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Catalytic Degradation of Nitrobenzene and Aniline in Presence of Ozone by Magnesia from Natural Mineral

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Abstract In this work, magnesia from natural brucite mineral has been used firstly for catalytic degradation of nitrobenzene and aniline in presence of ozone. Compared with single ozonation, the catalytic ozonation accelerated markedly the degradation of nitrobenzene and aniline. The influences of hydroxyl radical scavengers, pH values, and reaction temperatures on degradation were investigated. It was found that the essential of catalysis was the homogeneous catalysis of hydroxyl ions in water, which accelerated the generation of hydroxyl radicals. As a catalyst, magnesia from natural brucite has supplied an economical and feasible choice for catalytic ozonation of nitrobenzene and aniline in industrial wastewater.

Keywords Catalytic ozonation · Magnesia · Natural mineral · Nitrobenzene · Aniline

1 Introduction

Aromatic compounds are common pollutants in the effluents of several industries. Among these aromatic pollutants, nitrobenzene and aniline are toxic and suspected carcinogenic. Nitrobenzene is an important material for the production of aniline, aniline dyes, explosives, pesticides and drugs. It has also been used as a solvent in products such as paints, shoes and floor metal polishes [1, 2]. Aniline and its derivatives are commonly produced as by-products of the petroleum, paper, coal and chemical industries [3]. As a consequence, nitrobenzene and aniline appear as main contaminant in water sources especially in surface water and industrial wastewaters. Recently, considerable attention has been focused on the treatment of nitrobenzene and aniline in wastewater. Different methods have been proposed such as photo-catalytic process [4–7], wet air oxidation [1, 8, 9], catalytic electrochemical treatments [10–12] and ozonation [13–19].

As a promising advanced oxidation technology, catalytic ozonation has attracted great attention for degradation of nitrobenzene and/or aniline due to its high efficiency. Many catalysts, such as Fe^{2+}, TiO_2 MnO_x/GAC and ceramic honeycombs were developed [15–19]. However, the costs of most catalysts are still high, which is a drawback for practical application of catalytic ozonation. Therefore, seeking an economically feasible catalyst is a challenge with great significance and necessary for industrial wastewater treatment.

For their great cost advantages, many natural mineral have been used in water treatment field [20–24]. To the best of our knowledge, there is few report on natural mineral used as ozonation catalyst [25, 26]. Natural brucite is a kind of inexpensive and environment friendly alkali mineral. Recently, we have used natural brucite as ozonation catalyst for the degradation of organic dye [27]. Herein, the calcined product of natural brucite, magnesia has been successfully used for the catalytic ozonation of nitrobenzene and aniline. On this basis, an economically feasible catalytic ozonation technology was suggested. The catalytic mechanism was also investigated.

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2 Experimental

2.1 Preparation and Characterization of Catalyst

Natural brucite was exploited from Fengcheng of Liaoning Province in China, and its thermo-gravimetric (TG) curve was obtained through a Pyris1 thermo-gravimetric analyzer (PerKinElmer). The brucite sample was crushed and sieved into 100 mesh size and calcined at 723 K for 6 h in air. The composition of the calcined product, magnesia, was determined by X-ray diffraction (XRD) and X-ray fluorescence (XRF). XRD pattern was recorded on an X'TRA X-ray diffractometer (ARL, Switzerland) with Cu Kα radiation $\lambda = 1.5418$ Å and XRF result was obtained on a 9800 X-ray fluorescence (XRF) spectrometer (ARL, Switzerland).

2.2 Chemical Reagents

All the reagents used, such as nitrobenzene, aniline, t-butanol, sodium hydroxide, pure MgO and phosphate were all analytical grades without further purification. The water used in this work was distilled water.

