THE ROLE OF TiO_2 NPs CATALYST AND PACKING MATERIAL IN REMOVAL OF PHENOL FROM WASTEWATER USING AN OZONIZED BUBBLE COLUMN REACTOR

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Highlight
This research aims to enhance mass transfer and reaction rate of phenol degradation from wastewater in ozonation process using packed bubble column reactor.

Abstract
Phenol is present as a highly toxic pollutant in wastewater, and it has a dangerous impact on the environment. In the present research, the phenol removal from wastewater has been achieved using four treatment methods in a bubble column reactor (treatment by ozone only, using packed bubble column reactor with ozone, utilizing ozone with TiO_2 NPs catalyst in the reactor without packing, and employing ozone with TiO_2 NPs in the presence of packing). The effects of phenol concentration, ozone dosage, TiO_2 NPs additions, and contact time on the phenol removal efficiency were determined. It was found that at a contact time of 30 min, the phenol removal was 60.4, 74.9, 86.0, and 100% for the first, second, third, and fourth methods, respectively. The results indicated that the phenol degradation method using catalytic ozonation in a packed bubble column with TiO_2 NPs is the best treatment method. This study demonstrated the advantages of using packing materials in a bubble column reactor to enhance the mass transfer process in an ozonation reaction and then increase the phenol removal efficiency. Also, the presence of TiO_2 NPs as a catalyst improves the ozonation process via the production of hydroxyl routs. Additionally, the reaction kinetics of ozonation reaction manifested that the first order model is more applicable for the reaction. Eventually, the packed bubble column reactor in the presence of TiO_2 NPs catalyst provided a high-performance removal of phenol with a high economic feasibility.

Keywords
petroleum refineries; phenol degradation; TiO_2 NPs; multiphase flow reactor; catalytic ozonation reaction.

Introduction
The demand for petroleum and other energy resources is increasing with the population increase and global economic development. The petroleum refinery requires huge quantities of water for an operating unit, and then large amounts of wastewater are produced [1–3]. Phenol regards one of the most harmful materials produced in wastewater effluent from petroleum refineries and results in environmental risks as well as hinders the normal operations of the ecosystems [4]. Phenol is a toxic and dangerous substance for all living organisms, as it causes many dangerous symptoms to humans, animals, and plants [5–8]. Therefore, efficient treatment methods are needed to ensure that phenol is completely removed from the water. According to the EPA classifications, phenol

is selected as one of 129 priority contaminants that must be removed and controlled [5]. Many industrial methods are usually used for the removal of phenol from wastewater [9–14]. The advanced oxidation process (AOP) is considered one of the important methods used to treat polluted water [15–18]. Ozonation technology is one of the chief AOPs which increased the attention as a result of the finding of ozone's potential to efficiently degrade various types of organic pollution, especially the phenol [17]. Multiphase reactors are widely used in ozonation process to remove organic compounds from industrial wastewater, such as trickle bed reactor, fluidized bed reactor, membrane reactor, and bubble column reactor [19–25]. The performance of these reactors is highly managed by the operation of the hydrodynamics parameters in the reactor [26]. Bubble column reactor is one of the main multiphase reactors that have an efficient contact among the gas, liquid, and solid phases [27–32]. Accordingly, bubble column reactor employed in ozonation process due to its ability to eliminate the contaminants in water in the presence of oxidation agents such as ozone [12,33]. Many authors have investigated the ozonation process to remove the phenol from wastewater using different nanomaterials in a bubble column reactor [34–36]. Sridar et al. [37] employed FeO and ZnO NPs to remove the phenol from synthetic and industrial wastewater. The authors noted that the removal of phenol effectiveness for FeO was 82%. Also, the efficiency of phenol removal from industrial wastewater using ZnO was found to be relatively low when compared to synthetic phenol solution. Iboukhoulef et al. [38] applied an ozonation reaction with $BiFeO_3$ nanocatalyst to treat the olive mill wastewater. It was observed that the degradation process caused by $O_3/BiFeO_3/S_2O_{82}$ under alkaline circumstances proved to be the most effective. This degradation achieved a reduction of phenolic compounds by ~83% and a reduction of COD by 98%. Wang et al. [39] studied the degradation of wastewater effluent from refineries via catalytic ozonation by using activated carbon-supported copper oxide (CuO/AC). It was observed that the (CuO/AC) was a suitable supported catalyst for enhancing the ozonation degradation of heavy oil from wastewater. Salcedo, et al. [40] investigated the phenol degradation process using a natural catalyst of Sand-coated-carbon in a batch reactor. It was noticed that about 65% of degradation occurred with an average of 16 phenols, and 41% of wastewater was mineralized. Also, the authors found that, with the reaction half-time values ranging between 0.01 and 3.6 h, the photocatalysis process was effective in degrading phenols. Al-Ghouti et al. [41] studied the removal of phenol from wastewater using graphene oxide NPs. It was indicated that the increase in operating temperature was caused by a clear reduction in the adsorption capacity. Zazouli et al. [42] tested the removal of pentachlorophenol from wastewater by photocatalytic ozonation process using graphene-dioxide titanium nanocomposite. It was seen that by increasing the dose of used nanocomposite material, the removal efficiency was enhanced. The highest removal efficiency was noted to be 98.82%.According to a literature survey, it was observed that the phenol oxidizes slowly during the ozonation process in the bubble column. Moreover, the low solubility of ozone in water leads to low ozone activity, as well as the production of intermediate products that cannot react with the ozone, resulting in low mineralization efficiency, which must be addressed [40–44]. Therefore, the main aims of the present work are to apply a packed bubble column to enhance the mass transfer and the reaction mechanism of phenol degradation from wastewater in the ozonation process, and to investigate the influence of TiO_2 NPs on the activity of ozone gas to increase the phenol degradation in the reactor.

