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Degradation of Toluene in Treatment of Refinery Wastewater by Photocatalytic Oxidation Technology in a Bubble Column Reactor Using ZnO-TiO_2 Composite Nanocatalyst and Packing Material

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Abstract

Oxidation bubble column reactors (BCRs) are useful for treating wastewater because of their effective mass transfer and mixing capabilities. However, because of the low oxidation level of the pollutants, the BCRs' ability to remove toluene is restricted. A packing material and a ZnO-TiO_2 composite nanocatalyst in the BCR were used in this study to improve the degradation of toluene. Additionally, the superficial gas velocity (i.e., 0.4, 0.8, 1.2, 1.6, 2, 2.4, and 2.8 cm/s) was used to assess the gas holdup, pressure decrease, and diameter of the bubble. The optimal superficial gas velocity was determined to be 2.4 cm/s. Using packing materials and a ZnO-TiO_2 composite nanocatalyst in the BCR, a total (100 %) removal of toluene was accomplished at toluene concentrations of 10, 20, 30, and 40 ppm at reaction periods of 50, 60, 70, and 80 minutes, respectively. Additionally, two ZnO-TiO_2 composite nanocatalyst dosages (i.e., 0.04 and 0.12 g/L) were added to the reaction mixture; the ideal dose was determined to be 0.12 g/L. Therefore, four treatment methods (air and H_2O_2) alone, (air and H_2O_2/ packing), (air and H_2O_2/ZnO-TiO_2 composite nanocatalyst), and (air and H_2O_2/ packing/ZnO-TiO_2 composite nanocatalyst) were used to evaluate four toluene concentrations in the BCR (i.e., 10, 20, 30, and 40 ppm). Last but not least, the results gave a clear reaction mechanism explaining the oxides BCR, and the applied treatment process can be employed effectively to remove toluene from wastewater at a cheap cost, with minimal energy consumption, and with a straightforward operation.

Keywords: Toluene removal; oxidation reaction; Bubble column reactor; ZnO–TiO_2 nanocatalyst; packing material; hydroxyl radicals.

تحلل التولوين في معالجة مياه الصرف الصحي للمصافي بتقنية الأكسدة الضوئية في مفاعل عمود الفقاعات

الخلاصة

تُعد مفاعلات عمود الفقاعات المؤكسدة (BCRs) مفيدة في معالجة مياه الصرف الصحي نظرًا لقدرتها الفعالة على نقل الكتلة والخلط. ومع ذلك، نظرًا لانخفاض مستوى أكسدة الملوثات، فإن قدرة مفاعلات عمود الفقاعات المؤكسدة على إزالة التولوين محدودة. في هذه الدراسة، استخدمت مادة تعبئة ومحفز نانوي مركب من أوكسيد الزنك وأوكسيد التيتانيوم ($ZnO\text{-}TiO_2$) في مفاعل عمود الفقاعات المؤكسدة لتحسين تحلل التولوين. بالإضافة إلى ذلك، استُخدمت سرعة الغاز السطحية (0.4، 0.8، 1.2، 1.6، 2، 2.4، و2.8 سم/ثانية) لتقييم احتجاز الغاز، وانخفاض الضغط، وقطر الفقاعة. حُددت السرعة السطحية المثلى للغاز عند 2.4 سم/ثانية. باستخدام مواد تعبئة ومحفز نانوي مركب من أكسيد الزنك وأكسيد التيتانيوم في مفاعل BCR ، تمت إزالة التولوين بالكامل (100%) عند تركيزات تولوين 10، 20، 30، و40 جزء في المليون، خلال فترات تفاعل 50، 60، 70، و80 دقيقة على التوالي. إضافةً إلى ذلك، أُضيفت جرعتان من المحفز النانوي المركب من أكسيد الزنك وأكسيد التيتانيوم (0.04 و0.12 جم/لتر) إلى خليط التفاعل؛ وحُددت الجرعة المثالية بـ 0.12 جم/لتر. لذلك، استُخدمت أربع طرق معالجة (الهواء/ H_2O_2) فقط، ((الهواء /H_2O_2)+ حشوة) و(المحفز النانوي المركب $ZnO\text{-}TiO_2$ + (الهواء /H_2O_2))، و(المحفز النانوي المركب $ZnO\text{-}TiO_2$ + (الهواء/H_2O_2) + +حشوة) لتقييم أربعة تراكيز من التولوين في BCR وهي (10، 20، 30، و40 جزء في المليون). وأخيرًا، أوضحت النتائج آلية التفاعل وفسرت الاكسدة في BCR، ويمكن استخدام عملية المعالجة المطبقة بفعالية لإزالة التولوين من مياه الصرف الصحي بتكلفة منخفضة، وباستهلاك منخفض للطاقة وبعملية بسيطة.

1. Introduction

The petrochemical and petroleum refinery industries generate large amounts of wastewater that are contaminated, which is considered a worldwide environmental issue[1]. Numerous contaminants, including organic chemicals, heavy metals, greases, nitrates, phosphate, and biological elements, are typically found in petroleum effluent [2]. The most common types of contaminants found in wastewater from petroleum refineries are organic materials [3]. If wastewater is released without treatment, the high concentration of hydrocarbons in it is toxic and harmful to aquatic life, the environment, and human health [4]. Then, in accordance with the standard WHO criteria, effective wastewater treatment techniques are needed prior to release into the environment [5][6].The most prevalent hydrocarbons in petroleum effluent are low molecular weight hydrocarbons and BTEX (benzene, toluene, ethylbenzene, and xylene). Volatile aromatic hydrocarbons are known as BTEX [7]. They are extremely harmful to the environment and to people. According to the Environmental Protection Agency (EPA), benzene (C_6H_6) is an aromatic hydrocarbon that poses a risk [8]. Consequently, the global oil and gas industry has been pressured to develop water treatment technology [9].

According to the World Health Organization's (WHO) guidelines, the highest concentration of benzene in drinking water is 10 μg/L, while the maximum concentrations of toluene, ethylbenzene, and xylene are 700, 300, and 500 μg/L, respectively[10]. Many authors have recently proposed studies based on BTEX compounds because of their high concentration in urban ambient air and water and their propensity to cause cancer [11][12]. Global interest in

treating BTEX has increased as a result, particularly at the points of generation before it is released into the environment. The most prevalent source of BTEX is crude oil, and its byproducts, including gasoline, are the primary constituents of surface and ground water. These often result from crude oil spills at production wells, refineries, pipelines, storage and distribution terminals, and from the leakage of petroleum storage tanks [13]. Although toluene is the most dangerous of the BTEX compounds, it is nonetheless used in the chemical, pharmaceutical, and petrochemical sectors [14]. Interactions between BTEX chemicals are prevalent. Since the BTEX chemicals interact with one another, their coexistence suggests that their toxicity is increased [15].

