Enhancement of Ozonation Reaction for Efficient Removal of Phenol from Wastewater Using a Packed Bubble Column Reactor

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Abstract: *In the ozonation process, the phenol degradation in wastewater undergoes a low mass transfer mechanism. In this study, ozonized packed bubble column reactor was designed and constructed to remove phenol. The reactor's inner diameter and height were 150 and 8 cm, respectively. The packing height was kept constant at 1 m in accordance with the reactor hydrodynamics. The gas distributor was designed with 55 holes of 0.5 mm. The phenol removal efficiency was evaluated at ozone concentrations of 10, 15, and 20 mg/L, contact times of 15, 30, 45, 60, 75, 90, 105, and 120 min, and phenol concentrations of 3, 6, 9, 12, and 15 mg/L. The results indicated that the highest phenol removal efficiency of 100% was achieved at 30 min in presence of packing. Moreover, the use of packing improved the contact between the gas and liquid, which significantly enhanced the phenol degradation. Actually, a thin film over a packing surface enhances the mass transfer. Also, it was found that the phenol is degraded into CO_2 and H_2O through a series of reaction steps. Additionally, a kinetic study of a first-order reaction provided an efficient estimation of reaction parameters with a correlation factor of 0.997.*

Keywords: *wastewater treatment; phenol removal; advanced oxidation process; ozonation reaction; kinetics study*

INTRODUCTION

Most industrial processes, including those at chemical plants, in the petrochemicals industry, and in petroleum refining processes, discharge wastewater into the environment without being treated or reused [1]. Thus, these industrial activities continuously create large amounts of wastewater at high rates with varying quantities of pollutants [2]. Wastewater from petroleum refineries contains high levels of harmful materials (grease, sulfides, cyanides, suspended solids, heavy metals, and phenols) that can be fatal to humans as well as cause other environmental problems [3-8]. Phenol and its derivatives are usually produced in petroleum refineries as a result of operating unit activities. These materials are regarded as highly toxic compounds in the petroleum industry because they cause pollution in water supplies [9-12].

The ozonation process is one of the most advanced oxidation techniques employed to remove organic pollutants from wastewater [10,13]. In the ozonation technique, the hydroxyl group and other radicals are generated during the oxidation reaction, which provides a high removal percentage of organic materials [14-18]. Ozone gas is a strong oxidizing agent that is widely applied in wastewater treatment to remove microorganisms, organic, and inorganic compounds. Ozones are utilized in direct and indirect processes, which may produce hydroxyl radicals and other chemical by-products [19-22]. Furthermore, it is important to consider that the ozonation process is characterized by a low reaction rate. Accordingly, the chemical reaction required a long reaction time to degrade hydrocarbons. The limited reaction rate is attributed to the low mass transfer mechanism inside reactors. Then, the enhancement of the contact area between the gas phase (ozone) and the liquid phase (polluted wastewater) can improve the reaction rate of the ozonation process [6,20].

Moreover, due to the difficulty of degrading phenol compounds, many researchers have explored enhanced removal techniques depending on the phenol concentration, operating conditions, and reactor design [23-27]. The efficient removal of phenolic compounds from industrial wastewater requires a high-performance process with economic feasibility. Different reactor designs have been employed to remove phenol from wastewater, including a semi-batch reactor [28], fluidized bed reactor [29], trickle bed reactor, and bubble column reactor [30-33].

Karri et al. [34] investigated the removal of phenol using a fluidized-bed reactor and activated carbon from coconut shells. The authors noted that with a lower concentration of activated carbon and shorter contact times, about 96% phenol removal was achieved. Annisa et al. [35] evaluated the efficiency of ozonation procedures in the removal of phenolic compounds in a bubble column reactor. They found that at 60 min, the removal efficiency for 4-chlorophenol using ozonation was 62.79%, but for RB-19 dye, it was 99.70%. Yusoff et al. [36] studied the performance of a hybrid growth sequencing batch reactor under three toxicity conditions by adding phenol to activated sludge at full organic loading. The authors found that a treatment time of 30 min produced a clear reduction in the phenol and chemical oxygen demand (COD) by 61 and 52%, respectively.

Liu et al. [37] applied a fixed-bed reactor for the phenol removal process using stainless steel-graphene film as a metal-free catalyst. They noted that after a working time of 72 h, the catalyst provided full phenol removal and an impressive total organic carbon (TOC) removal of 80.7–91%. Zheng et al. [38] employed a fluidized bed reactor for the phenolic degradation process and observed that the activated carbon/lignite showed a higher rate of phenolic degradation in comparison with activated sludge reactors. The authors indicated that the adsorption capacity was 90 and 70% for fluidized and activated sludge reactors, respectively. Qin et al. [39] studied phenol removal in two stages (fixed-bed reactor and heterogeneous Fenton-reaction) using a Cu/Bi-Ce/Al_2O_3 catalyst. They noted that the highest phenol removal was 32.6% for two-stage operations. Al Ezzi [40] used an internal airlift loop reactor to remove phenol, with rice husk and granular activated carbon as adsorbent materials and hydrogen peroxide as an oxidant agent. After 60 min of treatment time, the phenol removal was 81 and 83% for the rice husk and activated carbon, respectively.

Hashim et al. [41] and Sang et al. [42] pointed to the importance of using packing materials to increase the contact between gas and liquid phases. The authors used packing materials in the fixed-bed reactor and micro-fixed-bed reactor, respectively. They found that the diffusion resistance was reduced efficiently when packing materials were applied inside the reactors. Furthermore, the main reason for using the packing is the low solubility of ozone in water. This low solubility leads to low mass transfer of ozone from the gas to the liquid phase and the high ozone demand for contaminants decomposition during ozonation. Then, adding packing material to the reactors is an efficient method for increasing the residence time, which causes the enhancing decomposition of ozone gas in an aqueous solution to improve ozone utilization and increase the removal efficiency of phenol degradation [10,43]. In comparison with other multiphase reactors, the bubble column reactor is characterized by having no moving parts, low maintenance, and simple operation [44] and can be applied in the ozone oxidation process with high performance [32,45]. From a reaction kinetics point of view, the ozonation reaction is dependent on the radical oxidation process. Then, species of reactive oxygen contribute significantly to minimizing the amount of pollutants in the wastewater [46-48]. According to a literature survey, the ozonation reaction operates with limited efficiency due to the low mass transfer rate between the gas and liquid in the reactor and due to the low contact surface area between these two substances. Therefore, it is desirable to develop an effective operational mechanism using a packed bubble column reactor to maximize phenol removal by enhancing ozone mass transfer in the reactor. Consequently, the ozone concentration and phenol degradation mechanism, as well as a kinetic study of packed and unpacked bubble columns, was evaluated.

