



## Preliminary kinetic study on the degradation of nitrobenzene by modified ceramic honeycomb-catalytic ozonation in aqueous solution

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### ABSTRACT

The kinetics of degradation of nitrobenzene in aqueous solution was investigated in the processes of ozone alone, ozone/ceramic honeycomb (CH), ozone/modified ceramic honeycomb (MCH). The results indicated that all reactions followed the pseudo-first-order kinetic model, and the degradation rate of nitrobenzene was accelerated in the presence of CH or MCH catalyst, and the more pronounced degradation rate was achieved in O<sub>3</sub>/MCH system. Under the experimental conditions of reaction temperature 293 K and initial pH 6.87, the rate constants were determined to be  $5.21 \times 10^{-2} \text{ min}^{-1}$  for O<sub>3</sub> alone,  $7.99 \times 10^{-2} \text{ min}^{-1}$  for O<sub>3</sub>/CH and  $15.45 \times 10^{-2} \text{ min}^{-1}$  for O<sub>3</sub>/MCH. The influencing factors, such as applied ozone concentration (0.987–2.732 mg L<sup>-1</sup>), initial concentration of nitrobenzene (50–250 μg L<sup>-1</sup>) and amount of catalyst (0–5 blocks) could yield respectively the positive effect on the pseudo-first-order rate constants for degradation of nitrobenzene in the three processes mentioned above. The results suggested that the modification process promoted the catalytic activity of raw CH catalyst, namely the impregnation of metals (Mn, Cu and K) maybe enhance the initiation of hydroxyl radical ( $\cdot\text{OH}$ ).

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### 1. Introduction

Ozone has recently received much attention in water treatment technology because of its high oxidation and disinfection potential [1]. Ozone was used for many different purposes such as disinfection and algae control, taste, odour and colour removal, oxidation of inorganic pollutants (iron, manganese), oxidation of organic pollutants as well as for the improvement of coagulation [2]. There were two main points of oxidant application in water treatment: pre-oxidation and intermediate oxidation. Generally, pre-oxidation was applied for the elimination of inorganic compounds, colour, taste, odour, turbidity and suspended solids. At this stage, the partial degradation of natural organic matter and inactivation of microorganisms occurred as well as the coagulation–flocculation–decantation step enhancement took place. On the other hand, intermediate oxidation was aiming at

degrading micropollutants, removing trihalomethanes precursors and increasing biodegradability of organic matters for the following biological process [1,3,4].

Ozonation alone has been shown to achieve very limited mineralization of organic compounds in drinking water treatment or removal of refractory COD of industrial effluents. Consequently, various advanced oxidation processes (AOPs, such as O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, Fenton and UV/Fenton reagents, photocatalytic oxidation with TiO<sub>2</sub>, wet air oxidation and wet peroxide oxidation processes, electron beam, catalytic ozonation) have been investigated as potential methods for degrading organic compounds [5]. Catalytic ozonation could be considered firstly as homogeneous catalytic ozonation, which was based on ozone activation by metal ions present in aqueous solution, and secondly as heterogeneous catalytic ozonation in the presence of metal oxides or metals/metal oxides on supports [1].

Over the last several years, heterogeneous catalytic ozonation has received increasing attention due to its potentially higher effectiveness in the degradation of refractory organic pollutants and lower negative effect on water quality. However, only few studies have been reported on the degradation of nitrobenzene in aqueous solution by heterogeneous catalytic ozonation processes. For example, when the granular activated carbon (GAC) was used as the

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catalyst, the degradation rate of nitrobenzene could be increased from 16.4% in the case of ozonation alone to 25.8% in the case of catalytic ozonation. For the Mn-loaded GAC/ozone catalytic process, the removal efficiency of nitrobenzene could reach 34.2–49.9%, about 1.5–2.0 times than that of the GAC/ozone oxidation process and 2.0–3.0 times than that of the ozonation alone for the removal of nitrobenzene [6]. The experimental results supported that in the  $\text{MnO}_x/\text{GAC}$  catalytic ozonation, the oxidation efficiency of nitrobenzene was higher at low pH (2.74–3.52) than that at high pH conditions (6.72–9.61), and higher pH was beneficial to the decomposition of ozone [7]. Furthermore, use of nano- $\text{TiO}_2$  powder as catalyst for the ozonation of nitrobenzene in water significantly improved the removal of this compound compared with ozonation alone. An increase of initial nitrobenzene concentration caused the enhancement of nitrobenzene removal by ozonation alone and catalytic ozonation. Whereas, increasing the dose of catalyst showed negligible influence on nitrobenzene removal. The experimental results confirmed that the degradation of nitrobenzene by  $\text{TiO}_2$ -catalyzed ozonation followed a radical-type mechanism [8].

In additional, catalytic ozonation with the prepared  $\text{FeOOH}$  substantially improved the degradation of nitrobenzene in water through enhanced generation of  $\cdot\text{OH}$ . The activity of the  $\text{FeOOH}$  was due to its highly hydroxylated surfaces in water. The results indicated that the uncharged surface hydroxyl groups of  $\text{FeOOH}$  in water could induce aqueous ozone decomposition to generate  $\cdot\text{OH}$  during the catalytic ozonation of nitrobenzene [9]. The research work also found that the presence of ceramic honeycomb significantly increased the degradation rate of nitrobenzene compared to the case of ozonation alone. The removal of nitrobenzene decreased sharply with addition of *tert*-butanol, suggesting that the degradation of nitrobenzene followed a radical-type mechanism [10]. The reaction mechanism of  $\cdot\text{OH}$  oxidation also could be confirmed by the investigation of oxidation products and pathway of ceramic honeycomb catalytic ozonation for the degradation of nitrobenzene in aqueous solution [11]. The previous study found that ceramic honeycomb exhibited many excellent characteristics such as high mechanical strength, chemical stability and higher catalytic activity [12].

