



Influencing mechanism of bicarbonate on the catalytic ozonation of nitrobenzene in aqueous solution by ceramic honeycomb supported manganese

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ABSTRACT

The influence of bicarbonate on degradation efficiency of nitrobenzene in aqueous solution by ceramic honeycomb supported manganese catalytic ozonation has been investigated. Under the lower concentration condition (25 and 50 mg L⁻¹), bicarbonate enhances the degradation efficiency of nitrobenzene, while bicarbonate presents the inhibition effect at the higher concentration (100–250 mg L⁻¹). The modification of ceramic honeycomb with Mn improves its resistibility to the negative effect of bicarbonate, and the inhibition effect of bicarbonate also can be decreased, respectively by increasing total applied ozone or amount of catalyst. The utilization efficiency of ozone increases with the increasing bicarbonate concentration (0–100 mg L⁻¹). The formation of H₂O₂ and the initiation of hydroxyl radical (\cdot OH) reach a maximum at the bicarbonate concentration 75 and 50 mg L⁻¹, respectively. The mechanism investigation suggests that bicarbonate plays an important role as a promoter of radical chain reactions accelerating the ozone mass transformation, causing the increases in the utilization efficiency of ozone, the formation of H₂O₂ and the initiation of \cdot OH at the lower concentration. Bicarbonate with the higher concentration exerts a negative effect on the degradation efficiency of nitrobenzene due to the predominance derived from its scavenging capacity of \cdot OH.

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1. Introduction

Ozonation is an attractive and increasingly important method for the degradation of organic pollutants in aqueous solution [1]. However, the recalcitrant organic pollutants are relatively difficult to be efficiently degraded by strong oxidants like ozone [2]. For instance, nitrobenzene, a major environmental pollutant due to its carcinogenesis and mutagenesis [3], resists to the degradation by ozonation alone due to the strong electron-withdrawing property of its nitro-group [4]. Therefore, various advanced oxidation processes (AOPs) have been developed as potential methods for degrading organic compounds, such as O₃/H₂O₂, O₃/UV, UV/H₂O₂, Fenton and UV/Fenton reagents, UV/TiO₂, electron beam and catalytic ozonation [5].

Since AOPs may require higher equipment and operating costs and so maybe difficult to use in practice, alternative lower cost AOPs with a relatively simpler operation need to be developed for the degradation of recalcitrant organic pollutants in aqueous solution [1]. As a novel AOP, heterogeneous catalytic ozonation has received increasing attention in recent years, which combines

ozone with solid phase catalyst [5]. The main catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides (MnO₂, TiO₂ and Al₂O₃) and also metals or metal oxides on metal oxide supports (e.g. Cu/Al₂O₃, Cu/TiO₂, Ru/CeO₂, TiO₂/Al₂O₃ and Fe₂O₃/Al₂O₃), the catalytic activity of which is mainly based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals (\cdot OH) [6]. The main advantage of heterogeneous catalytic ozonation is the ability to spontaneously separate the solid and liquid phases, and to increase ozone capability for the abatement of recalcitrant organic pollutants [7]. Consequently, heterogeneous catalytic ozonation has been attracting the interest of the scientific community dedicated to the study of ozone processes in water treatment. Several researches have been reported on the degradation of nitrobenzene in aqueous solution by the heterogeneous catalytic ozonation processes. It is seen that the presence of heterogeneous catalyst such as nano-TiO₂ [8], Mn-loaded granular activated carbon [9,10], ceramic honeycomb [11,12], Mn-ceramic honeycomb [13] and synthetic goethite [14] can enhance significantly the degradation efficiency of nitrobenzene compared with the case of ozonation alone, and the degradation of nitrobenzene mostly follows the \cdot OH oxidation mechanism in the systems mentioned above.

Bicarbonate, as the main form of inorganic carbon existing under neutral pH conditions, is present in surface and ground waters at

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concentrations typically in the range of 50–200 mg L⁻¹ [15]. Therefore, it is very important to assess the influence of bicarbonate on the degradation efficiency of target organic compounds because the concentration of bicarbonate ions is substantially higher (mg L⁻¹ level) than that of organic micropollutants (μg L⁻¹ level or ng L⁻¹ level) in water, specifically for the practical operation of organic compounds removal in wastewater treatment and drinking water supply with source water of the river and the lake. Though some work has been carried out for the investigation of the influence of bicarbonate on the heterogeneous catalytic ozonation for the degradation of organic compounds in aqueous solution, few researches have been reported in detail on the influencing mechanism of bicarbonate.

Nitrobenzene, as an indicator of •OH, is chosen as the target organic micropollutant due to its refractory nature to conventional chemical oxidation. Based on the previous work [13], the objective of this study was to investigate the influence of bicarbonate on the degradation efficiency of nitrobenzene in aqueous solution by the process of ceramic honeycomb supported manganese catalytic ozonation, and to elucidate preliminarily the influencing mechanism from the aspects of ozone mass transformation, the characteristic determination of catalyst, and the formation of H₂O₂ and •OH.

