

## Article

# Integrated Process for High Phenol Removal from Wastewater Employing a ZnO Nanocatalyst in an Ozonation Reaction in a Packed Bubble Column Reactor

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**Abstract:** The use of an ozonized bubble column reactor (OBCR) in wastewater treatment is advantageous due to its efficient mixing and mass transfer characteristics. Among all high-performance features, the ozonation reaction in a BCR undergoes a low dissolution of O<sub>3</sub> in the reactor with a limited reaction rate. In this study, the ozonation reaction of phenol in an OBCR was tested using a ZnO nanocatalyst and alumina balls as packing material. Three concentrations of O<sub>3</sub> were evaluated (i.e., 10, 15, and 20 ppm), and 20 ppm was found to be the optimum concentration for phenol degradation. Also, two doses (i.e., 0.05 and 0.1 g/L) of ZnO nanocatalysts were applied in the reaction mixture, with the optimal dose found to be 0.1 g/L. Accordingly, three phenol concentrations were investigated in the OBCR (i.e., 15, 20, and 25 ppm) using four treatment methods (i.e., O<sub>3</sub> alone, O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, O<sub>3</sub>/ZnO nanocatalyst, and O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/ZnO nanocatalyst). At a contact time of 60 min and phenol concentration of 15 ppm, the removal rate was 66.2, 73.1, 74.5, and 86.8% for each treatment method, respectively. The treatment experiment that applied the O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/ZnO nanocatalyst produced the highest phenol conversion into CO<sub>2</sub> and H<sub>2</sub>O in the shortest contact time for all phenol concentrations. Thus, the OBCR employed with a ZnO nanocatalyst plus packing material is a promising technology for the rapid and active removal of phenol because it enhances the number of hydroxyl radicals (•OH) generated, which ultimately increases the oxidation activity in the OBCR. Also, the results showed efficient flow characteristics in the OBCR, with channeling problems averted due to appropriate gas movement resulting from the use of packing materials. Finally, it was found that the ozonation process in an OBCR is an efficient method for phenol conversion with good economic feasibility.

**Keywords:** packing material; phenol degradation; hydroxyl radicals; contact time; channeling problem



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## 1. Introduction

Phenol is the most significant and prevalent organic water contaminant that appears in water resources. Surface water, drinking water, subsurface water, and landfills all include some traces of phenol [1]. Phenol is generally present in the effluents of many kinds of industries, including the petroleum industry (6–500 ppm), petrochemical industry (3–1220 ppm), and coal industry (10–6800 ppm) [2–5]. Discharge of phenol without removal poses serious health dangers to humans and the aquatic environment [6]. The toxic limit of phenol lies between 9 and 25 ppm for both human health and the standard aquatic system [7–10]. Exposing the human body to a high dose of phenol over a long time produces problems in breathing, the presence of tremors, muscle destruction, and many skin diseases [4,8]. Thus, the efficient removal of phenol from wastewater is critical for the safety and health of humans and the environment [11–14].

Phenol removal from polluted wastewater is achieved using various techniques, such as liquid–liquid extraction, air oxidation, catalytic wet air oxidation, and biological processes [7]. Moreover, some advanced techniques may be used to treat phenol, including catalytic photooxidation, Fenton mechanisms, membrane technology, electrochemical techniques, and ozonation processes [15–18]. The ozonation method has been used extensively in the treatment of wastewater. In this process, hydrocarbons are broken down into carbon dioxide and water. However, the ozonation process undergoes limited ozone gas utilization efficiency, and some harmful by-products may be generated during ozonation reactions [19–25]. This problem can be partially solved using the catalytic ozonation process. Then, management and control of a number of variables (i.e., a suitable amount of ozone, catalyst type, and reaction time) and the design and operation of the reactor can deliver high-performance phenol removal [8,20,26].

The ozonation reaction can be achieved in many types of reactors, including membrane reactors, stirred tanks, and fixed-bed, trickle-bed, fluidized-bed, and bubble column reactors [27–32]. Among all types of multiphase reactors, the bubble column reactor (BCR) has the ability to operate efficiently by providing the maximum contact between the gaseous phase and the polluted water (i.e., liquid phase) [33–35]. Moreover, the BCR can be improved by using packing material to increase the contact surface area between the reaction phases [36]. Such packing material provides a high diffusion rate in the system by enhancing the interfacial area. Also, BCRs are usually characterized by their economic operation because they do not include moving or stirring parts [32,37]. Furthermore, in comparison with other multiphase reactors, the BCR is distinguished by its high heat transfer with efficient operation [9,12]. Quan et al. [38], Zheng et al. [39], and Yang et al. [40] have pointed out the importance of the hydrodynamic parameters of the BCR in governing the reactor's performance. They demonstrated that the gas holdup, superficial gas velocity, flow regimes, pressure drop, reactor dimensions, and gas distribution type play a key role in determining the final efficiency of the reactor.

To enhance the removal of phenol or organic compounds and increase the dissolution of ozone gas, the ozonation system was developed by a number of researchers, some of whose work will be described below. Iboukhoulef et al. [41] studied the treatment of phenolic compounds from wastewater using an ozonation method in the presence of BiFeO<sub>3</sub> as a nanocatalyst. They found that the nanocatalyst operated efficiently for the degradation process in alkaline media, with a rate of phenolic compound degradation of ~83% and chemical oxygen demand (COD) reduction of 98%. Qiao et al. [42] evaluated the degradation of nitrobenzene using ozone and persulfate in a rotating packed-bed reactor, noting that the degradation efficiencies were 69.44 and 27.14% for the reaction in the presence of ozone gas alone and persulfate, respectively. Moreover, the result showed a degradation efficiency of 90.59% when using ozone/persulfate. Barlak et al. [43] developed a treatment process for micropollutant abatement in landfill leachate by employing an ozonation reaction in a BCR, using lava rock and expanded clay in the treatment method. They observed that both natural materials provided new technical approaches to enhance the treatment process. Wang et al. [44] studied the degradation of heavy oil from wastewater effluent from refineries via catalytic ozonation using CuO-activated carbon as a heterogeneous catalyst. The catalyst worked efficiently to improve the ozonation reaction with a low cost and high activity. Cao et al. [45] applied a micro-packed bed reactor with ozone to improve the dissolution rate of ozone and achieve high degradation of organic pollutants, noting that the phenol and COD removal recorded values of 100 and 86.4%, respectively, at optimal operating conditions. Yang et al. [46] evaluated the feasibility of the application of packed bubble columns in actual biotreated landfill leachate treatment, providing new information about the transformation of organic matter in leachates during ozonation. For example, their study demonstrated that a packed bubble column increased the removal and decreased the energy use when treating landfill leachate, thus promoting the application of ozonation. Alattar et al. [47] designed a packed BCR (PBCR) to enhance the diffusion and the reaction rate of phenol removal from wastewater with ozone gas and a TiO<sub>2</sub> nanocata-

lyst. They observed that the highest phenol removal (~100%) was achieved at a reaction time of 30 min using a  $\text{TiO}_2$  nanocatalyst and glass packing material with ozone.