In particular, further study is needed to explore the process of heterogeneous catalytic ozonation. Thus, the primary objective of this study was to determine the kinetic constants of degradation of nitrobenzene by the processes of  $\text{O}_3$  alone,  $\text{O}_3$ /ceramic honeycomb (CH) and  $\text{O}_3$ /modified ceramic honeycomb (MCH) in aqueous solution, and to investigate the influencing factors on the rate con-

stants, including applied ozone concentration, initial concentration of nitrobenzene and amount of catalysts.

## 2. Experimental

### 2.1. Materials and reagents

Ceramic honeycomb (Shanghai Pengyinaihuo Material Factory, China) with the constituent of cordierite was applied in the experiment. Monolithic CH was cylindrical with a diameter of 50 mm and a length of 50 mm; the cell density of CH was 400 square cells per square inch with a wall thickness of 0.4 mm. CH was rinsed with detergent to remove impurities and then dried at 373 K before ozonation experiment.

The model water was prepared by spiking  $50 \mu\text{g L}^{-1}$  nitrobenzene (Beijing Chemical Factory, China, purified by distillation pre-treatment, 99.80%) in distilled water (Harbin Wenjin Distilled Water Factory, China). Manganese nitrate (50% (w/w) solution, Beijing Chemical Factory, China, analytical grade reagent), potassium nitrate (Harbin Chemical Factory, China, analytical grade reagent) and copper nitrate (Tianjin Nankai Chemical Factory, China, analytical grade reagent) were used to modify the CH catalyst. The other chemicals such as sodium thiosulphate solution used in this experiment were all analytical grade reagents, and used without further purification. All the glassware except for the volumetric flasks were muffled overnight at 673 K. The volumetric flasks were washed by soaking them in chromic acid and then rinsing with distilled water.

### 2.2. Catalyst preparation

CH was washed by distilled water, and then dried at 373 K overnight in a drying vacuum oven prior to the impregnation. Modified ceramic honeycomb was prepared by wet impregnation of CH with appropriate concentration of metal ions (6%) in an aqueous solution of nitrate salt for metallic catalyst, which were  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{KNO}_3$ . All the catalysts were dried at room temperature for 12 h in air, then 393 K for 12 h, and calcined at 723 K for 4 h.

### 2.3. Ozonation procedure

The experiments were carried out in a cylindrical reactor (inside diameter of 50 mm and the volume of 3 L) made of stainless steel (Shown in Fig. 1), which was shielded to control reaction

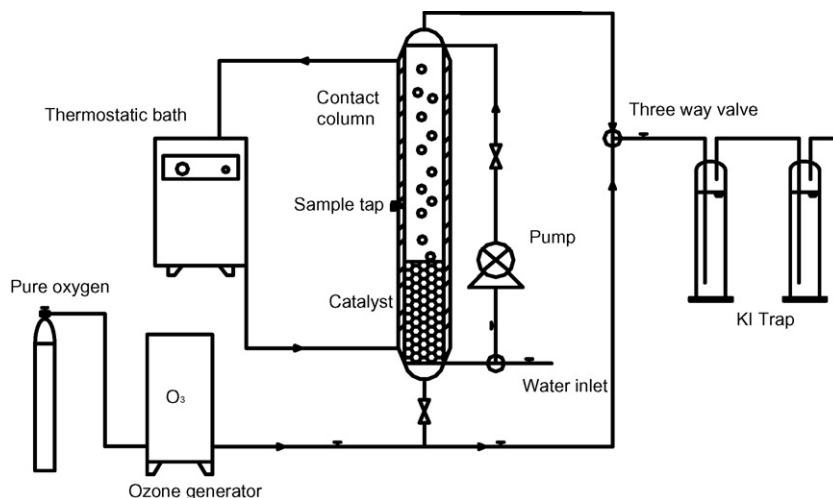


Fig. 1. Diagram of experimental ozonation system.

temperature constantly at 293 K by a low thermostatic bath (Ningbo Haishutianheng Apparatus Factory, China, model DC-3005A) flowing through the surrounding water jacket. Ozone was produced from pure oxygen (Harbin Gas Co. Ltd., 99.999%, China) through XFZ-5 ozone generator (Qinghua Tongli, China) at a power setting of 40 W, and was subsequently fed into ozonation reactor to contact thoroughly with water samples through a porous titanium sand plate at the bottom of the reactor. Before the experimental operation, the reactor was pre-ozonated for 4 min to satisfy any ozone demand, and then was washed several times with distilled water to exclude possible side effects. In the ozonation experiments, the model water (3 L) with nitrobenzene concentration of  $50 \mu\text{g L}^{-1}$  was pumped into the reactor by MP-20R magnetic pump (Shanghai Xishan Pump Co. Ltd., China) and then circulated at a rate of approximately  $4 \text{ L min}^{-1}$ . The catalysts were fed into the reactor by taking off its base. The ozonation time was controlled at 2 min for all the samples. Water samples (each being 50 mL) were taken from the reactor at various reaction times to analyze the residual concentration of nitrobenzene. The oxidative reaction was stopped with addition of a small amount of sodium thiosulphate solution.