■ EXPERIMENTAL SECTION

Materials

In the present experimental study, phenol (99.6% purity, Gryfskand Co., Poland), potassium iodide (98.2% purity), sodium thiosulfate (99.95% purity), and sulfuric acid (99.8% purity) were purchased from Sigma-Aldrich Company, USA. Also, pure starch was used in the experimental work.

Instrumentation

The instrumentations used in this study were TOC analyzer (TOC-L-CSH E200, Shimadzu, Japan), ozone generator type (DNA-Series Company, China), and bubble column reactor (locally designed and constructed from QF-glass).

Procedure

For the starter, the removal of phenol from wastewater was achieved using a packed bubble column. Fig. 1 illustrates the experimental apparatus of the packed bubble column reactor. The experimental operation in this reactor was conducted under a semi-batch operational mode. The reactor was constructed from QF-glass, 150 cm in height and 8 cm in diameter. Moreover, spherical glass beads with a diameter of 1.5 cm were used as packing material over a height of 100 cm inside the reactor. Also, gas distribution was designed and constructed from stainless steel supported at the reactor bottom. The gas distributor had 51 holes, 0.5 mm in diameter. Furthermore, an ozone generator with a capacity of 3-g/h dose (DNA-Series Company, China) was used to allow ozone gas into the bubble column reactor at a supply rate of 0 to 20 mg/L. The flow rate of ozone gas was controlled with the aid of a sensitive airflow meter supported inside the ozone generation system. Also, an air compressor was used to combine the water and phenol mixing inside the reactor before any run to ensure that a uniform mixture was achieved. A calibrated gas flow meter was used to control the ozone gas flow from the bottom of the reactor. The output ozone gas was collected at the reactor top and then passed over a column of a 2% solution of potassium iodide (KI) to convert O_3 into O_2. Additionally, the sampling draw zone was fitted

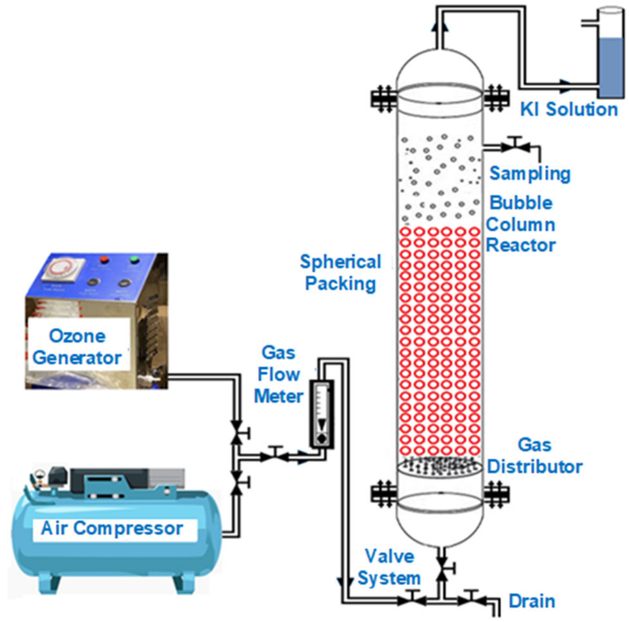

Fig 1. Schematic diagram of the experimental bubble column reactor apparatus

15 cm from the reactor top and sent to the TOC analyzer to measure the phenol concentration.

Simulated wastewater was prepared by mixing phenol with deionized water at different concentrations: 3, 6, 9, 12, and 15 mg/L. Dry air was fed to an ozone generator to produce ozone gas. The input ozone gas used in the treatment of phenol in the reactor ranged from 0 to 20 mg/L. The operating temperature was kept constant in the bubble column reactor at 25 °C for all experimental runs, and the treatment time for each run was 15 min. During the course of the test, a 5 mL sample of treated wastewater was collected from the sampling valve at the reactor top. Additionally, the experimental procedure was achieved using two different phenol treatment modes in bubble column reactors. The first was carried out in a bubble column reactor with ozone gas only. The second mode of treatment used ozone in the presence of packing (O_3/packing). Fig. 2 summarizes the two operating modes in the bubble column. At the end of each experiment, the phenol concentration was measured using a TOC analyzer (TOC-L-CSH E200, Shimadzu, Japan). Moreover, the reaction time (or contact time) was tested in the present experimental work of ozonation reaction at the two modes of operation. The contact time represents the accumulative