Numerous methods, including liquid-liquid extraction, air oxidation, catalytic wet air oxidation, and biological processes, are used to remove toluene from contaminated wastewater [16]. Furthermore, toluene can be treated using a variety of sophisticated methods, such as membrane technology, electrochemical methods, Fenton mechanisms, catalytic photo oxidation, and ozonation procedures [17][18].

From an industrial perspective, physicochemical, biological, and mechanical techniques are typically used to treat wastewater in petroleum refineries. Flotation, flocculation electrocoagulation, adsorption, chemical precipitation, and membrane reactors are the most often used treatment techniques[19][20]. Additionally, improved oxidation techniques can be applied to photocatalytic oxidation, Fenton, UV/O_3, UV/H_2O_2, O_3, and ultrasonography [21][22]. As a result, all of these methods are costly and involve intricate procedures. Thus, it is necessary to find a high-performance method that has a high rate of organic component removal. In petroleum refineries, the application of advanced oxidation processes (AOP) is considered a significant difficulty among all deployed methods for wastewater treatment. Hydrocarbons from wastewater can be effectively degraded by photocatalytic oxidation, which is a suitable and economical AOPs treatment technique [23][24].

The removal of a wide range of organic contaminants from wastewater using catalytic photochemical oxidation has gained popularity due to its ease of use, adaptability, and high effectiveness [25][26]. In this technique, a photocatalyst and UV light are used to create a highly reactive (2.8 V oxidation potential) hydroxyl radical (OH.), which transforms hydrocarbons in water into innocuous H_2O and CO_2. Refinery effluent containing hydrocarbons can be more easily oxidized thanks to the OH radical's unique wide range of selectivity and high oxidation activity [27][28]. SnO_2, WO_3, CeO_2, Fe_2O_3, ZnO, ZnS, CdS, SiO_2, and TiO_2 oxides are among the semiconductors that have been found to be effective photocatalysts in the photocatalytic degradation of organics [29][30]. Since TiO_2 is very effective, stable, readily available,

inexpensive, and easily recovered from treated wastewater, it has gained a crucial place among these for the oxidation of HCs in wastewater [31][32]. A UV/TiO_2 oxidation system has demonstrated significant activity in the degradation of various organic contaminants [29]. It has also been found to be an effective option for the degradation of hydrocarbons (HCs) in effluent from refineries. This strategy, however, has drawbacks, including high processing costs and the persistence of some oxidation products in the wastewater after treatment [33].

Unquestionably, the most common photocatalyst is TiO_2, which needs UV light to be activated. To prevent some disadvantages, such as charge recombination, its activity still has to be improved [34]. Numerous changes to the structure and properties of TiO_2 have been suggested in an effort to improve photocatalytic activity and produce catalysts that respond to visible light. Prior research has shown that the heterojunction of semiconductors with similar band gaps, such as ZnO and TiO_2, can have synergistic benefits by increasing the lifetime of the electron-hole pair and decreasing the recombination rate [35]. Nitrogen doping has been shown to reduce the band gap energy, which in turn enhances visible light activity [36]. Propose that interstitial nitrogen forms an N-O type connection encircled by three Ti atoms by binding to the interstitial O_2^- lattice. Although they don't specify a geometric arrangement of atoms, other publications refer to the interstitial nitrogen as Ti-O-N or Ti-N-O. [37].

The two primary methods of incorporating nitrogen into the TiO_2 structure are interstitial doping, which involves occupying interstitial spaces, and substitutional doping, which involves replacing oxygen with nitrogen. For substitutional nitrogen, the binding energy falls between 396 and 398 eV, while for interstitial nitrogen, it falls between 400 and 406 eV [37][38]. Numerous industrial reactors, including membrane reactors, fluidized bed reactors, trickling bed reactors, and bubble column reactors (BCRs), can be used to extract the hydrocarbon components from wastewater. In industrial operations, BCRs are among the most often used gas-liquid and gas-liquid-solid multiphase reactors. Easy operation, effective mixing, high heat and mass transfer rates, minimal maintenance costs, and low energy consumption are just a few of their many advantages [39][40].

One significant multiphase reactor that is frequently used in industrial processes to conduct homogeneous or heterogeneous reactions between gas, liquid, and solid phases is the bubble column reactor (BCR). High heat and mass transfer rates, a broad range of working conditions, an effective mixing rate, and minimal energy consumption because it has no moving parts are the characteristics of the BCR. Furthermore, key hydrodynamic characteristics (such as gas velocity, gas holdup, pressure drop, bubble rise velocity, H/D ratio, and gas distributor design) affect how

efficiently BCRs operate. Because of all these reasons, the BCR is favored and used in many wastewater treatment procedures to eliminate pollutants [41][42].

The mechanism of mass transfer between the liquid and gas phases is crucial to the utilization of bubble columns in wastewater treatment. For this reason, knowing the diffusion process's operating parameters will give you a clear idea of how to remove hydrocarbons from a BCR [43]. Effective contact between the reaction mixes is necessary for the breakdown of different hydrocarbon pollutants from wastewater effluent streams using BCRs. Hydrocarbons degrade in the liquid phase, and gas bubbles promote effective mass transfer. The polluting materials enter the system prior to the oxidation reaction [44][45]. The performance of the reactor is significantly influenced by the flow regime inside the BCR. Evaluation of the surface gas velocity can help determine the flow patterns and the precise hydrodynamic behavior because it is difficult to predict the flow behavior in a BCR. As a result, further research is required to determine how the gas-liquid-solids interact in a BCR to remove toluene from wastewater [46][47].

According to the literature, it is still challenging to comprehend how hydrodynamic factors affect the mass transfer mechanism in a BCR with air and packing materials present. Additionally, the air reaction typically shows low solubility and rapid air molecule breakdown [48]. In the liquid phase reaction within a BCR, each of these elements contributes to restricted mass transfer. As a result, different surface air velocities must be identified and their impact on the reactor's performance assessed [1][47]. In order to achieve high toluene removal from wastewater, the primary goal of the current work is to improve the degrading reaction utilizing a bubble column reactor. Additionally, the performance of the reactor will be assessed in relation to the influence of the hybrid photo catalyst and hydrodynamic behavior.

2. Materials and Methods

2.1. Materials

Numerous chemicals were used in the experimental runs, such as sulfuric acid (99.55% purity) from Sigma (USA), sodium thiosulfate (99.86% purity), potassium iodide (99.42% purity), hydroden peroxed (H_2O_2) (98% pure), and toluene (99.8% pure) from Mallinckrodt in HPLC grade. Additionally, ZnO-TiO_2 composite catalysts have been made before[49]. as well as the packing properties listed in Table (1) and the utilized packing material depicted in Figure (1).