#### 2.4. Analytical method

The concentration of ozone in the gas was measured by iodometric titration method (Ozone Standards Committee Method). The dissolved ozone in water was detected by spectrophotometer using the indigo method [13].

Typically a 50-mL sample containing nitrobenzene was extracted using a total volume of 1 mL benzene (Tianjin Kemiou Research and Development Centre of Chemicals, China, HPLC grade). Nitrobenzene was analyzed by injecting  $1 \mu\text{L}$  of the extracted headspace sample into GC-14C gas chromatography spectrometer (Shimadzu, Japan), using the high purity nitrogen (99.999%) as the mobile phase at a rate of  $34 \text{ mL min}^{-1}$ . The conditions of GC-14C gas chromatography spectrometer were as follows: column temperature: 433 K; injector and detector temperature: 483 K. The pH of aqueous solution was measured by Delta 320 pH acidometer (Shanghai Mettler-Toledo Apparatus Co. Ltd., China).

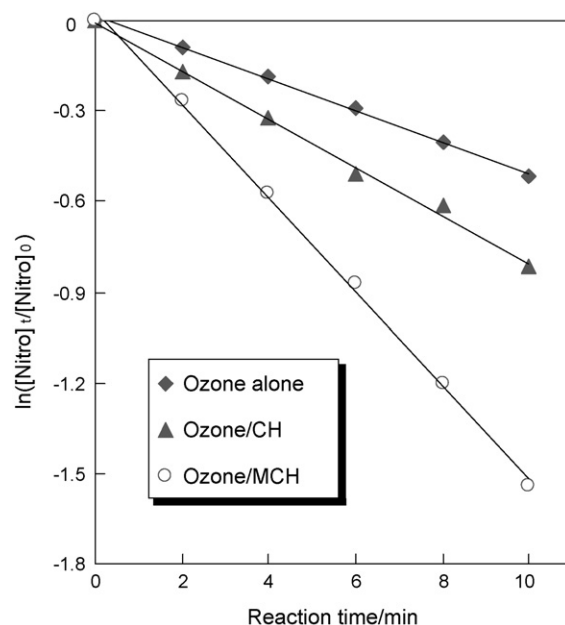
The phase composition of raw CH or MCH was studied by the method of X-ray diffraction analysis (XRD, DRON-3M) using a Siemens D-500 Kristalloflex X-ray powder diffractometer and  $\text{Cu K}\alpha$  radiation. The specific surface area of catalyst sample was measured according to the Brunauer–Emmet–Teller (BET) method with the krypton adsorption at liquid nitrogen temperature with a Micromeritics ASAP 2010 system. To measure the BET specific surface area of the catalyst monoliths, a particular home-made test tube was needed to host the sample.

### 3. Results and discussion

#### 3.1. The kinetics of nitrobenzene degradation in the different processes

The experiments were performed at initial nitrobenzene concentration of  $50 \mu\text{g L}^{-1}$ , applied ozone concentration of  $0.987 \text{ mg L}^{-1}$  and initial pH 6.87. It was found that  $\text{O}_3/\text{MCH}$  could greatly increase the degradation rate of nitrobenzene compared with those achieved by  $\text{O}_3$  alone and  $\text{O}_3/\text{CH}$ , and adsorption of nitrobenzene on the catalysts was too limited to have any influence on the degradation rate of nitrobenzene. The plots of  $\ln([\text{Nitro}]_t/[\text{Nitro}]_0)$  versus reaction time for representative kinetic runs were shown in Figs. 2 and 3.

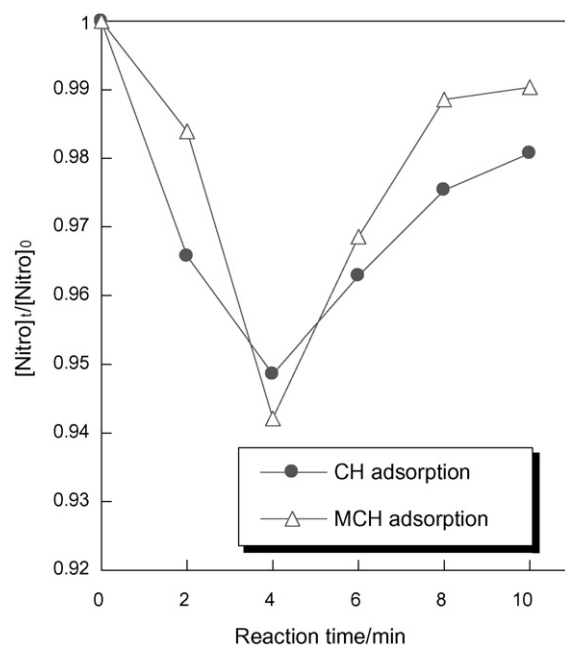
The processes included  $\text{O}_3$  alone,  $\text{O}_3/\text{CH}$ ,  $\text{O}_3/\text{MCH}$ , CH adsorption and MCH adsorption. The linearity in the plots demonstrated



**Fig. 2.** Pseudo-first-order plot of nitrobenzene degradation in the different processes, including  $\text{O}_3$  alone,  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$ . Reaction conditions: temperature 293 K; initial pH 6.87; initial concentration of nitrobenzene:  $50 \mu\text{g L}^{-1}$ ; amount of CH and MCH catalysts used in series: 5 doses; water background: distilled water; applied ozone concentration:  $0.987 \text{ mg L}^{-1}$ ;  $[\text{Nitro}]_t$ : the instantaneous concentration of nitrobenzene;  $[\text{Nitro}]_0$ : the initial concentration of nitrobenzene.

that the degradation rates were pseudo-first-order with respect to nitrobenzene in the processes of  $\text{O}_3$  alone,  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$ . Based on the experimental slopes, the pseudo-first-order kinetic constants were calculated and shown in Table 1.