Materials and Methods

Chemicals

In the present experimental work, many chemicals were used such as phenol (99.6% purity), and TiO_2 NPs (30 nm in size of 99.5% purity) were obtained from Sigma-Aldrich company. Iodide Potassium (99.6% purity), Sodium thiosulfate (99.6% purity), and Sulfuric acid (99.6% purity) were obtained from the Fluka company. Also, starch (99.6% purity) was used to determine the ozone concentration.

Experimental Setup and Procedure

In this investigation, a bubble column reactor was designed to carry out the experimental tests to remove the phenol from wastewater. Figure 1 shows the experimental system of packed bubble column reactor operated under a semi-batch mode, while Figure 2 illustrates a schematic diagram of the experimental apparatus. The reactor height was 150 cm, and its diameter was 8 cm. At a height of 100 cm, the reactor was packed with spherical glass beads of 1.5 cm in diameter. The gas phase was passed via the rector bottom using a gas distribution that was constructed from stainless steel with 52 holes of 0.5 mm in diameter. Moreover, the ozone gas (gas phase) was generated using an ozone generator device of 20 mg/L. A calibrated gas flow meter was used to regulate the flow rate input into reactor.

The reactor was equipped with a sampling valve that was supported at a height of 75 cm.

Figure 1. The experimental apparatus of packed bubble column reactor. *Source: Author.*

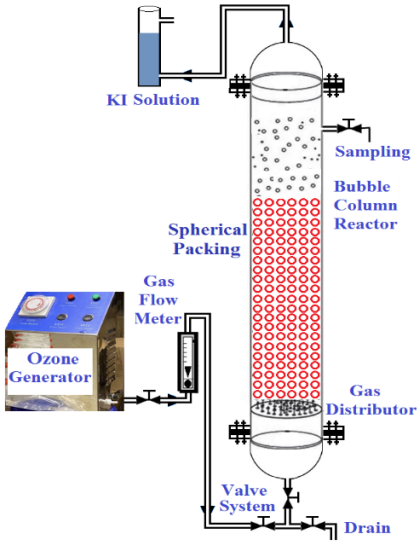

Figure 2. Schematic diagrams of experimental bubble column reactor apparatus. *Source: Author.*

Simulated polluted wastewater was synthesized by dissolving phenol in distilled water. Four concentrations of phenol solutions were prepared (i.e., 3, 6, 9, 12, and 15 mg/L). The ozonation process of phenol treatment was achieved using input ozone gas at concentrations of 10, 15, and 20 mg/L. Each experiment was evaluated under total ozonation time (contact time) for 120 min with a 15 min period of time for drawing the samples. Additionally, the concentration of ozone gas in the water was determined using the Indigo technique [18–20]. Actually, the experimental procedure was achieved using four different phenol treatment modes in bubble column reactors. The first one was carried out in a bubble column reactor with ozone gas only. The second mode of treatment was conducted using ozone in the

presence of packing (O_3/packing). The third treatment mode was achieved in the presence of ozone and TiO_2 NPs (O_3/TiO_2 NPs), while the final treatment mode was performed using ozone gas with packing and TiO_2 NPs (O_3/packing/TiO_2 NPs). Figure 3 summarizes the four stages of 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).