2.3 Ozonation Procedure

All the ozonation experiments were performed in a semi-continuous flow mode. In a typical catalytic ozonation procedure, 0.50 g of catalyst and 120 mL of simulative wastewater were mixed in a flask under stirring and thermostatic control. Then the ozone flow was fed into the bottom of the flask with continuous stirring. At given intervals, 3.0 mL of samples were taken from the reactor and centrifugalized for analytical determination. Ozone was produced from an ordinary grade air with an ozone generator, and the flow rate of ozone was 0.30 mg min^{-1}. The initial concentration of nitrobenzene solution and aniline solution were 100 and 200 mg L^{-1}, respectively. The contrast experiments of single ozonation (without catalyst) were carried out under same conditions.

2.4 Analysis

The concentrations of nitrobenzene and aniline were determined by high performance liquid chromatography (HPLC, LC-10AD, Shimadzu) with a reversed-phase C$_{18}$ waters column (4.6 × 250 mm, Cosmosil, Japan) at room temperature. Elution was carried out by pumping methanol and water (5:5 v/v) at a flow rate of 1.0 mL min^{-1}. An attached UV detector (SPD-10A, Shimadzu) was used at wavelength of 266 nm for nitrobenzene and at 230 nm for aniline. The pH values of the solutions were recorded by a pH S-2C analyzer (Lei Ci Instrumental Factory, Shanghai, China). The concentrations of Mg^{2+} and Ca^{2+} in water were determined with J-A1100 Inductively Coupled Plasma (ICP, Jarrell-Ash, USA).

3 Results and Discussion

3.1 Characterization of Catalyst

The main component of natural brucite used was $Mg(OH)_2$. As shown in Fig. 1, there was an evident weight loss at 600–700 K from the thermolytic dissociation of $Mg(OH)_2$. On this basis, the calcination temperature was determined at 723 K. The calcined product, magnesia, was obtained by calcining for 6 h in air. The XRF result of magnesia was listed in Table 1, which indicted that MgO was the main component with the percent (m/m) of 86.15%. There were also some impurities such as SiO_2, CaO and Fe_2O_3. The XRD pattern of magnesia was shown in Fig. 2. Three main diffraction peaks can be readily indexed to MgO (JCPDS 4–0829). Some weak diffraction peaks (a–f) from impurities were also observed.

3.2 Catalyst Activity

A preliminary set of experiments were performed to evaluate the influence of air flow and the adsorption. In this experiment, not ozone but air was fed into the flask for 2 h, while other experimental conditions were kept same with catalytic ozonation. Experimental results indicated that the ultimate concentration of nitrobenzene was 98 mg L^{-1} and that of aniline was 197.5 mg L^{-1}. These values were very close to the original concentration (100 and 200 mg L^{-1} for nitrobenzene and aniline, respectively). Therefore, it may be said that both the air flow and the adsorption could hardly affect the concentrations.

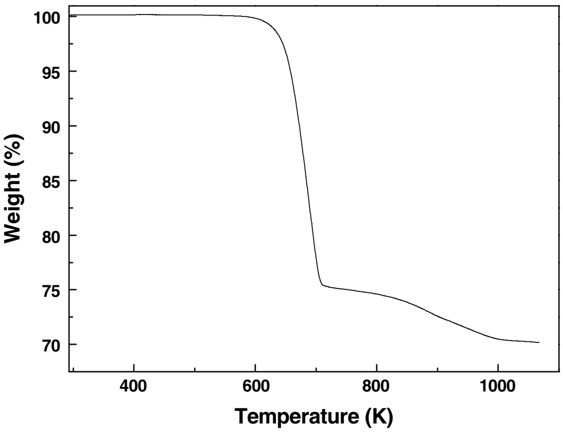

Fig. 1 Thermo-gravimetric curve of natural brucite

Table 1 XRF results of magnesia obtained from brucite

MgO	Al_2O_3	CaO	Fe_2O_3	MnO_2	P_2O_5	SiO_2	TiO_2	Burn-off	Total
86.15	0.28	1.46	0.87	0.06	0.43	2.15	0.07	8.57	100.04