It was found that adsorption of nitrobenzene on CH and MCH did not follow the pseudo-first-order kinetic model. The phenomenon



**Fig. 3.** Pseudo-first-order plot of nitrobenzene degradation in the adsorption processes. Reaction conditions: temperature 293 K; initial pH 6.87; initial concentration of nitrobenzene:  $50 \mu\text{g L}^{-1}$ ; amount of CH and MCH catalysts used in series: 5 doses; water background: distilled water;  $[\text{Nitro}]_t$ : the instantaneous concentration of nitrobenzene;  $[\text{Nitro}]_0$ : the initial concentration of nitrobenzene.

**Table 1**  
Pseudo-first-order rate constants of nitrobenzene degradation normalized in the different processes

Experiment	$k (\times 10^2 \text{ min}^{-1})$	$R^2$
Ozone alone	5.21	0.9979
Ozone/CH	7.99	0.9967
Ozone/MCH	15.45	0.9983
CH adsorption <sup>a</sup>	0.01	0.0004
MCH adsorption <sup>a</sup>	0.07	0.0237

$R^2$  is the square of correlation coefficient.

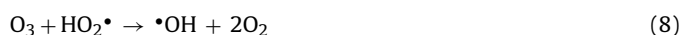
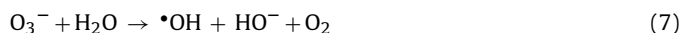
<sup>a</sup> The degradation efficiency of adsorption, namely behavior in the presence of catalyst but without ozone.

was due to a maximum adsorption of nitrobenzene at 4 min in both systems, and then nitrobenzene began to desorb from that moment, as presented in Fig. 3. This result represented the dynamic equilibrium between adsorption and desorption at that point.

The reaction of  $O_3$  alone with nitrobenzene followed a pseudo-first-order degradation rate law under the same experimental condition. This result was consistent with that of the literature [1]. The reasons were as follows.

At first, the chemistry of aqueous ozone was complex. It involved the decomposition of ozone via a chain reaction mechanism, resulting in the production of hydroxyl radical ( $\bullet OH$ ) species. The series of reactions showed that reaction of the hydroxyl ions with ozone produced one superoxide anion radical ( $O_2^{\bullet -}$ ) and one hyperoxyl radical ( $HO_2^{\bullet}$ ). These reactions comprised the initiation step of chain reaction mechanism. Addition of organic solutes could result in either the direct consumption of ozone before the chain reaction began and the production of ozonide anion radical ( $O_3^{\bullet -}$ ) by electron transfer [14]. Upon protonation within the aqueous system, the ozonide anion decomposed into  $\bullet OH$ . These radicals were now free to react with the organic solutes at rapid rates, the rate constants being in the order of  $10^8$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [13,15–20].  $\bullet OH$  reacted with the functional groups of the organic solutes producing organic radicals, which added  $O_2$  and then eliminated  $HO_2^{\bullet}/O_2^{\bullet -}$ . The formation of the  $O_2^{\bullet -}$  radical had a very high rate constant compared to the reactions with other solutes present in ozonated waters. It was thought that the production of highly selective  $O_2^{\bullet -}$  anion promoted the chain reaction to produce  $\bullet OH$ . The production of these radicals was beneficial for the destruction of organic solutes by radical reactions [17].

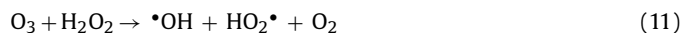
Moreover, in the bulk aqueous phase, ozone could be decomposed by hydroxide ion,  $OH^-$ , or the conjugate base of  $H_2O_2$  ( $HO_2^-$ ) to yield  $HO_2^{\bullet}$  and  $\bullet OH$  as shown below [21]:



$\bullet OH$  and  $HO_2^{\bullet}$  as reactive intermediates were formed from the above series of elementary reactions constituted a free radical chain reaction, leading to the decomposition of ozone. The chain termination steps were as follows:



The reaction of ozone with hydrogen peroxide would also contribute to the formation of  $\bullet OH$  and  $HO_2^{\bullet}$  as follows:



Furthermore, heterogeneous catalytic ozonation had potential as an alternative AOP because the presence of heterogeneous surface appeared to transfer ozone into solution more efficiently and also help to initiate the production of radical species from ozone [17].

