Removal of Phenol From Wastewater by High-Gravity Intensified Heterogeneous Catalytic Ozonation With Activated Carbon

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Abstract

In this study, the high-gravity technique is used to intensify the heterogeneous catalytic ozonation with activated carbon (AC) as the catalyst for removal of phenol from wastewater in a rotating packed bed (RPB), and the effects of high-gravity factor, inlet O_3 concentration, liquid-gas ratio and initial pH on the degradation and mineralization of phenol at room temperature are investigated. It is revealed that the degradation rate of phenol reaches 100% at 10 min and the removal rate of total organic carbon (TOC) reaches 91% at 40 min under the conditions of high-gravity factor $\beta=40$, inlet O_3 concentration = $90 \text{ mg}\cdot\text{L}^{-1}$, liquid flow rate = $80 \text{ L}\cdot\text{h}^{-1}$ and initial pH=11. Compared with the bubbling reactor (BR)/ O_3 /AC and RPB/ O_3 systems, the mineralization rate of phenol by the RPB/ O_3 /AC system is increased by 24.78% and 34.77%, respectively. Free radical quenching experiments are performed using tertiary butanol (TBA) and benzoquinone(BQ) as scavengers of $\cdot\text{OH}$ and $O_2\cdot^-$, respectively. It is shown that the degradation and mineralization of phenol are respectively attributed to the direct ozonation and the indirect oxidation by $\cdot\text{OH}$ generated from the decomposition of O_3 adsorbed on AC surface. $\cdot\text{OH}$ and $O_2\cdot^-$ are also detected by electron paramagnetic resonance (EPR). Thus, it is concluded that AC-catalyzed ozonation and high gravity technique had a synergistic effect on $\cdot\text{OH}$ initiation, which in turn can significantly improve the degradation and mineralization of organic wastewater.

1. Introduction

Phenol is a toxic organic compound with numerous applications in coal chemical, petrochemical, paper-making, dyeing and pharmaceutical industries (Yang et al. 2019a). However, it is highly carcinogenic, teratogenic and mutagenic in nature that may cause severe damage to both humans and animals even in a low amount (Naguib and Badawy 2019). Approximately 0.6 tons of phenol wastewater would be produced per ton of phenol obtained, and it is also estimated that 0.16–0.24 million tons of phenol wastewater will be released globally in 2021(Huang et al. 2015). Now, phenol has been listed as a priority pollutant in the United States and China. Therefore, it is of great significance to seek an economical and effective method to treat phenol wastewater (Bhausahab et al. 2016; Zhang et al. 2020).

Catalytic ozonation has gained considerable attention as an efficient wastewater treatment method, whereby $\cdot\text{OH}$ can be produced from catalytic decomposition of O_3 , which has strong oxidative capacity ($E^0 = 2.8\text{eV}$) and reacts non-selectively with organic pollutants present in wastewater(Jaafarzadeh et al. 2017). Importantly, most catalysts used in heterogeneous catalytic ozonation have the advantages of high catalytic activity(Ahmed et al. 2010), easy separation from the liquid phase, reusable, and no secondary pollution to the environment (Nawrocki et al. 2013; Wang et al. 2020).

Common heterogeneous catalysts include carbon materials, metal oxides, and supported metals or metal oxides (Afzal et al. 2020; Afzal et al. 2016; Xta et al. 2020). Activated carbon (AC) is a remarkable carbon-based heterogeneous catalyst for its unique advantages such as high efficiency, high stability, large specific surface area, and low cost(Ma et al. 2016). In heterogeneous catalytic ozonation, AC can act not

only as a catalyst but also as an adsorbent (Abdedayem et al. 2015; Wang et al. 2019). Jans et al. (1998) found that AC promoted the decomposition of dissolved O_3 into hydroxyl radicals. Mousavi et al. (2017) compared ozonation and AC-catalyzed ozonation for reducing chlorophyll a, turbidity, UV_{254} absorbance, dissolved organic carbon (DOC) and color from eutrophic water. Ozonation and AC-catalyzed ozonation reduced chlorophyll a from 49.5 to 9.7 and 4.7 $\mu g L^{-1}$, respectively; ozonation showed a 36% increase in DOC, while AC-catalyzed ozonation removed up to 76.0% of DOC; and more significant decline in water color and turbidity was achieved by AC-catalyzed ozonation. However, the degradation of organic pollutants is limited in conventional stirred reactors, because the mass transfer of O_3 from the gas to the liquid phase, which is the control step of heterogeneous catalytic ozonation, is low as a result of insufficient gas-liquid contact (Wang et al. 2019).