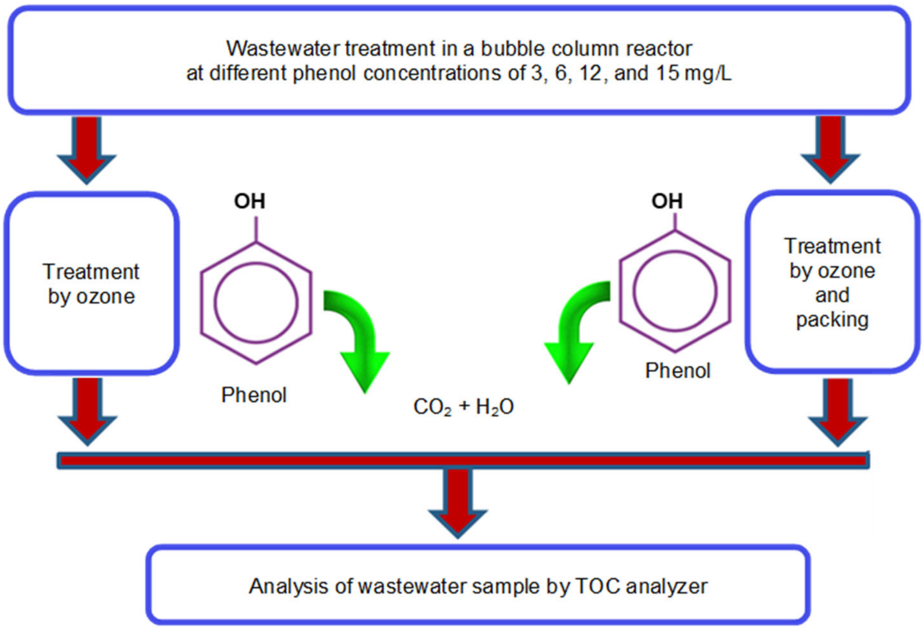

Fig 2. Modes of the ozonation process in the bubble column reactor in the absence and presence of packing inside the reactor

time to achieve phenol degradation. The sample was collected from the reactor every 15 min for a period of 2 h (15, 30, 45, 60, 75, 90, 105, and 120 min).

The ozone concentration in the wastewater was determined in mg/L using the indigo method [26] as a practical calibration. The following steps summarize the operating procedure of ozone gas quality evaluation. First, the generated ozone gas was passed directly into two containers containing a 2% KI solution for 10 min. Next, 10 mL of H_2SO_4 of 2 N was added to 200 mL of the KI solution. Then, the solution was titrated with sodium thiosulfate ($Na_2S_2O_3$) of 0.005 N till the yellow color of the iodine was no longer visible. At this point, two drops of starch were added. The titration procedure was continued until the blue color was no longer visible. The chemical reaction is presented in Eq. (1). Then, the total amount of consumed sodium thiosulfate in the titration process was estimated using Eq. (2) to calculate the generated ozone concentration in mg/L [17,26].

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \quad (1)$$

$$\text{Ozone concentration}\left(\text{mg / L}\right) = \frac{\left(A+B\right)\times N\times 24}{T} \quad (2)$$

where A is the amount of sodium thiosulfate used in the first container (mL); B is the amount of sodium thiosulfate used in the second container (mL); T is the ozone period (min); and N is the sodium thiosulfate normality.

RESULTS AND DISCUSSION

Effect of Phenol Concentration

The use of a bubble column reactor in the phenol removal process from wastewater is challenging due to the complex hydrodynamic characteristics of such a reactor. In addition, petroleum refineries produce wastewater with many organic pollutants; the phenol effluent from various operating units in the petroleum refinery ranges from 2–15 ppm [3,6,8]. The results in Fig. 3 show the variation in the phenol removal efficiency with the phenol concentration at different treatment times, indicating that the phenol removal efficiency decreased with increasing phenol concentration. For example, at a contact time of 30 min, the phenol concentration was 3 mg/L, and the phenol removal efficiency was 65.42%. Moreover, the removal efficiency of phenol was 52.32 and 38.69% at phenol concentrations of 9 and 15 mg/L, respectively. In other words, it was found that as the concentration of phenol increased in the wastewater, it required more treatment

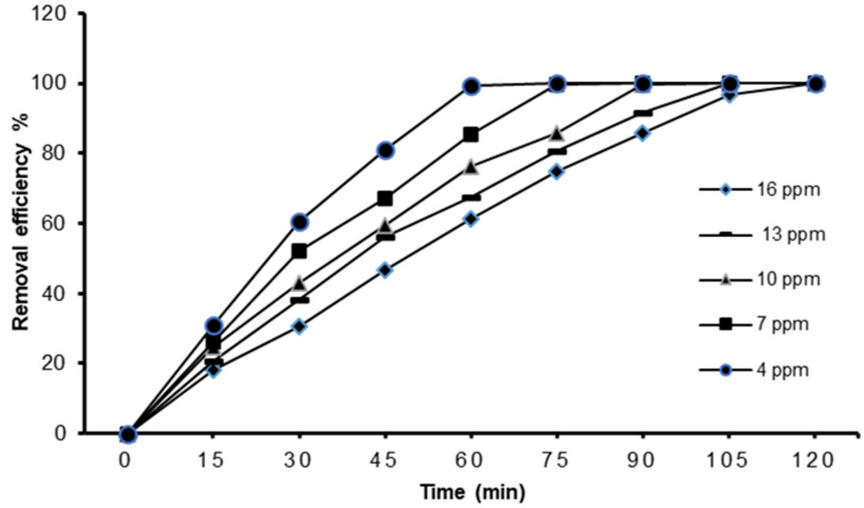

Fig 3. Variation in the phenol removal efficiency with the phenol concentration in the presence of ozone gas only in a bubble column reactor

time (contact time) in the reactor to obtain a high removal rate.

Furthermore, from the results in Fig. 3, it was noted that the contact time plays a major role in determining the phenol removal efficiency. As the contact time increased, the removal of phenol also increased. These results are attributed to the semi-batch operation mode in the bubble column, in which the degradation reaction of phenol continued with increasing contact time. Cheng et al. [22] and Barlak et al. [33] pointed to the importance of treatment time to produce higher rates of phenol degradation from wastewater. Also, Wang et al. [27] showed that the hydrodynamic parameters, such as column height, column diameter, gas distributor, bubble size, bubble rise velocity, and superficial gas velocity, provided optimal operating conditions in the treatment of organic pollutants from wastewater using a bubble column reactor.