Fig. (1). Packing utilized in the three tests' reactor.

Table (1): Characteristics of various packing types.

Parameter	Packing media
Color	Grey
Diameter (mm)	15
Length (mm)	15
Specific surface (m^2/m^3)	869
Porosity (%)	87

2.2. Equipment for Reaction

A packed bubble column reactor (BCR) made up the reaction apparatus. The reactor ran in semi-batch mode, where the gas phase (air) constantly entered the reactor in an upward flow direction while the liquid phase (polluted wastewater) remained stationary. A consistent operating temperature of 25ºC was used for all treatment experiments. Gas bubbles were produced by the gas-liquid phase interaction, which was dependent on the applied superficial gas velocity and other hydrodynamic parameters. The schematic diagram of a BCR's reaction equipment is shown in Figure (2). A cylindrical column of 190 cm in height and 9 cm in inner diameter was part of the system. An air compressor was used to supply the air. The device used sensitive flow air meters to gauge the airflow rate into the BCR. A stainless steel air distributor (also known as a twisted plate) with 62 0.6 mm holes was located in the bottom section of the BCR. It was dispersed in cycles throughout the plate sections. The pH was maintained at 7 during all experimental runs, and the air rate was set at 3 g/h.

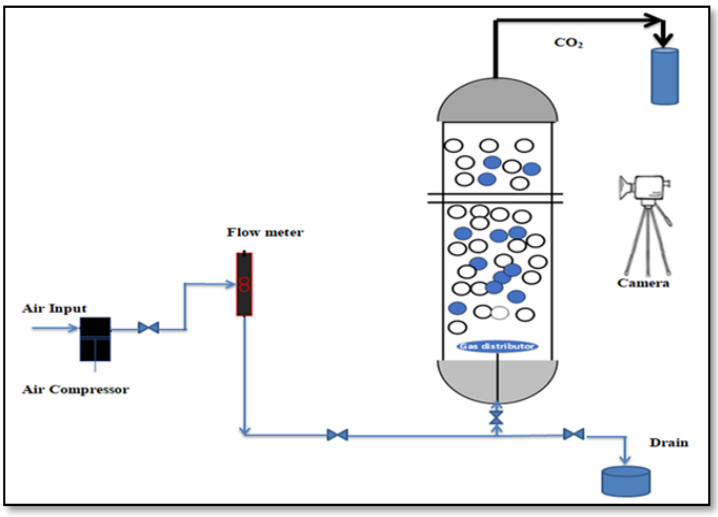

Fig. (2): Diagram of the BCR packed with packaging materials.

2.3. Procedure for Operations

Four treatment methods were used in the BCR to achieve the degradation reaction for toluene elimination in the current study. The first method was used with air and H_2O_2 present in the BCR. Using packing (with a large surface area) in the reactor with air and H_2O_2, the second method of toluene removal was accomplished. ZnO-TiO_2 composite catalyst nanoparticles (NPs) were used as nanocatalysts with air and H_2O_2 in the third treatment, and packing material and ZnO-TiO_2 composite catalyst nanocatalyst with air and H_2O_2 were combined in the fourth.

The four BCR operational approaches are summed together in Figure (3). Wastewater with varying toluene concentrations (10, 20, 30, and 40 ppm) was used. The BCR was supplied with air at a steady pace. The reactor's toluene material was treated for 5, 10, 20, 30, 40, 50, 60, 70, and 80 minutes. For every experiment, the bubble column reactor's operating temperature and pressure were maintained at 25ºC and 1 bar, respectively. A sample of the reaction mixture was taken from the sampling valve at the end of each experiment. A total organic carbon (TOC) analyzer (E200, Shimadzu Company, Japan) was used to measure the toluene concentration.

Additionally, the following formula was used to determine the toluene removal efficiency:

$$\text{Removal efficiency } \% = 1 - \left[\text{TOC}_{(t)}/\text{TOC}_{(IN)}\right] \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where TOC(t) is the TOC concentration measured in mg/L at any time, and TOC(IN) is the TOC concentration measured in mg/L at zero time (initial concentration).

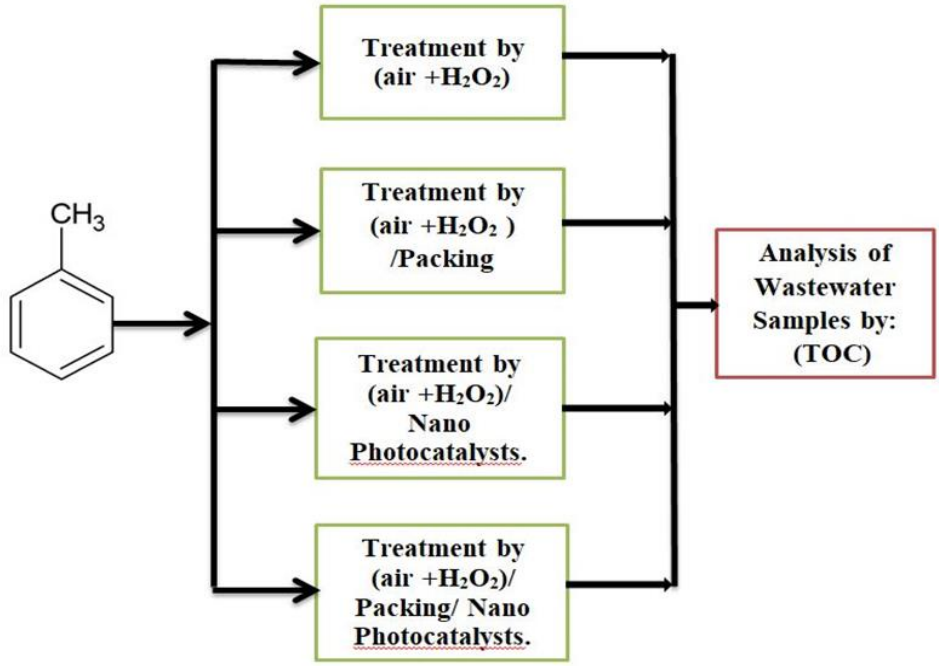

Fig. (3): The four experimental methods used in a BCR's reaction system to extract toluene from wastewater.