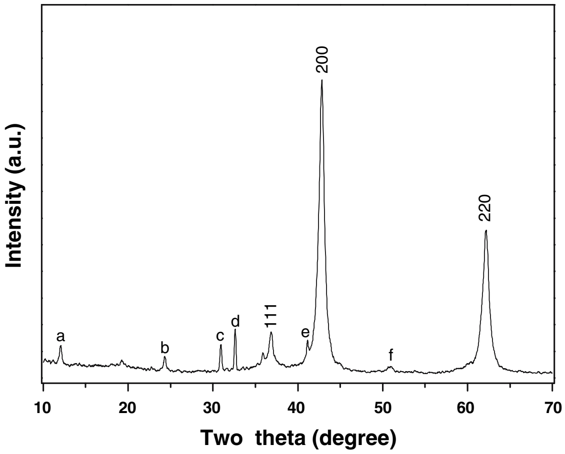

Fig. 2 XRD pattern of magnesia obtained from brucite

The degradation of nitrobenzene along with the react time under single ozonation and catalytic ozonation is displayed in Fig. 3A, in which C/C_0 means the ratio of residual contration to initial concentration. The results clearly indicated that magnesia played an important role for increasing the degradation efficiency. For example, after ozonation for 120 min, the residual concentration of single ozonation was 45.4 mg L^{-1} while that of catalytic ozonation was only 2.1 mg L^{-1}.

As shown in Fig. 3B, magnesia also revealed notable degradation efficiency for aniline. For instance, the residual concentration was 121 mg L^{-1} after single ozonation for 60 min, while that of catalytic ozonation was only 27.5 mg L^{-1}.

Based on the results, it can be said that magnesia had great catalysis on ozonation degradation of nitrobenzene and aniline. With mineral magnesia catalyst, a practical and economical oxidation technology is suggested.

3.3 Influence of Hydroxyl Radical Scavengers

According to traditional ozonation theory [28], molecular ozone can oxidize organic substance via a direct route, or a chain reaction with generation of hydroxyl radicals. In order to study the role of hydroxyl radical for degradation of nitrobenzene and aniline, contrast experiments were performed through investigate the influence of hydroxyl radical scavengers. Tert-butanol, which has the reaction rate constant of 6.0×10^{8} M^{-1} s^{-1} with hydroxyl radical [29] and 3.0×10^{-3} M^{-1} s^{-1} with ozone [30], was adopted as hydroxyl radical scavengers. In this experiment, 0.5 g of tert-butanol was added to 120 mL of reaction system.

As shown in Fig. 4A, tert-butanol had evident negative impact on both of single ozonation and catalytic ozonation of nitrobenzene. Therefore, it may be said that both single ozonation and catalytic ozonation of nitrobenzene followed the hydroxyl radical oxidation mechanism. It can be explained that, nitrobenzene is difficult to be oxidized by molecular ozone (the reaction rate constant k is 0.09 ± 0.02 M^{-1} s^{-1}) [30], while it can be easily oxidized by hydroxyl radical (the reaction rate constant k is 2.2×10^8 M^{-1} s^{-1}) [31]. In the catalytic process, the accelerated generation of hydroxyl radical resulted in the faster degradation of nitrobenzene.

The influence of tert-butanol on the degradation of aniline was also investigated. The result was shown in Fig. 4B. Different from that of nitrobenzene, tert-butanol had lesser negative impact on both single ozonation and catalytic ozonation of aniline. This result was coincident with the reported degradation mechanism of aniline, in which aniline could be oxidized by both O_3 and hydroxyl radical [16]. Because hydroxyl radicals react with aniline faster than molecular ozone, the degradation of aniline was

