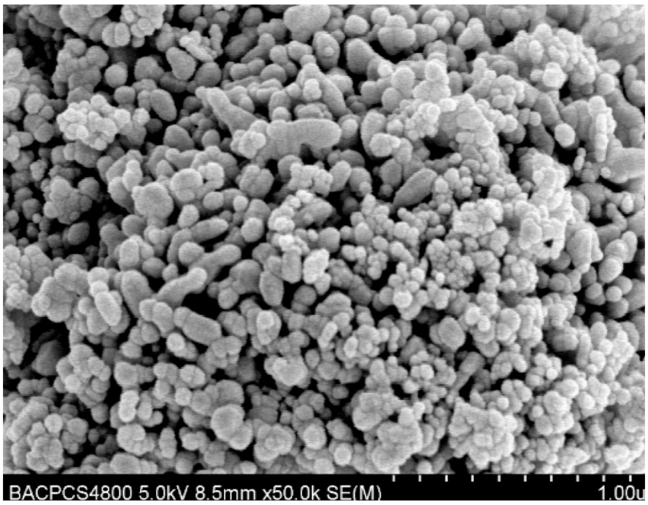

Fig. 3. (b) SEM image of the ZnO nanoparticle.

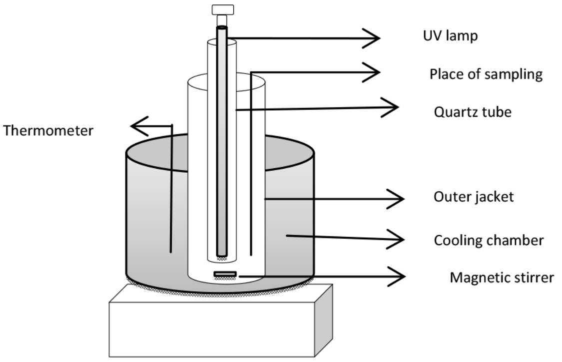

Fig. 4. Set up of photo catalytic reactor.

is oxidized by ozone and the product of the reaction is I_2, which immediately titrates with $Na_2S_2O_3$ until a pale yellow color appears. At the last step, when the starch is added, a blue color appears which is stripped by the extra $Na_2S_2O_3$ solution. The end point of titration is simply determined by the starch solution. To prepare and standardize $Na_2S_2O_3$ solution with iodometry method, we first create 100 ml of sodium thiosulphate solution 0.1 N and 100 ml of KI 0.1 N solution. After calculating the initial material content, we add the desired amount to beakers and add 1cc of chloroform and we bring it up to volume in volumetric flask. The brought up solution ($Na_2S_2O_3$) is transferred to the burette to do titration.

Finally, the percentage of phenol removal was determined by using the following equation:

$$RE = \frac{\left(C_i - C_t\right)}{C_i} \times 100 \tag{16}$$

where C_i initial phenol concentration (mg/L), C_t; final phenol concentration (mg/L).

3. Results and discussion

This study investigates the effect of various concentrations of phenol (10, 50 and 100 mg/L), pH (5 and 9), the effect of zinc oxide nanoparticles dose (0.1 and 0.2 g/L), the effect of contact time (5, 10, 20 and 30 min) and the effect of ozone concentration (10, 20 and 30 mg/L) on phenol removal efficiency by ultraviolet and photo catalyst processes (UV-ZnO).

3.1. The effect of UV and O_3 on the phenol removal

In this study, the effects of each process, including the photolysis process with UV, nanophoto catalyst (ZnO/UV), and ozonation (O_3) on the efficiency of removal of phenol from aqueous solutions are shown in Fig. 5. As seen in the figure, in the photolysis process, phenol removal is equal to 68.74% because in this situation, the lowest amount of hydroxyl radical is produced. Therefore, the efficiency of the phenol removal process is reduced. Phenol removal in the ozonation process with the contact time of 30 min was 96.64%.