There is evidence that ultrasonic, electric and high-gravity fields can act synergistically with catalysts to improve the decomposition and mass transfer of O_3 by increasing the gas-liquid-solid contact area (Qian et al. 2017). The rotating packed bed (RPB) is a novel gas-liquid reactor with excellent micromixing performance, high mass transfer efficiency and small size (Jiao et al. 2019). A high-gravity field is created by the centrifugal force resulting from the high-speed rotation of the packing, by which liquid can be sheared into films, threads and droplets in order to improve gas-liquid dispersion and mixing, reduce the mass transfer resistance, and improve the mass transfer efficiency. In short, the high-gravity field has the potential to intensify the heterogeneous catalytic ozonation (Anonymous et al. 2010; Jiao et al. 2010; Wu et al. 2017). Li et al. (2020) used RPB instead of a conventional reactor for FeOOH-catalyzed ozonation of nitrobenzene in aqueous solution, and the results showed that RPB as an effective gas-liquid reactor could improve the mass transfer rate and oxidative activity of O_3 . However, there have been few studies on AC-catalyzed ozonation for removal of phenol from wastewater in a high-gravity field.

In this study, AC is used as the packing of RPB to provide contact and reaction sites for gas, liquid and solid phases and to catalyze the decomposition of O_3 . The effects of high-gravity factor(β), liquid-gas ratio Q_L/Q_G , inlet O_3 concentration C_{O_3} , initial phenol concentration and initial pH on the removal rate of phenol and TOC are investigated. In order to understand the synergistic effects of RPB and heterogeneous catalytic ozonation with AC, the degradation and mineralization of phenol by RPB/ O_3 , RPB/ O_3 /AC, BR/ O_3 /AC, and RPB/AC systems are compared. In order to understand the mechanism of heterogeneous catalytic ozonation with AC in RPB, free radical quenching experiments are performed using TBA and BQ as the scavengers of $\cdot OH$ and $O_2\cdot^-$, respectively.

2. Experimental

2.1 Chemicals and equipment

AC was purchased from Henan Changge Xinyuan Chemical Co., Ltd. (Henan, China); Phenol, potassium iodide, sodium thiosulphate and radical scavengers (ter-butanol (TBA) and p-benzoquinone (p-BQ)) were analytically pure and purchased from Tianjin Guangfu Reagent Co., Ltd. (Tianjin, China). The main

instruments used in this study include a Dionex Ultimate 3000 (USA) instrument for high-performance liquid chromatography, a pH analyzer (PHS-3C; Shanghai Analytical Instrument Co., Ltd., China), an ozone generator (OZV-8; Shandong Lvbang Photoelectric Equipment Co., Ltd., China; a rotating packed bed (High Gravity key Laboratory of Central North University of China; porosity: 0.46 m³/m³; inner diameter of the packing: 29 mm; outer diameter of the packing: 95 mm; packing height: 60mm), a TOC analyzer for measurement of TOC concentrations (Aurora, O.I. Analytical, USA), and Electron paramagnetic resonance (EPR; MS-5000x, Bruker, Germany).

2.2 Experimental setup

The experiment was carried out by semi-batch operation at an ambient temperature of 25°C±2°C in the RPB, as shown in Fig. 1. Briefly, 2 L of phenol solution was pumped into RPB at a flow rate of 40–100 L/h, and then sprayed on the inner edge of the rotor through the liquid distributor. After that, the liquid was sheared into microelements to increase the contact area as it flowed in the circumferential direction under the action of centrifugal force. A certain concentration of ozone was fed from the bottom of the RPB at a flow rate of 60 ~ 120 L/h and fully contacted with the liquid in a cross-flow manner. The reacted phenol solution flowed back to the storage tank by gravity for recycling, and the effluent gas was absorbed by 5% KI solution. Samples were collected at different times for further analysis and characterization. In the control experiments, the same experiment was conducted using Pall ring packing in a conventional bubbling reactor.

2.3 Analytical methods

The gaseous ozone concentrations at the inlet and outlet were measured by a gaseous ozone detector (3S-J5000; China), The solution pH was measured by a pH meter (PHS-3C; China). The concentrations of phenol and intermediate products were determined by high-performance liquid chromatography (HPLC; Dionex UltiMate 3000) with a C18 reversed column, where the wavelength of the UV detector was set at 276 nm and the mobile phase was the CH₃OH/DI water (60: 40) with a flow rate of 0.9 mL min⁻¹. The TOC concentrations were determined by a TOC analyzer (Aurora, O.I. Analytical). The removal efficiency of phenol and TOC was evaluated using the following equation.

$$\eta(\%) = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

where η (%) is defined as the removal efficiency of phenol or TOC, and C_0 and C are the concentrations of phenol or TOC at time $t = 0$ or t (mg L⁻¹), respectively.

3. Results And Discussion

3.1 Characterization of AC

The surface and structural properties of AC used in this study were characterized by scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), as shown in Fig. 2. It is seen from

Fig. 2A that the AC surface is spongy with many porous structures and irregularly distributed cavities, which indicates that AC has a high porosity (Banat et al. 2010; Rivera-Utrilla et al. 2011). In Fig. 2B, the basic characteristics of the raw material activated carbon are as follows: the peak at 3425 cm^{-1} is attributed to the presence of phenolic hydroxyl groups and carboxylic acid on the AC surface; the peaks at 2924 cm^{-1} and 2847 cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of C-H in CH_2 , respectively; the peak at 1627 cm^{-1} is attributed to the stretching vibration of $\text{C}=\text{C}$; while the peak at $1044\text{--}1049\text{ cm}^{-1}$ is attributed to the stretching vibration of CO (Lei et al. 2007). O_3 molecules can react with oxygen-containing groups on the AC surface to form a five-membered ring structure via hydrogen bonds, which in turn is decomposed into free radicals via electron transfer. Thus, AC provides a catalytic environment for decomposition of O_3 into $\cdot\text{OH}$ and consequently enhance the degradation of phenol in wastewater.