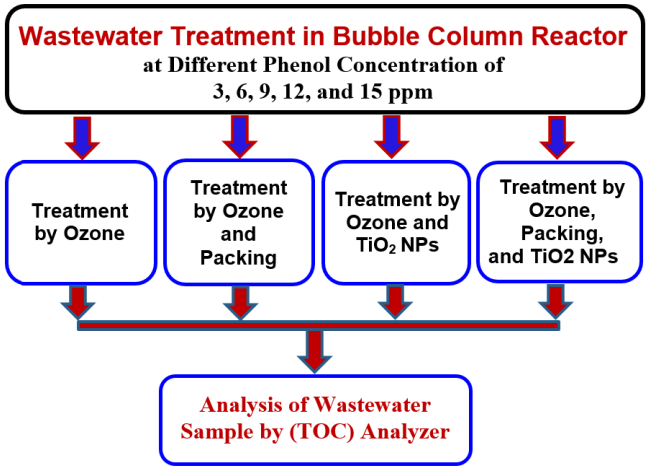

Figure 3. The four treatment stages of phenol removal in the bubble column reactor. *Source: Author.*

Results and Discussion

Evaluation of Phenol Removal Efficiency Using Ozone Only

In order to evaluate the influence of the concentration of phenol on the removal rates in all stages of treatment, four phenol concentrations of 3, 6, 9, 12, and 15 mg/L were investigated. The pH value was kept constants for all experiments at the value of 7. Also, the ozone concentration and the TiO_2 NPs dose were set at 50.3 mg/min and 0.1 g, respectively. Figure 4 displays the results of phenol degradation with contact time (treatment time) using ozone only in a bubble column reactor. The results evinced that at a contact time of 30 min, the phenol removal % recorded values were 60.42%, 52.19%, 43.09%, 38.33%, and 30.69% for phenol concentrations of 3, 6, 9, 12, and 15 mg/L, respectively. Also, the result elucidated that the best contact time was measured to be 75, 90, 105, and 120 min for phenol concentrations of 6, 9, 12, and 15 mg/L, respectively. Moreover, it was observed that a reaction time of 60 min is required to ensure the complete removal of phenol at an initial phenol concentration of 3 mg/L. Then, it was seen that as the initial phenol concentration was increased, the period of reaction time increased too. Accordingly, the contact time is regarded a major factor determining the removal efficiency of phenol. The same results were reported by Park et al. [21] and Nirmala et al. [23].

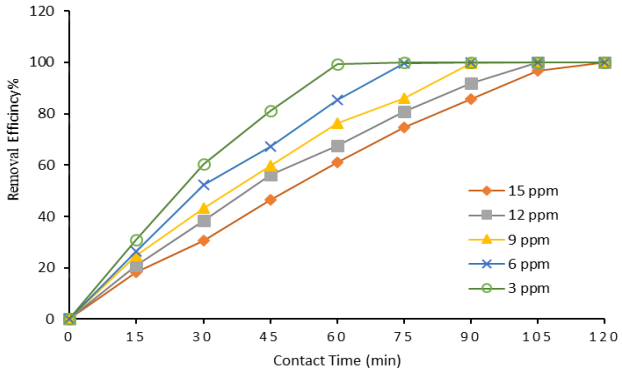

Figure 4. Effect of the initial phenol concentration on the removal rates using ozone only. *Source: Author.*