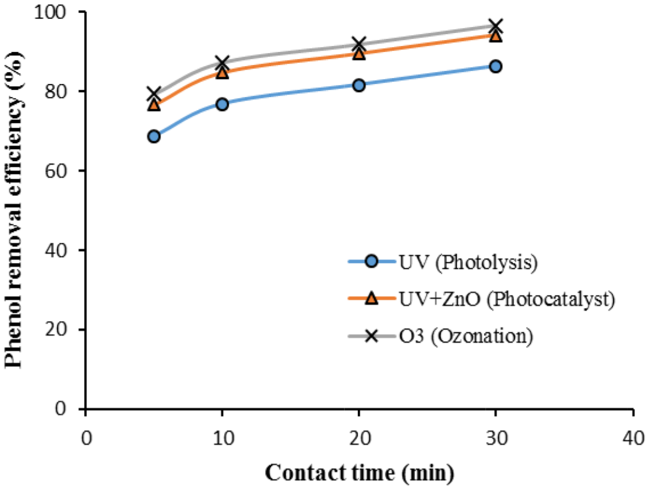

Fig. 5. Efficiency of separate and combined processes in phenol removal (phenol concentration 10 mg/L, nanoparticle dose 0.1 g/L, pH 5, ozone concentration 30 mg/L).

The oxidation potential of hydroxyl radicals is 2.33 V and the oxidation potential of ozone is 2.07 V [35,36].

3.2. Effect of pH

The initial pH of the solution is one of the important parameters in the various processes of treating the pollutants from aqueous solutions [37,38]. As shown in Fig. 6a, the highest phenol removal efficiency in the nanophoto catalyst process at pH = 5 was 94.42% at 30 min. Therefore, the efficiency of phenol degradation in nanophoto catalyst process is higher at acidic pH than alkaline pH. The greater the degradation of phenol in an acidic environment (pH = 5) can be explained as follows: in acidic environments, there are more H^+ ions which can lead to the formation of $^{\bullet}H$ radicals. $^{\bullet}H$ can also be produced in three ways: (a) water molecules react with cavities in electron-cavity pairs to form $^{\bullet}H$ and H^+. H^+ is combined with electrons from electron-cavity pairs; (b) during the process, $^{\bullet}OH$ will attack the aromatic ring and break the carbon-hydrogen bond. Hydrogen is replaced by $^{\bullet}OH$, and $^{\bullet}H$ is formed; (c) UV rays create the energy necessary to break the covalent bonds. Therefore, $^{\bullet}H$ may also be produced by breaking the oxygen-hydrogen bond in water molecules and phenol molecules, or the hydrogen-carbon bond in the molecular phenol [39]. During the process, H^+ and $^{\bullet}H$ are also formed by the oxygen present in the solution, which forms the radicals of $HO_2^{\bullet}$, eventually transforming into $^{\bullet}OH$ radicals [39]. Therefore, with the presence of other $^{\bullet}OH$ radicals produced in the photo catalyst process, phenol degradation is increased. Phenol also produces H^+ and $C_6H_5O^-$ (lower in acidic environments and more in the alkaline environment) as a hydroxide holder group when it is in water-soluble form. Because acidic products are obtained in the phenol degradation process, thus there is a probability for lowering pH due to the production of these products. So these conditions can partly increase the process efficiency [37–39].

In addition to the above reasons, the greater efficiency of the phenol degradation in the acidic environment by ZnO can be attributed to the positive charge of the nanoparticle. According the documented reasons based on the positive charge of zinc oxide in the acidic medium [40,41], it can be concluded that the dominant charge of ZnO in the acidic environment is positive which can absorb phenoxic anions in the environment [42].

As shown in Fig. 6b, the highest phenol removal efficiency in the ozonation process at pH = 9 occurs at 64.96% over a period of 30 min. Therefore, the efficiency of phenol degradation in the ozonation process at alkaline pH is higher than that of acidic pH. The most degradation of phenol in alkaline medium (pH = 9) can be explained as follows: in alkaline environments due to indirect oxidation of phenol and increased production of free radicals of hydroxide, and also increased radicals at high pHs, the removal efficiency increases. But with reduced pH due to reduced production of free radicals and direct oxidation of pollutants by ozone, the efficiency of phenol removal decreases. During the process, $^{\bullet}OH$ attacks the aromatic ring. The carbon-hydrogen bond breaks. Hydrogen is replaced by $^{\bullet}OH$ and $^{\bullet}H$ is formed [39–43].