3.2 Effects of process parameters on the degradation and mineralization of phenol by RPB/ O_3 /AC

3.2.1 Effects of high-gravity factor

The high gravity factor β is a dimensionless measure of the intensity of the high gravity field, and is the ratio of inertial acceleration to gravitational acceleration (Yang et al. 2019):

$$\beta = \frac{G}{g} = \frac{r\omega^2}{g} = \frac{N^2 r}{900} \quad (1)$$

where ω is the rotational angular velocity of the rotor (s^{-1}), r is the average radius of the rotor (m), g is the gravitational acceleration ($9.8\text{ m}^2\cdot\text{s}^{-1}$), and N is the rotational speed of the rotor (rpm)

Figure 3A shows that the removal rate of phenol increases with the increase of high-gravity factor, and at 10 min it reaches 100% at $\beta = 40$ but only 80% at $\beta = 10$. It is clear that a higher high-gravity factor can make the droplets smaller and the films thinner in RPB, and thus increase the volume mass transfer coefficient and the decomposition rate constant of O_3 . Because of this, more O_3 is dissolved in the solution, resulting in an increase in liquid-phase O_3 concentration and subsequently AC-catalyzed decomposition of O_3 into $\cdot\text{OH}$ (Qin et al. 2018). Combined with Fig. 3B, it should be noted that at $\beta = 40$, the removal rate of phenol reaches 100% at 10 min, at which the removal rate of TOC is only 30% due to the generation of large amounts of intermediate products during the degradation of phenol. Thus, the mineralization rate of phenol should also be taken into consideration. It is revealed that as the high-gravity factor increases from 10 to 50, the mineralization rate of phenol at 40 min is increased from 31–78%, because the gas-liquid-solid contact area is increased as the wastewater is sheared into finer droplets, threads and films at a higher centrifugal force. As β increases, the gas-liquid-solid interface can also be renewed faster, leading to the transfer of more O_3 into the solution and consequently the generation of more $\cdot\text{OH}$ from the decomposition of O_3 . However, similar mineralization processes of

phenol are noted between $\beta = 40$ and $\beta = 50$, as β reaches a certain level, the gas-liquid-solid contact area has reached the peak. Thus, a high-gravity factor higher than $\beta = 40$ does not necessarily guarantee high mineralization efficiency of phenol. Given the high energy consumption and cost at high high-gravity factor, the optimal high-gravity factor is set to $\beta = 40$.

3.2.2 Effects of gas phase O₃ concentration

Figure 4A shows that as the inlet O₃ concentration is increased from 25 mg·L⁻¹ to 90 mg·L⁻¹, the removal rate of phenol at 40 min is increased from 44–100%. Figure 4B shows that at a given inlet O₃ concentration, the mineralization rate of phenol by the RPB/O₃/AC system is increased as the reaction proceeds. It is also seen that the mineralization rate of phenol at 40 min is 41% at C_{O3}= 25 mg·L⁻¹ but 91% at C_{O3}= 90 mg·L⁻¹. According to the Henry's law, the equilibrium concentration of O₃ in water

$\int_0^t [O_3] dt$ will increase with increasing inlet O₃ concentration, and thus more ·OH will be produced from AC-catalyzed decomposition of O₃. Elovitz et al. (1999) have revealed that the ·OH concentration is proportional to $\int_0^t [OH] dt$ and $\int_0^t [O_3] dt$. Increasing the gas-phase O₃ concentration can also increase its partial pressure and thus drives the dissolution of O₃, and the dissolved O₃ can contact sufficiently with the functional groups on the AC surface to produce ·OH (Álvarez et al. 2005; Li et al. 2018; Shao et al. 2021). Thus, both the degradation and mineralization rates of phenol are significantly improved at higher inlet O₃ concentrations.

3.2.3 Effects of initial pH

Initial pH is expected to have an effect on the decomposition of O₃ into ·OH by affecting the charges of hydroxyl groups present on the catalyst surface. In this study, the effects of initial pH on the removal rate of phenol and TOC by the RPB/O₃/AC system are investigated over a range of pH = 3.0 ~ 11.0. As shown in Fig. 6A and 6B, the removal rate of phenol first increases rapidly with the increase of pH, and it reaches 100% within 20 min at a phenol concentration of 100 mg/L, which is in good agreement with previous results. It is also seen that the removal rate under alkaline conditions is much higher than that under acidic conditions. This is because O₃ molecules can react with hydroxide to form ·OH under alkaline conditions that can facilitate the ozonation process (Staehelin and Hoigne 1982); while under acidic conditions, O₃ molecules are less likely to be decomposed into free radicals, and only direct ozonation occurs for degradation of organic pollutants by breaking the double bond or the aromatic ring (Turhan and Uzman 2008; Xiong et al. 2020). In addition, ·OH has higher oxidative capacity than O₃ as its redox potential (E⁰ = 2.80 V) is higher than that of O₃ (E⁰ = 2.07V). Thus, Zeng et al. (2013) found that the reaction rate of phenol with ·OH (k = 2.10×10⁹-4.50×10⁹ M⁻¹s⁻¹) was much higher than that with and O₃ (k = 1.6×10³ M⁻¹s⁻¹). These results indicate that an alkaline environment is more favorable for AC-catalyzed ozonation.