Ozonation undergoes a limited reaction rate due to the low mass transfer process in a BCR. Accordingly, it is necessary to enhance the mineralization performance by increasing the solubility of ozone in the mixture inside the reactor [48–52]. Therefore, the main objective of the present work was to increase the mineralization of phenol by enhancing mass transfer using alumina balls as packing material while also improving the reaction rate using a ZnO nanocatalyst.

## 2. Materials and Methods

### 2.1. Chemicals

The experimental investigations were carried out in a bubble column reactor (BCR) using many chemicals, such as phenol (99.6% purity, Gryfskand Co., Ltd., Gryfino, Poland), with sulfuric acid (99.55% purity), sodium thiosulfate (99.9% purity), and potassium iodide (99.5% purity, Fluka Co., Ltd., Buchs, Switzerland). Moreover, zinc oxide nanoparticles (99.85% purity, Sadhika Co., Ltd., Haryana, India) were applied as a nanocatalyst in the reaction system. Furthermore, alumina balls ( $\text{Al}_2\text{O}_3$ , 99.1% purity, QS-Advanced Materials Inc., New York, NY, USA) were employed as packing material in the BCR.

### 2.2. Experimental Apparatus

The phenol removal was conducted in a BCR operating in semi-batch mode. Figure 1 illustrates the schematic representation of the reaction system. The reactor was constructed from QF glass with a height of 150 cm and a diameter of 8 cm. The ozonation reaction was achieved using  $\text{O}_3$  as a gas phase and wastewater polluted by phenol (i.e., simulated wastewater) as the liquid phase in the reactor. An ozone generator device (OZ-30, Carl Roth, Karlsruhe, Germany) was used to supply the BCR with the required amount of  $\text{O}_3$ . Alumina balls ( $\text{Al}_2\text{O}_3$  of 19 mm in diameter) were utilized as a packing media in the BCR. The packing material was arranged in the reactor up to a height of 100 cm from the reactor bottom. Moreover, ZnO nanoparticles were employed as an active nanocatalyst in the reaction system. The ZnO nanocatalyst characterizations were analyzed and described in reference [11]. Accordingly, the phenol removal was carried out using four treatment methods (i.e.,  $\text{O}_3$  alone,  $\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{O}_3/\text{ZnO}$  nanocatalyst, and  $\text{O}_3/\text{Al}_2\text{O}_3/\text{ZnO}$  nanocatalyst). Figure 2 summarizes the four phenol removal methods, with Figure 3 presenting photographs of the four applied experimental methods. Additionally, a stainless steel gas distributor was fixed in the bottom zone of the reactor, containing 52 holes, each one 0.5 mm in diameter. Moreover, the  $\text{O}_3$  flow rate input into the reactor was managed using an accurate gas flow meter.

Actually, the volume of phenol solution without  $\text{Al}_2\text{O}_3$  packing was 4.5 L, while with  $\text{Al}_2\text{O}_3$  packing at a height of 100 cm, it was 3.25 L. Accordingly, in both cases, the concentration of phenol in the solution was kept constant at the required concentration (in mg/L).

### 2.3. Experimental Procedure

Three concentrations of phenol were tested (i.e., 15, 20, and 25 ppm), to simulate the industrial limitations in petroleum refineries [26,34,37]. Moreover, three concentrations of  $\text{O}_3$  were evaluated in the reaction system (i.e., 10, 15, and 20 ppm). The phenol removal in each treatment method was achieved at various reaction times from 10 to 100 min. A sample of treated wastewater at each reaction time was drawn from the sampling valve fixed at a height of 25 cm from the reactor top. Before being used in the reactor, the ZnO nanocatalyst was mixed with polluted wastewater and subjected to a sonication process for 15 min to ensure high nanoparticle distribution in the reaction mixture. Two doses (i.e., 0.05 and 0.1 g/L) of the ZnO nanocatalyst were applied in the reaction mixture. It is important to mention here that the pH value was kept constant at  $7 \pm 0.2$  in order to apply a real neutral pH limit of industrial wastewater in the petroleum industry.

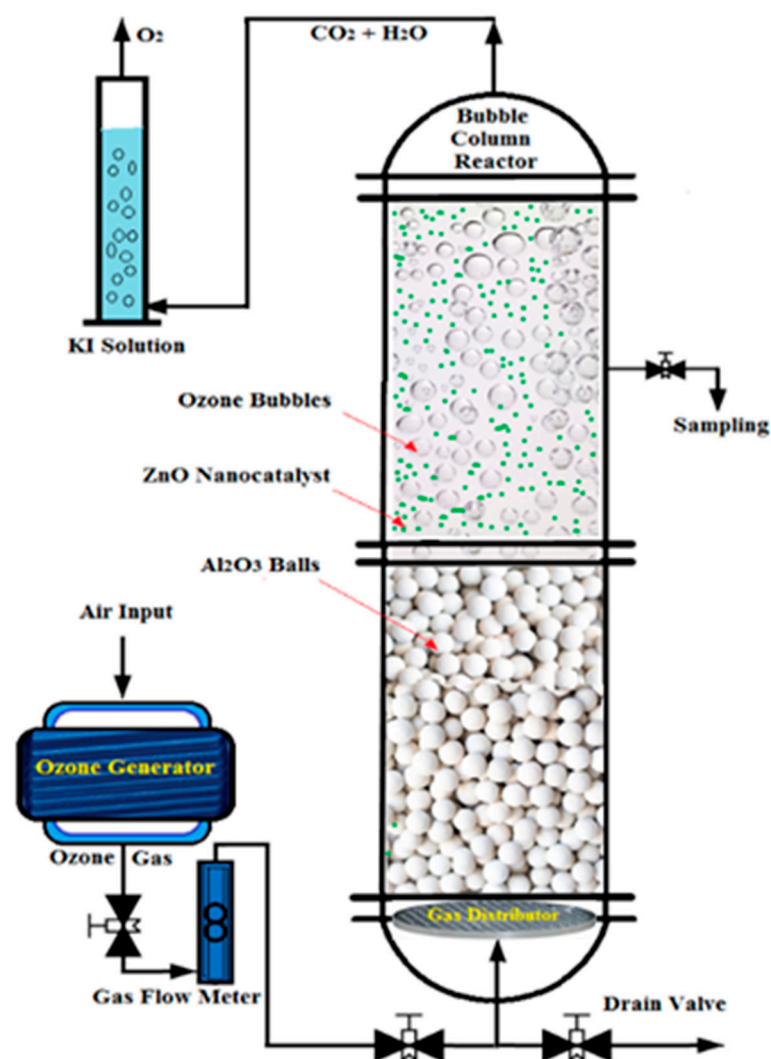


Figure 1. Schematic representation of the BCR system for phenol removal from wastewater.