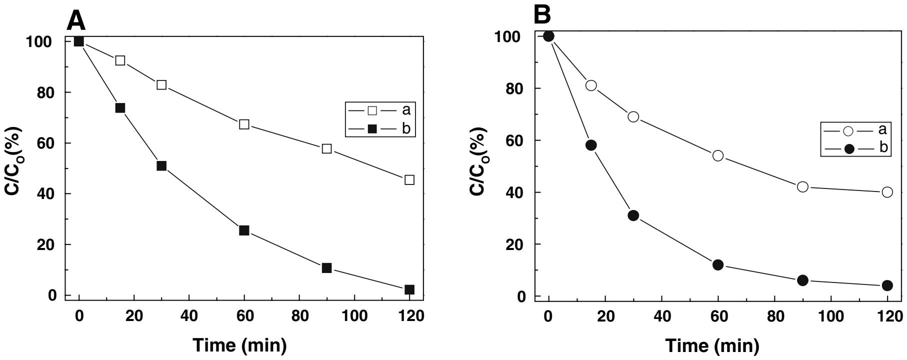

Fig. 3 (**A**) Degradation of nitrobenzene under single ozonation (a) and catalytic ozonation (b). (**B**) Degradation of aniline under single ozonation (a) and catalytic ozonation (b). Reaction temperature: 293 K

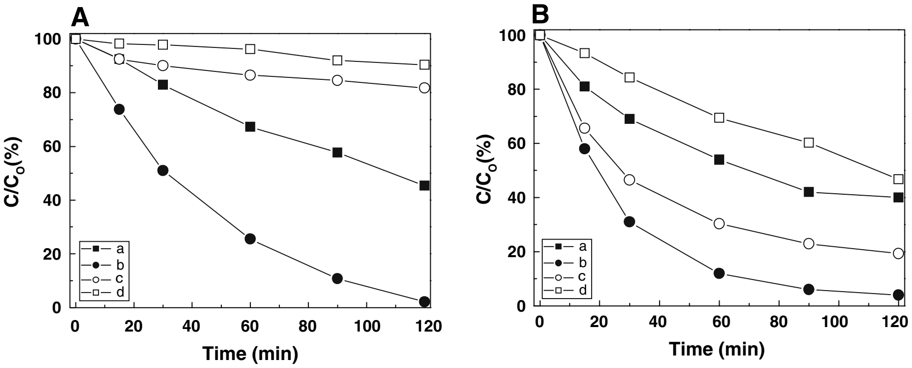

Fig. 4 (**A**) Influence of tert-butanol on ozonation of nitrobenzene. (a) single ozonation, (b) catalytic ozonation, (c) catalytic ozonation with tert-butanol added, (d) single ozonation with tert-butanol added. (**B**) Influence of tert-butanol on ozonation of aniline. (a) single ozonation, (b) catalytic ozonation, (c) catalytic ozonation with tert-butanol added, (d) single ozonation with tert-butanol added. Reaction temperature: 293 K

greatly accelerated through the enhanced generation of hydroxyl radical in catalytic ozonation.

The original concentrations of nitrobenzene (100 mg L^{-1}) and aniline (200 mg L^{-1}) were uniform in our experiments. When we compared the ozonation rates of nitrobenzene and aniline (see Fig. 3A and B), it can be observed that the ozonation rates of aniline were faster than those of nitrobenzene. This may be interpreted by their difference on degradation mechanisms, i.e. nitrobenzene could be oxidized by hydroxyl radical only, and aniline could be degraded by both O_3 and hydroxyl radical.

3.4 Influence of Reaction Temperatures

The influences of reaction temperatures on catalytic ozonation of nitrobenzene and aniline were investigated respectively at 293, 303 and 313 K. As shown in Fig. 5A and B, the degradation rates of nitrobenzene slightly increased with rise of temperature, while the degradation rates of aniline decreased at higher temperatures. It is known that ozone is very unstable in water. The increase of temperature may lead to two results: (1) lower the concentration of ozone in solution; (2) accelerate the generation of hydroxyl radical. Therefore, it may be explained that the increase in degradation of nitrobenzene was due to the increasing of hydroxyl radicals at higher temperatures. As in the case of aniline, the effect (1) was greater than (2), which results in the degradation of aniline decreased along with increase of temperature. This result is also consistent with degradation mechanism described in Sect. 3.3.