Figure 6B shows that the removal rate of TOC varies in the range of 70 ~ 82%, and thus it is concluded that initial pH has smaller effects on the mineralization of phenol than on the degradation of phenol by the RPB/O₃/AC system. This is because large amounts of small carboxylic acid molecules are produced during the degradation process of phenol, such as oxalic acid, maleic acid and fumaric acid (Zhang et al. 2021), which make the reaction system more acidic. Figure 6A shows that the phenol concentration decreases rapidly within the first 5 min and then stabilizes gradually probably due to the decrease of pH. Thus, the RPB/O₃/AC system could not take full advantage of its high oxidative capacity under alkaline conditions. The adsorption capacity of AC also plays a role in the removal of TOC. However, Miao et al. (2013) found that an alkaline environment was not conducive to the adsorption of phenol by AC. For these reasons, initial pH has a significant effect on the removal of phenol by the RPB/O₃/AC system but no obvious effect on the mineralization of phenol.

3.2.4 Effects of liquid-gas ratio

As the mass transfer of O₃ is liquid film controlled, there is a need to increase the turbulence of the liquid in order to enhance the mass transfer of O₃. It is known that the higher the liquid flow rate is, the higher the

volume mass transfer coefficient of O₃ and then the $\int_0^t [O_3] dt$ will be (Chen et al. 2005). However, the residence time of the liquid in RPB that depends heavily on the liquid-gas ratio would be greatly reduced in case of high turbulence, which can adversely affect the contact between O₃ and the liquid and subsequent ozonation of phenol. In this experiment, the gas flow rate is set to $Q_G=60 \text{ L}\cdot\text{h}^{-1}$ and the liquid flow rate is varied to obtain different liquid-gas ratios. Figure 6A and 6B show that the removal rates of phenol and TOC increase with the increase of Q_L/Q_G , indicating that the benefits brought about by turbulence outweigh the negative impacts brought about by the short residence time. As the Q_L/Q_G ratio is increased from 40/60 to 100/60, the mineralization rate of phenol at 40 min is significantly increased from 49–88%, which can be attributed to excellent dispersion of liquid in the packing and the high mass transfer efficiency as a result of the high liquid flow rate in the cross flow (Wei et al. 2020). Thus, the optimal liquid-gas ratio is set to 100/60 in this experiment.

3.2.5 Comparison of different technologies

The removal rates of phenol and TOC by BR/O₃/AC, PRB/O₃/AC, BR/O₃, and PRB/O₃ systems are compared. Figure 7A shows that for the RPB/AC system, the removal rate of phenol reaches equilibrium after 20 min and reaches a saturation state (30%) after 40 min, indicating that AC is capable of adsorbing phenol. Thus, AC can act not only as an excellent adsorbent but also as an excellent catalyst. For the RPB/O₃ system, the removal rate of phenol reaches 100% after 30 min, because O₃ can easily undergo electrophilic substitution reactions with unsaturated aromatic compounds like phenol (Xiong et al. 2020) due to its high oxidative capacity. For the RPB/O₃/AC and BR/O₃/AC systems, the removal rate of phenol reaches 100% after 20 min, which is attributed to the ability of AC to catalyze the degradation of intermediate products. It should be noted that the removal rate of phenol by the RPB/O₃/AC system is higher than that by the BR/O₃/AC system, which implies that RPB is more capable of enhancing the mass

transfer of O_3 and thus the catalytic ozonation of phenol. The rapid renewal of the liquid-solid interface in RPB provides more adsorption sites of O_3 and thus contributes to the generation of $\cdot OH$ and subsequent catalytic ozonation of phenol (Yang et al. 2019). Thus, the highest removal rate of phenol is obtained with the use of the RPB/ O_3 /AC system.

Figure 7B shows the mineralization rate of phenol by BR/ O_3 /AC, PRB/ O_3 /AC, BR/ O_3 , and PRB/ O_3 systems. It is evident that the removal of TOC lags behind that of phenol. At 40 min, the mineralization rate of phenol by the RPB/AC system is as low as 23%, which indicates that AC-catalyzed ozonation rather than adsorption is the major contributor to the mineralization of phenol. The low mineralization rate of phenol by the RPB/ O_3 system (41%) is probably due to the selective reaction of O_3 with organic pollutants. However, a higher mineralization rate is obtained using BR/ O_3 /AC and RPB/ O_3 /AC systems, because $\cdot OH$ is generated from AC-catalyzed decomposition of O_3 and it has a much higher reaction rate constant with phenol ($2.1 \times 10^9 M^{-1} \cdot s^{-1}$) compared with that of O_3 (Ku et al. 2011). As expected, the mineralization rate of phenol by the RPB/ O_3 /AC system is 24% higher than that by the BR/ O_3 /AC system, confirming again that RPB is more capable of enhancing the mass transfer and decomposition of O_3 to $\cdot OH$, and AC-catalyzed ozonation and high gravity technique act synergistically to improve the mineralization of phenol.