3. Results and Discussion

3.1. Behavior of Flow in the BCR

The performance of the BCR is influenced by its hydrodynamic characteristics. The flow regimes in the BCR are known to be strongly influenced by the mixture's physical characteristics, pressure drop, gas holdup, and gas velocity [50][51][52]. The relationship between the gas holdup and the superficial gas velocity in the BCR with air alone and with air plus a ZnO-TiO_2 composite nanocatalyst is depicted in Figure 4. At the applied gas velocity (0.4, 0.8, 1.2, 1.6, 2, 2.4, and 2.8 cm/s), homogenous bubbly flow accounted for the bulk of the flow. Additionally, the bubbles had a low rise velocity and a consistent size distribution. The BCR was able to operate better when the air superficial velocity was higher. Because it directly affects hydrodynamic characteristics including gas holdup, bubble size, and rising velocity, it was also discovered that the surface gas velocity significantly affected the BCR's performance. Using air with a ZnO-TiO_2 composite nanocatalyst in the BCR produced slightly different gas holdup findings than using air alone, as Figure (4) illustrates. The presence of the ZnO-TiO_2 composite nanocatalyst is responsible for this variance in the hydrodynamic behavior.

Additionally, at low gas velocities, the bubbles were uniformly distributed throughout the reactor and had a spherical overall shape. As a result, the bubble size increased and altered, taking on ellipsoidal or slug-like shapes, at greater gas velocities (i.e., 2.8 cm/s). Bubbles congregating and

expanding into larger bubbles can explain this behavior. According to a number of writers, such as Sharma et al. [53], and Alattar et al. [54], the gas velocity significantly affects the size and structure of the bubbles in a BCR. The mass transfer process inside the reactor with the gas velocity is influenced by the effective interfacial area, which rises in response to a noticeable increase in the gas holdup value in the reactor.

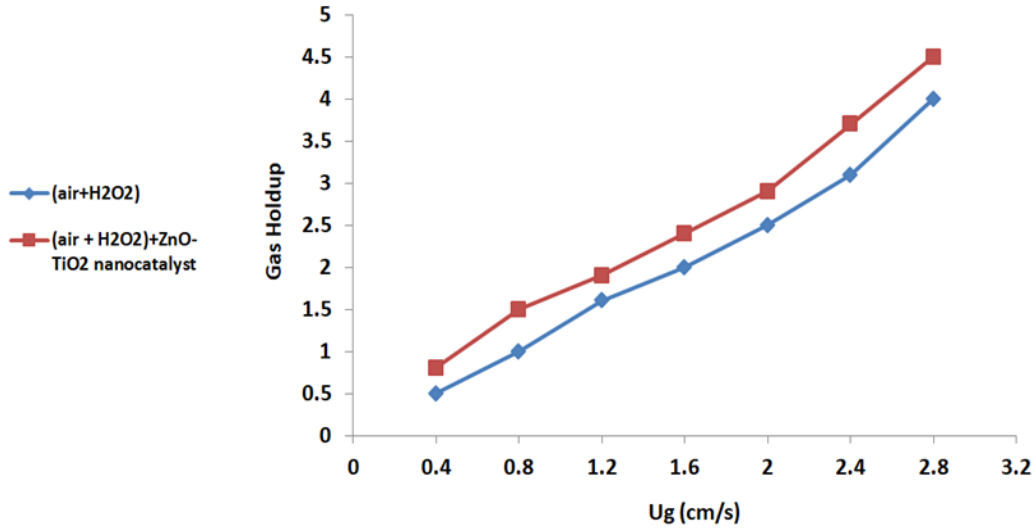

Fig. (4): Impact of superficial gas velocity on the behavior of gas holdup in a BCR with air as the reactor's gas phase.

3.2. Degradation of Toluene in a BCR with Just (Air and H_2O_2) Present.

The four toluene concentrations used in the experiment were 10, 20, 30, and 40 ppm. In the BCR, the toluene degradation response was assessed in relation to the treatment duration. The correlation between reaction time and toluene removal percentage at different concentrations is shown in Figure (5). With a total reaction time of 50 minutes, the toluene removal at concentrations of 10, 20, 30, and 40 ppm was 68.1, 64.3, 60, and 55.2%, respectively. The optimal reaction times were found to be 60, 70, and 80 minutes for the three toluene concentrations of 10, 20, and 30 ppm, respectively. Additionally, a reaction time of 80 minutes was required to accomplish about 92% toluene elimination at an initial toluene concentration (low concentration) of 10 ppm. Furthermore, the length of the reaction time rose in tandem with the starting toluene concentration. Consequently, the toluene concentration in the reactor determined the necessary reaction time, and this parameter is the primary determinant of BCR performance. Previous studies have emphasized the importance of reaction time in the decomposition of toluene. [16], [46], [55].

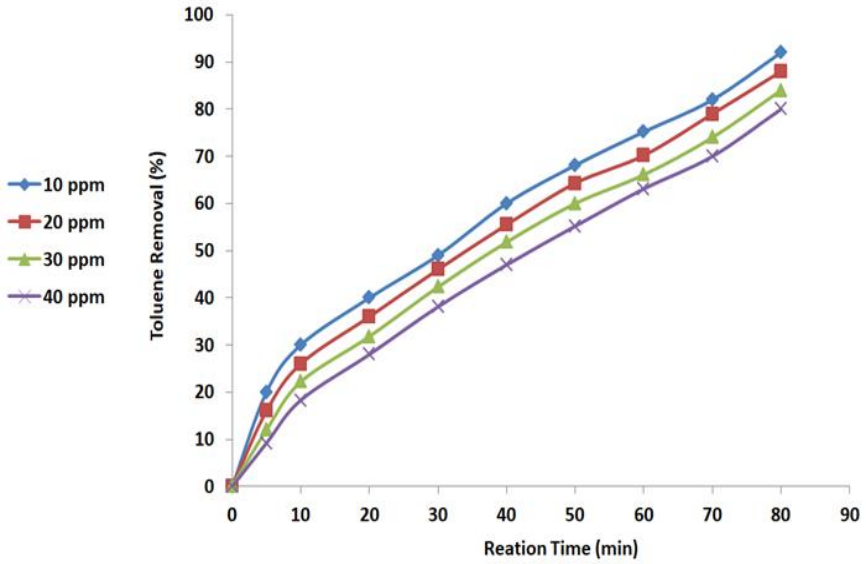

Fig. (5): Impact of reaction duration on toluene degradation in a BCR employing only air and H_2O_2.

3.3. Impact of the Dosage of ZnO Nanocatalyst

The toluene degradation process in the BCR was enhanced by the use of a ZnO-TiO_2 composite nanocatalyst as a catalytic material. Therefore, two doses of the ZnO nanocatalyst (i.e., 0.04 and 0.12 g/L) were administered in the reactor with packing in order to determine the proper nanocatalyst dose needed for the reaction. The impact of the catalyst dose on the rate of toluene degradation at different contact times is depicted in Figure (6). The findings showed that the amount of ZnO-TiO2 composite nanocatalyst had a significant impact on the rate at which toluene broke down. The toluene removal rates for nanocatalyst dosages of 0.04 g/L and 0.12 g/L at a 60-minute treatment period were 83.6% and 87.2%, respectively.

