



Photocatalytic degradation of phenol in water solutions using ZnO nanoparticles immobilized on glass

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Original Article

Abstract

Phenol and its derivatives are pollutant compounds that are present in the wastewater of many industries. The objective of this study was to investigate the photocatalytic degradation of phenol in water containing various concentrations of sodium chloride. A laboratory study was conducted to evaluate the performance of UV/ZnO process on the efficiency of phenol removal from saline water with ZnO nanoparticles fixed on glass using UVC radiation. The effects of pH, contact time, sodium chloride concentrations, and the initial concentration of phenol on the photocatalytic removal of phenol were studied. The photocatalytic degradation of phenol showed suitable efficiency under the absence of sodium chloride (100% phenol removal at a concentration of 5 mg/l and during 120 minutes). However, the removal efficiency decreased in the presence of a concentration of 30 g/l of sodium chloride (92.4%). Additionally, phenol photocatalytic degradation efficiency decreased as a result of an increase in the initial concentration of phenol and the efficiency increased as a result of a decrease in pH (pH = 3). The results obtained from this study indicated that ZnO nanoparticles or ultraviolet rays alone cannot remove phenol fully and have a much lower efficiency in comparison with the photocatalytic degradation of phenol. Thus, the photocatalytic degradation process (UV/ZnO) is an effective method of removing phenol from saline water solutions.

KEYWORDS: Degradation, Phenol, Water Pollution, Nanoparticles

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Introduction

Most industrial wastewaters have high concentrations of salt and dangerous organic pollutants. Different industries including petroleum refineries, petrochemical plants, olive oil production, pesticide production, and textile, leather, food, and agricultural

industries produce phenolic wastewaters.^{1,2} Aromatic pollutants, especially phenol and its derivatives, are frequently found in the environment due to their widespread use.³ Phenol is a cyclic hydrocarbon which is colorless in pure form and is highly soluble in water, and therefore, it is likely to be present in water sources. Due to their distinct properties, including toxicity, effect on the flavor and odor of water, and adverse effects on human health and living creatures, phenolic compounds are

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classified as priority pollutants by the US Environmental Protection Agency (USEPA).^{4,5} Phenol is quickly absorbed through the skin and can lead to skin and eye burns upon contact. Excessive contact with phenol can lead to coma, seizures, cyanosis, and death.⁶ Due to the high toxicity of phenolic compounds, EPA has recommended the permissible level of 1 mg/l in effluents to be released into the environment.⁷ Additionally, the World Health Organization (WHO) has considered a concentration of 0.001 mg/l of phenolic compounds in drinking water as the maximum permissible concentration.⁸ Biological treatment, extraction from solution, reverse osmosis, chemical oxidation, and electrochemical methods are the most important methods of removal of phenol and phenolic compounds from saline wastewaters. High costs, low efficiency, and the generation of dangerous and toxic byproducts are among the factors which limit the use of some of these methods of removal.⁹

Recently, another technique called advanced oxidation has been used for the removal of contaminants which involves the generation of very strong oxidation agents such as hydroxyl radicals.¹⁰ The photocatalytic degradation process is considered as a novel treatment method, because the catalyst can be easily activated under normal temperature and pressure.¹¹ This method is a possible technique for the removal of organic and non-organic pollutants from the air and water.¹² In photocatalytic degradation, pollutants are degraded under the radiation of UV rays and in the presence of metal oxide particles like ZnO and TiO₂.¹³ One of the advantages of ZnO over TiO₂ is that ZnO can absorb the higher ultraviolet (UV) spectrum, and this is due to the absorption threshold of this compound which is at the 425 nm wavelength.¹⁴ Additionally, ZnO is less toxic, is cheaper, and in some cases it is more active than TiO₂.¹⁵