3.3 Mechanisms

3.3.1 Free radical scavengers

In the AC-catalyzed ozonation process, many reactive oxygen species (ROS) are formed from the decomposition of O_3 , such as $\cdot OH$, $O_2 \cdot^-$ and 1O_2 with a redox potential of 2.8 V, 1.35V and 2.22V, respectively (Li et al. 2020). In the quenching experiment, two free radical scavengers, TBA and BQ, are added to eliminate $\cdot OH$ and $O_2 \cdot^-$ (Sl et al. 2019) in order to understand their unique contributions to the degradation of phenol by the RPB/ O_3 /AC system. Figure 8 shows that the addition of excess TBA results in a 9% decrease in the degradation rate of phenol from 100–91% at 40 min, indicating that direct ozonation plays a more important role in the degradation of phenol than indirect oxidation by $\cdot OH$. However, the addition of excess BQ results in a 23% decrease in the degradation rate of phenol. BQ can scavenge O_3 , $\cdot OH$ and $O_2 \cdot^-$, and as $O_2 \cdot^-$ accounts for only a small portion, O_3 also plays a main role in the degradation of phenol (Yu et al.). However, as the mineralization rate of phenol by RPB/ O_3 and RPB/ O_3 /AC systems is 41% and 75% at 40 min, respectively, it is inferred that the degradation and mineralization of phenol are respectively attributed to the direct ozonation and the indirect oxidation by $\cdot OH$ from the decomposition of O_3 adsorbed on AC surface.

3.3.2 Types of free radicals by EPR

In order to determine the reactive species for the degradation of phenol by the RPB/ O_3 /AC system, the types of free radicals are determined by electron paramagnetic resonance (EPR). In Fig. 9A, the DMPO-

·OH signal is clearly detected with an intensity ratio of 1:2:2:1 in the RPB/O₃/AC system (Qiao et al. 2019). In Fig. 9B, the O₂·⁻ signal is also detected when the aqueous phase is replaced with ethanol solvent ($k_{\text{OH,EtOH}} = (1.2-2.8) \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) to inhibit ·OH under the same conditions (Bing et al. 2015). This verifies that the AC in the RPB/O₃/AC system can enhance the decomposition of O₃ to ·OH and O₂·⁻ which in turn are involved in the indirect oxidation of phenol.

4. Conclusions

In this study, the high-gravity technique is used to enhance the heterogeneous catalytic ozonation with AC as the catalyst for removal of phenol from wastewater in RPB. As expected, RPB can significantly enhance the mass transfer and decomposition of O₃ to ·OH and, as a consequence, the degradation and mineralization of phenol. Under the same conditions, the mineralization rate of phenol by the RPB/O₃/AC system at 40 min (74.8%) is 24.78% higher than that by the BR/O₃/AC system. The quenching experiment reveals that the addition of excess TBA and BQ results in 9% and 23% decrease in the degradation rate of phenol at 40 min, respectively. It is concluded that the degradation and mineralization of phenol are attributed to the direct ozonation and the indirect oxidation by ·OH from the decomposition of O₃ adsorbed on AC surface, respectively. Thus, the combination of high-gravity technique with AC-catalyzed ozonation allows for rapid degradation and deep mineralization of phenol. The free radical quenching experiment confirms that O₂·⁻ and ·OH are the main reactive species involved in the mineralization of phenol. In conclusion, AC-catalyzed ozonation and high gravity technique act synergistically to induce the formation of ·OH, which in turn significantly improves the degradation and mineralization of organic wastewater.

Declarations

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Availability of data and materials All data generated or analyzed during this study were included in this article.

Author contribution Shengjuan Shao and Xin Ding were in charge of the experiment. Youzhi Liu, Zhixing Li and Jiabin Jing analyzed the experimental data. Jingwen Zhang and Weizhou Jiao were major contributors in writing the manuscript. All authors read and approved the final manuscript. All authors of this manuscript have directly participated in the planning, execution, and analyses of this study.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