2. Materials and methods

2.1. Materials and reagents

The model water was prepared by spiking 50 μg L⁻¹ nitrobenzene (Beijing Chemical Factory, China, purified by distillation pretreatment, 99.80%) in Milli-Q water (Millipore Q Biocel system). Manganese nitrate (50% w/w solution, Beijing Chemical Factory, China), and all other chemicals used in the experiments were analytical grade reagents. Bicarbonate alkalinity (as CaCO₃) was added by using NaHCO₃.

Catalyst preparation and ozonation procedure were performed according to the methods described in the previous studies [13]. In addition, compared to the scavenging effect of buffer solution (HCO₃⁻, CO₃²⁻, H₂PO₄⁻, and HPO₄²⁻), the degradation of trace initial nitrobenzene concentration 50 μg L⁻¹ led to a slight change of initial pH which could not affect the experiment, and could be neglected. Therefore, the experiments were carried out in this study without adding any buffer solution to maintain the pH at a constant value. However, addition of bicarbonate in aqueous solution caused a remarkable change of initial pH. In order to eliminate the influence and obtain parallel comparison, initial pH was adjusted to 7.0 immediately prior to the every batch experiment by addition of aqueous sodium hydroxide or hydrochloric acid.

2.2. Analytical method

The concentration of nitrobenzene was determined by a GC-14C gas chromatograph (Shimadzu, Japan) [13]. The concentration of ozone in the gas was measured by the iodometric titration method [16]. The concentration of residual ozone in aqueous solution was measured by a spectrophotometer using the indigo method [17]. The concentration of ozone was controlled at 1.0 mg L⁻¹. The concentration of H₂O₂ formed in the oxidation system was determined by the photometric method [18]. Electron paramagnetic resonance (EPR) experiments were conducted for the determination of •OH generated in the catalytic ozonation process [8]. An inductive coupled plasma emission spectrometer (ICP, optima 5300DV, PerkinElmer, USA) was used to determine the concentration of metal ion in aqueous solution.

X-ray power diffraction (XRD, Input Gokv Zokw Co. Ltd., Japan, Model A-41L-Cu) was used to analyze the crystal phase of the catalyst in monochromatized Cu Kα radiation using a curved graphite monochromator on a diffracted beam with operating voltage of 45 kV and current of 50 mA. The specific surface area of the catalyst sample was measured according to the Brunauer–Emmet–Teller (BET) method with the krypton adsorption at liquid nitrogen temperature on a Micromeritics ASAP 2020 instrument. To measure the BET specific surface area of the catalyst monoliths, a particular home-made test tube was used. The density of surface hydroxyl groups was measured according to a saturated deprotonation method described by Laiti and Tamura [19,20]. The pH at the point of zero charge (pH_{PZC}) was measured with a mass titration method [21,22].

3. Results and discussion

3.1. Influence of bicarbonate on degradation efficiency of nitrobenzene

The influence of bicarbonate on the degradation efficiency of nitrobenzene was investigated in the processes of ozonation alone, ozonation/ceramic honeycomb, ozonation/Mn-ceramic honeycomb, adsorption of nitrobenzene on ceramic honeycomb and adsorption of nitrobenzene on Mn-ceramic honeycomb. The results are shown in Fig. 1.

Fig. 1 shows the dependence of degradation efficiency of nitrobenzene on the different bicarbonate concentration (0–250 mg L⁻¹). Nitrobenzene is hardly adsorbed on ceramic honeycomb or Mn-ceramic honeycomb. Therefore, adsorption of nitrobenzene can be neglected compared to ozonation alone and catalytic ozonation. In particular, it is also to be noted that adsorption of nitrobenzene is not significantly dependent on bicarbonate concentrations. For the process of ozonation alone, bicarbonate presents a negative effect on the degradation of nitrobenzene, namely the higher bicarbonate concentration, the lower degradation efficiency of nitrobenzene is obtained.

Under the same experimental conditions, the degradation of nitrobenzene undergoes a complicated evolution in the process

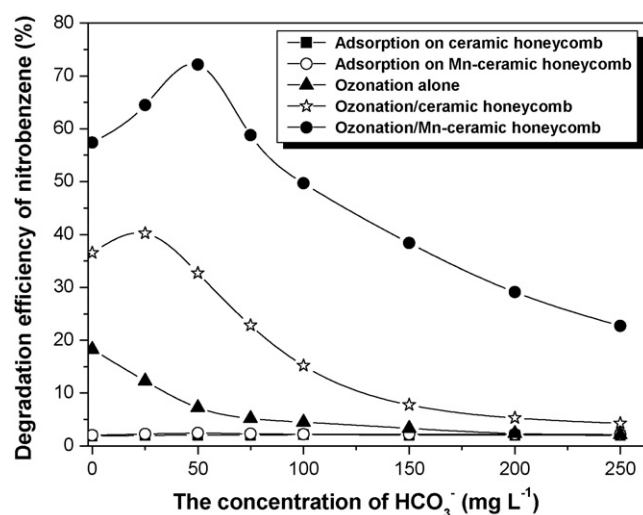


Fig. 1. Comparison of the degradation efficiency of nitrobenzene at different concentrations of bicarbonate in the different processes (reaction conditions—temperature: 293 K; initial pH: 7.0; initial nitrobenzene concentration: 50 μg L⁻¹; concentration of total applied ozone: 1.0 mg L⁻¹; amount of ceramic honeycomb and Mn-ceramic honeycomb catalysts used, respectively in catalytic ozonation: 3 blocks; loading percentage of Mn (wt.%): 1.0%; concentration of bicarbonate: 0–250 mg L⁻¹; reaction time: 10 min).