Therefore, the rate of compounds disappearance in the ozonation system, whether directly or indirectly, was usually assumed to be the combination of the two bimolecular reactions, namely, one in which the compound concerned reacted with ozone in a direct manner and an indirect reaction via  $\bullet OH$  produced by its decomposition. The kinetics of the two reactions was assumed to be second-order (first-order in the concentrations of ozone,  $\bullet OH$  and the compounds that react with the former) [21]. The degradation rate of nitrobenzene in the processes of ozonation alone and catalytic ozonation could be expressed as follows:

$$-\frac{d[\text{Nitro}]}{dt} = k_{O_3} [\text{Nitro}] [O_3] + k_{HO^{\bullet}} [\text{Nitro}] [HO^{\bullet}] \quad (12)$$

where,  $k_{O_3}$  and  $k_{HO^{\bullet}}$  were, respectively, the first-order degradation rate constants for ozonation and  $\bullet OH$  reaction. In this study, the concentrations of  $O_3$  and  $\bullet OH$  only varied over fairly narrow range. Therefore, Eq. (12) could be rewritten as

$$-\frac{d[\text{Nitro}]}{dt} = k_{app} [\text{Nitro}] \quad (13)$$

where  $k_{app}$  was the apparent degradation rate constant of the whole system. Thus the reaction was a pseudo-first-order degradation reaction based on Eq. (13), where:

$$k_{app} = k_{O_3} [O_3] + k_{HO^{\bullet}} [HO^{\bullet}] \quad (14)$$

As a consequence, ozonation alone and catalytic ozonation all followed apparent pseudo-first-order kinetics model. As shown in Fig. 2 and Table 1, the degradation rate of nitrobenzene by  $O_3/CH$  was observed to be slower than that of  $O_3/MCH$ , and that of  $O_3$  alone was the slowest in the three processes. The presence of CH or MCH in aqueous solution was found to enhance the degradation rate of nitrobenzene at relative low initial concentration of nitrobenzene ( $50 \mu\text{g L}^{-1}$ ). These observations were consistent with the previous developed theory that heterogeneous catalyst could act as a promoter of radical-type chain reactions [22]. If it could be assumed that the enhancement of the degradation in both catalytic ozonation systems was attributed to the increase of  $\bullet OH$  initiation, it was obvious that MCH had a higher catalytic activity than CH.

Mn, Cu and K, as the modifiers, was found to increase greatly the specific surface area under the experimental conditions to values as high as  $4.37 \text{ m}^2/\text{g}$ , namely more than 12 times higher than  $0.35 \text{ m}^2/\text{g}$  of the raw CH monolith. Furthermore, the result of XRD analysis identified that the bulk crystalline phase of CH catalyst was  $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ , which was the standard structure of  $\alpha$ -cordierite. Comparing to the result obtained with the raw CH catalyst, the modification process led to the appearance of additional peaks of  $\text{MnO}_2$  and  $\text{CuO}$ . The experimental phenomenon in Fig. 2 might suggest that CH catalyst had the activity to initiate  $\bullet OH$ . The surface characteristics of the catalysts showed that the modification of CH with Mn, Cu and K resulted in the appearance of novel crystalline phase and the increase of specific surface area, which could enhance the synergetic effect on CH catalyst to accelerate the formation of  $\bullet OH$ , which was a less selective, one of the most reactive free radicals and one of the strongest oxidants.

Ozone in aqueous solution could react either directly with target substrates or indirectly via reactions with its free radical

**Table 2**

The known overall second-order reaction rate constants for reaction of nitrobenzene with O<sub>3</sub> and •OH

Reference	$k_{O_3}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{OH}$ (M <sup>-1</sup> s <sup>-1</sup> )
[5,15,16]	0.09 ± 0.02	NA
[23]	NA	3.9 × 10 <sup>9</sup>
[24]	NA	2.2 × 10 <sup>8</sup>
[15]	3.9 × 10 <sup>-2</sup> ± 1.1 × 10 <sup>-3</sup>	NA

NA: not applicable.

decomposition products [22]. The known overall second-order reaction rate constants for ozone with nitrobenzene were listed in Table 2.

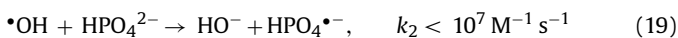
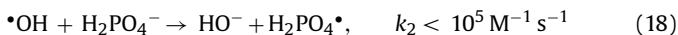
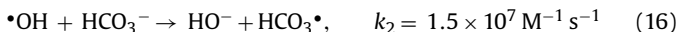
According to the data shown in Table 2, the degradation rate of nitrobenzene in O<sub>3</sub> alone system should be very slight compared to that of •OH oxidation due to the obvious different level between  $k_{O_3}$  and  $k_{HO\cdot}$ . However, the results in Table 1 indicated that there was no remarkable difference order between  $k_{O_3}$  and  $k_{OH\cdot}$  detected in the present experiment. The reasons were as follows.

On the one hand, for the O<sub>3</sub> alone system, only slightly partial degradation of nitrobenzene occurred via the direct molecular ozone mechanism. While ozone reacted with nitrobenzene mostly through a radical-type reaction involving •OH induced by the ozone self-decomposition in aqueous solution under the present experimental conditions [11]. The chemical properties of ozone depended on its molecule structure. Due to the two extreme forms of resonance structures, molecular ozone could react as a dipole, an electrophilic or nucleophilic agent [1]. Therefore, ozone was very unstable in water because of the high reactivity. The half-life of molecular ozone varied from a few seconds up to few minutes and depended on pH, water temperature and concentrations of organic and inorganic compounds in water [1,25]. The pH of aqueous solution significantly influenced ozone decomposition in water. Basic pH caused an increase of ozone decomposition. At pH < 3 •OH did not influence the decomposition of ozone. For 7 < pH < 10, the typical half-life of ozone was from 15 up to 25 min [1,25].