1. Abdedayem A, Guiza M, Ouederni A (2015) Copper supported on porous activated carbon obtained by wetness impregnation: effect of preparation conditions on the ozonation catalyst's characteristics. *CR Chim* 18:100-109. <https://doi.org/10.1016/j.crci.2014.07.011>
2. Afzal S, Quan X, Chen S, Wang J, Muhammad D (2016) Synthesis of manganese incorporated hierarchical mesoporous silica nanosphere with fibrous morphology by facile one-pot approach for efficient catalytic ozonation. *J Hazard Mater* 318: 308-318. <https://doi.org/10.1016/j.jhazmat.2016.07.015>
3. Afzal S, Pan K, Duan D, Wei Y, Chen L (2020) Heterogeneous activation of peroxymonosulfate with cobalt incorporated fibrous silica nanospheres for the degradation of organic pollutants in water. *Appl Surf Sci* 542:148674. <https://doi.org/10.1016/j.apsusc.2020.148674>
4. Ahmed S, Rasul MG, Martens WN, Brown R, Hashib MA (2010) Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments. *Desalination* 261:3-18. <https://doi.org/10.1016/j.desal.2010.04.062>
5. Álvarez P, García-Araya J, Beltrán F, Masa FJ, Medina F (2005) Ozonation of activated carbons: effect on the adsorption of selected phenolic compounds from aqueous solutions. *J Colloid Interf Sci* 283:503-512. <https://doi.org/10.1016/j.jcis.2004.09.014>
6. Banat F, Al-Asheh S, Al-Makhadmeh L (2010) Utilization of raw and activated date pits for the removal of phenol from aqueous solutions. *Chem Eng Technol* 27, 80-86. <https://doi.org/10.1002/ceat.200401868>
7. Bhausahab S, Korake S (2016) Review on removal of phenol from wastewater using low cost adsorbent. *Int J Eng Sci* 6:2278-7798.
8. Bing J, Hu C, Nie Y, Min Y, Qu J (2015) Mechanism of catalytic ozonation in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ aqueous suspension for destruction of ibuprofen. *Environ. Sci Technol* 49:1690-1697. <https://doi.org/10.1021/es503729h>
9. Chen YH, Chang CY, Su WL, Chiu CY, Yu H, Chiang PC, Chang CF, Shie JL, Chiou CS, Chiang SI (2010) Ozonation of CI reactive black 5 using rotating packed bed and stirred tank reactor. *J Chem Technol Biot* 80:68-75. <https://doi.org/10.1002/jctb.1159>
10. Chen YH, Chiu CY, Chang CY, Huang YH, Yu YH, Chiang PC, Shie JL, Chiou CS (2005) Modeling ozonation process with pollutant in a rotating packed bed. *Ind Eng Chem Res* 44:21-29. <https://doi.org/10.1021/ie0401657>
11. Elovitz MS, Gunten UV (1999) Hydroxyl radical/ozone ratios during ozonation processes. I The Rct Concept Ozone-*Sci Eng* 21:239-260. <https://doi.org/10.1080/01919519908547239>

12. Huang K, Wang J, Wu D, Lin S (2015) Copper hydroxyl sulfate as a heterogeneous catalyst for the catalytic wet peroxide oxidation of phenol. *Rsc Adv* 5:8455-8462. <https://doi.org/10.1039/C4RA15878D>
13. Jaafarzadeh N, Ghanbari F, Ahmadi M (2017) Efficient degradation of 2,4-dichlorophenoxyacetic acid by peroxymonosulfate/magnetic copper ferrite nanoparticles/ozone: a novel combination of advanced oxidation processes. *Chem Eng J* 320:436-447. <https://doi.org/10.1016/j.cej.2017.03.036>
14. Jiao WZ, Liu YZ, Qi GS (2010) Gas pressure drop and mass transfer characteristics in a cross-flow rotating packed bed with porous plate packing. *Ind Eng Chem Res* 49:3732-3740. <https://doi.org/10.1021/ie9009777>
15. Jiao W, Luo S, He Z, Liu Y (2016) Applications of high gravity technologies for wastewater treatment: A review. *Chem Eng J* 313:912-927. <https://doi.org/10.1016/j.cej.2016.10.125>
16. Ku Y, Huang YJ, Chen HW, Hou WM (2011) Decomposition of acetone by hydrogen peroxide/ozone process in a rotating packed contactor. *Water Environ Res* 83:588-593. <https://doi.org/10.2175/106143010X12851009156961>
17. Lei L, Li G, Zhang X, Su Y (2007) Catalytic oxidation of highly concentrated real industrial wastewater by integrated ozone and activated carbon. *Appl Catal A- Gen* 327:287-294. <https://doi.org/10.1016/j.apcata.2007.05.027>
18. Li P, Wei X, Shao S, Gao W, Liu Y (2020a) Degradation of nitrobenzene in wastewater by $O_3/FeOOH$ in a rotating packed bed. *Chem Eng Process* 153:107981. <https://doi.org/10.1016/j.cep.2020.107981>
19. Li W, Yan J, Yan Z, Song Y, Jiao W, Qi G, Liu Y (2018) Adsorption of phenol by activated carbon in rotating packed bed: Experiment and modeling. *Appl Therm Eng* 142:760-766. <https://doi.org/10.1016/j.applthermaleng.2018.07.051>
20. Li X, Ma J, He H (2020) Recent advances in catalytic decomposition of ozone. *J Environ Sci* 94:14-31. <https://doi.org/10.1016/j.jes.2020.03.058>
21. Ma D, Chen L, Wu Y, Liu R (2016) Evaluation of the removal of antiestrogens and antiandrogens via ozone and granular activated carbon using bioassay and fluorescent spectroscopy. *Chemosphere* 153:346-355. <http://dx.doi.org/10.1016/j.chemosphere.2016.03.073>
22. Miao Q, Tang Y, Xu J, Liu X, Xiao L, Chen Q (2013) Activated carbon prepared from soybean straw for phenol adsorption. *J Taiwan Inst Chem E* 44:458-465. <https://doi.org/10.1016/j.jtice.2012.12.006>
23. Mousavi S, Dehghanzadeh R, Ebrahimi SM (2017) Comparative analysis of ozonation (O_3) and activated carbon catalyzed ozonation (ACCO) for destroying chlorophyll a and reducing dissolved organic carbon from a eutrophic water reservoir. *Chem Eng J* 314:396-405. <https://doi.org/10.1016/j.cej.2016.11.159>
24. Naguib DM, Badawy NM (2019) Phenol removal from wastewater using waste products. *J Environ Chem Eng* 8:103592. <https://doi.org/10.1016/j.jece.2019.103592>
25. Nawrocki J (2013) Catalytic ozonation in water: Controversies and questions. discussion paper. *Appl Catal B-Environ* 142: 465-471. <https://doi.org/10.1016/j.apcatb.2013.05.061>