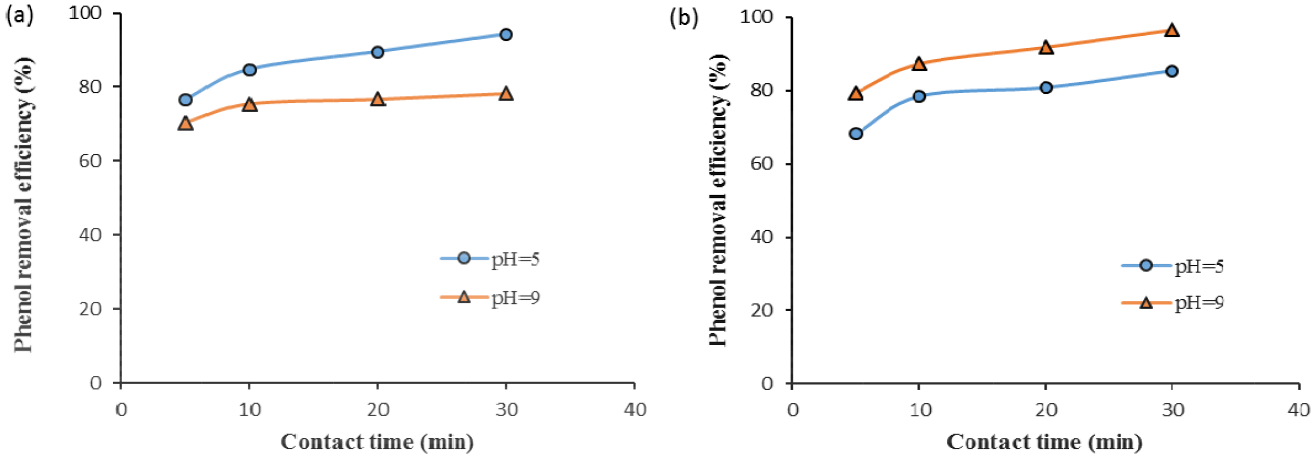

Fig. 6. The effect of pH on the removal efficiency using a) UV/ZnO (phenol concentration 10 mg/L, nanoparticle dose 0.1 g/L) and b (O_3) (phenol concentration 10 mg/L, ozone concentration 30 mg/L).

3.3. The effect of the initial phenol concentration

The effect of phenol initial concentration on the removal efficiency in photo catalyst and ozonation processes is shown in Figs. 7a, b. The removal efficacy in the range of 10–100 mg/L of phenol has been investigated in both processes. As shown in Fig. 7, in the photo catalyst process, when the phenol concentration ranges from 10 mg/L to 100 mg/L, the reaction speed is reduced as the other conditions are stable (nanoparticle concentration and pH). At acidic pH (pH = 5) where the nanoparticle dose is 0.1 g/L, contact time is 30 min and the phenol concentration is 10 mg/L, phenol removal percent would be 94.24. The removal efficiency for phenol concentration of 50 mg/L and 100 mg/L is 74% and 45.88%, respectively.

Studies conducted by Sobczyski et al. showed that the degradation rate decreases at high concentrations of phenol. The studies considered the formation of polycarbonate compounds as the reason for this issue which are insoluble in water and may stick on the catalyst surface and cause a decrease in the efficiency of photo catalytic reactions at high concentrations [44]. According to a study by Kashif et al., the reason for reducing the degradation efficiency with increasing initial phenol concentration is that the phenol absorbed light is greater than that light absorbed by the catalyst. Therefore, phenol-absorbed light is not effective for degradation [42]. Other studies have shown that, given the fact that radical hydroxyl production and super oxide do not increase the phenol breakdown thus, a smaller number of phenol molecules are reacted with the radicals produced. Therefore, the efficiency of phenol removal is reduced [40–43]. On the other hand, considering the competition between phenol and intermediate products, by increasing the initial concentration of phenol and increasing the concentration of intermediate products, as well as reducing the phenol content in the environment, a significant amount of the radicals formed are used to degrade intermediate products to easier products [42,43].

3.4. The effect of ZnO

The results showed that phenol removal efficiency in nanophoto catalyst process with zinc oxide nanoparticles dose of 0.1 and 0.2 g/L at 30 min of contact time is 94.24 and 71.56%, respectively. The use of nanoparticles results in increased the removal efficiency due to increased concentrations of produced radicals. As expected, the number of photons absorbed will also increase. As a result, available activated sites increase [42,46] and the number of adsorbed phenol molecules will also increase [42]. As shown in Fig. 8, when the nanoparticle concentration ranges from 0.1 to 0.2 g/L, the reaction speed decreases with the stability of other conditions (initial phenol concentration and pH), in fact, the catalyst increase can even reduce the penetration of light in the solution and increase the diffusion of light from the surface of the nanoparticles. By increasing the catalyst dose, the penetration of light in the solution decreases. Also, the accumulation and deposition of the catalyst occurs [39,40].