of catalytic ozonation. The degradation efficiency of nitrobenzene reaches the maximum of 40% in the process of ozonation/ceramic honeycomb at bicarbonate concentration of 25 mg L^{-1} , and then decreases to 4% at 250 mg L^{-1} bicarbonate, indicating an enhancement at the lower concentration and an inhibition at the higher concentration. The degradation efficiency of nitrobenzene in the ozonation/Mn–ceramic honeycomb system reaches the maximum value of 72% at bicarbonate concentration of 50 mg L^{-1} . After this critical concentration point, the degradation efficiency declines steadily to 23% with increasing bicarbonate concentration to 250 mg L^{-1} .

The previous study confirmed that nitrobenzene is oxidized primarily by $\bullet\text{OH}$ in the processes of ozonation alone, ozonation/ceramic honeycomb and ozonation/Mn-ceramic honeycomb under the present experimental conditions [13]. From the phenomenon shown in Fig. 1, some characteristics can be described as follows: (1) bicarbonate may inhibit the oxidation of nitrobenzene by scavenging $\bullet\text{OH}$ in the process of ozonation alone; (2) due to the introduction of heterogeneous catalysts, bicarbonate presents the synergistic effect with catalytic surface to accelerate the degradation of nitrobenzene at the lower bicarbonate concentration; (3) the modification of ceramic honeycomb with Mn improves its resistibility to the negative effect of bicarbonate. Therefore, the experiment focused more attention on the investigation of the influence of bicarbonate on the degradation efficiency of nitrobenzene in the process of Mn-ceramic honeycomb catalytic ozonation.

3.2. Influence of bicarbonate on degradation efficiency at different variables

Like bicarbonate existing in surface and ground waters, some variables influence remarkably the degradation of organic compounds and the practical operation of wastewater treatment and drinking water supply with source water of the river and the lake. Therefore, we also investigated the influence of bicarbonate on the degradation efficiency of nitrobenzene under the different conditions.

3.2.1. Total applied ozone

The influence of bicarbonate on the degradation efficiency of nitrobenzene was evaluated at the different ozone concentrations. The results are presented in Fig. 2.

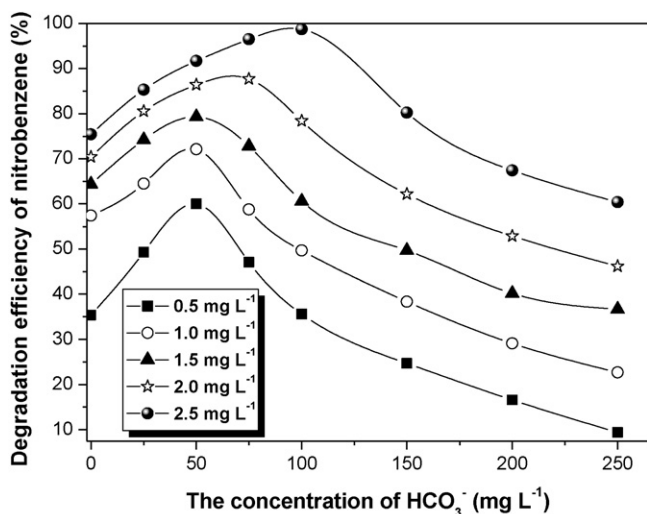


Fig. 2. Evolution of the degradation efficiency of nitrobenzene with the concentration of bicarbonate in the process of Mn-ceramic honeycomb catalytic ozonation at different ozone concentrations (reaction conditions as in Fig. 1; ozone concentration: $0.5\text{--}2.5 \text{ mg L}^{-1}$).

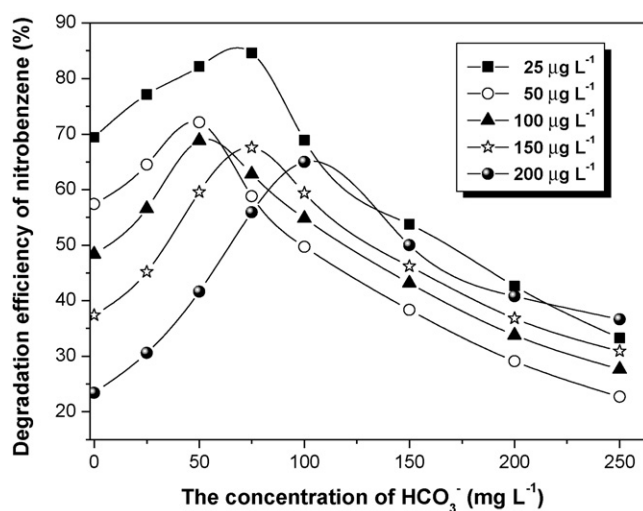


Fig. 3. Evolution of the degradation efficiency of nitrobenzene with the concentration of bicarbonate in the process of Mn-ceramic honeycomb catalytic ozonation at different initial nitrobenzene concentrations (reaction conditions as in Fig. 1; initial nitrobenzene concentration: $25\text{--}200 \mu\text{g L}^{-1}$).