Influence of Packing on the Phenol Degradation Rate

Figure 5 illustrates the relationship between phenol removal efficiency and contact time using ozone and packing in a bubble column reactor. The results indicated that the phenol degradation rate increased with the decreasing of phenol dose. At a contact time of 30 min, the phenol removal efficiency was 74.98%, 52.97%, and 38.22% for phenol concentrations of 3, 9, and 5 mg/L, respectively. Also, at the time of 45 min, the removal efficiency was 100% at a phenol concentration of 3 mg/L. Moreover, at 15 mg/L of phenol concentration, the phenol removal was achieved 100% at a contact time of 105 min. Consequently, the addition of packing to the bubble column reactor enhances the removal of phenol efficiency significantly due to the improvement in the contact area between gas and liquid, and then a high mass transfer rate was obtained. Furthermore, the use of packing in bubble column reactor will work on lowering the ozone utilization efficiency, and then low mass transfer retardation will be achieved. Therefore, adding the packing material to the bubble column reactor is considered an efficient method for enhancing the decomposition of ozone gas in an aqueous solution to improve the ozone utilization and increase the removal efficiency of phenol degradation [18–23]. Also, many investigators, such as Deshpande et al. [15], Xiong et al. [33], Sukkar et al. [36] indicated that the presence of packing inside different types of reactors enhances the mass transfer and the reaction rate dramatically.

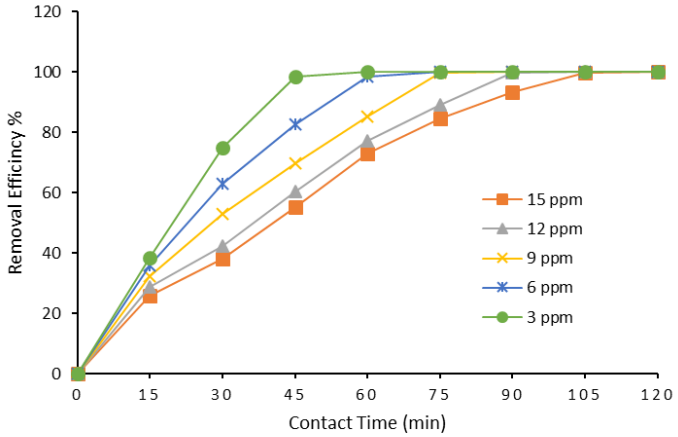

Figure 5. Effect of packing and ozone on the reactor performance to remove the phenol. *Source: Author.*

The use of a catalyst to initiate the reaction mechanism is considered an important task to improve the ozonation process and the high phenol degradation rate. Figure 6 clarifies the effect of the addition of TiO_2 NPs as a catalyst on the phenol removal efficiency with contact time**.** The catalyst addition was 0.1 g of TiO_2 NPs. The result in this figure exhibited that the TiO_2 NPs addition enhanced the phenol degradation rate in comparison with the treatment with ozone only (Figure 4). For a contact time of 30 min, the value of phenol removal % was 86.04%, 62.45%, and 48.16% for phenol concentrations of 3, 9, and 15 mg/L, respectively. Also, it was found that at a concentration of 3 mg/L, the complete removal of phenol (100%) was achieved at 45 min of contact time. On the other hand, for a phenol concentration of 15 mg/L, a contact time of 105 min is required for the complete removal of phenol from wastewater. A comparison between the results of phenol removal efficiency at 45 min of contact time depicted that a value of 100% and 81.22% was achieved for the presence and absence of TiO_2 NPs catalyst, respectively.

Actually, when the ozone gas was used in the reactor without TiO_2 NPs, the phenol ozonation process was found to be rather limited, due to the slow reaction of ozone with phenol (degradation reaction). These results were clearly noted in Figure 6 mainly due to the enhancement and high conversion of phenol accomplished in the catalytic ozonation process owing to the action of free radicals generated by the self-decomposition of ozone on the active site of the TiO_2 NPs, thus an increase in the removal rate of phenol by catalytic ozonation at the gas-liquid interface [6,12,33]. The same results were obtained by Parvin and Ali [24] in their work; they found that after 30 min, the change of TOC for ozone/ZnO NPs and ozone alone was 54.9% and 27.4%, respectively. This result indicates the rapidly mineralized pollutants by the heterogeneous catalytic ozonation using the ZnO NPs than ozone alone.