3.5. The effect of injected ozone

Three concentrations (10, 20 and 30 mg/L) were used to evaluate the effect of injected ozone in repeated experi-

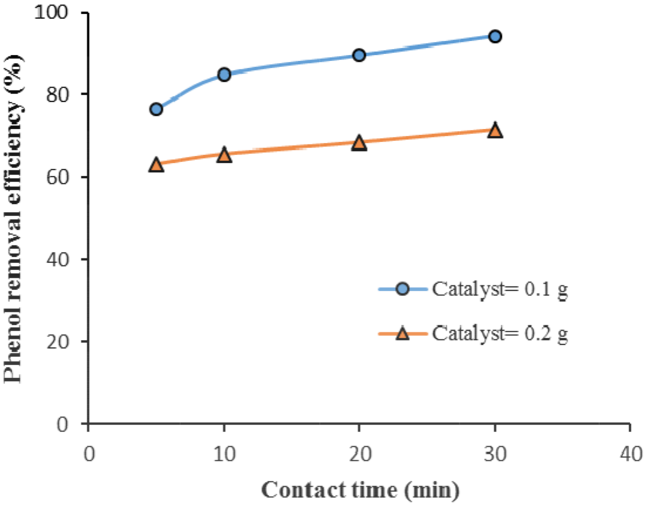

Fig. 8. The effect of ZnO nanoparticles for removal of phenol (pH 5, phenol concentration 10 mg/L).

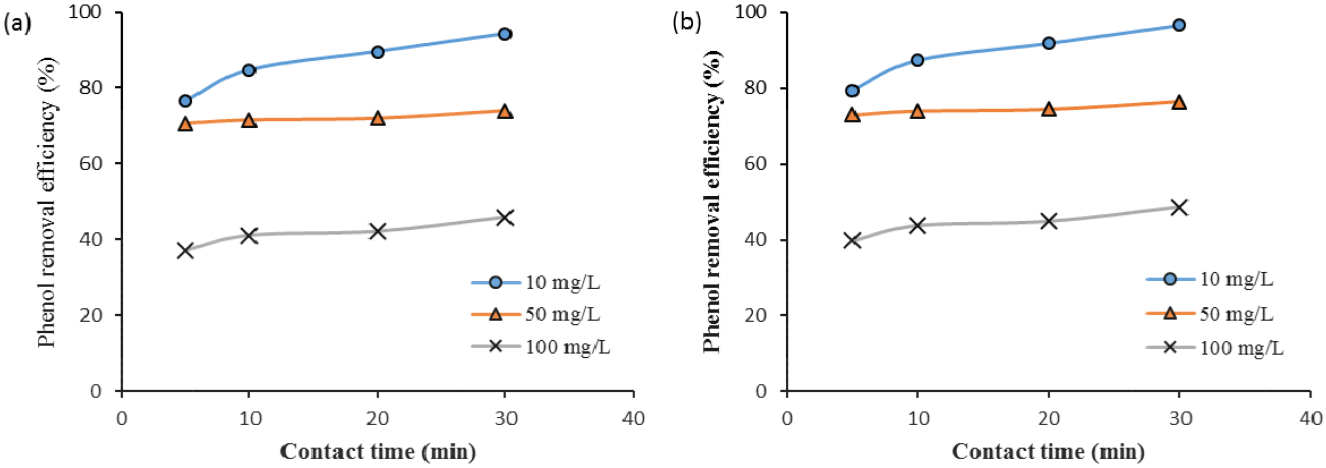

Fig. 7. The effect of phenol initial concentration on the removal efficiency using a) UV/ZnO (pH 5, nanoparticle dose 0.1 g/L) and b (O_3) (ozone concentration 30 mg/L).

ments. The results presented in Fig. 9 show that, when the concentration of injected ozone ranges from 10 to 30 mg/L, the reaction speed increases with the constant values of other conditions (initial phenol concentration and pH). In all experiments, increasing the concentration of injected ozone increases the phenol removal efficiency. The highest phenol removal rate at 30 min of contact with an initial concentration of 30 mg/L of ozone is 96.66%. The effect of injected ozone concentrations with the further degradation of phenol can be explained as follows: Ozone, which is in the rank of the strongest oxidizing agents, either reacts directly with the phenol or indirectly with production of radical hydroxide. The reaction between ozone and organic molecules involves the addition of oxygen to the benzene ring, the breaking of binary rings, and the oxidation of alcohols. The final products are from phenol oxidation by ozone, water and carbon dioxide. Intermediate products of phenol oxidation include Catechol and O-quinone. Studies have shown that with increasing concentrations of injected ozone, the phenol removal rate is also increased [57–59].