As can be observed in Fig. 2, the degradation efficiencies of nitrobenzene at the different ozone concentrations all reach a maximum and then decrease gradually. In the interval ozone concentrations of $0.5\text{--}1.5 \text{ mg L}^{-1}$, the maximum appears at a bicarbonate concentration of 50 mg L^{-1} . While the further increase in total applied ozone to 2.0 and 2.5 mg L^{-1} leads to an increase in the optimum bicarbonate concentration to 75 and 100 mg L^{-1} , respectively, at which the maximum degradation efficiency of nitrobenzene 88% and 99% can be obtained. Therefore, it is deduced that total applied ozone exhibits the obvious positive effect to avoid the inhibition derived from the presence of bicarbonate. This phenomenon indicates that the increase in the ozone concentrations can improve the initiation of $\bullet\text{OH}$, resulting in its sufficient quantity to resist the negative effect of bicarbonate in aqueous solution. Another possible explanation for the results is that the increasing ozone concentration maybe enhances the synergistic effect generated from heterogeneous catalyst and bicarbonate, leading to the degradation acceleration of nitrobenzene.

3.2.2. Initial nitrobenzene concentration

The influence of bicarbonate on the degradation efficiency of nitrobenzene was performed by varying initial nitrobenzene concentration from 25 to $200 \mu\text{g L}^{-1}$. The results are shown in Fig. 3.

From the results of Fig. 3, bicarbonate seems to present a relatively complex influence on the degradation efficiency of nitrobenzene at the different initial nitrobenzene concentrations. The degradation efficiency of nitrobenzene shows the maximum 85% at a bicarbonate concentration of 75 mg L^{-1} at an initial nitrobenzene concentration of $25 \mu\text{g L}^{-1}$. For another two systems with initial nitrobenzene concentration of 50 and $100 \mu\text{g L}^{-1}$, the maximum conversions of 72% and 69% are obtained at a bicarbonate concentration of 50 mg L^{-1} . It means that though the synergistic effect of bicarbonate exists, the resistance of reactive system to negative effect decreases because the increase in consumed quantity of $\bullet\text{OH}$ is accompanied with the increase in initial nitrobenzene concentration. Finally, it amazingly falls back to bicarbonate concentration of 75 and 100 mg L^{-1} , respectively, at initial nitrobenzene concentration of 150 and $200 \mu\text{g L}^{-1}$. In this case, the resistance increases as a result of the increase in competitive ability for the scavenger of $\bullet\text{OH}$ with the increasing initial nitrobenzene concentration.

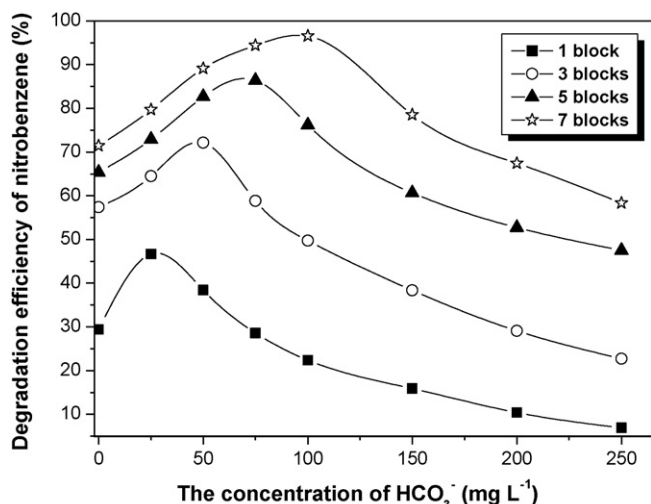


Fig. 4. Evolution of the degradation efficiency of nitrobenzene with the concentration of bicarbonate in the process of Mn-ceramic honeycomb catalytic ozonation at different amount of catalyst (reaction conditions as in Fig. 1); amount of Mn-ceramic honeycomb catalysts used: 1–7 blocks.

3.2.3. Amount of catalyst

Since amount of catalyst is a key condition for the three phase heterogeneous reactions (gas–liquid–solid reactions) in aqueous solution, it is important to examine the influence of this parameter over the reactive systems studied here. Fig. 4 shows the evolution of degradation efficiency of nitrobenzene with bicarbonate concentration at the different amounts of catalyst.

As indicated in Fig. 4, the degradation efficiency of nitrobenzene increases with the increasing amount of catalyst at the same bicarbonate concentration, and the critical bicarbonate concentration of the maximum increases from 25 to 100 mg L^{-1} in the interval 1–7 blocks amount of catalyst. It seems reasonable because the increase in amount of catalyst can enhance the initiation of $\cdot\text{OH}$, resulting in the increasing resistance of negative effect and the enhancement of degradation efficiency of nitrobenzene.