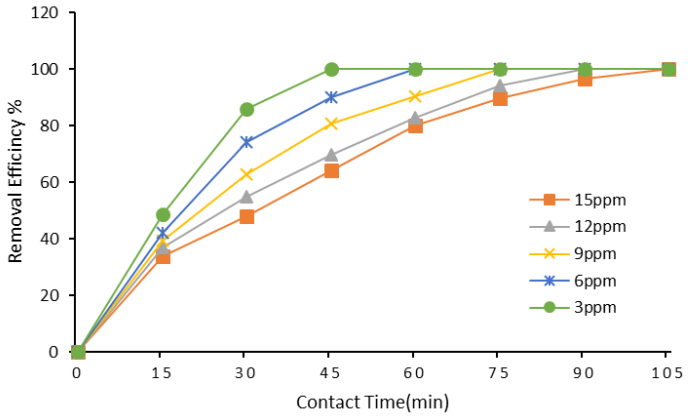

Figure 6. Effect TiO_2 NPs addition as a catalyst with ozone on the phenol removal rates. *Source: Author.*

Influence of TiO_2 NPs and Packing on the Phenol Degradation Rate

The results of the fourth stage of phenol treatment were achieved using TiO_2 NPs in presence of packing in a bubble column reactor. Figure 7 demonstrates the influence of contact time on the removal efficiency of phenol in the presence of TiO_2 NPs and packing in the reactor. The results revealed that at a contact time of 30 min and a phenol concentration of 3 mg/L, a percentage of 100% of phenol removal was observed. Also, it was found that the removal efficiency of phenol at 9 and 15 mg/L was 79.32% and 64.11%, respectively. Then, it was noted that the presence of TiO_2 NPs in a packed bubble column reactor improved the reaction mechanism of phenol degradation significantly. As an example, at a phenol concentration of 15 mg/L, 90 min of treatment time was needed to achieve the phenol removal of 100%. These results mainly evinced that the use of TiO_2 NPs in a packed bubble column reactor is higher than that of the other previous three treatment methods. At a contact time of 30 min and a phenol concentration of 3 mg/L, the treatment results for O_3 gas only, O_3/packing, O_3/TiO_2 NPs, and O_3/packing/TiO_2 NPs were 60.42%, 74.98%, 86.04%, and 100%, respectively. These results indicated that the use of a packed bubble column is considered to provide an increased interfacial contact area, lower ozone gas rising velocity, longer ozone gas stagnation time, increased contact time, and higher mass transfer coefficient. All these factors enable the ozonation process to increase the phenol removal efficiency.

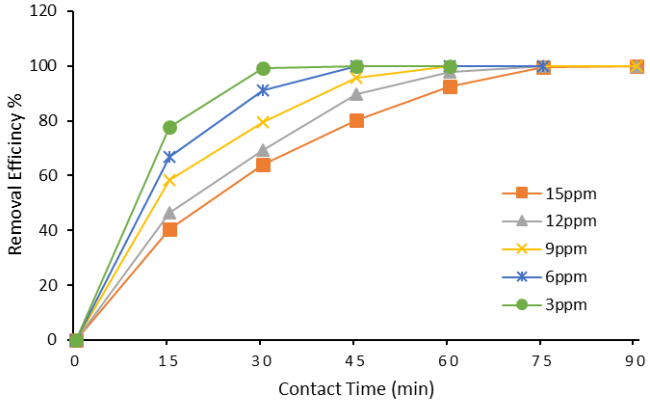

Figure 7. Effect of TiO_2 NPs and packing on the phenol removal rates in the reactor. *Source: Author.*

Effect of Ozone Concentration

The influence of ozone gas concentration on the phenol degradation process was evaluated in the present study. Three levels of ozone were tested (i.e., 10, 15, and 20 mg/L), while the concentration of phenol was kept constant at 3 mg/L. Figure 8 reveals the effects of the ozone dose on the phenol removal rate. From this figure, it was noted

that at the treatment time of 30 min, the ozone dose of 10, 15, and 20 mg/L provided a phenol removal efficiency of 73.34, 88.95, and 99.43%, respectively. Then, the results in this figure indicated that as the ozone dose increased in the bubble column reactor, faster phenol degradation was achieved. Actually, when the system operated with high concentrations of ozone, the degradation ability of organic materials increased dramatically with a short treatment time. The same finding was noted by Mohsen et al. [28] via their investigation on the catalytic ozonation of caffeine. It was found that with the increasing of ozone concentration, the pollutants removal rate increased too. Furthermore, it was observed that the phenol degradation efficiency arrived at 100% when the reaction was carried out at an ozone concentration of 2.5 mg/L and 5 mg/L at treatment times of 80 min and 60 min, respectively. Then, it was seen that as the ozone concentration was increased, the treatment time required lower contact time to achieve 100% removal of phenol. Accordingly, many authors have also noted that the increase in ozone concentration will provide better phenol removal efficiency [12,29,40]. Then, the experimental results in figure 8 clearly portrayed the importance of increasing the ozone concentration in the aqueous phase to get a significant impact on the rate of organic materials oxidation.