3.5 Influence of Solution pH

As an alkali oxide, magnesia can partly hydrate and resolve in water. Thus addition of magnesia enhanced the alkalinity of solution. In catalytic ozonation of nitrobenzene and aniline, the pH values of solution were above 11. It is known that hydroxyl ions can accelerate the generation of hydroxyl radical [28, 32–34]. At alkaline conditions, O_3 molecules can react with hydroxyl ions and eventually produce the stronger oxidant hydroxyl radicals:

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^{\bullet} \tag{1}$$

$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + HO^{\bullet} \tag{2}$$

or alternatively:

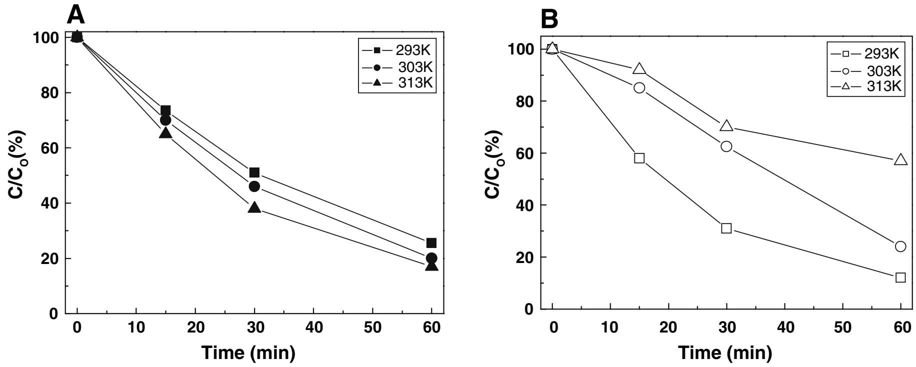

Fig. 5 (**A**) Influence of temperature on catalytic ozonation of nitrobenzene. (**B**) Influence of temperature on catalytic ozonation of aniline

Table 2 pH values of nitrobenzene solutions before and after reaction under different conditions

Sample No.	1	2	3	4	5	6	7	8	9
Reagent	None	Phosphate	Brucite	MgO	Magnesia	NaOH	NaOH	NaOH	NaOH
Before ozonation	6.80	6.86	10.59	10.40	11.14	11.50	12.32	13.14	13.82
After ozonation	4.95	6.78	9.24	10.16	11.14	10.7	12.00	13.07	13.80

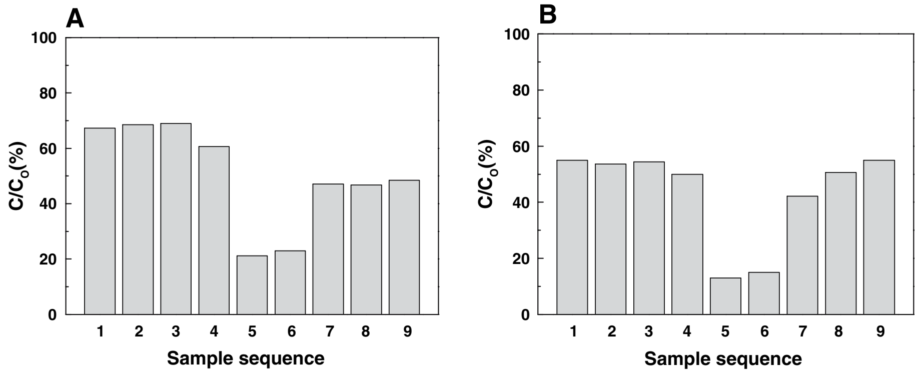

Fig. 6 (**A**) Influence of pH on ozonation of nitrobenzene. (**B**) Influence of pH on ozonation of aniline. Ozonation time: 60 min. Reaction temperature: 293 K

Table 3 pH values of aniline solution before and after reaction under different conditions