Many researchers have studied the removal of various refractory organic pollutants using

photocatalytic processes. However, few articles have investigated the efficiency of this technique in saline environments. In a study on the photocatalytic degradation of phenol via UV/TiO₂ in solutions with various salt concentrations, Azevedo et al. were able to obtain a removal efficiency of 90% for a phenol concentration of 50 mg/l and a pH of 7.¹⁶ In a study on the photocatalytic degradation (UV/TiO₂) of humic acid in saline water, Al-Rasheed and Cardin reported that the rate of photocatalytic degradation of humic acid was slower in water with high salinity (46 g/l) in comparison with water with low salinity (2.7 mg/l).¹⁷ Kashif and Ouyang studied the inhibitory effects of some anions on the photocatalytic degradation of phenol.¹⁸ The results of their study showed that chloride ions have a negative effect on the process. In an investigation of the effect of various concentrations of sodium chloride, sulfate, and nitrate on the photocatalytic degradation of 2-phenylphenol, Khodja et al. concluded that these anions have highly negative effects on the degradation of this pollutant.¹⁹

Due to the higher capability of ZnO in the absorption of the UV spectrum in comparison with TiO₂, ZnO nanoparticles were used in the present study. Additionally, given the difficulty of separating the nanoparticles during their use in the form of a suspension and the need for special equipment for their filtration from the solution, photocatalysts fixed on glass, which are completely neutral substances, were used in the present study.

The objective of this research was to study the performance of the photocatalytic UV/ZnO process in the removal of phenol in four saline concentrations (0, 10, 20, and 30 g/l), taking into account the effects of other parameters such as solution pH, initial concentration of phenol, and contact time.

Materials and Methods

This research was discontinuously conducted

on a laboratory scale in a plexiglass reactor with a capacity of 1 l. This reactor consists of two segments. The first segment functioned as a media on which ZnO fixed on glass and the solution containing the pollutant (a combination of various concentrations of phenol and NaCl) were placed. The second segment functioned as the cover of the reactor which allowed 5 lamps to be installed on its walls. UV_c lamps and their electrical transformers were placed in a wooden case in the cover segment with a distance of 1 cm from the reactor media in order to prevent the dissemination of the rays into the environment. This reactor has an entry orifice and an exit orifice which are situated on its two sides and the entry orifice is lower than the exit orifice. The entry and exit orifices are connected by a special tube to a peristaltic pump with a maximum rotational speed of 120 rpm so that complete mixing occurs inside the reactor. Figure 1 shows a diagram and figure of this reactor.

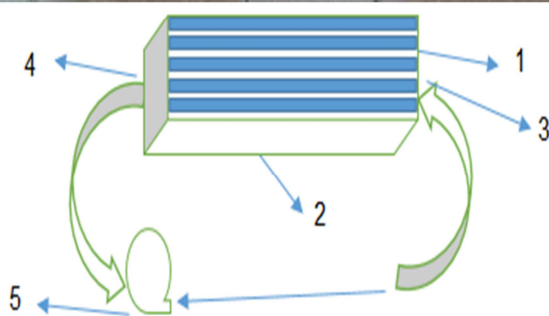
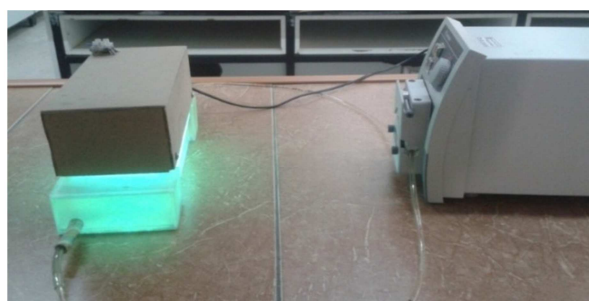


Figure 1. A figure and diagram of the noncontinuous rotational reactor

1. The reactor cover and the lamps attached to it; 2. The glass bed containing fixed zinc oxide nanoparticles; 3. Entry orifice; 4. Exit orifice; and 5. Peristaltic pump