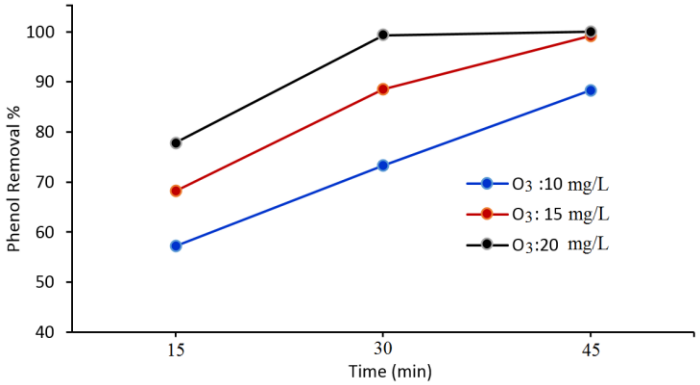

Figure 8. Effect of ozone concentration on phenol removal efficiency at different contact times (phenol dose of 3 mg/L and TiO_2 NPs catalyst of 0.1 g). *Source: Author.*

Effect of TiO_2 NPs Catalyst Dosage

In this section, the TiO_2 NPs were used as a catalytic material to improve the reaction of phenol degradation. Accordingly, from an economic point of view, determining the optimal dosage of nanocatalyst is regarded the most important criterion for a high reaction performance. Four dosages of TiO_2 NPs catalyst were tested (0.025, 0.05, 0.1, and 0.2 g/L) at an ozone concentration of 20 mg/L in the presence of packing material. The phenol concentration was 3 mg/L for all sets of experiments. Figure 9 elucidates the effect of catalyst dose on the degradation of phenol at different treatment times. The results indicated that the dose of TiO_2 NPs catalyst plays a significant impact on the rate of phenol degradation. Accordingly, it was noted that at 30 min of reaction time using ozonation treatment in the presence of packing material, the use of TiO_2 NPs catalyst of 0.025, 0.05, and 0.1 g/L provided a phenol removal of 80.45 and 92.62, and 99.35%, respectively. Actually, the increasing of TiO_2 NPs catalyst will initiate the formation of more active sites on the catalyst surface, and then more (OH) radicals will be generated in the reaction system. Such operation leads to a significant improvement in the phenol degradation mechanism with a high mass transfer rate. Moreover, at a contact time of 30 min, it was found that when the TiO_2 NPs catalyst concentration was 0.1 and 0.2 g, the phenol removal efficiency was 99.35%, and 95.25% respectively. It is important to mention here that the best TiO_2 NPs catalyst dose was 0.1 g which provides the highest phenol degradation (100%) within the shorter time of 30 min. Moreover, it was noted that the increase of TiO_2 NPs catalyst amount was not influenced by the reaction mechanism for further phenol degradation. In fact, increasing the dose of the catalyst can lead to the accumulation and precipitation of the catalyst causing inactivation of some TiO_2 NPs surface active sites and a reduction of free radicals generated. Also, one can demonstrate that the catalyst dose had a positive effect on the conversion of phenol in the catalytic ozone process under a high dosage of TiO_2 NPs. These results

the pollutant removal efficiency decreased. Also, the same result was noted by Jose et al. [30].

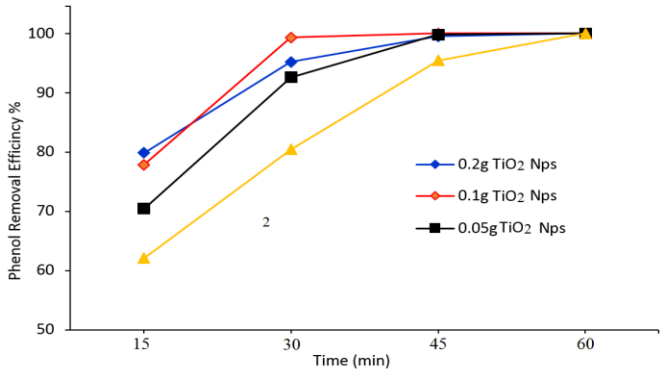

Figure 9. Effect of TiO_2 NPs dose on the removal rates of phenol at different dosages of TiO_2 NPs catalyst in the presence of packing material. *Source: Author.*

Evaluation of Phenol Degradation Kinetics

In the present study, the kinetics of phenol degradation by the ozonation process was studied. A mole balance was achieved in the reaction system to provide a clear description for the phenol degradation reaction. Two reaction orders were assumed for the present kinetics study (first order and second order). The reaction rate constants were determined depending on the different concentrations of the phenol in the reaction system [35]. Equations 1 and 2 illustrate the mole balance for the first and second order assumption, respectively.