26. Qiao J, Luo S, Yang P, Jiao W, Liu Y (2019) Degradation of nitrobenzene-containing wastewater by ozone/persulfate oxidation process in a rotating packed bed. *J Taiwan Inst Chem E*. 99:1-8. <https://doi.org/10.1016/j.jtice.2019.02.015>
27. Qian Z, Chen Q, Grossmann IE (2017) Optimal synthesis of rotating packed bed reactor. *Comput Chem Eng* 105:152-160. <https://doi.org/10.1016/B978-0-444-64241-7.50391-8>
28. Qin YJ, Luo S, Geng S, Jiao WZ, Liu YZ (2018) Degradation and mineralization of aniline by O₃/Fenton process enhanced using high-gravity technology. *Chinese J Chem Eng* 26:8-14 <https://doi.org/10.1016/j.cjche.2018.01.018>
29. Rivera-Utrilla J, Sánchez-Polo M, Gómez-Serrano V, Álvarez P, Alvim-Ferraz M, Dias JM (2011) Activated carbon modifications to enhance its water treatment applications. An overview. *J Hazard Mater* 187:1-23. <https://doi.org/10.1016/j.jhazmat.2011.01.033>
30. Shao S, Lei D, Song Y, Liang L, Jiao W (2021): Cu–MnO_x/γ-Al₂O₃ catalyzed ozonation of nitrobenzene in a high-gravity rotating packed bed. *Ind Eng Chem Res* 60:2123-2135. <https://doi.org/10.1021/acs.iecr.0c05751>
31. Si A, Ytab C, Jz A, Wh A, Wc A, Fga C, Zhe HA, Llab C (2019) Advanced and green ozonation process for removal of clofibric acid in water system: preparation and mechanism analysis of efficient copper-substituted MCM-48. *Sep Purif Technol* 211:684-696. <https://doi.org/10.1016/j.seppur.2018.10.031>
32. Staehelin J, Hoigne J (1982) Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environ Sci Technol* 16:621-653. <https://doi.org/10.1021/es00104a009>
33. Turhan K, Uzman S (2008) Removal of phenol from water using ozone. *Desalination* 229:257-263. <https://doi.org/10.1016/j.desal.2007.09.012>
34. Wang D, Liu L, Ma L, Wang F, Shao L (2019) Modeling and experimental studies on ozone absorption into phenolic solution in a rotating packed bed. *Ind Eng Chem Res* 58:7052-7062. <https://doi.org/10.1021/acs.iecr.9b00787>
35. Wang J, Chen H (2020) Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. *Sci Total Environ* 704:1-17. <https://doi.org/10.1016/j.scitotenv.2019.135249>
36. Wang X, Xu J, Liu J, Liu J, Liu W (2019) Mechanism of Cr(VI) removal by magnetic greigite/biochar composites. *Sci Total Environ* 700:134414. <https://doi.org/10.1016/j.scitotenv.2019.134414>
37. Wei X, Shao S, Ding X, Jiao W, Liu Y (2020) Degradation of phenol with heterogeneous catalytic ozonation enhanced by high gravity technology. *J Cleaner Prod* 248:119179.1-119179.10. <https://doi.org/10.1016/j.jclepro.2019.119179>
38. Wu TW, Hung YT, Chen MT, Tan CS (2017) CO₂ capture from natural gas power plants by aqueous PZ/DETA in rotating packed bed. *Sep Purif Technol* 186:309-317. <https://doi.org/10.1016/j.seppur.2017.05.040>
39. Xiong W, Cui W, Li R, Feng C, Chen N (2020) Mineralization of phenol by ozone combined with activated carbon: performance and mechanism under different pH levels. *Environ Sci*