To fix ZnO nanoparticles, the thermal fixing method was used.²⁰ First, sandblasted glass surfaces suited to the size of the reactor were prepared. Then, the pieces of glass were placed in a 50% solution of sodium hydroxide for 24 hours. After removal from the solution, they were washed with distilled and tap water. In the next stage, a 3% suspension of ZnO nanoparticles was prepared and mixed using a shaker (Behdad Co., Iran) for half an hour. Moreover, to distribute the ZnO nanoparticles homogeneously in the solution, it was placed in an ultrasonic bath (SONER 203 H, Rocker Scientific Co., Taiwan) machine with a frequency of 50 KHz under the influence of ultrasonic waves. Then, 5 cc of this suspension in which the nanoparticles were completely separated was spread evenly on each piece of glass, each of which had been dried and weighed. The pieces of glass were placed in a hot air oven (DSL 60, Texcare Instrument Co., India) at a temperature of 40 to 50 °C for 6 hours so that they would dry slowly. Then, the temperature of the hot air oven was raised to 110 °C for one hour, and in the final stage, the pieces of glass were placed in an electric furnace (FT 1200, Meta Therm Furnace Pvt. Ltd., India) at a temperature of 450 °C for 1 hour.²⁰ Ultimately, to set aside the pieces of glass on which nanoparticles were poorly fixed and were not stable enough, they were rinsed with distilled water along the reactor flow.

In the present study, phenol with a purity of 99% was purchased from Merck & Co., Germany. ZnO nanoparticles with laboratory level purity were purchased from the British DPH Company. X-ray diffraction (XRD) tests were performed using a Philips PNA analytical diffractometer and scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) system using Seron AIS2300C on the nanoparticles powder and on the nanoparticles fixed on the glass. All chemicals used in this study including chloridric acid and sodium

hydroxide (used to adjust the pH), sodium chloride (for the preparation of the saline solution), and the reagents used in the colorimetry of phenol including potassium ferricyanide, phosphate buffer, and ammonium hydroxide were bought from Merck & Co. Other equipment used in this study included 5 ultraviolet 6 watt lamps (Philips), UV meter (UVc-254, Lueter, Germany), pH meter (Hana-211, Germany), UV/vis spectrophotometer (2100 Unico, US), and peristaltic pump (Heidolph pump drive 5001, Germany).

First, a stock phenol solution (1 g phenol in 1000 cc distilled water) was prepared. Next, in order to produce the calibration curve, various concentrations were prepared from this solution. Additionally, in later stages of the experiment, the same solution was used to prepare the desired samples of phenol with the concentrations required for the experiments via dilution with distilled water. To determine the concentration of phenol in unknown and standard samples, the direct colorimetry method was used with 4-aminoantipyrine as the reagent at a wave length of 500 nanometers, using the 5530D colorimetry method as presented in the standard methods for the examination of water and wastewater.²¹ To make the concentration of phenol in the studied samples similar to the amount found in industrial wastewaters, the phenol solutions were prepared in five concentrations of 5, 10, 20, 40, and 80 mg/l. Moreover, four concentrations of sodium chloride (0, 10, 20, and 30 g/l) were mixed with various concentrations of phenol to obtain saline wastewater. To determine the optimum pH in photocatalytic degradation, the experiments were carried out in five amounts of pH (i.e., 3, 5, 7, 9, and 11). To adjust the pH, 0.1 normal hydrochloric acid and sodium hydroxide solutions were used. During each process and at time intervals of 30, 60, 90, 120, 150, and 180 minutes, samples were taken from

the solution content of the reactor. It is also necessary to state that after each stage of the experiments, the used glass surfaces were heated at a temperature of 450 °C in the furnace to reactivate them and make sure that the performance of the fixed nanoparticles was acceptable. To compare the results, the samples were exposed to UV rays alone, ZnO nanoparticles alone, or both UV rays and ZnO nanoparticles in separate stages. It should also be mentioned that all experiments were carried out at laboratory temperatures. All experiments were conducted in triplicate.

To analyze the data, repeated measures model and longitudinal models (generalized linear models) were used in SPSS software (version 21, SPSS Inc., Chicago, IL, USA).

Results and Discussion

The X-ray diffraction result of ZnO nanoparticles used in the present research is presented in Figure 2. In figures 3 and 4, the nanoparticles fixed on glass surfaces, and the physical properties, size, degree of purity, and the composition of the particles are illustrated.