The experiments were performed at initial pH 6.87, which was the natural value of distilled water used. As mentioned above, ozone had a relatively rapid rate of self-decompose under this experimental conditions, namely could produce substantially •OH, which could react unselectively with organic compounds. Therefore, where:

$$k_{app} \approx k_{HO\cdot} [HO\cdot] \quad (15)$$

All kinetic runs were studied in the experiments without adding any buffer solution because they could scavenge •OH. The reactions and the rate constants were shown as follows [4,25]:



where  $k_2$ , was the second-order degradation rate constant of reaction.

Consequently, the presence of these •OH scavengers resulted in the significant decrease of the degradation rate of nitrobenzene. As far as the ozonation alone system was concerned, this action was beneficial to investigate  $k_{O_3}$  by reducing the contribution of •OH derived from the scavengers. However, this phenomenon could also yield the negative effect on CH or MCH catalytic ozonation, leading to the reduction of degradation rate by consuming •OH competitively. Therefore, concerning the comparative characteristic, the

method of buffer solution was not introduced in the processes of ozonation alone and catalytic ozonation.

On the other hand, for the processes of CH and MCH catalytic ozonation, there were some scavengers and factors to influence significantly the degradation of nitrobenzene. For instance, the typical representatives of the negative effect were listed in Eqs. (5) and (10). The  $k_2$  of Eq. (5) was  $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , indicating that ozone could compete strongly with target substance in reaction with •OH. In the same way, •OH played an important role as self-scavenger in Eq. (10). Furthermore, there were several compounds with inhibition of the radical chain reaction process existing in distilled water system. The inhibitors (CH<sub>3</sub>-COO<sup>-</sup>, alkyl-(R), HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, humic substances) were the compounds that consumed •OH without regenerating superoxide anion. Because the reaction of •OH was not selective, •OH could react rapidly with the primary radical inhibitors, such as carbonates and bicarbonates, as shown in Eqs. (16) and (17), apparent rate constants of which were only slightly lower than that of •OH with nitrobenzene. It was the reason why the presence of radical scavengers in water could cause the total inhibition of free radical chain reaction. The reactions of •OH with radical scavengers were the main disadvantage of all oxidative degradation processes based on •OH oxidation [1]. As the literature mentioned, one must consider the potential presence of free-radical inhibitors in the medium [23]. Specifically, the concentration of inorganic carbon was found to rise, probably as a result of the transformation of carbonic acid into carbonate and bicarbonate. This might have somehow inhibited the formation of •OH and decreased the reaction rate. The reasons mentioned above led to the decrease order of  $k_{HO\cdot}$  obtained in the present experiment compared to that shown in Table 2.

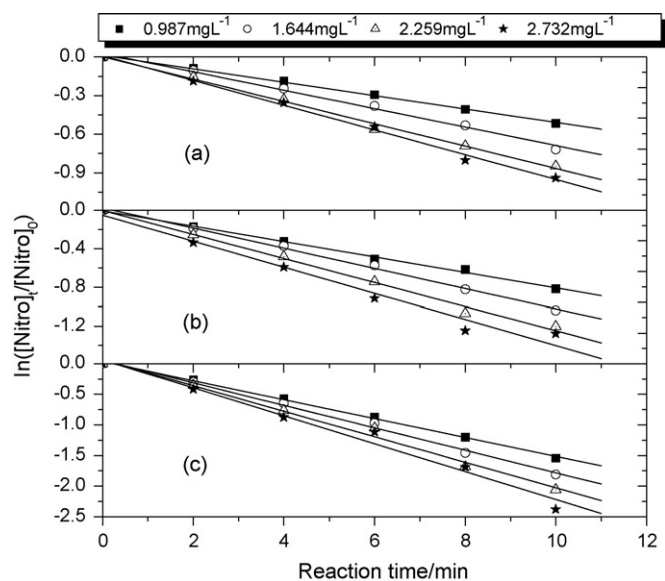
### 3.2. The effect of applied ozone concentration on the kinetics

The effect of applied ozone concentration was studied ([O<sub>3</sub>] = 0.987–2.732 mg L<sup>-1</sup>) on pseudo-first-order plot for the degradation of nitrobenzene in different processes. The results were listed in Fig. 4.

As described in Fig. 4, all the reactions followed pseudo-first-order kinetic model at different applied ozone concentrations. The results demonstrated that simple addition of ozone to the processes of O<sub>3</sub> alone, O<sub>3</sub>/CH and O<sub>3</sub>/MCH accelerated the degradation rate of nitrobenzene by a rate constant of (5.21–9.61) × 10<sup>-2</sup> min<sup>-1</sup>, (7.9–13.48) × 10<sup>-2</sup> min<sup>-1</sup> and (15.45–22.78) × 10<sup>-2</sup> min<sup>-1</sup>, respectively, depending on [Nitro]<sub>0</sub> = 50 μg L<sup>-1</sup>. It also could be seen that the degradation rates of nitrobenzene in different processes presented respectively an enhanced trend with increasing applied ozone concentrations. This phenomenon was consistent with the literature, which reported that an increase of ozone dose resulted in a linear increment of the instantaneous ozone demand in the river water and a higher concentration of •OH was observed in water containing a greater number of constituents that demanded ozone [26].