Effect of Packing on Ozonation Reaction

Fig. 4 illustrates the results of the phenol treatment process in the presence of ozone gas using a packed bubble column reactor at different contact times. It shows that a dramatically high activity for phenol degradation was noted for all tested phenol concentrations. For example, at a contact time of 30 min,

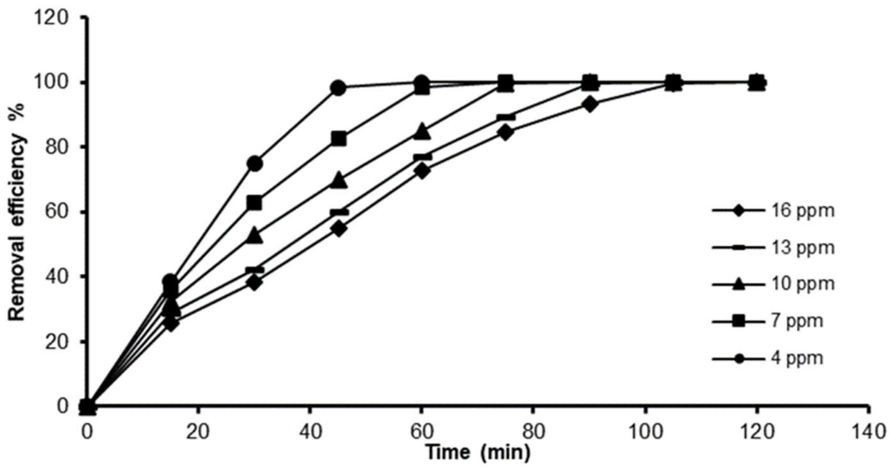

Fig 4. Variation in the phenol removal efficiency with the phenol concentration in the presence of ozone gas and packing in a bubble column reactor

for a phenol concentration of 3 mg/L, the phenol removal efficiency value was 74.98%. Moreover, the removal efficiency of phenol was 47.01 and 41.22% for phenol concentrations of 9 and 15 mg/L, respectively. In addition, for a reaction time of 45 min and at a phenol concentration of 3 ppm, the results showed a removal of 100%, while at the highest phenol concentration of 15 ppm, a phenol removal rate of 100% was achieved at a contact time of 105 min**.** The addition of spherical packing to the bubble column reactor significantly enhanced the phenol removal efficiency due to the high surface area. Accordingly, the available surface area improved the mass transfer operation between the gas and liquid contact, leading to a high phenol degradation performance.

The comparison of the results shown in Fig. 3 and 4 indicated that the best removal efficiency of phenol was achieved when the reactor used packing material (Fig. 4). Then, the use of packing material in the bubble column reactor provided a clear increase in the interfacial area with low ozone gas rising velocity. Actually, the long pathway of ozone gas along the packing height will enhance contact time and provide an efficient mass transfer mechanism. This enables the enhancement of the exposures of ozone in the aqueous solution, which improves ozone utilization efficiency and increases phenol degradation. The same result was noted by Hashim et al. [41] and Sang et al. [42].

To understand the activity of the ozonation process with a variation in the phenol dose, Fig. 5 illustrates the effectiveness of phenol removal at different phenol concentrations at a contact time of 45 min. The removal efficiency was 98.43, 77.53, 65.82, 60.207, and 55.11% at phenol dosages of 3, 6, 9, 12, and 15 mg/L, respectively. Also, it was found that when the phenol concentration increased in the wastewater mixture in the packed bubble column reactor, the removal efficiency decreased. This behavior is attributed to the need for a long contact time to provide an efficient phenol degradation process. Additionally, it was observed that the phenol dosage is a significant variable in the ozonation process performance in the presence or absence of packing in a bubble column reactor. These results agree with the reported trends [10,22,27].

Effect of Ozone Dosage on Phenol Degradation

The degradation of phenol in a bubble column reactor was investigated at various ozone gas concentrations (10, 15, and 20 mg/L) in the absence or presence of packing inside the reactor. Fig 6 shows the effects of the ozone concentration on the phenol removal efficiency at a phenol concentration of 3 mg/L and an operating temperature of 25 °C. The results indicated that the concentration of ozone in the aqueous phase had a significant impact on the phenol oxidation rate. As shown in Fig. 6, the experiments that used high ozone

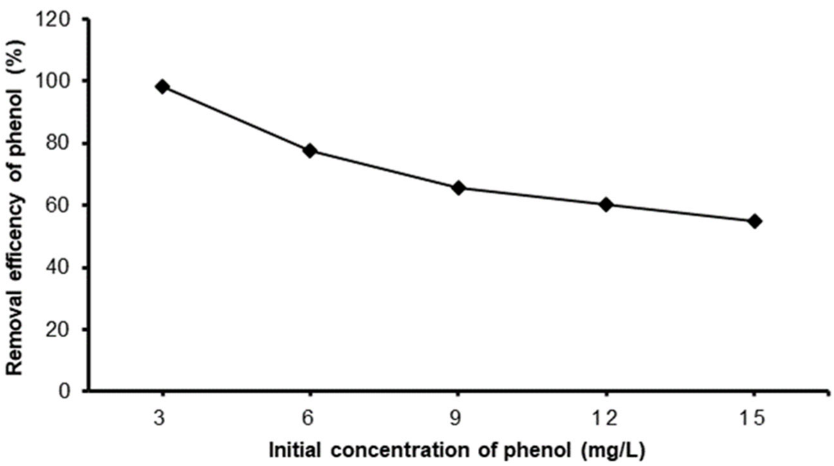

Fig 5. Effect of phenol dosages on the phenol removal efficiency at a contact time of 45 min using an O_3/packing mode with an ozone concentration of 20.6 mg /L

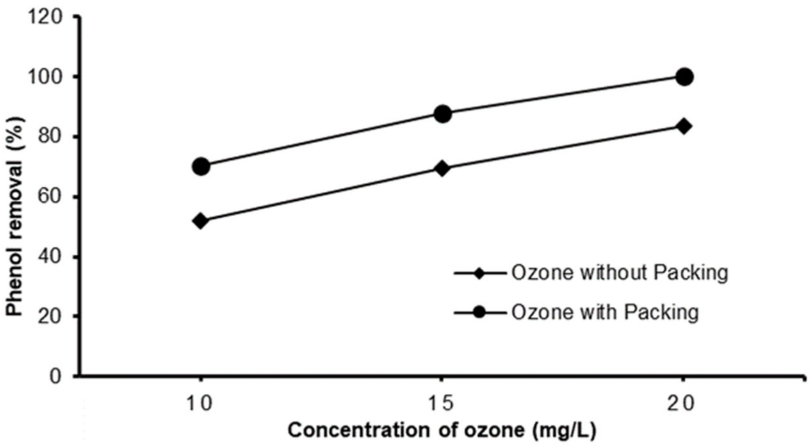

Fig 6. Influence of the ozone dosage on the phenol degradation process in a bubble column reactor in the presence and absence of packing (at 3 mg/L phenol concentration and 45 min of contact time)