3.3. Investigation of influencing mechanism

The previous study confirmed that, as shown in the route (1) of Fig. 5, the modification of ceramic honeycomb with Mn can cause the enhancement of density of surface hydroxyl groups which results in the accelerations of ozone decomposition and initiation of $\cdot\text{OH}$, leading to the increase in degradation efficiency of nitrobenzene [13]. Therefore, bicarbonate maybe influences the interaction of heterogeneous catalytic surface or the evolution of ozone in the present gas–liquid–solid reaction.

3.3.1. Characteristics conversion of catalyst surface

It was reported that several natural water constituents can cause permanent blockage of the catalysts active surface sites and the decrease of their catalytic activity, such as inorganic ions: phosphates or carbonates [6]. On the one hand, bicarbonate maybe influences mainly heterogeneous catalytic aspect according to the route (2) of Fig. 5. In this case, bicarbonate ion likely can occupy the active surface site on heterogeneous catalytic surface, resulting in the blockage of active surface site which reduces the initiation of $\cdot\text{OH}$. If this situation happens, the characteristics of catalyst surface must be influenced, specifically the density of surface hydroxyl groups and pH_{PZC} . Therefore, the experiment determined the conversion of density of surface hydroxyl groups and pH_{PZC} with the concentration of bicarbonate after the Mn-ceramic honeycomb catalytic ozonation. However, the results (not shown) indicate that

there is no obvious conversion of density of surface hydroxyl groups after the Mn-ceramic honeycomb catalytic ozonation in the interval concentration of bicarbonate 0–250 mg L^{-1} . Additionally, pH_{PZC} does not present a remarkable conversion due to the very good positive correlation between density of surface hydroxyl groups and pH_{PZC} confirmed in the previous study [13]. Except for the two characteristics mentioned above, the measurement results also illustrate bicarbonate with the different concentrations does not cause the conversions of the crystalline phase and the specific surface area. As a consequence, it can be deduced that the introduction of bicarbonate has no influence on the characteristics of catalyst surface. Another evaluation about the influence of bicarbonate on heterogeneous catalytic surface shown in the route (2) of Fig. 5 is the lifetime of Mn-ceramic honeycomb catalyst.

3.3.2. Degradation efficiency of nitrobenzene under reuse condition

The lifetime of catalyst reflects the poisoning of catalyst after the reaction. The experiment investigated the degradation efficiency of nitrobenzene under reuse condition. The results (not shown) depict that the degradation efficiency of nitrobenzene almost remain constantly after 40 times reuse of catalyst at different bicarbonate concentrations. On the contrary, if the route (2) of Fig. 5 is considered as the influencing mechanism of the present heterogeneous catalytic ozonation, the degradation efficiency of nitrobenzene must decrease continuously with the increasing reuse times due to the blockage of active surface site derived from bicarbonate. Therefore, the experimental phenomenon of reuse implies bicarbonate with the different concentrations does not produce the poisoning of catalyst, and the influence of bicarbonate on the degradation efficiency of nitrobenzene by the Mn-ceramic honeycomb catalytic ozonation does not follow the mechanism of route (2) in Fig. 5.

On the other hand, bicarbonate maybe influences the evolution of ozone according to the route (3) in Fig. 5, namely ozone mass transformation in the process of Mn-ceramic honeycomb catalytic ozonation.

3.3.3. Influence of bicarbonate on utilization efficiency of ozone and H_2O_2 formation

We determined all the aspects corresponding to ozone mass transformation, including the concentration of total applied ozone, the concentration of residual ozone, the concentration of offgas ozone and the concentration of consumed ozone. Consequently, the utilization efficiency of ozone can be calculated and presented in Fig. 6(a).

The results in Fig. 6(a) depict that the utilization efficiency of ozone increases with the increasing bicarbonate concentration from 0 to 100 mg L^{-1} , and then remain constantly the maximum in both the systems with addition of nitrobenzene and without it, meaning a positive relationship between bicarbonate concentration and the utilization efficiency of ozone at the fixed total applied ozone 1.0 mg L^{-1} .

Fig. 6(b) illustrates the conversion of accumulated concentration of H_2O_2 formation with bicarbonate concentration in the process of Mn-ceramic honeycomb catalytic ozonation. It can be observed that the concentration of H_2O_2 formation always increases as bicarbonate concentration increases (0–250 mg L^{-1}) in the system without addition of nitrobenzene. This positive effect indicates the introduction of bicarbonate can promote the formation of H_2O_2 . However, the concentration of H_2O_2 formation increases with the increasing bicarbonate concentration from 0 to 75 mg L^{-1} and decreases slowly in the interval 75–250 mg L^{-1} after the maximum in the system with addition of nitrobenzene, suggesting an existence of complicated influencing mechanism.