As mentioned above, nitrobenzene should be degraded very slowly by O<sub>3</sub> alone. However, under the experimental conditions, the reaction of nitrobenzene with O<sub>3</sub> alone appeared to be enhanced due to the effects of higher reaction temperature 293 K, initial pH 6.87 and due to indirect reactions with •OH, which was the product of ozone self-decomposition [11]. The kinetic data indicated that the combined O<sub>3</sub>/MCH system was much more effective in degrading nitrobenzene than either O<sub>3</sub> alone or O<sub>3</sub>/CH system. This apparent synergic effect might be attributed to the initiated ability of •OH derived from the heterogeneous surface of catalyst.

Moreover, as for the linear increase of rate constant with applied ozone concentration, the explanation might be that, under the



**Fig. 4.** Pseudo-first-order plot for the degradation of nitrobenzene by the three processes at different applied ozone concentrations. Reaction conditions: temperature 293 K; initial pH 6.87; initial concentration of nitrobenzene:  $50 \mu\text{g L}^{-1}$ ; amount of CH and MCH catalysts used in series: 5 doses; water background: distilled water; applied ozone concentration: 0.987, 1.644, 2.259 and  $2.732 \text{ mg L}^{-1}$ ;  $[\text{Nitro}]_t$ : the instantaneous concentration of nitrobenzene;  $[\text{Nitro}]_0$ : the initial concentration of nitrobenzene; (a) ozone alone; (b) ozone/CH; (c) ozone/MCH.

experimental conditions, the increase of applied ozone concentrations could increase the turbulence in the gas–liquid interface, which then enhanced the ozone mass transfer rate from gas phase to liquid [27]. In addition, it was very likely that when the ratio of ozone/nitrobenzene increased, applied ozone concentration has a higher chance to be present in excess, resulting in the term  $k_{\text{app}}$  in Eqs. (14) and (15) actually being increased.

### 3.3. The effect of initial concentration of nitrobenzene on the kinetics

To explore the effect of initial concentration of nitrobenzene on pseudo-first-order plot for the degradation of nitrobenzene, the kinetic experiments ran at various initial concentrations of nitrobenzene ( $[\text{Nitro}]_0 = 50\text{--}250 \mu\text{g L}^{-1}$ ) in different processes, including  $\text{O}_3$  alone,  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$ . The results of this series were listed in Fig. 5.

It could be observed from Fig. 5(a) that the degradation of nitrobenzene by  $\text{O}_3$  alone followed pseudo-first-order kinetic model at different initial concentrations of nitrobenzene between 50 and  $250 \mu\text{g L}^{-1}$ , with fixed applied ozone concentration ( $[\text{O}_3] = 0.987 \text{ mg L}^{-1}$ ). Fig. 5(b) and (c) also showed the same result, namely the degradation of nitrobenzene by CH or MCH catalytic ozonation, under the same experimental conditions, was complied with pseudo-first-order kinetic model, respectively.

The results also represented that pseudo-first-order rate constant increased with the increase of initial concentration of nitrobenzene at the concentration scope applied in this study. It was due to the contribution of reactant concentration level. In the experiments, the concentration level of applied ozone was in milligram range, but that of nitrobenzene was in microgram range. The ratio of initial concentration  $[\text{O}_3]/[\text{Nitro}]_0$ , was in the scope of 10.12–50.58. As a consequence, ozone was sufficiently enough to react with nitrobenzene in the three processes used by the present study. With the increase of initial concentration of nitrobenzene, it might enhance the probability of impact between  $\text{O}_3$  molecular or

$\bullet\text{OH}$  and nitrobenzene, resulting in the improvement of oxidation rate. Both in ozonation alone and catalytic ozonation systems, it could be observed that initial concentration of nitrobenzene was a significant and sensitive factor, namely it was important to direct and indirect reactions of nitrobenzene with ozone.

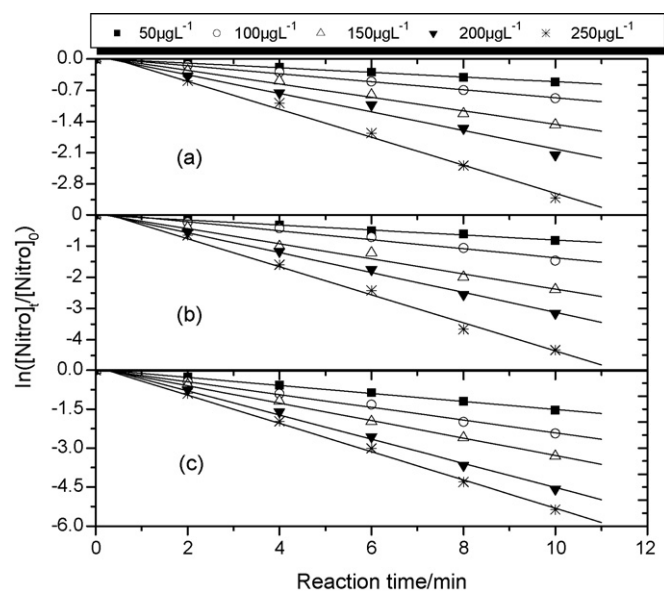
Furthermore, the intermediates of ozonation might also catalyze the formation of  $\bullet\text{OH}$ , which might improve the overall oxidative reaction, and this effect was enhanced as the available concentration of nitrobenzene was increased.

On the other hand, the results might be explained from the reaction kinetics. Theoretically, ozonation of target substance was first-order with respect to ozone and target substance, respectively [2]. Obviously, the rate of ozonation should increase with the concentrations of both ozone and target substance. When applied ozone concentration was constant, as described above, ozonation became pseudo-first-order with respect to target substance, and the reaction rate increased linearly with the concentration of target substance [27].