Sample No.	1	2	3	4	5	6	7	8	9
Reagent	None	Phosphate	Brucite	MgO	Magnesia	NaOH	NaOH	NaOH	NaOH
Before ozonation	6.93	6.80	10.45	10.37	11.35	11.50	12.60	13.48	14.17
After ozonation	5.88	6.58	9.12	10.20	11.13	10.9	11.36	13.35	14.11

$$2\mathrm{HO}_2^{\bullet} \rightarrow \mathrm{O}_2 + \mathrm{H}_2\mathrm{O}_2^{\bullet} \tag{3}$$

$$\mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2^{\bullet-} \rightarrow \mathrm{OH}^- + \mathrm{HO}^{\bullet} + \mathrm{O}_2 \tag{4}$$

In order to study the effect of hydroxyl ions in our experiment, the influence of different pH values on the degradation of nitrobenzene and aniline was investigated. Samples of 1–9 were prepared before ozonation as follows: sample 1 was a original solution without regulation, sample 2 was obtained by adding 0.34 g mixed phosphate in the original solution, sample 3 was obtained by adding 0.5 g natural brucite (without calcination), sample 4 was obtained by adding 0.5 g pure MgO, sample 5 was obtained by adding 0.5 g magnesia, and samples 6–9 were obtained by adding proper amount of sodium hydroxide.

For nitrobenzene, the pH values of solution before and after ozonation were listed in Table 2, and the residual concentrations of nitrobenzene after ozonation for 60 min were shown in Fig. 6A. For aniline, the pH values before and after ozonation were listed in Table 3, and the residual concentrations of aniline after ozonation for 60 min were shown in Fig. 6B. These results indicated that the alkalinity of the solutions had great effect on the ozonation of nitrobenzene and aniline. Especially, sample 6 (sodium hydroxide solution) which had a similar pH with sample 5 (magnesia) revealed similar catalysis effect on the ozonation of both nitrobenzene and aniline. Therefore, it may be said that the catalysis of magnesia is correlated closely to homogeneous hydroxyl ions in water. In addition, a slight decline in the pH values after ozonation was observed from Tables 2 and 3 because some acidic by-products produced during the ozonation process [16, 35].

Compared with that of sample 3 (natural brucite) and sample 4 (pure MgO), the pH value of sample 5 (magnesia) was higher. In order to search the reason for the higher pH value, the concentrations of Mg^{2+} in these solutions were determined. The concentrations of Mg^{2+} were 4.66, 2.98, and 13.8 mg L^{-1} in samples 3, 4 and 5, respectively. Then it may be said that $Mg(OH)_2$ in sample 5 was more soluble than that in other samples, which resulted in higher pH value.

As shown in Fig. 6A and B, magnesia supplied optimum pH conditions for catalytic ozonation of nitrobenzene and aniline. In fact, magnesia played a buffering control role for optimum pH conditions. At much higher pH such as 12, 13 and 14, the degradation efficiency decreased. The negative effect may be due to the reaction as follows [29]: $HO\cdot + OH^-\cdot \rightarrow H_2O + \cdot O^-$ ($k = 1.2 \times 10^{10}$ L M^{-1} s^{-1}). In strong alkaline solution, HO· is rapidly converted to its conjugate base $\cdot O^-$. Compared with hydroxyl radicals ($E_0 = 2.33$ V), oxide radical ion has a lower oxidation potential of 1.77 V. Especially, oxide radical ion has a low tendency to add to double bonds or to aromatic rings (2–3 orders of magnitude less than rate coefficient of hydroxyl radicals) [36], results in a lower reactivity with nitrobenzene and aniline.

Owing to the dissolved hydroxyl ions from magnesia in solution, the catalytic ozonation occurred actually in homogeneous reaction. In application of magnesia, the problem of secondary pollutant can be avoided because Mg^{2+} is proper ions in water. Thus, magnesia supplied an economical and feasible choice for catalytic ozonation of nitrobenzene and aniline.

4 Conclusion

Magnesia from natural mineral was found to be a promising catalyst for ozonation of nitrobenzene and aniline in water. In this process, the essential of catalysis was the homogeneous catalysis of hydroxyl ions in water, which accelerated the generation of hydroxyl radicals. Magnesia played buffering control role for optimum pH conditions. As a catalyst without secondary pollutant, magnesia is economical and feasible for application in water treatment.

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