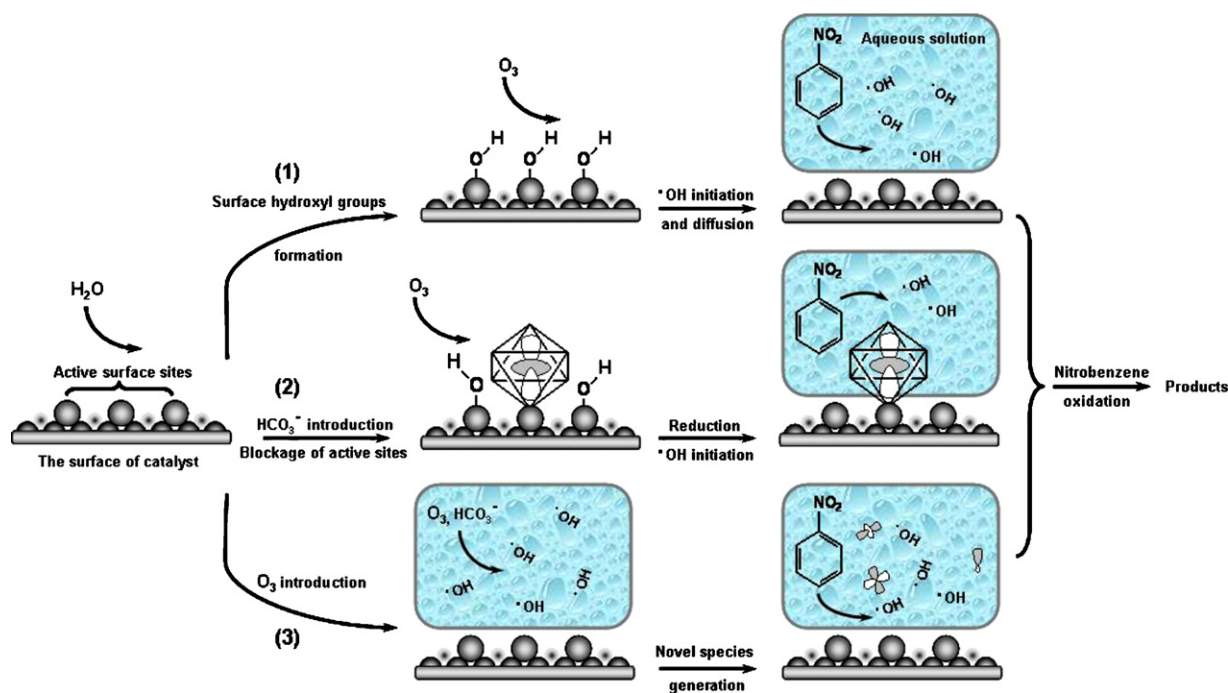


Fig. 5. Probable influencing mechanism proposed of bicarbonate on the degradation efficiency of nitrobenzene in aqueous solution by the process of Mn-ceramic honeycomb catalytic ozonation.

Simultaneously, it also can be found that the system with addition of nitrobenzene at every bicarbonate concentration ($\leq 100 \text{ mg L}^{-1}$) all has a relatively higher utilization efficiency of ozone in Fig. 6(a). The reason of this phenomenon is probably because addition of nitrobenzene consumes much more quantity of oxidative intermediate species, accelerating the transformation of reaction equation and the decomposition of ozone. The curved profile in Fig. 6(b) illuminates the addition of nitrobenzene also accelerates the disappearance of accumulated H_2O_2 , maybe resulting in the initiation of $\bullet\text{OH}$ formation during the course of reactions.

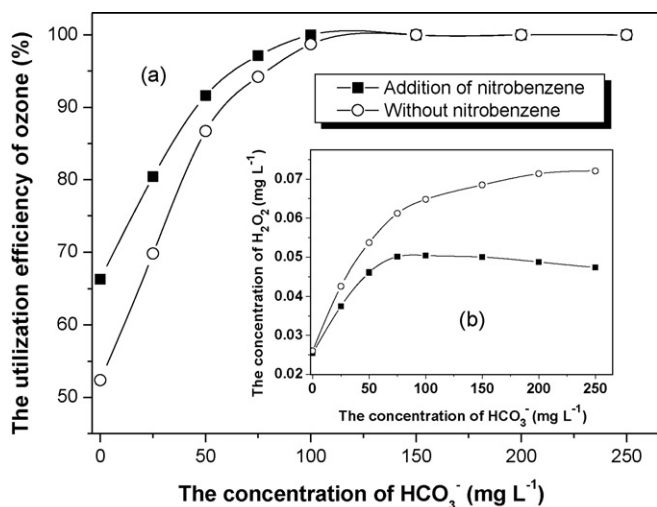


Fig. 6. Evolution of the utilization efficiency of ozone and the concentration of H_2O_2 formation with the concentration of bicarbonate during the Mn-ceramic honeycomb catalytic ozonation in the presence and absence of nitrobenzene (reaction conditions as in Fig. 1; (a) evolution of the utilization efficiency of ozone with the concentration of bicarbonate during the Mn-ceramic honeycomb catalytic ozonation in the presence and absence of nitrobenzene; (b) evolution of the concentration of H_2O_2 formation with the concentration of bicarbonate during the Mn-ceramic honeycomb catalytic ozonation in the presence and absence of nitrobenzene).