In order to compare this study with other studies, the efficiency of various methods for removal of phenol using photo catalytic process and ozonation from aqueous solutions were investigated. The summary of the research presented in Table 1.

4. Conclusions

According to the empirical findings, the main results of this study are as follows:

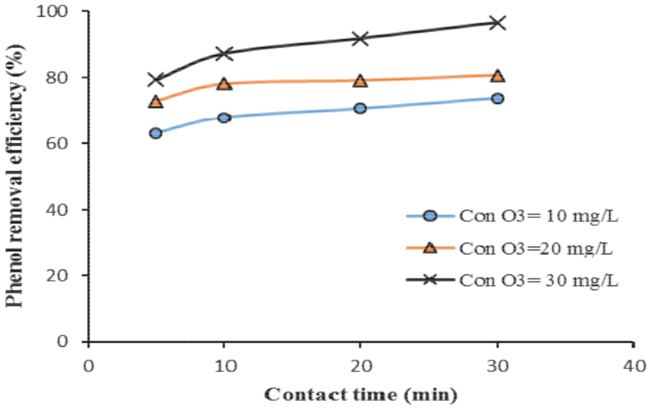

Fig. 9. The effect of dose of ozone for removal of phenol (pH 9, phenol concentration 10 mg/L).

- To remove phenol at low concentrations, the use of UV radiation alone is sufficient at low doses. But if the degradation of these materials are considered at high concentrations, it is better to use catalysts such as ZnO with UV light to reduce irradiation time.
- Generally, the phenol removal rate by the UV/ZnO nanophoto catalytic process is faster than the ultraviolet radiation alone.
- The lack of complete phenol degradation in the photo catalyst process indicates that phenol is not completely degraded to the final products (water and car-

Table 1
The efficiency of various methods for removal of phenol from aqueous solutions

Processes	Experimental conditions			Removal			Ref
	Phenol concentration	Ozone concentration	Adsorbent dose	Contact time	pH	Percentage	
UV/ZnO	25 mg/L	–	0.05 g	90 min	7	14.2	49
ZnO photo catalyst	30 mg/L	–	1 g/L	30 min	5	56	50
(UV + US)/ ZnO	40 mg/L	–	0.1 g/L	90 min	5.5	73.8	51
UV/ZnO	40 mg/L	–	0.1 g/L	90 min	5.5	33.2	51
UV/ZnO	25 mg/L	–	0.4 g/L	5 h		5.5	52
O_3	300 mg/L	0.75 mg/min	0.2 g/L	60 min	6.5	38.9	53
UV/TiO_2	10 mg/L	–	0.2 g/L	4 h	7	99	54
UV/ZnO	50 mg/L	–	0.6 g/L	6 h	3	100	55
UV/TiO_2	100 mg/L	–	0.2 w/w %	60 min	5	77.5	56
O_3	3000 mg/L	7.06 mg/L	–	240 min	12	80.17	57
O_3	100 mg/L	60 mg/L	–	4 min	6.8	77.4	58
UV/TiO_2/O_3	100 mg/L	27 mg/L	0.2 g/L	60 min	7	53.6	59
O_3	50 cm^3/min	50 mg/dm^3	–	240 min	6	21.5	59
Catalyzed by laccase	4 mM	–	–	30 min	5	77.7	58
Photo-oxidation by UV	60 mg/L	–	–	60 min	3	94	59
Ozonation	10 mg/L	30 mg/L	0.1 g/L	30 min	9	96.64	Present study
UV/ZnO	10 mg/L	–	0.1 g/L	30 min	5	94.24	Present study

bon dioxide). Therefore, prolonging the process time in order to completely decompose the phenol before turning it into non-toxic products is essential to prevent their harmful effects in the environment.

- Ozone is a strong oxidizer that has long been used as a disinfectant in water and sewage and is able to respond quickly to most toxic compounds. In this study, the effect of parameters such as concentration of injected ozone and initial concentration of phenol and pH were investigated. Reducing the initial concentration of phenol causes increased degradation. Also, the use of this process will be more efficient for sewage with alkaline pH. Increasing the concentration of injected ozone increases the phenol removal efficiency.
- Phenol with ozonation process at pH of 9 and using the photo catalyst process (UV/ZnO) at pH of 5 has the highest efficiency.
- Ozonation process in comparison with the photo catalyst process of (UV/ZnO) indicates higher phenol removal efficiency.

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Conflict of Interest

The authors of this article declare that they have no conflict of interests.

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