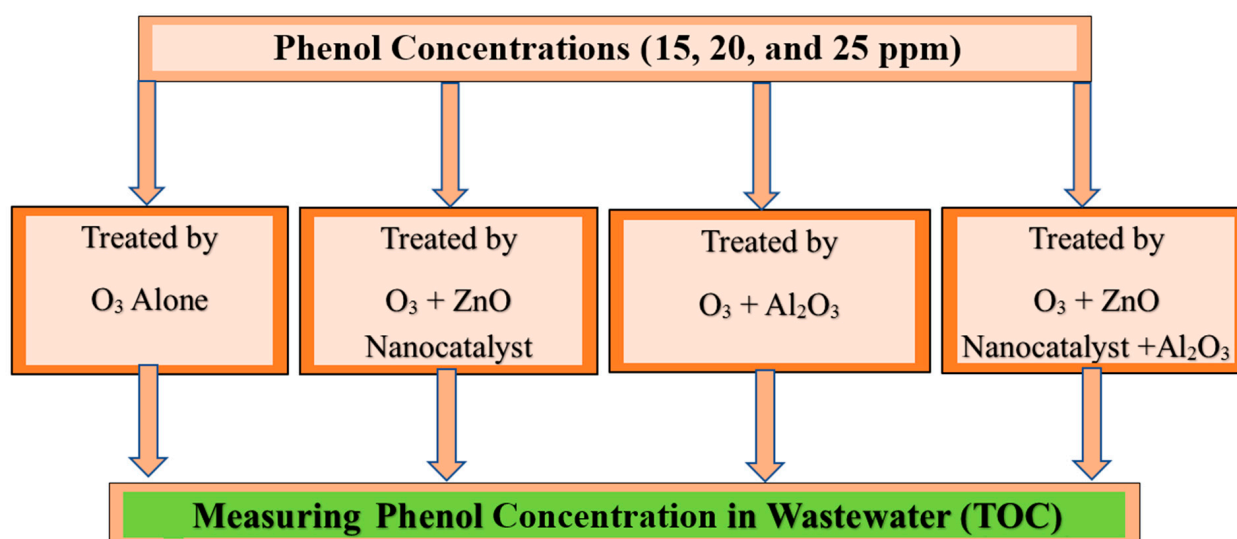


Figure 2. Four experimental methods of phenol removal by ozonation reaction in a BCR.





**Figure 3.** Photos of the reaction apparatus of the BCR applying the four experimental methods: (a)  $O_3$  gas alone, (b)  $O_3$ /ZnO nanocatalyst, (c)  $O_3$ / $Al_2O_3$ , and (d)  $O_3$ / $Al_2O_3$ /ZnO nanocatalyst.

#### 2.4. Measurement Methods

Moreover, the phenol concentration measurements were determined based on measuring the total organic carbon (TOC) in the wastewater samples. The TOC measurements were achieved by employing a TOC-L-CSH E200 device (Shimadzu, Kyoto, Japan). The operating mode of the TOC analyzer was based on the combustion of the organic carbon in the sample to produce carbon dioxide. The measurements depended on the standard test method (ASTM D7573) using an NDIR detector for the produced  $CO_2$  gas. In this method, the nitrogen gas was used as a carrier gas. Moreover, the phenol removal efficiency was calculated using the following formula:

$$\text{Removal efficiency \%} = 1 - [TOC_{(t)}/TOC_{(IN)}] \times 100 \quad (1)$$

where  $TOC_{(IN)}$  is the TOC concentration measured in mg/L at zero time (initial concentration), and  $TOC_{(t)}$  is the TOC concentration measured in mg/L at any period of time.

Additionally, the ozone gas analysis was achieved using the Indigo method [51]. In this method, the concentration of unreacted ozone was calculated using a potassium iodide (KI) solution. Actually, the produced gas from the ozone generator was passed through two containers, each one containing a concentration of 2% potassium iodide (KI) solution of 250 mL volume for 10 min. About 200 mL of KI solution was removed after ozonized gas had been in the air for 10 min. Then, 10 mL of  $\text{H}_2\text{SO}_4$  was added to the mixture and titrated with sodium thiosulfate of 0.005 N until the iodine's yellow hue was no longer discernible in the mixture. Then, two drops of starch were added as an indication. Once the blue tint had vanished, the titration was repeated, and the total amount of sodium thiosulfate consumed was determined. Accordingly, the concentration (ppm) of unreacted ozone gas can be determined using the following formula [6,51]:

$$\text{Unreacted ozone (ppm)} = [(A_1 + A_2) + N + 24]/t \quad (2)$$

where  $A_1$ : Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  used in the first KI container;  $A_2$ : Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  used in the second KI container;  $N$ :  $\text{Na}_2\text{S}_2\text{O}_3$  normality;  $t$ : Ozonation reaction time (min).

To ensure the validity of the resulting experimental values, all samples were measured twice. Accordingly, an error evaluation process was achieved for the ozone gas flow, phenol removal, pressure drop, and contact time using statistical evaluation methods. The uncertainty calculations were applied to the reaction parameters. All experiments were performed in triplicate. Then, the standard deviation of the experimental results fell in a range from 0.005 to 8.16%. The measurements were achieved using the SPSS Statistics Analysis program (version 2023). In addition, all experimental instruments were calibrated to reduce the experimental error values. Table 1 illustrates the estimated values of the experimental uncertainties.