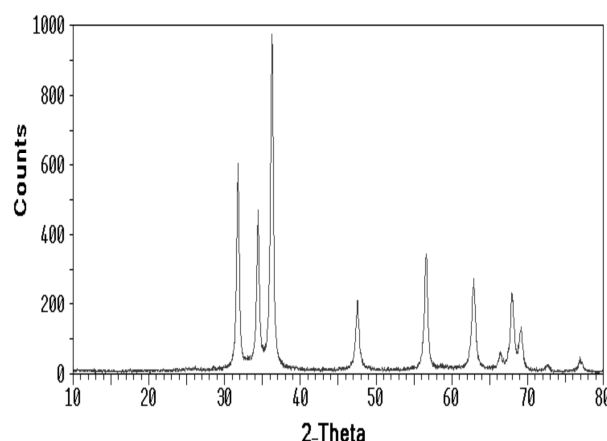


Figure 2. X-ray diffraction results of ZnO nanoparticles

The results obtained from XRD patterns indicate that the ZnO nanoparticles used had a hexagonal structure and were of a high degree of purity. Additionally, sharp peaks indicate

good crystallization of the ZnO nanoparticles. The results obtained from SEM micrographs also showed that the size of the ZnO nanoparticles used in this study was less than 100 nm. Furthermore, after fixing them on glass, porosity rates remained at a desirable level and the dimensions of the nanoparticles was still at the nano level. In addition, considering the EDX spectrum, only ZnO nanoparticles could be observed on the glass surfaces and there were no other impurities.

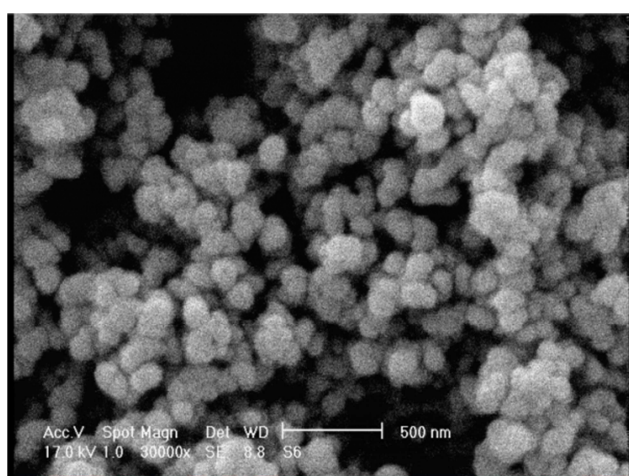


Figure 3. Scanning electron microscope (SEM) micrograph of ZnO nanoparticles fixed on glass with a magnitude of 30000

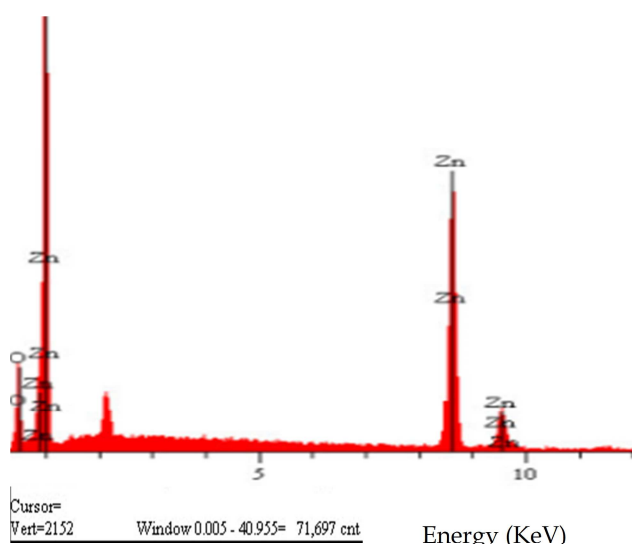


Figure 4. The results of X-ray spectroscopy (EDX) analysis of ZnO nanoparticles fixed on glass

The results of the adsorption of phenol on the surface of ZnO nanoparticles are presented in figure 5. In this figure, it can be observed that the adsorption of phenol on the surface of the nanoparticles is negligible if compared with the photocatalytic degradation of phenol in the UV/ZnO process. A survey of the effect of the separate contact of the synthetic wastewater containing the pollutant with ZnO nanoparticles, as shown in figure 5, showed that phenol removal rates were negligible after 180 minutes of contact time. Gaya et al., in a study on the effect of ZnO alone on the removal of 4-chlorophenol with a concentration of 50 mg/l, observed no considerable change in the concentration of the pollutant after 300 minutes.²²