(1) $\ln C_t/C_0 = -k_1 t$ First order assumption

(2) $C_t = C_0/ (1 + C_0 k_2 t)$ Second order assumption

Figures 10 and 11 view the theoretical and experimental results. Applying the validity of the first and second models was done by using equations (1) and (2), which were evaluated using the values of determining the coefficient (R^2). However, the kinetic reaction rate factor (ka) of the first-order model was calculated by the slope of the best fit line of the Ln (C_t/C_o) vs. the time (t), and the second-order model was calculated by the slope of the best fit line plot of ($1/C_t$) vs. the time (t) [36]. The results of these measurements can be seen in Table 1 and Table 2, respectively. As a result of the high well of (R^2) values that were achieved (>0.9), it is evident that the first-order model provided a good fit for the kinetic data, as shown in Figure 10. In addition, the use of the packed ozonation technique resulted in a considerable rise in the reaction rate value. These results are in accordance with the results of Fadhil and Nada [29], and Melahat et al. [37]. Additionally, four lines appear in Figure 10 with four colors as indications for the four phenol treatment stages in the bubble column reactor at the assumption of a first-order reaction kinetics. The blue one refers to the ozonation process with ozone gas only. The gray color refers to using of TiO_2 NPs catalyst (O_3/TiO_2). While the red color refers to the treatment stage in presence of packing (O_3/packing). Finally, the orange color refers to the treatment stage in presence of TiO_2 NPs catalyst and packing material (O_3/TiO_2/packing) in the reactor. On the other, Figure 11 shows the reaction kinetics of the second-order assumption. The red color refers to the ozonation process, the orange color refers to the (O_3/TiO_2) treatment, the gray color refers to the (O_3/packing) treatment level, and the blue color refers to (O_3/TiO_2/packing) stage.

Table 1. Experimental kinetic data of phenol reaction using first order equation assumption. *Source: Author.*

Type of Treatment	**Y = Ln(C_o/C_t), and x = t**	**k_1 (1/min)**	**R^2 (1/min)**
O_3 only	y = 0.0386x - 0.1133	0.07469	0.9726
O_3/packing	y = 0.0511x - 0.1177	0.08911	0.9844
O_3/ TiO_2 NPs	y = 0.0752x - 0.1051	0.13624	0.9893
O_3/packing/TiO_2 NPs	y = 0.1112x + 0.0521	0.1681	0.9971

Table 2. Experimental kinetic data of phenol reaction using second order equation assumption. *Source: Author*

Type of Treatment	Y = Ln(C_o/C_t), and x = t	k_2 (l/mg. min)	R^2 (l/mg. min)
O_3 only	y = 0.0298x + 0.1405	0.02978	0.905
O_3/packing	y = 0.0458x + 0.0675	0.04575	0.9154
O_3/ TiO_2 NPs	y = 0.0632x + 0.1554	0.06081	0.9285
O_3/packing/TiO_2 NPs	y = 0.074x + 0.4699	0.07397	0.9395

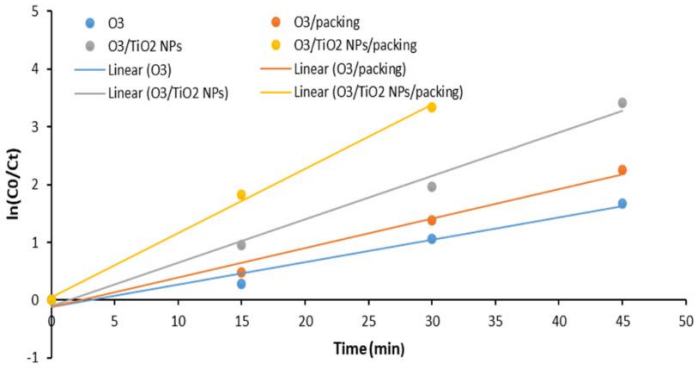

Figure 10. Assumption of first-order reaction kinetics of phenol degradation. *Source: Author.*