**Table 1.** Measured values of the experimental uncertainties.

Variable	Units	Uncertainty (%)
Ozone Flow Rate	m/s	$\pm 0.006$
Gas Holdup	[-]	$\pm 1.042$
Pressure Drop	Pa	$\pm 3.310$
Contact Time	min	$\pm 0.371$
pH (Constant at value of 7)	-	$\pm 0.200$
TOC Measurements	%	$\pm 8.160$

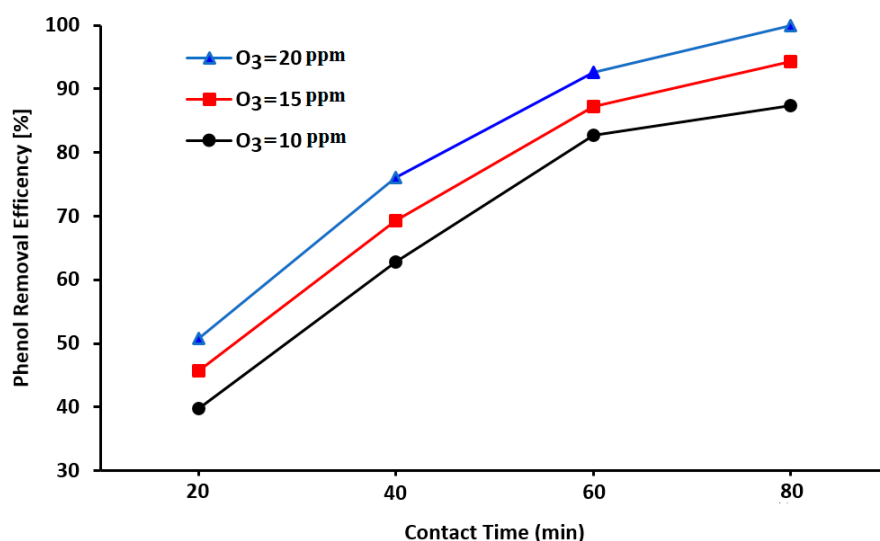
On the other hand, the flow channeling problem across the alumina packing material in the OBCR was evaluated by employing an imaging analysis method of raising gas bubbles. This method was achieved by taking a series of photographs using a high-resolution camera with a video recorder system (Canon, model-RF-S18, Tokyo, Japan). All photographs were taken in a specified section at a height of 100 cm from the gas distributor. Accordingly, image processing software (MATLAB, 9.10-R2021a) was applied to enhance the images of the bubble size and alumina balls in the reactor.

### 3. Results and Discussion

#### 3.1. Effect of the Ozone Concentration on the Phenol Conversion

The ozone gas concentration is the primary factor in the ozonation process, as it typically provides the main requirements for the oxidation reaction. Figure 4 demonstrates the effect of the ozone gas concentration on the rate of phenol elimination at different reaction times, at a phenol concentration of 15 ppm with a ZnO nanocatalyst (0.1 g/L). Three concentrations of ozone were evaluated in the packed bubble column reactor (PBCR) (i.e., 10, 15, and 20 ppm). As displayed in Figure 4, the 20 ppm ozone concentration showed the highest phenol removal rates at all contact times. For example, at a treatment time of 80 min, the phenol removal was 87.4, 94.3, and 100% at ozone concentrations of 10, 15, and

20 ppm, respectively. Therefore, it was decided to apply an ozone concentration of 20 ppm for all of the following experimental runs.



**Figure 4.** Effect of the ozone concentration on the phenol removal rates in a PBCR.

Mukherjee et al. [16] and John et al. [23] have pointed out that the limited selectivity of the ozonation reaction and the low solubility of ozone in the liquid phase reduce the utilization capacity of ozone gas in the reaction mixture. Accordingly, the oxidation process in the presence of ozone gas alone could not completely convert phenol to CO<sub>2</sub> and H<sub>2</sub>O. Hence, a nanocatalyst and packing material were used in the reactor and enhanced the catalytic ozonation reaction by decomposing the ozone gas and generating more active hydroxyl radicals in the reaction mixture. The main characteristic of the ozonation reaction is the formation of a large number of hydroxyl radicals ( $\bullet\text{OH}$ ) in the reactor. These radicals have a higher value of oxidation potential ( $\sim 2.80$  V) in comparison with ozone gas alone (2.08 V). Therefore, the oxidation process can achieve a high phenol degradation rate [25,31,36].

### 3.2. Effect of the ZnO Nanocatalyst Dose

A ZnO nanocatalyst was employed as a catalytic material to improve the phenol degradation reaction in the BCR. Accordingly, to establish the appropriate nanocatalyst dose required for the reaction, two doses of the ZnO nanocatalyst were applied (i.e., 0.05 and 0.1 g/L) in the presence of alumina balls in the reactor. Figure 5 shows the effect of the catalyst dose on the phenol degradation rate at various contact times. The results indicated that the amount of ZnO nanocatalyst considerably influenced the rate of phenol decomposition. At a treatment time of 70 min, the phenol removal was 83.6% and 87.2% for nanocatalyst doses of 0.05 g/L and 0.1 g/L, respectively. This occurred because the presence of the ZnO nanocatalyst in the reaction mixture enhanced the ozonation process by converting more ozone into hydroxyl radicals. Moreover, the large surface area of the nanocatalyst (215 m<sup>2</sup>/g) provided additional active sites that also supported the formation of more hydroxyl radicals. All of these factors improved the phenol degradation reaction and mass transfer rates in the reaction system. Yang et al. [3], Lian et al. [33], and Alattar et al. [47] have indicated that the mass of the catalyst highly influences the reaction mechanism and also the process of conversion of hydrocarbons into carbon dioxide and water. However, limited work has focused on the influence of nanocatalysts on the ozonation process. It is commonly understood that the ozonation reaction in aqueous solutions is a very complicated task and that there is a lack of effective nanocatalysts needed to provide an adequate number of active sites [27,32]. The number of active sites on the nanocatalyst was the predominant parameter affecting the outcome, so

the higher the catalyst dose, the more active sites, which thereby increased the reaction's performance. Thus, the catalyst positively impacted the phenol conversion in the ozonation system. Also, the catalytic reaction of phenol in the ozonation process in the presence of the ZnO nanocatalyst comprised the heterogeneous reaction of a three-phase system (i.e., ozone, wastewater, and nanocatalyst), in which the nanocatalyst was a crucial factor in determining the phenol-removing mechanism [28,43].