This happened as a result of the ZnO-TiO2 composite nanocatalyst's increased production of hydroxyl radicals in the reaction mixture, which accelerated the oxidation process. Furthermore, the nanocatalyst's enormous surface area (350 m^2/g) offered more active sites, which in turn promoted the production of more hydroxyl radicals. The mass transfer rates and toluene degradation reaction in the reaction system were enhanced by each of these elements. Studies have shown that the mass of the catalyst significantly influences the reaction mechanism and the conversion of hydrocarbons to carbon dioxide and water. However, little research has been conducted on how nanocatalysts affect the oxidation process [17][10]. It is well known that the oxidation reaction in aqueous solutions is a highly challenging process and that there aren't enough efficient nanocatalysts to supply a sufficient number of active sites [56][57][58]. The primary factor influencing the result was the number of active sites on the nanocatalyst; greater catalyst doses resulted in more active sites, which improved the performance of the process. Thus,

in the oxidation process, the catalyst had a favorable effect on the conversion of toluene. Additionally, the catalytic reaction of toluene in the oxidation process with the ZnO-TiO2 composite nanocatalyst included the heterogeneous reaction of a three-phase system (i.e., wastewater, air and H_2O_2, and nanocatalyst), where the nanocatalyst played a critical role in identifying the mechanism that removed the toluene [14][16].

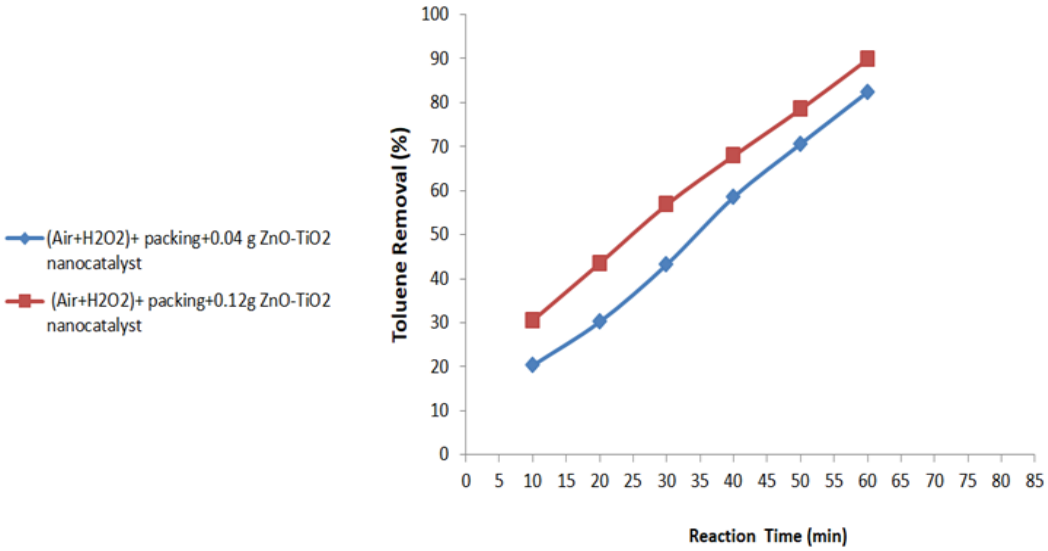

Fig. (6): Effect of ZnO nanocatalyst dosage on PBCR oxidation reaction.

3.4. The impact of initial toluene concentrations on the rate of removal

Experimental evaluation was conducted in a BCR at varying concentrations of toluene to assess the four applied treatment methods: (air and H_2O_2), (air and H_2O_2) /packing, (air and H_2O_2) / ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2) /packing/ ZnO-TiO_2 composite nanocatalyst. The evaluation process's objective was to identify the best treatment strategy that eliminated toluene as quickly and efficiently as possible. Consequently, three toluene concentrations (10, 20, 30, and 40 ppm) were examined. At a toluene concentration of 10 ppm, Figure (7) displays the outcomes of the toluene removal at different contact times in the BCR. The outcome showed that the toluene elimination and contact time were directly correlated. The breakdown of toluene into carbon dioxide and water then increased with the length of contact. The same outcomes were observed in the research of Hamed Hassani et al. [59] and Hamad AlMohamadi et al. [60]. For each treatment technique of (air and H_2O_2), (air and H_2O_2) /packing, (air and H_2O_2) /ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2) /packing/ZnO-TiO_2 composite nanocatalyst, the toluene removal was 74.1, 85.2, 90.1, and 100% for a chosen random contact duration of 60 minutes, respectively. The treatment employing the (air and H_2O_2) /packing/ ZnO-TiO_2 composite nanocatalyst yielded the maximum toluene degradation

performance, achieving the full conversion of toluene (100%) at a contact time of 50 minutes, according to a comparison of the results with the four treatment techniques. Furthermore, the (air and H_2O_2) /packing approach needed 80 minutes of contact time to achieve full conversion, but the treatment method employing the (air and H_2O_2) / ZnO-TiO_2 composite nanocatalyst achieved full conversion at 70 minutes.

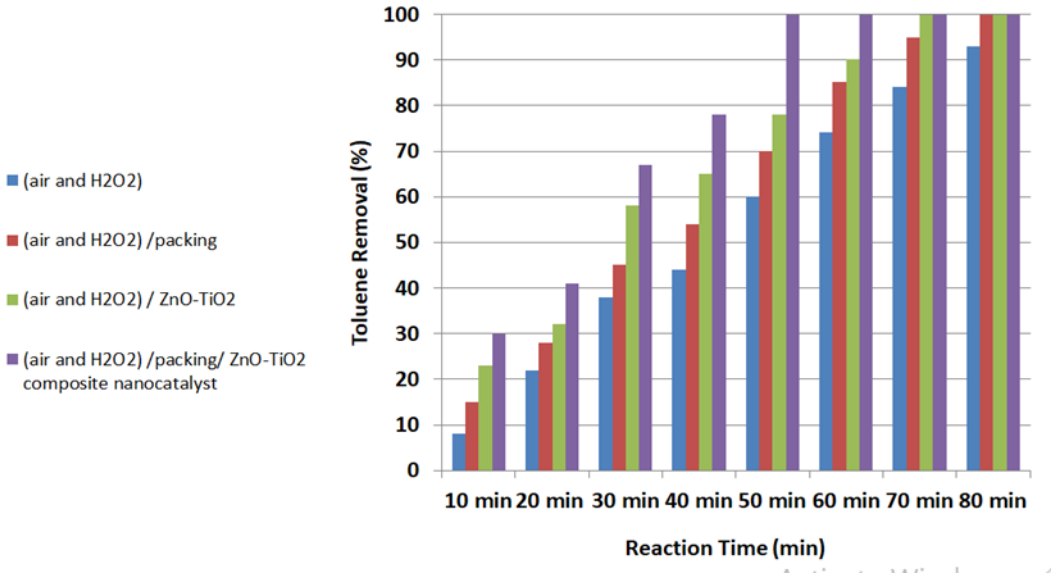

Fig. (7): Toluene is converted during the oxidation process in a BCR utilizing the four treatment techniques, at a toluene concentration of (10 ppm)