Technol 1:100005. <https://doi.org/10.1016/j.esse.2019.100005>

40. Xta B, Cw A, Fga B, Wen HA, Hya B, Sza B, Yza B, Yl A (2020) Mn-Fe-Ce multiple oxides with Al₂O₃ coating supported onto honeycomb cordierite monoliths for NO catalytic oxidation. *Colloid Surface A* 611:125790. <https://doi.org/10.1016/j.colsurfa.2020.125790>
41. Yang G, Mo S, Xing B, Dong J, Yuan J (2019) Effective degradation of phenol via catalytic wet peroxide oxidation over N, S, and Fe-tridoped activated carbon. *Environ Pollut* 258:113687. <https://doi.org/10.1016/j.envpol.2019.113687>
42. Yang PA, Luo SB, Liu HA, Jiao WA, Liu YA (2019) Aqueous ozone decomposition kinetics in a rotating packed bed. *J Taiwan Inst Chem E* 96:11-17. <https://doi.org/10.1016/j.jtice.2018.10.027>
43. Yu G, Wang Y, Cao H, Zhao H, Xie Y (2020) Reactive oxygen species and catalytic active sites in heterogeneous catalytic ozonation for water purification. *Environ Sci Technol* 54:5931-5946. <https://doi.org/10.1021/acs.est.0c00575>
44. Zeng Z, Zou H, Li X, Arowo M, Sun B, Chen J, Chu G, Shao L (2013) Degradation of phenol by ozone in the presence of fenton reagent in a rotating packed bed. *Chem Eng J* 229:404-411. <https://doi.org/10.1016/j.cej.2013.06.018>
45. Zhang M, Zhang Z, Liu S, Peng Y, Ki SY (2020) Ultrasound-assisted electrochemical treatment for phenolic wastewater. *Ultrason Sonochem* 65:105058. <https://doi.org/10.1016/j.ultsonch.2020.105058>
46. Zhang M, Yin D, Guo J, Wu H, Feng X (2021) Ternary catalyst Mn-Fe-Ce/Al₂O₃ for the ozonation of phenol pollutant: performance and mechanism. *Environ Sci Pollut* 28:32921-32932. <https://doi.org/10.1007/s11356-021-13006-5>

Figures

Fig.1

Figure 1

Diagram of experimental setup (1- oxygen cylinder, 2- ozone generator, 3- gas flowmeter, 4-valve, 5- rotating packed bed, 6- valve, 7- liquid flowmeter, 8- peristaltic pump, 9- storage tank, 10-gaseous ozone detector, 11- exhaust gas absorption device)

Fig.2 (A)

(B)

Figure 2

(A) The SEM image and (B)FTIR spectra of AC

Fig.3. (A) (B)

Figure 3

Effects of high-gravity factor on (A) the removal rate of phenol and (B) the mineralization rate of TOC (T=25°C, CB=100 mg·L⁻¹, ms=25 g·L⁻¹, QG=60 L·h⁻¹, CO₃=75 mg·h⁻¹, QL=80 L·h⁻¹, pH=6)

Fig.4 (A) (B)

Figure 4

Effects of inlet O3 concentration on (A) the removal rate of phenol and (B) the mineralization rate of TOC (T=25°C, CB=100 mg·L⁻¹, ms=25 g·L⁻¹, QG=60 L·h⁻¹, β=40, QL=80 L·h⁻¹, pH=6)

Figure 5

Effects of initial pH on (A) the removal rate of phenol and (B) the mineralization rate of TOC (T=25°C, CB=100 mg·L⁻¹, ms=25 g·L⁻¹, QG=60 L·h⁻¹, β=40, CO3=75 mg·L⁻¹, QL=80 L·h⁻¹)

Figure 6

Effects of liquid-gas ratio on (A) the removal rate of phenol and (B) the mineralization rate of TOC (T=25°C, CB=100 mg·L⁻¹, ms=25 g·L⁻¹, QG=60 L·h⁻¹, β=40, CO3=75 mg·L⁻¹, pH=6)

Fig.7 (A) **(B)**

Figure 7

(A) The removal rate of phenol and (B) the mineralization rate of TOC by BR/O3/AC, PRB/O3/AC, BR/O3, and PRB/O3 systems (T=25°C, CB=100 mg·L⁻¹, ms=25 g·L⁻¹, QG=60 L·h⁻¹, β=40, CO3=75 mg·L⁻¹, QL=80 L·h⁻¹, pH=6).

Fig.8

Figure 8

The removal rate of phenol in the presence of TBA and BQ ($T=25^{\circ}\text{C}$, $\text{CB}=100\text{ mg}\cdot\text{L}^{-1}$, $\text{ms}=25\text{ g}\cdot\text{L}^{-1}$, $\text{QG}=60\text{ L}\cdot\text{h}^{-1}$, $\beta=40$, $\text{CO}_3=75\text{ mg}\cdot\text{L}^{-1}$, $\text{QL}=80\text{ L}\cdot\text{h}^{-1}$, $\text{pH}=6$).

Fig.9 (A) (B)

Figure 9

The EPR spectra of the RPB/O3/AC system in aqueous solution measured with 150 mM DMPO. (A) DMPO- $\cdot$ OH in aqueous phase; and (B) DMPO-O₂⁻ in ethanol solvent (T=25°C, QG=60 L·h⁻¹, β=40, CO₃=75 mg·L⁻¹, QL=80 L·h⁻¹, pH=6).