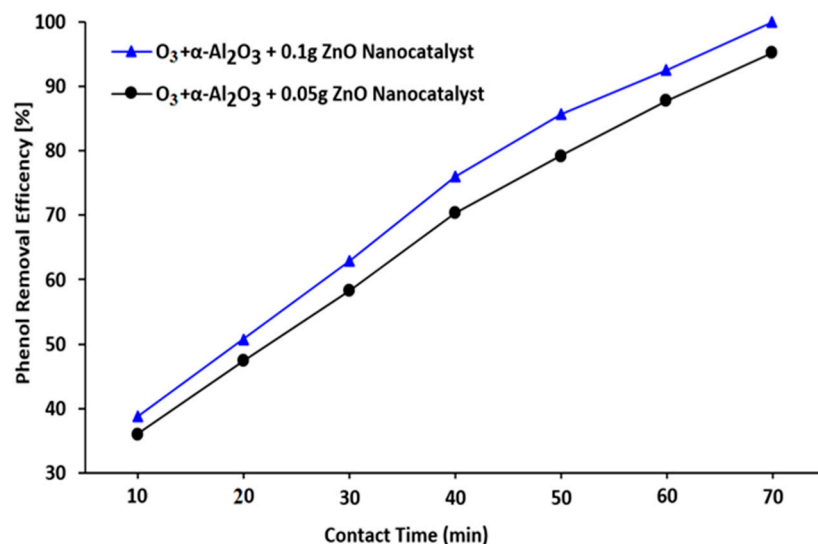


Figure 5. Impact of the ZnO nanocatalyst dose on the ozonation reaction in a PBCR.

### 3.3. Evaluation of the Channeling Flow Problem

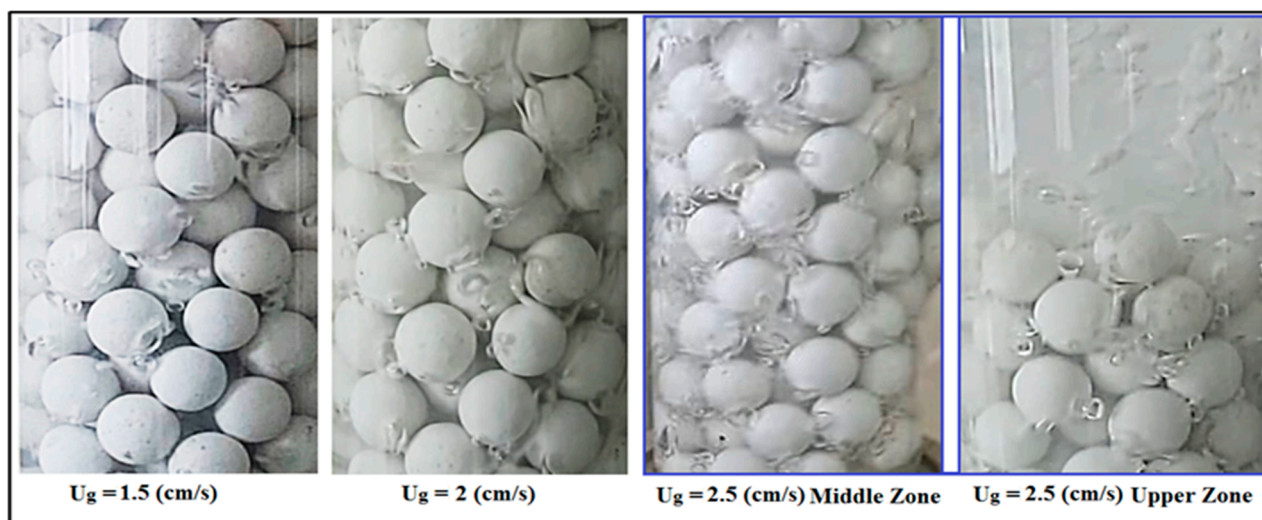
The gas flow through the packing materials usually undergoes what is called a channeling problem. This occurs when the gas flow is much higher in some zones than in others [21,47]. From a fluid flow perspective, this is undesirable, as it substantially reduces the interfacial surface area, which then retards the mass transfer process in the reactor. Such a loading point in the reactor occurs when the velocity of the gas records high values that restrict the flow of liquid in the multiphase reactor [28]. In the present work, no channeling problem was observed as a result of the gas bubble distribution and the void (40%) between the packing materials (alumina balls). Figure 6 represents the ozone gas flow over the packing materials at different superficial gas velocities. The gas and liquid movements were stable over time, and a high contact area was available for an effective reaction performance.

Yang et al. [3], Sukkar et al. [13], and Manjrekar and Dudukovic [24] have indicated that the channeling problem must be avoided because after this point of high velocity, the pressure drops will provide a higher rate that will carry off all liquid, creating a flooding point. Moreover, Cao et al. [45] reported that channeling appears along with low fluid flow, which produces dry zones due to a maldistribution of the packing materials. These dry zones over packing reduce the gas–liquid contact activity. Therefore, in this study, alumina balls were chosen deliberately to serve as the structural packing material in the reactor to produce a uniform gas flow distribution, as shown in Figure 6. Further, these packings were regularly arranged to avoid a channeling problem by applying steady ozone gas velocity in the BCR (i.e., a homogenous flow regime).

From the present experimental investigations, it was observed that the applied hydrodynamic parameters in the OBCR, such as superficial gas velocity and gas distributor design, as well as gas holdup, were selected and managed carefully to provide the highest performance. The main advantages presented by an OBCR involve high liquid phase treatment, efficient mass transfer operation at low consumed energy, high reaction selectivity, an efficient control system, and simple catalyst and packing load. Moreover, the low maintenance cost of this reactor type provides specialized criteria in comparison with



other multiphase reactors. The same observations were confirmed by many authors such as Majhool et al. [11], Liu et al. [14], and Yang et al. [46].



**Figure 6.** Photographs showing the monitoring of the ozone flow across the alumina balls in the ozonation process to evaluate the channeling problem in a BCR at different superficial ozone velocities of 1.5, 2, and 2.5 cm/s (at the middle and upper zones).

### 3.4. Influence of the Initial Phenol Concentrations on the Removal Rate

The four applied treatment methods (i.e.,  $O_3$  alone,  $O_3/Al_2O_3$ ,  $O_3/ZnO$  nanocatalyst, and  $O_3/Al_2O_3/ZnO$  nanocatalyst) were evaluated experimentally in a BCR at different phenol concentrations. The goal of the evaluation process was to determine the optimal treatment method that removed phenol at the highest rate and in the shortest contact time. Accordingly, three phenol concentrations were tested (i.e., 15, 20, and 25 ppm). Figure 7 shows the results of the phenol removal at various contact times in the BCR at a phenol concentration of 15 ppm. The result indicated that the phenol removal was directly proportional to the contact time. Then, as the contact time increased, the degradation of phenol into carbon dioxide and water also increased. The same results were noted in the work of Zheng et al. [39] and Wang et al. [44].