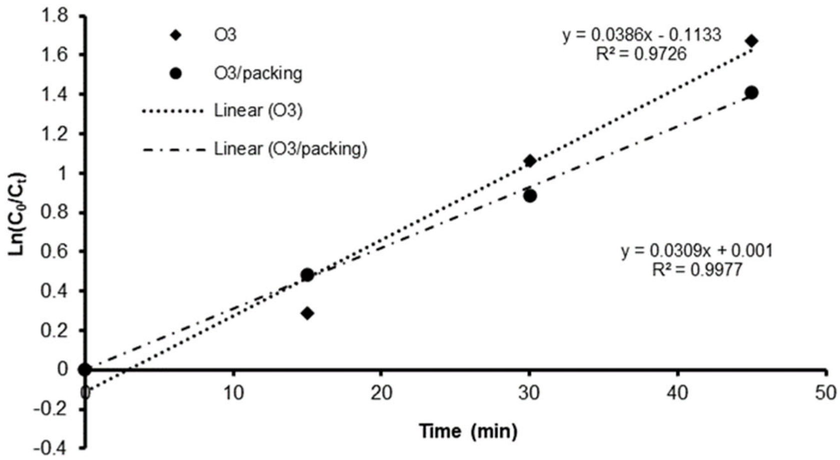

Fig 7. Evaluation of the first-order reaction kinetics for the ozonation process

dosage provided fast phenol removal efficiency. For example, at an ozone dosage of 10, 15, and 20 mg/L, the removal rate was 52.00, 69.30, and 83.60%, respectively, in the absence of packing inside the reactor; however, in the presence of packing, values of 70.50, 88.00, and 98.75%, respectively, were achieved. Also, in their investigations, Dehghani et al. [9] and Xiao et al. [19] showed that the increase of ozone doze increases the phenol removal efficiency.

Reaction Kinetics Study

The present work studied the kinetics of the phenol degradation process using ozonation technology. The evaluation was achieved by applying two reaction orders (first- and second-order), depending on the phenol reaction mechanism. Accordingly, for each assumed reaction order, the reaction rate constant was estimated depending on the various phenol concentrations [47]. Then, the mass balance equations for phenol at a given time of the first- and second-order reactions were estimated using Eq. (3) and (4), respectively.

$$\ln\frac{C_t}{C_0} = k_1 t \tag{3}$$

$$C_t = \frac{C_0}{1 + C_0 k_2 t} \tag{4}$$

where C_t is the concentration of phenol at any time (t); C_0 is the initial concentration of phenol; k_1 and k_1 are the reaction rate constants for the first- and second-order reactions, respectively, and t is the reaction time.

Fig. 7 and 8 show the comparison between the theoretical and experimental results of the ozonation

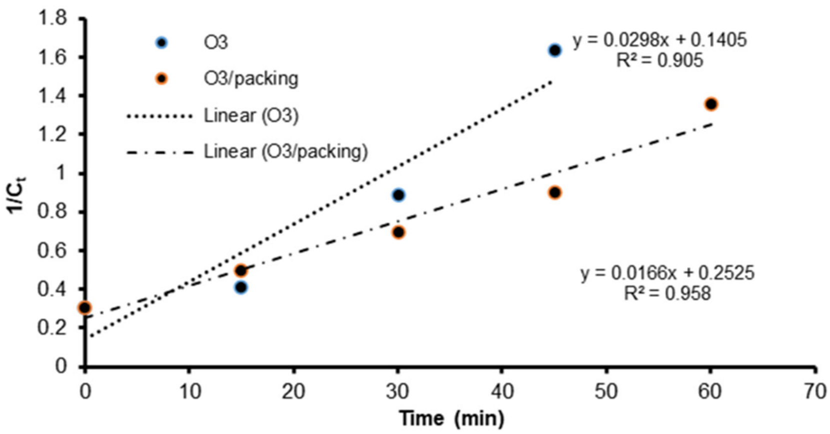

Fig 8. Evaluation of the second-order reaction kinetics for the ozonation process

process for the first- and second-order reactions, respectively. The correlation factor (R^2) was used to validate or refute the reaction order assumption. The k_1 of the first-order reaction was calculated and plotted in Fig. 7 as the slope of the best-fit line of ln (C_t/C_0) vs. time. For the second-order reaction model, the best fit of the line plot of $1/C_t$ vs. time provided the required slope, as shown in Fig. 8 [46]. Additionally, the use of the packed bubble column reactor provided a considerable rise in the k value for the ozonation process. These results agree with the findings of Barlak et al. [33] and Dai et al. [46].

Table 1 shows the results of the calculation process. It was found that the highest value of R^2 (0.9977) was obtained for the assumption of the first-order model with a perfect fitting for the kinetic data achieved. The result indicated that the presence of packing material in the bubble column reactor showed a clear increase in the k_1 value. It was noted that the k_1 increased from 0.078 to 0.096 for the assumption of first-order reaction with R^2 (0.9977). On the other hand, the second-order assumption provides a low R^2 value of (0.9580) in comparison with the first assumption. Then, it was concluded that the addition of packing material improves the phenol degradation in the ozonation process. This is attributed to the increased ozone concentration in the reaction mixture, which enhances the mass transfer rate, contact time, and reaction rate.