With an initial toluene concentration of 20 ppm, Figure (8) illustrates how the applied treatment procedure affects the amount of toluene elimination. More contact time was needed to attain high levels of toluene elimination as the concentration of toluene rose from 10 ppm (Figure 7) to 20 ppm. Removal percentages of 68.1, 79.1, 85.3%, and 100% were recorded for the toluene removal results for the reaction with (air and H_2O_2), (air and H_2O_2)/ packing, (air and H_2O_2)/ ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2) /packing at a contact time of 60 minutes. Additionally, the results showed that the (air and H_2O_2)/packing/ZnO-TiO_2 composite nanocatalyst removed almost 100% of the toluene at a contact duration of 60 minutes. Furthermore, during 80 minutes of contact time, toluene was completely converted when the (air and H_2O_2)/ZnO-TiO_2 composite nanocatalyst or (air and H_2O_2)/ packing was used. Similarly, previous studies have demonstrated that oxidation methods require longer reaction times to remove higher concentrations of toluene or other organic compounds [61], [62], [59]. It often takes more time to convert these chemical compounds into intermediate ones because it's a complex process.

Furthermore, the results demonstrated that because of the high concentration of toluene in the wastewater, the interaction between the gas and liquid required greater reaction time to achieve

the necessary elimination of toluene. Previous studies have shown that the initial concentration of organic compounds in contaminated wastewater has a significant impact on the economic feasibility of wastewater treatment methods [63], [64]. Then, in certain applicable treatment procedures, the passive oxidation process typically results in the production of intermediate components as the pollutant concentration decreases with reaction time. Furthermore, the current ZnO-TiO_2 composite nanocatalyst and packing combination improved the oxidation process in the BCR to obtain high toluene conversion in a shorter reaction time by utilizing oxidation technology. It is evident that the packing's presence encouraged the development of a thin coating over these packing materials' outside. By supplying more hydroxyl radicals, this thin layer improved the mass transfer mechanism and therefore increased the conversion of packing in the oxidation process.

As previously mentioned, the primary factor that transforms toluene into carbon dioxide and water is these hydroxyl radicals (•OH) [46] [60].

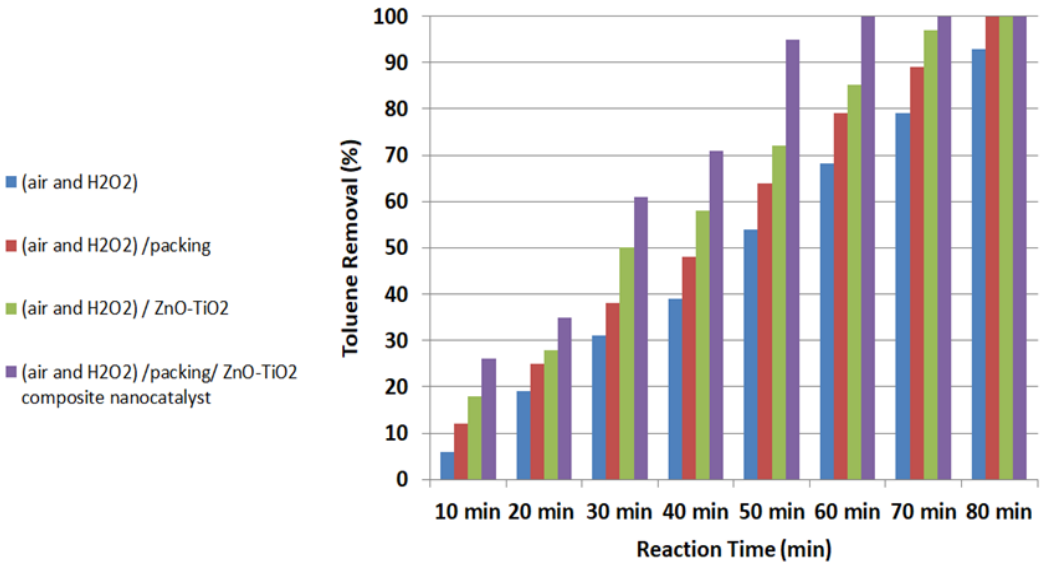

Fig. (8): Toluene is converted during the oxidation process in a BCR utilizing the four treatment techniques, at a toluene concentration of (20 ppm).

Using the four treatment techniques, Figure (9) shows the toluene removal rates at the maximum concentration (30 ppm). Figures (7) and (8) show that the removal efficiency trend was the same as in the earlier situations, but extra contact time was required in this instance. Therefore, the rise in toluene concentration led to a decrease in toluene removal efficiency. The toluene removal for the four treatment methods air and H_2O_2, (air and H_2O_2) /packing, (air and H_2O_2) / ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2) /packing/ ZnO-TiO_2 composite nanocatalyst was 61.1, 72.2, 80.3, and 97% at a contact duration of 60 minutes, respectively. The ZnO-TiO_2

composite nanocatalyst, which was packed with air and H_2O_2, completely removed toluene after a reaction time of 70 minutes.

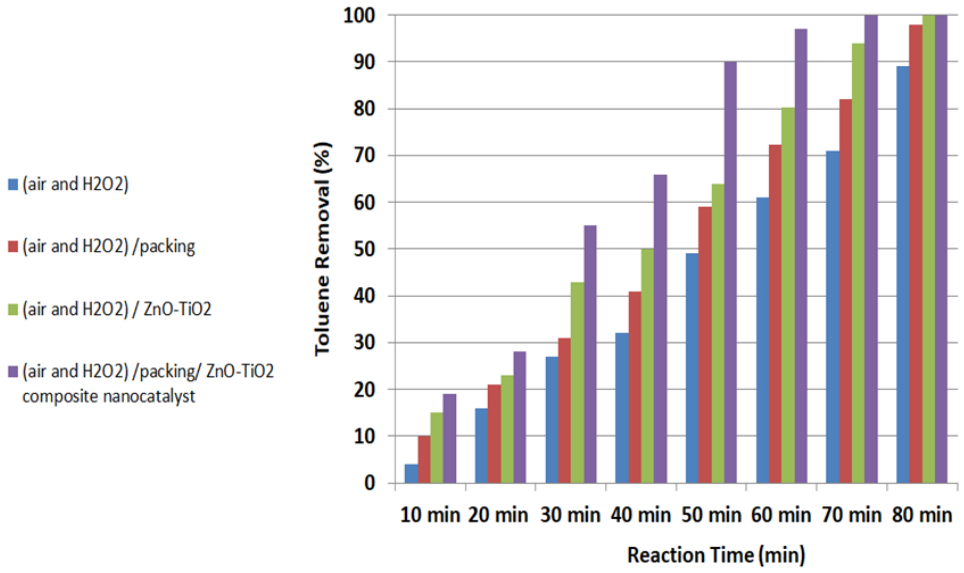

Fig. (9): Toluene is converted during the oxidation process in a BCR utilizing the four treatment techniques, at a toluene concentration of (30 ppm).