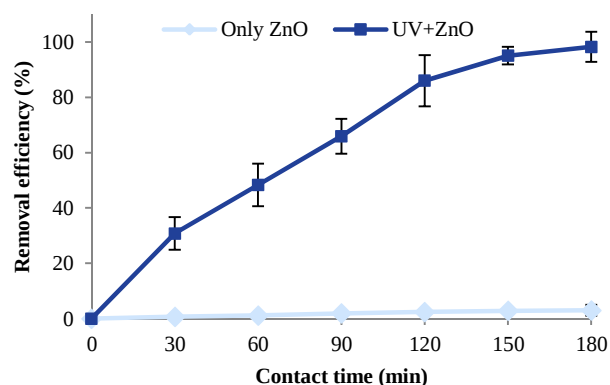


Figure 5. Comparison of the efficiency of ZnO nanoparticles alone and the UV/ZnO process in the removal of phenol (pH = 3, Phenol = 20 mg/l, and NaCl = 10 g/l)

The results of the effect of UV radiation alone on the removal of phenol are presented in figure 6 (A and B). Results show that although the use of UV rays alone can be effective in the removal of lower concentrations of phenol, in higher concentrations, the removal efficiency is reduced considerably. Moreover, it is less effective in comparison with the photocatalytic process of UV/ZnO. Phenol removal efficiency was higher at the lowest studied concentration (5 mg/l), but, at higher concentrations (80 mg/l), the removal

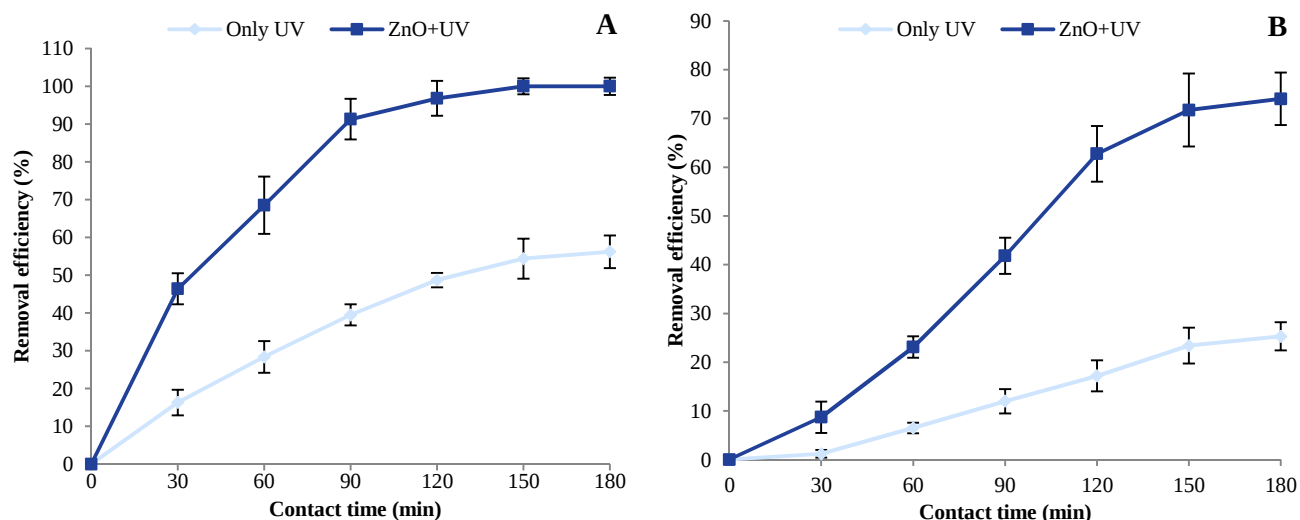


Figure 6. Comparison of the use of UV rays alone and the UV/ZnO process in the removal of phenol ($\text{pH} = 3$, $\text{NaCl} = 10 \text{ g/l}$, radiation intensity = $3950 \mu\text{W}/\text{cm}^2$, and (a) $C_{\text{phenol}} = 5 \text{ mg/l}$, (b) $C_{\text{phenol}} = 80 \text{ mg/l}$)

efficiency decreased because not enough hydroxyl radicals (the main factor for pollutant degradation) were generated.²³ Given the above-mentioned issues, it can be said that the use of these processes alone is not highly effective in the removal of phenol. Thus, it is necessary to modify the process and use the nano-photocatalytic process UV/ZnO in order to achieve higher removal efficiencies.