Phenol Degradation Process Mechanism

Applying the principles of ozone treatment to wastewater in petroleum refineries requires a deep understanding because ozone gas can play several roles in the treatment process. Our understanding of the degradation mechanism of phenol allowed the reaction paths to operate clearly and safely, which is especially important as phenol presents a great danger to human health and the environment. Many authors have indicated that the degradation of phenol requires many stages, which eventually produce carbon dioxide and water. These stages depend mainly on the phenol

Table 1. Results of the experimental kinetic data of the phenol ozonation reactions for the first- and second-order assumptions

First-order Assumption			
Type of treatment	$y = Ln(C_0/C_t)$ and $x = t$	k_1 (1/min)	R^2
O_3 only	y = 0.0386 x – 0.1133	0.0780	0.9726
O_3 in the presence of packing	y = 0.0309 x + 0.0010	0.0960	0.9977
Second-order Assumption			
Type of Treatment	$y = 1/C_t - 1/C_0$ and $x = t$	k_2 (1/mg min)	R^2
O_3 only	y = 0.0298 x + 0.1405	0.0081	0.9050
O_3 in the presence of packing	y = 0.0166 x + 0.2525	0.0128	0.9580

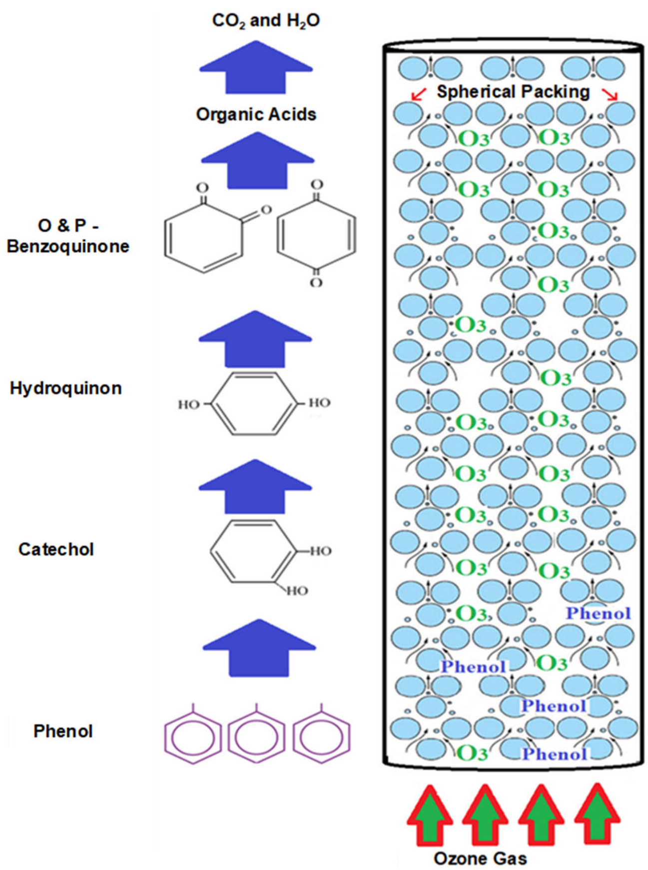

Fig 9. Phenol degradation mechanism by ozone in the packed bubble column

concentration in the wastewater and on the type of reactor used [5,22,28].

The current research employed a bubble column reactor, which is considered one of the most complex multiphase reactors due to the high interaction between the hydrodynamic properties that determine the reactor's performance. Therefore, the use of a packed bubble column provided an efficient contact surface area between the ozone gas and the aqueous solution, which included phenol. Thus, the mass transfer operation was enhanced by using an efficient reaction mechanism. From a diffusion point of view, the formation of a thin film over the spherical packing in the reactor plays a major role in providing efficient mass transfer operation. Actually, this thin film is characterized by low resistance to diffusion, and then a high phenol degradation process was achieved [21,27]. Water and carbon dioxide are the end products of phenol degradation via various advanced oxidation stages. Fig. 9 summarizes the chief stages in the degradation process of phenol into different kinds of compounds. The first step in the oxidation of phenol results in the formation of catechol and hydroquinone, while the next step results in the formation of *o*-benzoquinone and *p*-benzoquinone [25,47]. Additionally, the ozone gas that rises from the reactor bottom is responsible for the breakdown of aromatic compounds into new products of organic acids. After that, *o*-benzoquinone and *p*-benzoquinone undergo decomposition, which results in the formation of oxalic acid, propionic acid, formic acid, and acetic acid. Finally, these acids undergo an oxidation process to produce CO_2 and H_2O [10,18,36].

CONCLUSION

The packed bubble column reactor was used efficiently in the ozonation process to remove phenol from wastewater with a high rate and a low contact time. The effectiveness of the phenol and TOC removal was achieved at an ozone rate of 3 g/h and a contact time of 45 min. The results indicated that the use of packing inside the reactor greatly enhanced the amount of phenol removal and its efficiency. The phenol removal efficiency was measured at 99.45 and 81.52% in the presence and absence of packing in the reactor, respectively. Furthermore, it was found that the presence of packing inside the reactor enhanced the mass transfer process by improving the contact surface area between the gas and liquid in the reactor, increasing the phenol removal efficiency. Furthermore, from the two assumed kinetic models that describe the phenol reaction's kinetics, it was observed that the first-order assumption was optimal, with a R^2 of 0.9977 in relation to the experimental result. Additionally, a deep understanding of the reaction mechanism of phenol degradation was achieved, which explained the stages in the transformation of phenol into carbon dioxide and water. Finally, the use of packing in a bubble column reactor in the ozonation process was an effective method for the removal of phenol from industrial wastewater with a low cost and simple operation.

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■ REFERENCES

[1] Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P.R., and Reshma, B., 2021, Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development, *Chemosphere*, 280, 130595.

[2] Singh, R., Dutta, R.K., Naik, D.V., Ray, A., and Kanaujia, P.K., 2021, High surface area *Eucalyptus* wood biochar for the removal of phenol from petroleum refinery wastewater, *Environ. Challenges*, 5, 100353.

[3] Mao, G., Han, Y., Liu, X., Crittenden, J., Huang, N., and Ahmad, U.M., 2022, Technology status and trends of industrial wastewater treatment: A patent analysis, *Chemosphere*, 288, 132483.

[4] Chowdhary, P., Bharagava, R.N., Mishra, S., and Khan, N., 2020, "Role of Industries in Water Scarcity and Its Adverse Effects on Environment and Human Health" in *Environmental Concerns and Sustainable Development: Volume 1: Air, Water and Energy Resources*, Eds. Shukla, V., and Kumar, N., Springer, Singapore, 235–256.