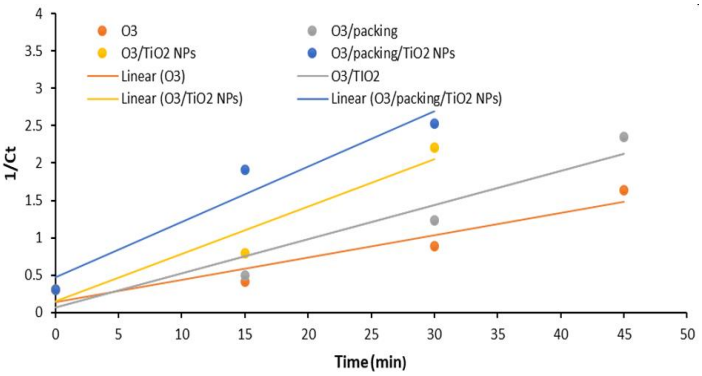

Figure 11. Assumption of second-order reaction kinetic of phenol degradation. *Source: Author.*

Impact

Effluents from petroleum refineries contain many hazardous materials, which have contributed to the presence of dangerous environmental impacts. The use of TiO_2 NPs catalyst in a packed bubble column reactor will have a high economic impact at the industrial scale by providing clean water with zero phenol. From an environmental point of view, wastewater pollution with organic compounds especially phenol is considered a major environmental problem. The treatment of wastewater in the present work regards will contribute to reusing water in operating units in petroleum refineries efficiently. Such a challenge to reduce the pollution of wastewater is highly desirable and has an enormous impact on industrial, economic, and environmental impacts. Moreover, a bubble column reactor is characterized by simple operation and no need to move or agitate parts. The agitations processes are usually achieved due to the rising of gas bubbles (ozone gas). Accordingly, the consumed energy in such reactor type is very low in comparison with other types of industrial multiphase reactors such as fluidized bed reactors or moving bed reactors. Furthermore, the use of TiO_2 NPs as a heterogeneous catalyst with packing material contributes to improving phenol removal from wastewater significantly by enhancing the ozonation process. Also, the presence

of packing material in the bubble column reactor solves the problem of the low solubility of ozone gas in water. Then, the packing material contributes to obtaining a higher concentration of ozone with higher solubility in water. Such contribution will enhance economic savings by using all generated amounts of ozone gas to increase the performance of the treatment system. The highest phenol removal of 100% was achieved at a contact time of 30 min. As a result, by increasing the contact surface area between the gas and liquid phases, the mass transfer process in the reactor will increase. Accordingly, the phenol degradation reaction was enhanced dramatically within a shorter time and then with low operational costs. Finally, the process of wastewater treatment using ozonation technology in a packed bubble column reactor allows for the promotion of sustainability by providing high-quality water with simple operation and low economic cost. It is also worth noting that the using catalytic ozonation process is eco-friendly practices where phenol decomposes into CO_2 and H_2O without any secondary pollutants that harm the environment and reduce negative factors.

Conclusions

In the present work, it was found that the use of TiO_2 NPs catalyst in a packed bubble column reactor provided a significant removal efficiency of phenol from wastewater effluent from petroleum refineries. Actually, the ozonation process was enhanced due to the effect of TiO_2 NPs as a catalyst and the presence of packing with a removal rate of 100% at a shorter contact time. Moreover, the results manifested that the presence of packing in the reactor improved the mass transfer process with a high contact area between gas and solid, and a low resistance to mass transfer was achieved. At a phenol concentration of 3 mg/L, the ozone dose of 3 g/h, pH = 7, and TiO_2 NPs of 0.1 g/l, the phenol removal efficiency provided the best contact increased, the mass transfer rate of the ozone gas increased, and then the removal of phenol increased. Additionally, the TiO_2 NPs catalytic improved the ozonation process via increasing the reaction of ozone in the active site of the catalytic led to the generation of hydroxyl routs which is considered better oxidation than ozone, so better removal of efficiency was got. Finally, the use of TiO_2 NPs in a packed bubble column reactor in the degradation of phenol is regarded an efficient process with low economic cost compared to other methods.

Conflict of interest

There are no conflicts to declare.

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