The results obtained from the study of the effects of pH variation in the UV/ZnO process with 5 amounts of pH are presented in figure 7. As seen in figure 7, the phenol removal efficiency was higher under acidic conditions than under basic conditions; the highest removal efficiency for the studied concentrations of phenol was at pH of 3 (90.2%) and the lowest removal efficiency was at pH of 11 (71.3%).

Two reasons can be mentioned for this phenomenon. The first reason may be the fact that higher numbers of H^+ ions are present in the acidic environment which leads to the formation of $\text{H}^\bullet$ radicals which also form $\text{HO}_2^\bullet$ radicals with the oxygen present in the solution, which finally convert to $\text{OH}^\bullet$ radicals.²³ Electrostatic reactions between phenol and the surface of the catalyst are

known as another factor affecting the pH. This phenomenon can be explained by the surface properties of ZnO.

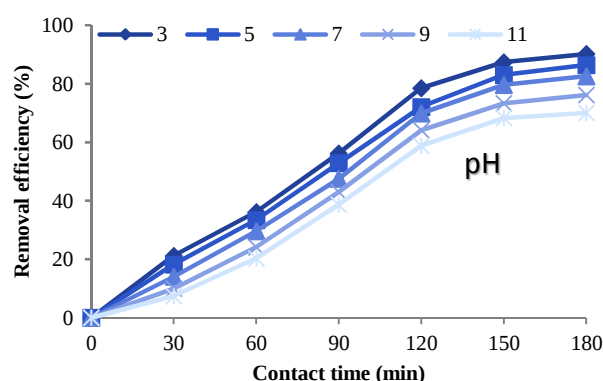


Figure 7. The effect of pH on the removal of phenol in the UV/ZnO process (the initial concentration of phenol = 40 mg/l , $\text{NaCl} = 10 \text{ g/l}$, and radiation intensity = $3950 \mu\text{W}/\text{cm}^2$)

In this study, the pH_{zpc} (point of zero charge) of the ZnO nanoparticles was about 8.60. At pH levels higher than this, the surface charge of the ZnO nanoparticles was negative, while at pH levels lower than this, the particles had a positive surface charge.²⁴ Many ionic compounds like phenols have negative charges (anionic compounds) which can be easily attracted to the surface of ZnO particles at pH

levels less than pH_{zpc} . However, at pH levels higher than pH_{zpc} , ZnO nanoparticles repel each other because they have negative charges.²⁵ The results obtained from the statistical analysis also showed that the difference in the mean phenol removal rates was significant at various pH levels ($P < 0.001$). In their investigation of the effect of pH (2.5 to 12.5) on the removal of phenol and benzoic acid using the UV/ZnO photocatalytic process, Mrowetz and Selli reported that the highest removal efficiency was obtained at the pH of 2.5.²⁶

The results of the phenol removal efficiency at various concentrations of sodium chloride (0, 10, 20, 30 g/l) are shown in figure 8. As can be seen in figure 8, an increase in the concentration of sodium chloride (NaCl) leads to a reduction in the removal efficiency. The highest removal efficiency (92.4%) was obtained in the absence of sodium chloride, and the lowest removal efficiency (81.12%) was obtained for the 30 g/l concentration of sodium chloride at the same contact time (180 minutes).