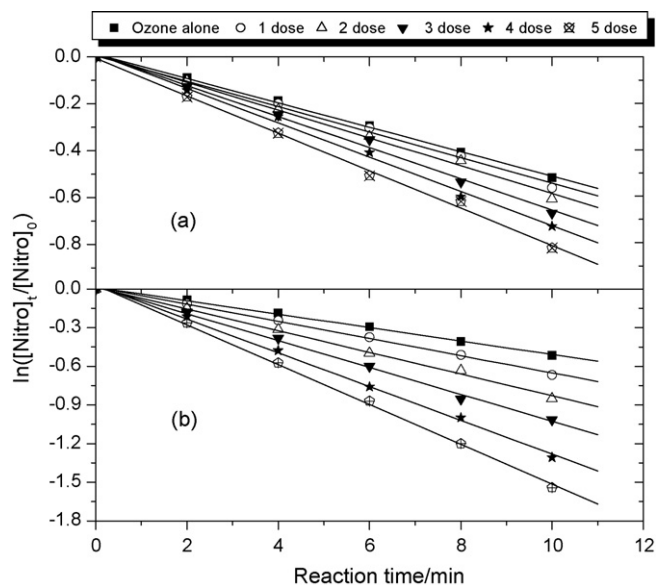
### 3.4. The effect of amount of catalysts on the kinetics

The experiments were performed at different amount of catalysts (0–5 doses) in order to investigate the effect on the degradation rate constants, running at initial nitrobenzene concentration of  $50 \mu\text{g L}^{-1}$ , applied ozone concentration of  $0.987 \text{ mg L}^{-1}$  and initial pH 6.87. Fig. 6 showed the alteration of the plots for the degradation of nitrobenzene in the processes of  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$ .

In the  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$  systems, the degradation of nitrobenzene also followed pseudo-first-order kinetics at different amount of catalysts (0–5 doses), as summarized by the linearity of the curves in Fig. 6. The effect of amount of catalysts on the primary degradation rate was significant, as expected, confirming the positive influence of amount of catalysts on the process kinetics [23]. The phenomenon might be attributed to the heterogeneous surfaces of catalysts, which could transfer ozone into solution



**Fig. 5.** Pseudo-first-order plot for the degradation of nitrobenzene by the three processes at different initial concentrations of nitrobenzene. Reaction conditions: temperature 293 K; initial pH 6.87; initial concentration of nitrobenzene: 50, 100, 150, 200 and  $250 \mu\text{g L}^{-1}$ ; amount of CH and MCH catalysts used in series: 5 doses; water background: distilled water; applied ozone concentration:  $0.987 \text{ mg L}^{-1}$ ;  $[\text{Nitro}]_t$ : the instantaneous concentration of nitrobenzene;  $[\text{Nitro}]_0$ : the initial concentration of nitrobenzene; (a) ozone alone; (b) ozone/CH; (c) ozone/MCH.



**Fig. 6.** Pseudo-first-order plot for the degradation of nitrobenzene by the two processes at different amount of catalysts. Reaction conditions: temperature 293 K; initial pH 6.87; initial concentration of nitrobenzene:  $50 \mu\text{g L}^{-1}$ ; amount of CH and MCH catalysts used in series: 0, 1, 2, 3, 4 and 5 doses; water background: distilled water; applied ozone concentration:  $0.987 \text{ mg L}^{-1}$ ;  $[\text{Nitro}]_t$ : the instantaneous concentration of nitrobenzene;  $[\text{Nitro}]_0$ : the initial concentration of nitrobenzene; (a) ozone/CH; (b) ozone/MCH.

more efficiently and decompose ozone into  $\bullet\text{OH}$ . The result of this study suggested that the catalysts initiated the radical-type reaction, thereby causing an increase rate of nitrobenzene degradation. Similarly, it also indicated that different amount of catalysts had different catalytic ability to generate  $\bullet\text{OH}$ . Furthermore, it demonstrated that the modification process was benefit to increase the catalytic activity of raw CH catalyst, namely the impregnation of metals (Mn, Cu and K) enhanced its catalytic activity in initiating  $\bullet\text{OH}$ . The study of reaction mechanism was needed in the future research work.

#### 4. Conclusions

The use of MCH catalyst, composed of Mn, Cu and K deposited on CH, during the ozonation of aqueous solution containing nitrobenzene enabled an interesting improvement of the degradation rate compared with  $\text{O}_3$  alone and  $\text{O}_3/\text{CH}$ . All kinetics runs followed the pseudo-first-order kinetics law in the three processes selected by the present experiment. The experimental results demonstrated that the rate constants in the processes of  $\text{O}_3$  alone,  $\text{O}_3/\text{CH}$  and  $\text{O}_3/\text{MCH}$  were  $5.21$ ,  $7.99$  and  $15.45 \times 10^{-2} \text{ min}^{-1}$ , at the reaction temperature 293 K and initial pH 6.87. The pseudo-first-order rate constants for the degradation of nitrobenzene in the three processes were enhanced respectively as applied ozone concentration increased from  $0.987$  to  $2.732 \text{ mg L}^{-1}$ , initial concentration of nitrobenzene increased from  $50$  to  $250 \mu\text{g L}^{-1}$  and amount of catalysts increased from 0 to 5 doses. The experimental phenomenon indicated that the modification process could increase the catalytic activity of CH by the enhancement of  $\bullet\text{OH}$  initiation.

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