[5] Saxena, G., Chandra, R., and Bharagava, R.N., 2017, "Environmental Pollution, Toxicity Profile and Treatment Approaches for Tannery Wastewater and Its Chemical Pollutants" in *Reviews of Environmental Contamination and Toxicology Volume 240*, Eds. de Voogt, P., Springer International Publishing, Cham, Switzerland, 31–69.

[6] Singh, S., and Shikha S., 2019, Treatment and recycling of wastewater from oil refinery/petroleum industry, *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Eds. Singh, R.L., and Singh, R.P., Springer, Singapore, 303–332.

[7] Mousa, N.E., Mohammed, S.S., Shnain, Z.Y., Abid, M.F., Alwasiti, A.A., and Sukkar, K.A., 2022, Catalytic photodegradation of cyclic sulfur compounds in a model fuel using a bench-scale falling-film reactor irradiated by a visible light, *Bull. Chem. React. Eng. Catal.*, 17 (4), 755–767.

[8] Sun, Y., Liu, Y., Chen, J., Huang, Y., Lu, H., Yuan, W., Yang, Q., Hu, J., Yu, B., Wang, D., Xu, W., and Wang, H., 2021, Physical pretreatment of petroleum refinery wastewater instead of chemicals addition for collaborative removal of oil and suspended solids, *J. Cleaner Prod.*, 278, 123821.

[9] Dehghani, M.H., Karamitabar, Y., Changani, F., and Heidarinejad, Z., 2019, High performance degradation of phenol from aqueous media using ozonation process and zinc oxide nanoparticles as a semiconductor photocatalyst in the presence of ultraviolet radiation, *Desalin. Water Treat.*, 166, 105–114.

[10] Alattar, S.A., Sukkar, K.A., and Alsaffar, M.A., 2023, The role of TiO_2 NPs catalyst and packing material in removal of phenol from wastewater using ozonized bubble column reactor, *Acta Innovations*, 46, 93–105.

[11] Karamah, E.F., Adripratiwi, I.P., and Anindita, L., 2018, Combination of ozonation and adsorption using granular activated carbon (GAC) for tofu industry wastewater treatment, *Indones. J. Chem.*, 18 (4), 600–606.

[12] Wang, Y., Yang, W., Yin, X., and Liu, Y., 2016, The role of Mn-doping for catalytic ozonation of phenol using Mn/γ-Al_2O_3 nanocatalyst: Performance and mechanism, *J. Environ. Chem. Eng.*, 4 (3), 3415–3425.

[13] Centurião, A.P.S.L., Baldissarelli, V.Z., Scaratti, G., de Amorim, S.M., and Moreira, R.F.P.M., 2019, Enhanced ozonation degradation of petroleum refinery wastewater in the presence of oxide nanocatalysts, *Environ. Technol.*, 40 (10), 1239–1249.

[14] Alardhi, S.M., Albayati, T.M., and Alrubaye, J.M., 2020, Adsorption of the methyl green dye pollutant from aqueous solution using mesoporous materials MCM-41 in a fixed-bed column, *Heliyon*, 6 (1), e03253.

[15] Rayaroth, M.P., Aravindakumar, C.T., Shah, N.S., and Boczkaj, G., 2022, Advanced oxidation processes (AOPs) based wastewater treatment-unexpected

nitration side reactions-a serious environmental issue: A review, *Chem. Eng. J.*, 430, 133002.
[16] Almukhtar, R., Hammoodi, S.I., Majdi, H.S., and Sukkar, K.A., 2022, Managing transport processes in thermal cracking to produce high-quality fuel from extra-heavy waste crude oil using a semi-batch reactor, *Processes*, 10 (10), 2077.
[17] Liu, X., Su, X., Tian, S., Li, Y., and Yuan, R., 2021, Mechanisms for simultaneous ozonation of sulfamethoxazole and natural organic matters in secondary effluent from sewage treatment plant, *Front. Environ. Sci. Eng.*, 15 (4), 75.
[18] Jiao, W., Shao, S., Yang, P., Gao, K., and Liu, Y., 2021, Kinetics and mechanism of nitrobenzene degradation by hydroxyl radicals-based ozonation process enhanced by high gravity technology, *Front. Chem. Sci. Eng.*, 15 (5), 1197–1205.
[19] Xiao, J., Xie, Y., and Cao, H., 2015, Organic pollutants removal in wastewater by heterogeneous photocatalytic ozonation, *Chemosphere*, 121, 1–17.
[20] Wei, C., Zhang, F., Hu, Y., Feng, C., and Wu, H., 2017, Ozonation in water treatment: The generation, basic properties of ozone and its practical application, *Rev. Chem. Eng.*, 33 (1), 49–89.
[21] Sukkar, K.A., Al-Zuhairi, F.K., and Dawood, E.A., 2021, Evaluating the influence of temperature and flow rate on biogas production from wood waste via a packed-bed bioreactor, *Arabian J. Sci. Eng.*, 46 (7), 6167–6175.
[22] Cheng, W., Quan, X., Li, R., Wu, J., and Zhao, Q., 2018, Ozonation of phenol-containing wastewater using $O_3/Ca(OH)_2$ system in a micro bubble gas-liquid reactor, *Ozone: Sci. Eng.*, 40 (3), 173–182.
[23] Temesgen, T., and Han, M., 2021, Ultrafine bubbles as an augmenting agent for ozone-based advanced oxidation, *Water Sci. Technol.*, 84 (12), 3705–3715.
[24] Awad, A.M., Sukkar, K.A., and Jaed, D.M., 2022, Development of an extremely efficient Iraqi nano-lubricating oil (base-60) employing SiO_2 and Al_2O_3 nanoparticles, *AIP Conf. Proc.*, 2443, 030049.
[25] Oputu, O.U., Fatoki, O.S., Opeolu, B.O., and Akharame, M.O., 2020, Degradation pathway of ozone oxidation of phenols and chlorophenols as followed by LC-MS-TOF, *Ozone: Sci. Eng.*, 42 (4), 294–318.
[26] Bader, H., and Hoigné, J., 1981, Determination of ozone in water by the indigo method, *Water Res.*, 15 (4), 449–456.
[27] Wang, Z., Guo, K., Liu, H., Liu, C., Geng, Y., Lu, Z., Jiao, B., and Chen, D., 2020, Effects of bubble size on the gas–liquid mass transfer of bubble swarms with Sauter mean diameters of 0.38–4.88 mm in a co-current upflow bubble column, *J. Chem. Technol. Biotechnol.*, 95 (11), 2853–2867.
[28] Saputera, W.H., Putrie, A.S., Esmailpour, A.A., Sasongko, D., Suendo, V., and Mukti, R.R., 2021, Technology advances in phenol removals: Current progress and future perspectives, *Catalysts*, 11 (8), 998.
[29] Piao, M., Zou, D., Ren, X., Gao, S., Qin, C., and Piao, Y., 2019, High efficiency biotransformation of bisphenol A in a fluidized bed reactor using stabilized laccase in porous silica, *Enzyme Microb. Technol.*, 126, 1–8.
[30] Shnain, Z.Y., Abid, M.F., and Sukkar, K.A., 2021, Photodegradation of mefenamic acid from wastewater in a continuous flow solar falling film reactor, *Desalin. Water Treat.*, 210, 22–30.
[31] Prasetyaningrum, A., Arum Kusumaningtyas, D., Suseno, P., Jos, B., and Ratnawati, R., 2018, Effect of pH and gas flow rate on ozone mass transfer of K-carrageenan solution in bubble column reactor, *Reaktor*, 18 (4), 177–182.
[32] Lima, V.N., Rodrigues, C.S.D., Sampaio, E.F.S., and Madeira, L.M., 2020, Insights into real industrial wastewater treatment by Fenton's oxidation in gas bubbling reactors, *J. Environ. Manage.*, 265, 110501.
[33] Barlak, M.S., Değermenci, N., Cengiz, I., Özel, H.U., and Yildiz, E., 2020, Comparison of phenol removal with ozonation in jet loop reactor and bubble column, *J. Environ. Chem. Eng.*, 8 (5), 104402.
[34] Karri, R.R., Jayakumar, N.S., and Sahu, J.N., 2017, Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon, *J. Mol. Liq.*, 231, 249–262.