Using the four treatment techniques, Figure (10) shows the toluene removal rates at the maximum concentration (40 ppm). In this instance, considerably longer contact time was required, but the removal efficiency trend was the same as in the earlier cases (see Figures 8 and 9). Therefore, the rise in toluene concentration led to a decrease in toluene removal efficiency. After 60 minutes of contact, the tolune elimination rates for the four treatment methods (air and H_2O_2, (air and H_2O_2) /packing, (air and H_2O_2) / ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2) /packing/ZnO-TiO_2 composite nanocatalyst were 56, 67.1, 74.2, and 93.3%, respectively. At a reaction period of 80 minutes, the ZnO-TiO_2 composite nanocatalyst (air and H_2O_2)/packing completely removed toluene.

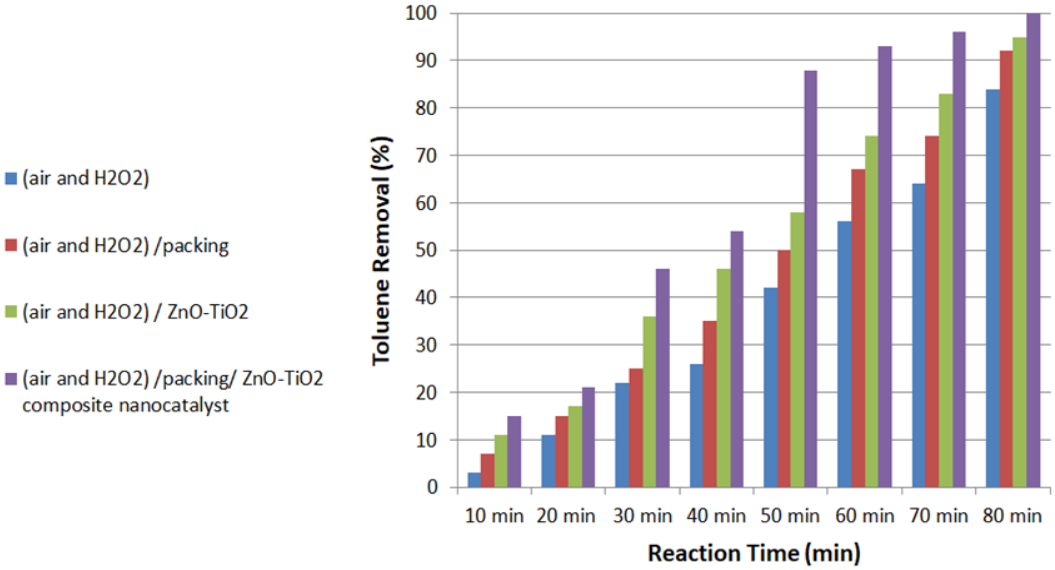

Fig. (10): Toluene is converted during the oxidation process in a BCR utilizing the four treatment techniques, at a toluene concentration of (40 ppm).

Lastly, in this work, the primary requirement for the OBCR's operation was a high and consistent toluene removal rate. The outcomes of other authors' toluene removal methods were contrasted with the current method's, which employed a ZnO-TiO_2 composite nanocatalyst and packing media. Out of all the treatment methods used in this study, (air and H_2O_2), (air and H_2O_2)/ packing, (air and H_2O_2) /ZnO-TiO_2 composite nanocatalyst, and (air and H_2O_2)/ packing/ ZnO-TiO_2 composite nanocatalyst, Figure (7) shows that the (air and H_2O_2) /packing/ZnO-TiO_2 composite nanocatalyst offered the highest toluene degradation efficiency, achieving complete conversion of toluene (100%) at a shorter contact time of 50 minutes. The high mass transfer process and the widely distributed nanocatalyst were responsible for the enhancement of the degradation reaction. Several studies have reported the use of different treatment methods and reactor systems for the removal of toluene from contaminated media [50], [61], [65]. They illustrate the reactors' combined drawbacks, which include high running costs, restricted toluene removal, and catalyst charging, all of which have a detrimental effect on the rate of toluene degradation [16][18][66].

3.5. Oxidation Reaction Mechanism

In order to control the primary phases of the oxidation reaction, a thorough understanding of toluene degradation in the BCR is required. The reaction mechanism of the oxidation reaction by (air+H_2O_2) in the BCR with packing and the ZnO-TiO_2 nanocatalyst is explained by equations (2–9) [1][64]. It demonstrates that the nanocatalyst enhanced the catalytic oxidation process and degraded more toluene by increasing the formation of hydroxyl radicals ($OH^{\bullet}$).

$$ZnO\text{-}TiO_2 + \Delta Egab\ (UV) \longrightarrow ZnO\text{-}TiO_2\ (e^-_{CB} + h^+_{VB}) \quad \text{.....(2)}$$

$ZnO\text{-}TiO_2$ (h^+_{VB}) + H_2O ⟶ $ZnO\text{-}TiO_2$+ H^++ OH^- ……...…(3)

$ZnO\text{-}TiO_2$ (h^+_{VB})+ OH^- ⟶ $ZnO\text{-}TiO_2$+ $OH^\bullet$ ……..….... (4)

$ZnO\text{-}TiO_2(e^-_{CB})$ + O_2 ⟶ $ZnO\text{-}TiO_2$+ $O_2^{\bullet -}$ ……...…. (5)

$O_2^{\bullet -}$ + H^+ ⟶ $HO_2^{\bullet -}$ ……..... (6)

$2HO_2^{\bullet -}$ ⟶ H_2O_2 +O_2 ……...…. (7)

H_2O_2 + e^- ⟶ OH^- + $OH^\bullet$ ……. …. (8)

Toluene + $OH^\bullet$ ⟶ degradation products ……. …. (9)

Strong oxidizing agents, these radicals aid in the breakdown of toluene. In the reaction system, the hydroxyl radicals speed up the catalytic oxidation process, converting more toluene. Additionally, the $ZnO\text{-}TiO_2$ nanocatalyst increased the removal efficiency by producing more hydroxyl radicals, which gave the oxidation process an effective, active catalytic surface [16][59][66].