For a selected random contact time of 60 min, the phenol removal was 66.2, 73.1, 74.5, and 86.8% for each treatment method of  $O_3$  alone,  $O_3/Al_2O_3$ ,  $O_3/ZnO$  nanocatalyst, and  $O_3/Al_2O_3/ZnO$  nanocatalyst, respectively. A comparison of the results with the four treatment methods showed that the treatment using the  $O_3/Al_2O_3/ZnO$  nanocatalyst provided the highest phenol degradation performance, which attained the complete conversion of phenol (100%) at a contact time of 80 min. Moreover, the treatment method using the  $O_3/ZnO$  nanocatalyst achieved complete conversion at a contact time of 90 min, while the  $O_3/Al_2O_3$  required 100 min of contact time to accomplish the complete conversion.

Figure 8 shows the influence of the applied treatment method on the amount of phenol removal using an initial phenol concentration of 20 ppm. As the phenol concentration increased from 15 ppm (Figure 7) to 20 ppm, more contact time was required to achieve high levels of phenol removal. The phenol removal results for the reaction with  $O_3$  gas alone,  $O_3/ZnO$ ,  $O_3/Al_2O_3$  nanocatalyst, and  $O_3/Al_2O_3/ZnO$  nanocatalyst at the contact time of 60 min recorded removal percentages of 61.5, 76.3, 78.1 and 80.8%, respectively. Also, the results indicated a complete phenol removal of ~100% at a contact time of 90 min using the  $O_3/Al_2O_3/ZnO$  nanocatalyst. Moreover, the use of either the  $O_3/ZnO$  nanocatalyst or  $O_3/Al_2O_3$  produced a complete conversion of phenol at 100 min of contact time. Similarly, Lima et al. [17], Zou et al. [19], and Yaqoob et al. [35] have shown that a higher concentration of phenol or any organic compound required a longer time to be removed by ozonation.

technology. The conversion of these organic compounds into intermediate ones is usually a complicated process and thus requires more time.

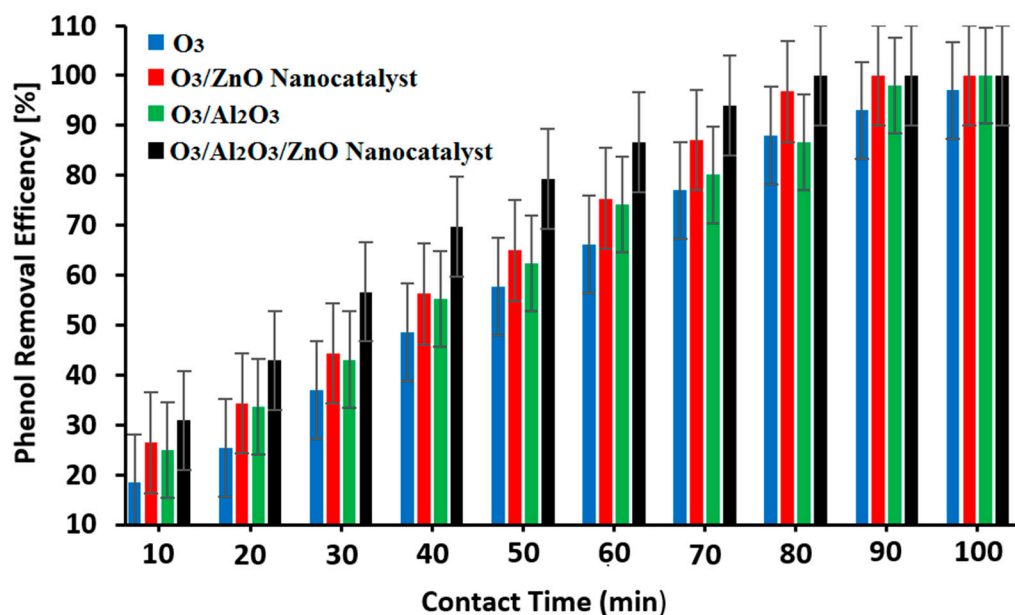


Figure 7. Conversion of phenol in the ozonation process in a BCR using the four treatment methods at a phenol concentration of 15 ppm.