3.3.4. Influence of bicarbonate on the initiation of $\bullet\text{OH}$

The initiation of $\bullet\text{OH}$, an active oxidative species, is the important characteristic and common objective of AOPs, and the major secondary oxidant formed from the decomposition of ozone in aqueous solution is the $\bullet\text{OH}$ [2]. Moreover, the reaction rate constant of nitrobenzene with $\bullet\text{OH}$ is $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [23], while the rate constant for reaction of nitrobenzene with molecular ozone is only $0.09 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$ [24], and these reaction rate constants coincide with the result obtained in the previous study that nitrobenzene is degraded mainly by the oxidation of $\bullet\text{OH}$ in the process of Mn-ceramic honeycomb catalytic ozonation [13]. In order to confirm the influencing mechanism, the experiments were performed for monitoring the evolution of $\bullet\text{OH}$ formation by means of spin-trapping/EPR technique which can detect unstable radicals by measuring the intensity of DMPO-OH adduct signal in aqueous solution. The results are summarized in Fig. 7.

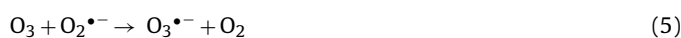
Fig. 7(a) exhibits the characteristic spectrum of the DMPO-OH adduct that coincides with the one demonstrated previously by other research group [25]. Fig. 7(b) represents the variation of intensity of DMPO-OH adduct signal with the concentration of bicarbonate corresponding to the experiment carried out in the systems with addition of nitrobenzene and without it, illustrating that the formation of $\bullet\text{OH}$ occurs in both the systems. Also, notice that under the same bicarbonate concentration condition, the system without addition of nitrobenzene can obtain a higher intensity of DMPO-OH adduct signal, implying a higher concentration of $\bullet\text{OH}$ formation compared to that of the system with addition of nitrobenzene. This is attributed to the presence of nitrobenzene, a $\bullet\text{OH}$ scavenger, which can compete with bicarbonate to react with $\bullet\text{OH}$ ($8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) [36], causing the decrease in the determination concentration of $\bullet\text{OH}$ formation. Combined the results of Figs. 6 and 7, it is concluded that in the system with addition of nitrobenzene, the higher consumption of $\bullet\text{OH}$ induces the transformation of reaction equation, resulting in the increase in utilization efficiency of ozone and the decrease in the equilibrium concentration of H_2O_2 .

3.3.5. Discussion on the influencing mechanism

According to the results obtained, the influencing mechanism of bicarbonate on the degradation of nitrobenzene in the process of Mn-ceramic honeycomb catalytic ozonation is established as follows.

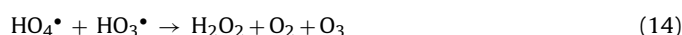
For heterogeneous catalytic ozonation in the presence of metal oxides or metals/metal oxides on supports, the efficiency of the catalytic process depends to a great extent on the properties of catalyst surface, which influence the properties of the surface active sites and ozone decomposition reactions in aqueous solutions [6]. The result of XRD analysis identifies that the crystalline phases of Mn-ceramic honeycomb are $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ and MnO_2 [13]. The most important chemical properties of catalyst are chemical stability and especially the presence of active surface sites, which are responsible for catalytic reactions [6]. The ICP determination indicates there is no metal leaching under the every bicarbonate concentration selected by the present study. Additionally, the relative long lifetime of catalyst suggests Mn-ceramic honeycomb is provided with a good chemical stability. Furthermore, as the catalytic active surface site, the surface hydroxyl group plays an important role in the process of Mn-ceramic honeycomb catalytic ozonation, resulting in the acceleration of ozone decomposition and $\cdot\text{OH}$ initiation [13]. The experimental results illustrate that bicarbonate does not present any influence on the surface characteristics of catalyst, including density of surface hydroxyl groups, pH_{PZC} and specific surface area. Consequently, the influence of bicarbonate on degradation efficiency of nitrobenzene does not derive from the interaction between bicarbonate and heterogeneous catalytic surface.

On the one hand, molecule ozone in aqueous solution can react with the surface hydroxyl group, resulting in the formation of HO_2^- , $\text{HO}_2\cdot$, $\text{O}_3^{\cdot-}$, $\text{HO}_3\cdot$ and $\text{O}_2^{\cdot-}$ through the initiation steps of radical species from the catalyst surface [27]. On the other hand, ozone decomposes in aqueous solution through the following chain reactions [28,29].



Obviously, the chemistry of aqueous ozone is complex due to the production of intermediate species of HO_2^- , $\text{HO}_2\cdot$, $\text{O}_3^{\cdot-}$, $\text{HO}_3\cdot$, $\text{O}^{\cdot-}$, $\text{O}_2^{\cdot-}$ and $\text{HO}_4\cdot$ [2,30,31]. In the following interactional stage, the species formed from heterogeneous surface can diffuse rapidly from the catalyst surface or the solid/water interface to aqueous solution, and take part in the next state of radical chain generation according to the series complex matrix reactions including the initiation, the propagation and the termination, which occur mainly in the homogeneous aqueous phase, in the presence of molecule ozone and H_2O molecule [27]. Accordingly, H_2O_2 and $\cdot\text{OH}$ are formed during the course of chain reactions.