[35] Annisa, N., Nadisti, M.S., Karamah, E.F., and Bismo, S., 2018, Degradation of batik dye wastewater in basic condition by ozonation technique in bubble column reactor, *E3S Web Conf.*, 67, 04019.

[36] Yusoff, N.A., Ong, S.A., Ho, L.N., Wong, Y.S., Mohd Saad, F.N., Khalik, W.F., and Lee, S.L., 2019, Performance of the hybrid growth sequencing batch reactor (HG-SBR) for biodegradation of phenol under various toxicity conditions, *J. Environ. Sci.*, 75, 64–72.

[37] Liu, F., Zhang, H., Yan, Y., and Huang, H., 2020, Graphene as efficient and robust catalysts for catalytic wet peroxide oxidation of phenol in a continuous fixed-bed reactor, *Sci. Total Environ.*, 701, 134772.

[38] Zheng, M., Bai, Y., Han, H., Zhang, Z., Xu, C., Ma, W., and Ma, W., 2021, Robust removal of phenolic compounds from coal pyrolysis wastewater using anoxic carbon-based fluidized bed reactor, *J. Cleaner Prod.*, 280, 124451.

[39] Qin, W., Ren, M., Lu, Y., and Yang, S., 2022, High effective degradation of phenol with Cu/Bi-Ce/Al_2O_3 heterogeneous Fenton-like catalyst in a two-stage fixed-bed reactor, *Sep. Purif. Technol.*, 299, 121733.

[40] Al Ezzi, A.A.R., 2022, Removal of phenol by expanded bed airlift loop reactor, *Iran. J. Chem. Chem. Eng.*, 41 (1), 154–162.

[41] Hashim, M.A., Kundu, A., Mukherjee, S., Ng, Y.S., Mukhopadhyay, S., Redzwan, G., and Gupta, B.S., 2019, Arsenic removal by adsorption on activated carbon in a rotating packed bed, *J. Water Process Eng.*, 30, 100591.

[42] Sang, L., Tu, J., Cheng, H., Luo, G., and Zhang, J., 2020, Hydrodynamics and mass transfer of gas–liquid flow in micropacked bed reactors with metal foam packing, *AIChE J.*, 66 (2), e16803.

[43] Pishgar, R., Kanda, A., Gress, G.R., Gong, H., Dominic, J.A., and Tay, J.H., 2018, Effect of aeration pattern and gas distribution during scale-up of bubble column reactor for aerobic granulation, *J. Environ. Chem. Eng.*, 6 (5), 6431–6443.

[44] Karamah, E.F., and Nurcahyani, P.A., 2019, Degradation of blue KN-R dye in batik effluent by an advanced oxidation process using a combination of ozonation and hydrodynamic cavitation, *Indones. J. Chem.*, 19 (1), 41–47.

[45] Ayanda, O.S., Adeleye, B.O., Aremu, O.H., Ojobola, F.B., Lawal, O.S., Amodu, O.S., Oketayo, O.O., Klink, M.J., and Nelana, S.M., 2023, Photocatalytic degradation of metronidazole using zinc oxide nanoparticles supported on acha waste, *Indones. J. Chem.*, 23 (1), 158–169.

[46] Dai, Q., Chen, L., Chen, W., and Chen, J., 2015, Degradation and kinetics of phenoxyacetic acid in aqueous solution by ozonation, *Sep. Purif. Technol.*, 142, 287–292.

[47] Sumegová, L., Derco, J., and Melicher, M., 2013, Influence of reaction conditions on the ozonation process, *Acta Chim. Slovaca*, 6 (2), 168–172.

[48] Yang, P., Luo, S., Liu, H., Jiao, W., and Liu, Y., 2019, Aqueous ozone decomposition kinetics in a rotating packed bed, *J. Taiwan Inst. Chem. Eng.*, 96, 11–17.