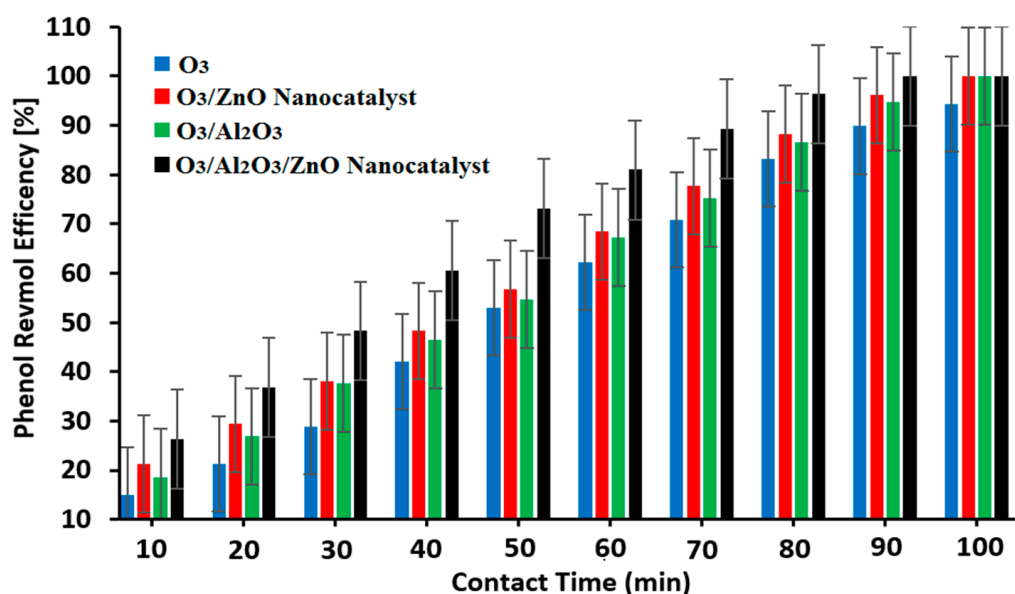
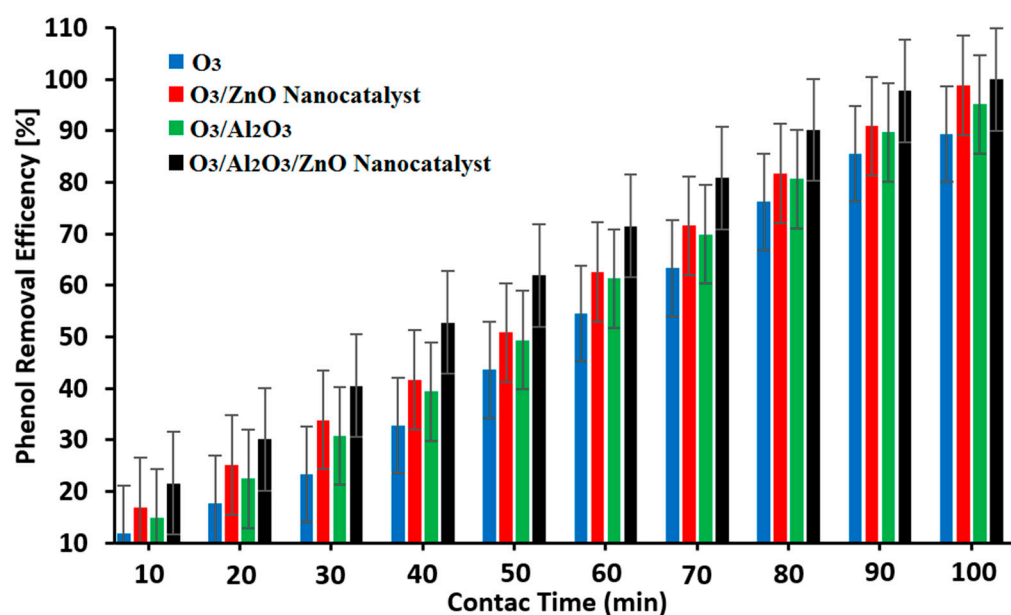


Figure 8. Conversion of phenol in the ozonation process in a BCR using the four treatment methods at a phenol concentration of 20 ppm.

Additionally, the results showed that the contact between the gas and liquid needed more reaction time to achieve the required removal of phenol due to the high concentration of phenol in the wastewater. Quan et al. [38] and Wang et al. [44] have indicated that the economic feasibility of any wastewater treatment process is highly dependent on the initial concentration of organic compounds in the polluted wastewater. Then, the reduction in the pollutant concentration with reaction time normally includes the generation of intermediate components due to the inactive oxidation process in some applied treatment technologies. Moreover, the use of ozonation technology in the present ZnO nanocatalyst and alumina balls combination enhanced the ozonation process in the BCR to achieve high phenol

conversion in a shorter reaction time. As can be seen, the presence of the alumina balls supported the formation of a thin film over the outer surface of these packing materials. This thin film worked to improve the mass transfer mechanism and then enhanced the conversion of phenol in the ozonation process by providing more hydroxyl radicals ( $\bullet\text{OH}$ ). As stated previously, these hydroxyl radicals are the main variable responsible for converting phenol into carbon dioxide and water [1,21].

Figure 9 illustrates the removal rates of phenol at the highest concentration (25 ppm) using the four treatment methods. As in the previous cases, the same trend of removal efficiency was noted (see Figures 7 and 8), but in this case, even more contact time was needed. As a result, the phenol removal efficiency decreased due to the increase in the phenol concentration. At a contact time of 60 min, the phenol removal was 54.7, 60.1, 62, and 72.8% for the four treatment methods of  $\text{O}_3$  alone,  $\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{O}_3/\text{ZnO}$  nanocatalyst, and  $\text{O}_3/\text{Al}_2\text{O}_3/\text{ZnO}$  nanocatalyst, respectively. The complete removal of phenol occurred at a reaction time of 100 min using the  $\text{O}_3/\text{Al}_2\text{O}_3/\text{ZnO}$  nanocatalyst.



**Figure 9.** Conversion of phenol in the ozonation process in a BCR using the four treatment methods at a phenol concentration of 25 ppm.

Finally, a high and stable phenol removal rate was the main criterion for the operation of the OBCR in this work. The results of the present technique that used ZnO nanocatalyst and alumina balls as packing media were compared with the results of other authors who applied different techniques for phenol removal. In the present study, among all used treatment methods of  $\text{O}_3$  alone,  $\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{O}_3/\text{ZnO}$  nanocatalyst, and  $\text{O}_3/\text{Al}_2\text{O}_3/\text{ZnO}$  nanocatalyst, it can be seen from Figure 7 that the  $\text{O}_3/\text{Al}_2\text{O}_3/\text{ZnO}$  nanocatalyst provided the highest phenol degradation efficiency, which achieved the complete conversion of phenol (100%) at a shorter contact time of 80 min. The enhancement in the degradation reaction was caused by the high mass transfer process as well as the highly dispersed nanocatalyst. Many authors have applied different approaches and reactors for phenol removal, such as Wu et al. [7], Lima et al. [15], Cheng et al. [36], and Alattar et al. [47]. They demonstrate the combined disadvantages of these reactors: the catalyst charging, limited phenol removal, and high operating cost are significant aspects that negatively influence the phenol degradation rate [1,45,49]. Table 2 illustrates the comparison between the results of the present study with the results of various studies on different operating techniques and parameters. From this table, it was observed that the results of the phenol degradation rate (of 100%) are higher than the corresponding removal rates of other reaction techniques.