It should be noticed that the results obtained in Fig. 6(b) represent the equilibrium concentration of H_2O_2 in the process of Mn-ceramic honeycomb catalytic ozonation. On the one hand, H_2O_2 can be formed according to the reactions [30–32].



On the other hand, H_2O_2 also can be consumed by reacting with other intermediate species produced in the reactions mentioned above through the termination steps [30–37].

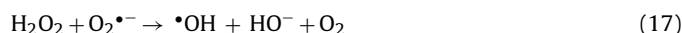
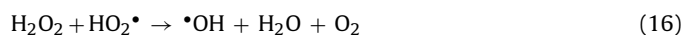
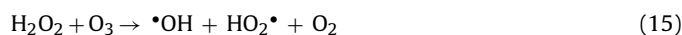
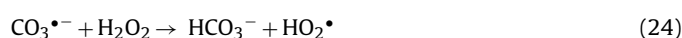
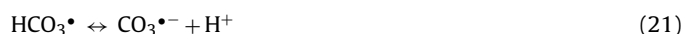


Fig. 7(b) confirms that under the lower concentration (25 and 50 mg L^{-1}), the introduction of bicarbonate can accelerate the initiation of $\cdot\text{OH}$ in both the systems. This phenomenon is ascribed to the positive effect of bicarbonate that plays the role of a promoter for the decomposition of ozone in the presence of H_2O_2 . The relational chain reactions are as follows [26].



According to the reactions (20)–(24) followed by (4)–(7), accelerated initiation of $\cdot\text{OH}$ can be obtained. However, contrary to what happens at lower concentration, further increase in bicarbonate concentration from 50 to 250 mg L^{-1} leads to a remarkable decrease in the intensity of DMPO-OH adduct signal, namely the higher bicarbonate concentration inhibits the initiation of $\cdot\text{OH}$. The possible explanation for this result is that, under the condition of fixed low total applied ozone 1.0 mg L^{-1} , the lower concentration of H_2O_2 is formed and the scavenging effect is enhanced with the increasing bicarbonate concentration.

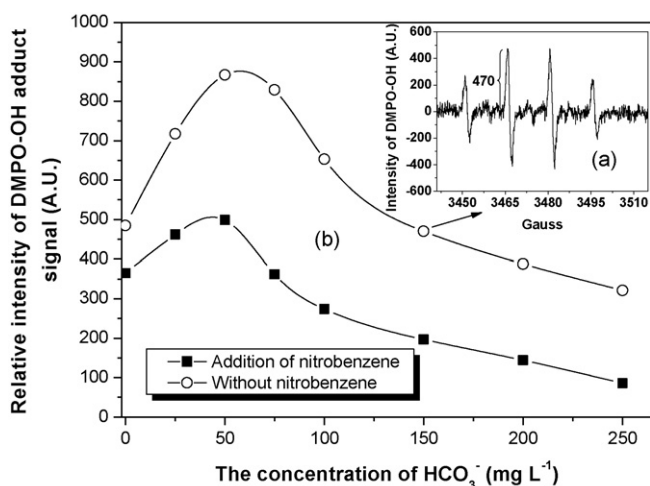


Fig. 7. Evolution of the relative intensity of DMPO-OH adduct signal with the concentration of bicarbonate during the Mn-ceramic honeycomb catalytic ozonation in the presence and absence of nitrobenzene (reaction conditions as in Fig. 1; initial DMPO concentration: 100 mmol L^{-1}).

In conclusion, the modification of ceramic honeycomb with Mn, the co-catalyst, increases the density of surface hydroxyl group on ceramic honeycomb which is the major active site and the essential role of the components in the catalytic ozonation, resulting in the increase of catalytic activity of the raw catalyst. Bicarbonate acts as a promoter and an inhibitor for the degradation of nitrobenzene, respectively, at the lower concentration and the higher concentration in the present study. The synergistic effect mentioned above between bicarbonate and heterogeneous catalyst should refer to the enhancement function of degradation efficiency of nitrobenzene derived from the initiation acceleration of $\bullet\text{OH}$, which is ascribed to the radical chain multiplication reactions composed of bicarbonate and intermediate species, the generation acceleration of which is determined by the introduction of heterogeneous catalyst [27].

4. Conclusions

This paper presents an influence investigation of bicarbonate on the degradation efficiency of nitrobenzene in aqueous solution by Mn-ceramic honeycomb catalytic ozonation. The main conclusions are summarized below.

- Bicarbonate presents the negative effect on the degradation of nitrobenzene in the process of ozonation alone. The maximum degradation efficiency of nitrobenzene can be obtained at bicarbonate concentration of 25 and 50 mg L⁻¹ bicarbonate, respectively, in the processes of ozonation/ceramic honeycomb and ozonation/Mn-ceramic honeycomb.
- The increasing total applied ozone or amount of catalyst, respectively can decrease the inhibition of bicarbonate.
- Bicarbonate can act as a promoter and an inhibitor for the degradation of nitrobenzene, respectively, at the lower concentration and the higher concentration, which is determined by the different participation function of bicarbonate in radical chain reactions. The formation of H₂O₂ and the initiation of $\bullet\text{OH}$ occur during the oxidation reaction.

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