As a result, the combination of the $ZnO\text{-}TiO_2$ nanocatalyst and packing material in the reaction system demonstrated a high degree of toluene degradation in the current experiment.

When the $ZnO\text{-}TiO_2$ nanocatalyst was added to wastewater that contained toluene, the reaction surface area and gas holdup clearly increased, and the nanocatalyst particles dispersed widely. All of these elements encouraged the reaction mixture to contain a large amount of air, which greatly enhanced the toluene breakdown process by producing carbon dioxide and water. Consequently, using this approach resulted in higher-performance elimination in a BCR and a quicker reaction time for toluene degradation [44][61][67].

Figure (11) Proposed photocatalysis and aqueous phase oxidation via [68][69]. The Russell reaction breaks down the tetroxide into molecular oxygen, benzaldehyde, and benzyl alcohol. In a "Russell-like" reaction, the benzylperoxy radical can also combine with a hydroperoxy radical to generate a monoalkyl tetroxide, which then breaks down into benzaldehyde, molecular oxygen, and water. [70][71].

The breakdown of the three primary intermediate products involves a secondary, less significant process that results in the creation of mono-hydroxylated isomers: an attack at the ring (Figure 11). When compared to the non-hydroxylated primary intermediate products, the tiny levels of these hydroxylated products demonstrate that the photocatalytic system's principal pathway is the first $OH^\bullet$ radical addition to the aromatic ring [71].

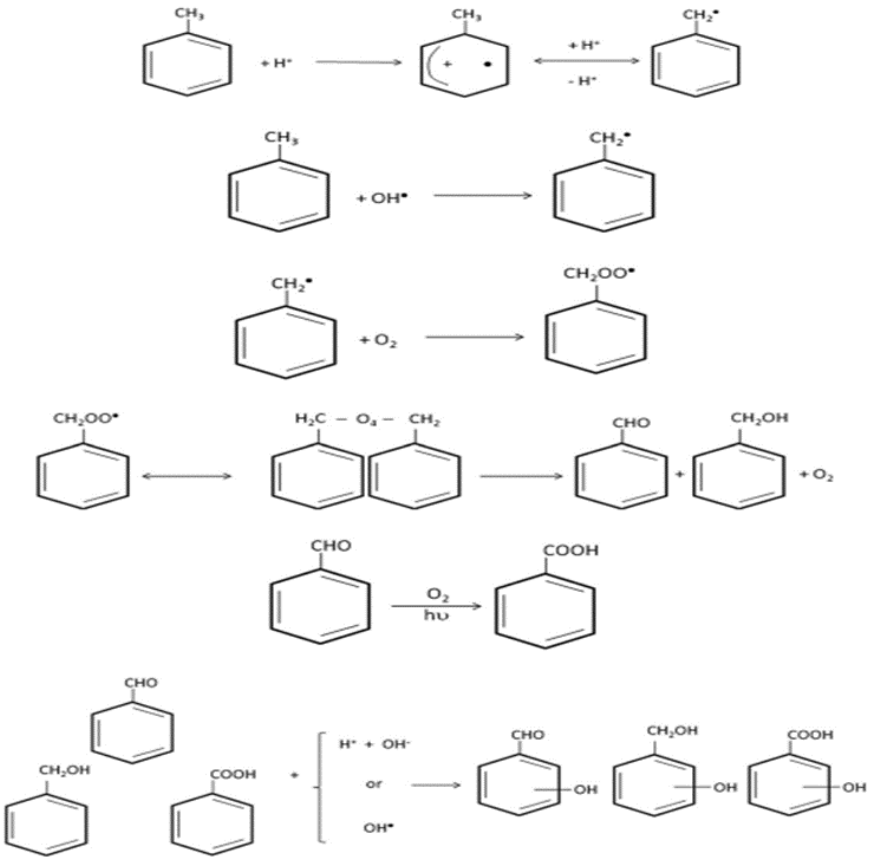

Fig. (11): Toluene's photocatalytic oxidation processes.

4. Conclusions

This work used packing media and a ZnO-TiO_2 composite nanocatalyst to enhance the poor rate of mineralization of toluene contaminants from wastewater.

The findings showed that because packing increases the total surface area of contact between the liquid and gas phases, it is appropriate for a high mass transfer mechanism. Additionally, the high void fraction of the packing material (45%) kept the reactor's internal pressure drop within a reasonable range without affecting the rate of reaction. Furthermore, it was discovered that the ZnO-TiO_2 composite nanocatalyst significantly increased the rate of toluene degradation by strengthening the mechanism of toluene degradation.

According to the experimental findings, the oxidation reaction took longer to complete when the concentration of toluene in the reaction system rose. The maximum toluene removal values were also demonstrated by the ZnO-TiO_2 composite nanocatalyst and the presence of packing. Furthermore, the performance of the BCR in the reaction process was found to be significantly influenced by its hydrodynamic characteristics. For toluene to be completely (100%) degraded,

reaction times of 50, 60, 70, and 80 minutes were needed for concentrations of 10, 20, 30, and 40 ppm.

Furthermore, it was discovered that the (air and H_2O_2) /packing/ ZnO-TiO_2 composite nanocatalyst method offered the best toluene degradation performance (100%) at a contact time of 50 minutes for an initial toluene concentration of 10 ppm out of the four experimental techniques used in their mineralization process.

Additionally, the flow evaluation study showed that the presence of the ZnO-TiO_2 composite nanocatalyst enhanced the catalytic process because of the highly active sites within the catalyst pores, and that no channeling issues were observed as a result of the gas bubble movement via the packing because of the proper gas void fraction. Furthermore, more hydroxyl radicals ($^{\bullet}OH$) were formed in the BCR as a result of the oxidation reaction being aided by the ZnO-TiO_2 composite nanocatalyst and packing. The breakdown mechanism of toluene into CO_2 and H_2O was accelerated by these potent oxidizing radicals.

The development of a thin layer atop the packing facilitated high toluene elimination by increasing the reaction rate from the perspective of mass transfer. No prior research has examined the toluene oxidation process in conjunction with a ZnO-TiO_2 composite nanocatalyst in the presence of a packing material in a BCR, according to a survey of the literature.

In order to convert toluene in wastewater in a shorter amount of time, the proposed reaction mechanism in this work offers a better knowledge of the oxidation process. Lastly, the primary factor supporting the reaction mechanism was thought to be the toluene reaction along the packed BCR height.

Author Contributions Statement: All authors have actively participated in all sections of this research and contributed to every stage of the work. All authors have read and approved the final version of the manuscript.

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