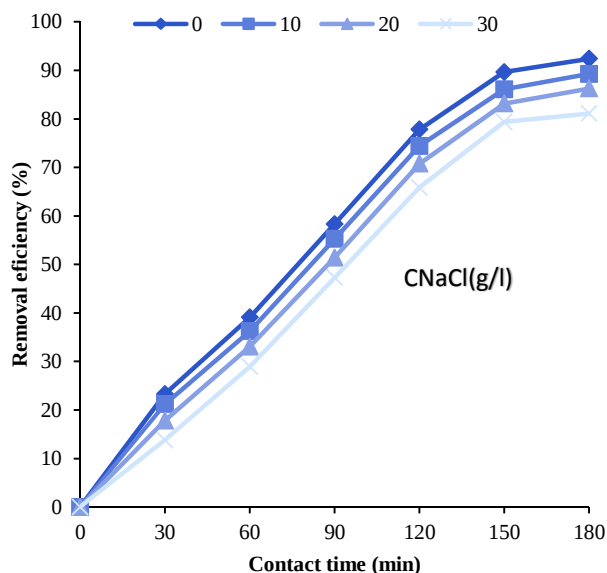


Figure 8. The effect of various concentrations of sodium chloride on the removal of phenol in the UV/ZnO process (pH = 3, phenol = 40 mg/l, and radiation intensity = $3950 \mu\text{W}/\text{cm}^2$)

Regarding the negative effect of the various concentrations of NaCl on the photocatalytic degradation of phenol and the reduction of removal efficiency with the increase in saline concentration (NaCl) in the studied solution (Figure 8), it can be said that the reduction in the efficiency of the process can be attributed to the presence of chloride ions, because chloride ions are able to adsorb hydroxyl radicals.²⁷ Additionally, it seems that the inhibitory effect of sodium chloride is due to the joining of the chloride ions to electrons and optical cavities. The chloride ions, which have been adsorbed to these cavities and have been oxidized, are converted to chlorine atoms, and then, again are reduced as chloride ions by the electrons.¹⁶ The results obtained from the repeated measures model statistical analysis also indicated a significant difference in the mean phenol removal efficiency at various NaCl concentrations ($P = 0.004$). Moreover, the results suggest that sodium chloride has a negative effect on the oxidation of phenol. Papadam et al.²⁸ and LAmour et al.²⁹ obtained similar results in their studies.

The study of the effect of initial concentration of phenol on photocatalytic degradation (for the optimum pH obtained in the previous stage) has shown that as the initial concentration of phenol increased, the photocatalytic degradation rates decrease (Figure 9).

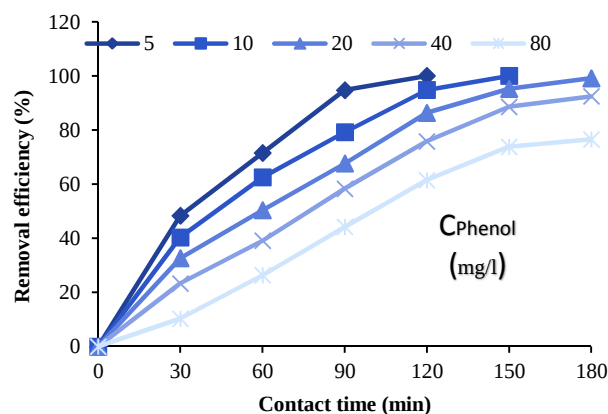


Figure 9. The effect of the initial concentration of phenol and contact time on the removal of phenol in the UV/ZnO process (pH = 3, and radiation intensity = $3950 \mu\text{W}/\text{cm}^2$)

Therefore, removal efficiency has an inverse relationship with the initial concentration of phenol. Additionally, the time needed to achieve a desirable removal efficiency increased as the initial concentration of phenol was raised. After 120 minutes and at an acidic pH, the highest removal efficiency (100%) was achieved at the lowest concentration (5 mg/l), and the lowest removal rate at a concentration of 80 mg/l and a contact time of 180 minutes was 76.5%.