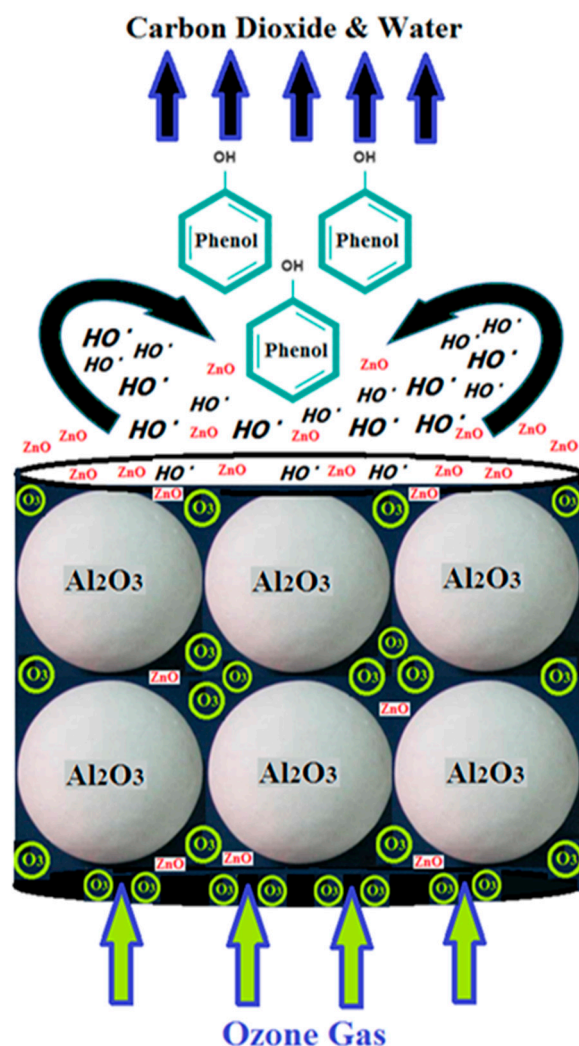
**Table 2.** Comparison of phenol and organic pollutants degradation rate achieved by various studies using different treatment technologies.

Authors	Pollutants	Technology	Removal Rate
Wu et al. [7]	Phenol and nitrobenzene degradation	Applying microbubble technique ( $>50\ \mu\text{m}$ )	Ozone mass transfer rates were 1.3–1.5 times higher than those of conventional bubble aeration.
Lima et al. [15]	Hydroquinone	Using $\text{H}_2\text{O}_2$ as an oxidizing agent in Fenton's technique in a bubble column reactor	Hydroquinone degradation was achieved at 39% of total of TOC
Alsaffar et al. [23]	Bisphenol	Photocatalytic degradation technology using Er-Fe/ $\text{TiO}_2$ modified catalyst	90% removal of Bisphenol
Qiao et al. [42]	Nitrobenzene	Degradation process in rotating ozonized packed bed reactor using $\text{Na}_2\text{S}_2\text{O}_8$ as persulfate oxidizing agent	90.59% degradation efficiency
Alattar et al. [47]	Phenol concentration of 15 ppm	Glass beads and $\text{TiO}_2$ nanocatalyst in bubble column reactor	100% at 105 min in presence of $\text{TiO}_2$ nanocatalyst
The present work	Phenol concentration of 15 ppm	Bubble column reactor utilizing alumina balls and ZnO nanocatalyst	100% at 80 min

### 3.5. Reaction Mechanism of the Ozonation Reaction

Building a complete understanding of phenol degradation in the OBCR is needed to manage the main stages in the ozonation reaction. Figure 10 represents a schematic diagram detailing the reaction mechanism of the ozonation reaction in the OBCR in the presence of alumina balls as packing and the ZnO nanocatalyst. The nanocatalyst improved the catalytic ozonation process and degraded more phenol in the reactor. This was achieved by enhancing the formation of more hydroxyl radicals ( $\bullet\text{OH}$ ) in the OBCR. These radicals are strong oxidizing agents in the reaction mixture that improve the phenol degradation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [31,36]. As a result of the hydroxyl radicals' activities in the catalytic ozonation process, more phenol could be converted within a shorter contact time. Further, the main ozonation reaction was achieved at the reactor bottom, which was full of  $\text{Al}_2\text{O}_3$  balls. The reaction in the presence of the alumina balls provided an efficient and high contact area between the gas and liquid phases. Accordingly, more hydroxyl radicals were formed. Then, the mass transfer process and reaction rate increased in the OBCR.

Additionally, the presence of a ZnO nanocatalyst in the reaction mixture of the three-phase system provided an efficient and active catalytic surface area for the ozonation reaction. Also, this step generated extra hydroxyl radicals, which supported the removal efficiency in the reactor. The ZnO nanocatalyst, which operates according to heterogeneous catalyst principles, was applied to increase the mass transfer between the ozone gas and polluted wastewater (i.e., liquid phase). The total surface morphology of the nanocatalyst enhanced the phenol degradation reaction due to the highly active sites within the catalyst pores. Thus, excellent reaction activity, selectivity, and stability were achieved in the OBCR for all contact times. Notably, the ZnO nanocatalyst has structural features that inherently provide plentiful and ordered pore specifications and adsorption sites [8,19]. All of these factors play a constant role in the formation of additional free radicals for the phenol oxidation process, and then, an improved mass transfer operation and reaction rate can occur [3,47].



**Figure 10.** Schematic diagram representing the phenol conversion mechanism using ozone, alumina balls, and ZnO nanocatalysts in the OBCR.

#### 4. Conclusions

The low rate of mineralization of phenol pollutants from wastewater was increased by using alumina balls as packing media as well as a ZnO nanocatalyst. The results showed that the optimal  $O_3$  gas concentration and ZnO nanocatalyst dose were 20 ppm and 0.1 g/L, respectively. Moreover, among the four experimental methods used in the mineralization process, it was found that the  $O_3/Al_2O_3/ZnO$  nanocatalyst method provided the highest phenol degradation performance (100%) at a contact time of 80 min for an initial phenol concentration of 15 ppm. Furthermore, the flow evaluation study indicated that no channeling problem was observed as a result of the gas bubble movement via the alumina balls due to the appropriate gas void fraction of 0.4. Also, it was noted that the presence of ZnO nanocatalyst improved the catalytic ozonation process due to the highly active sites within the catalyst pores. Additionally, the ZnO nanocatalyst and alumina balls enhanced the ozonation reaction to form more hydroxyl radicals ( $\bullet OH$ ) in the OBCR. These strong oxidizing radicals increased the phenol degradation mechanism into  $CO_2$  and  $H_2O$ . From a mass transfer point of view, the formation of a thin layer over the alumina balls contributed to enhancing the reaction rate, fostering high phenol removal. A review of the literature found no previous studies that have investigated the phenol ozonation process combined with ZnO nanocatalysts in the presence of alumina balls as a packing material in an OBCR. Accordingly, the suggested reaction mechanism in the present work provides more understanding of the ozonation process in order to convert phenol in wastewater within a



shorter reaction time. Finally, the reaction of phenol along the packed OBCR height was considered as the chief factor in supporting the reaction mechanism.

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