In investigating the effect of the initial concentration of phenol and contact time on photocatalytic degradation, as can be seen in figure 9, as the initial concentration of phenol increased, the photocatalytic degradation rates decreased. In explaining this issue, it can be stated that, in the photocatalytic process, as a result of the increase in the amount of influent pollutant, the likelihood of collision of the pollutant particles with the oxidizing agent (i.e., hydroxyl) is reduced, which leads to a reduction in the efficiency of the removal system at higher concentrations. Another reason for this issue is the generation of byproducts which are more reactive than phenol and which react with the present radicals or are adsorbed onto the surface of the photocatalyst; therefore, these byproducts compete with phenol in adsorption onto active sites on the ZnO surface and in reacting with

hydroxyl radicals.^{26,30} The results obtained from statistical analysis have demonstrated the significant difference between mean phenol removal efficiencies at its various concentrations ($P < 0.001$). Pardeshi and Patil³¹ and Chiou et al.³² have also reached similar results in their studies. Moreover, Zamankhan et al.³³, in a study on the removal of phenol using the photocatalytic method and ZnO nanoparticles, concluded that an increase in contact time leads to an increase in the removal efficiency of phenol.

Kinetics results of phenol removal through the photocatalytic process are shown in figure 10. Two models, the pseudo-first-order and the pseudo-second-order, were used to determine a possible mechanism involved in the degradation. The R^2 for pseudo-first-order kinetics ($R^2 = 0.93$) was higher than the pseudo-second-order ($R^2 = 0.75$).

The removal of phenol in the UV/ZnO process fit the pseudo-first-order reaction patterns well ($R^2 = 0.93$). The photocatalytic oxidation kinetics of many organic compounds have often been modeled with the Langmuir-Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface.¹⁴ The results of this study are in agreement with that of the studies by Behnajady et al.¹⁴ and Alalm and Tawfik.³⁴

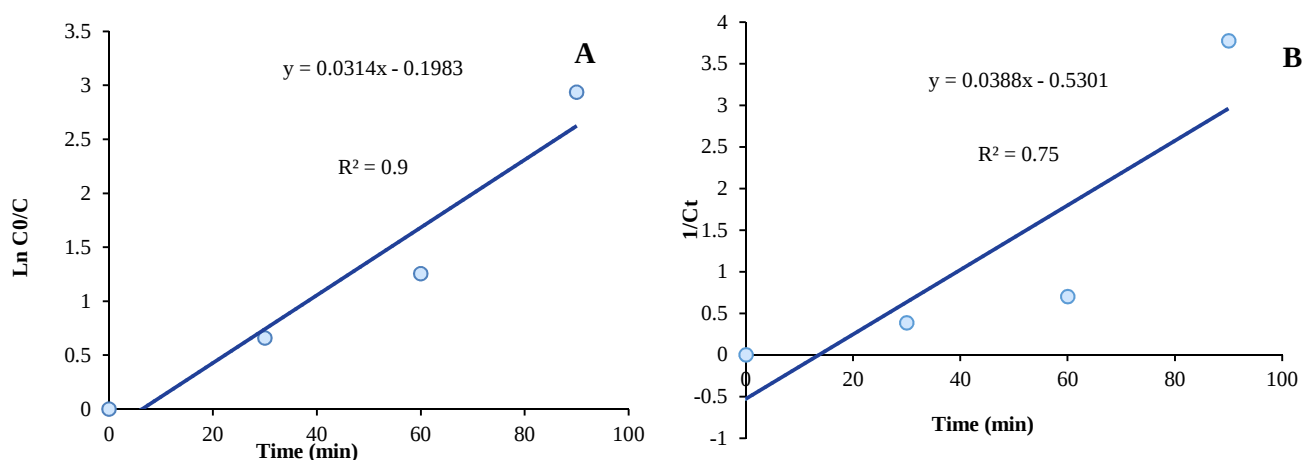


Figure 10. Phenol removal kinetics in the UV/ZnO process: (A) the pseudo-first-order and (B) the pseudo-second-order (pH = 3, retention time = 90 minutes, and phenol concentration = 5 mg/l)

Conclusion

In this study, the removal of phenol from saline wastewaters using the UV/ZnO photocatalytic process was investigated. In general, the results obtained from this study show that the use of the UV/ZnO process even in wastewaters containing anions like chloride, which is a scavenger of hydroxyl radicals and has an inhibitory effect on the process, was an effective method in removing phenol. However, at higher concentrations of sodium chloride (30 g/l), the time needed for achieving the desirable treatment levels increased. Additionally, ZnO nanoparticles alone or UV rays alone have a lower efficiency in the removal of phenol in comparison with the UV/ZnO photocatalytic process.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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