



Ozonation catalyzed by iron silicate for the degradation of p-chloronitrobenzene in aqueous solution

*Yue Liu¹, Lei Yang¹, Zhonglin Chen² and Jimin Shen²

¹School of Energy & Environment Engineering, Zhongyuan University of Technology, Zhengzhou, China

²State Key Laboratory of Urban Water Resources and Environment, School of Municipal & Environmental Engineering, Harbin Institute of Technology, Harbin, China

ABSTRACT

The prepared iron silicate was characterized using X-ray diffraction (XRD) and Fourier transformation infrared (FT-IR). The characterization studies showed that the Fe-O-Si bond is formed on the surface of the amorphous iron silicate which contains abundant functional groups. Iron silicate was used as an ozonation catalyst, and it showed significant activity in the decomposition of ozone in aqueous solution. The catalytic ozonation removal effectiveness of p-chloronitrobenzene (pCNB) was investigated under various physicochemical conditions. Both the adsorption and the single ozonation were not effective for the degradation of pCNB, but the presence of iron silicate in ozonation process could substantially enhance the pCNB removal efficiency. The hydroxyl radical scavenger experiment confirmed that iron silicate catalytic ozonation followed a radical-type mechanism. Better process removal efficiency should be at neutral pH than that at acidic pH or alkaline pH. It is concluded that the iron silicate was an efficient catalyst for pCNB degradation in aqueous solution.

Keywords: catalytic ozonation, iron silicate, ozonation alone, pCNB.

INTRODUCTION

Ozone is commonly used in water treatment due to its high capacity for oxidation and disinfection. However, it has been reported that most of the organic compounds are not degraded completely by ozonation alone and sometimes toxic intermediates are produced[1]. This case has led to the research on how to enhance the efficiency of ozonation for various applications, and many catalytic ozonation has been developed. Compared with the ozonation alone, the advantages of catalytic ozonation are enhanced ozone utilization, increased efficiency of pollutant removal rate and improved organic matter mineralization [2]. 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, supported metals or carbons[3]. In recent years, heterogeneous catalytic ozonation has received much attention due to its potentially higher effectiveness in the degradation of refractory organic pollutants and lower negative effect on water quality. However, most catalysts in some literatures are often not disclosed. At present, selecting active species and its preparation technology is the key problem to heterogeneous catalytic ozonation process. Iron silicate which was impregnated with iron oxide and silicon oxide has been synthesized in the laboratory. Some papers has been demonstrated that iron silicate is the most effective metal silicate for ozone decomposition in the aqueous solution[4]. So the characteristics of iron silicate catalytic ozonation of contaminants in water are interesting to researchers.

PCNB is widely used in fields of raw materials such as pesticide, herbicide, dyestuffs, wood anticorrosion, medicine, photography film, antioxidant, gasoline additive, antiseptic and so on [5-6]. The previous experiments [7] on animals and human implied that pCNB could damage liver and spleen, and it also could cause many kinds of diseases such as

the high-iron-hemoglobin and anemia, and it even could cause gene mutation. p-Chloronitrobenzene (pCNB) is a representative of halogenated nitroaromatic compounds which are not readily biodegradation, and this compounds without any treatment discharge into aqueous environment may cause environmental pollution problems[8]. Therefore, the remediation of pCNB in aqueous solution is of environmental concern, and the methods for removal of this compound from aqueous environmental systems must be developed.

The objective of this study were as follow:(1) to characterize the as-synthesized iron silicate for application as a heterogeneous catalyst in ozonation;(2) to investigate the catalytic efficiency of iron silicate for the decomposition of pCNB in aqueous solution.

EXPERIMENTAL SECTION

Materials. pCNB(99.5% purity, Chem Service, USA) was obtained from USA Chem Service. Other chemicals (KI, HNO₃, Na₂SiO₃·9H₂O, Fe(NO₃)₃, NaOH, Na₂SO₃) were analytical grade without further purification. The iron silicate was synthesized in the laboratory as described in the literature[4]. The stock solution of pCNB was prepared at 100mg/L by dissolving 100mg pCNB into 1000mL the ultra-pure water (18MΩ CM). All the glassware equipments used in the experiments were soaked in the solution of H₂SO₄-K₂Cr₂O₇ overnight, and then washed by the tap water and the distilled water for three times, respectively.

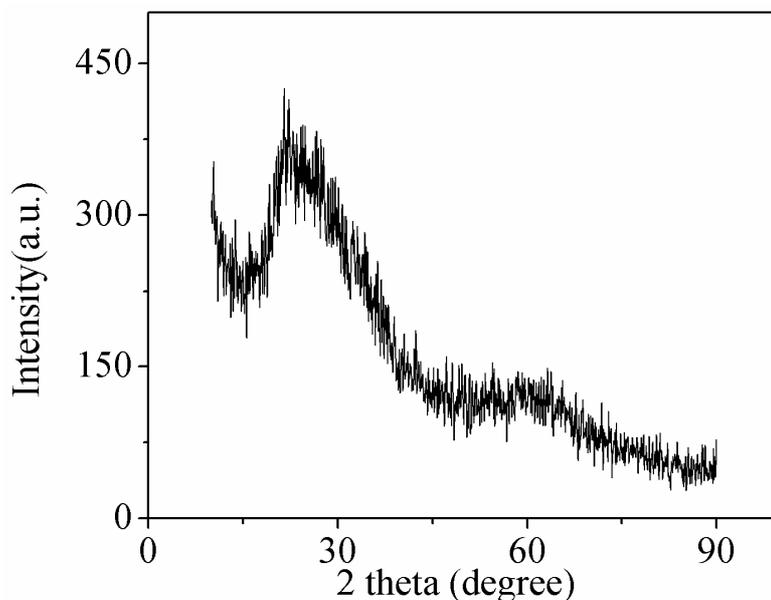
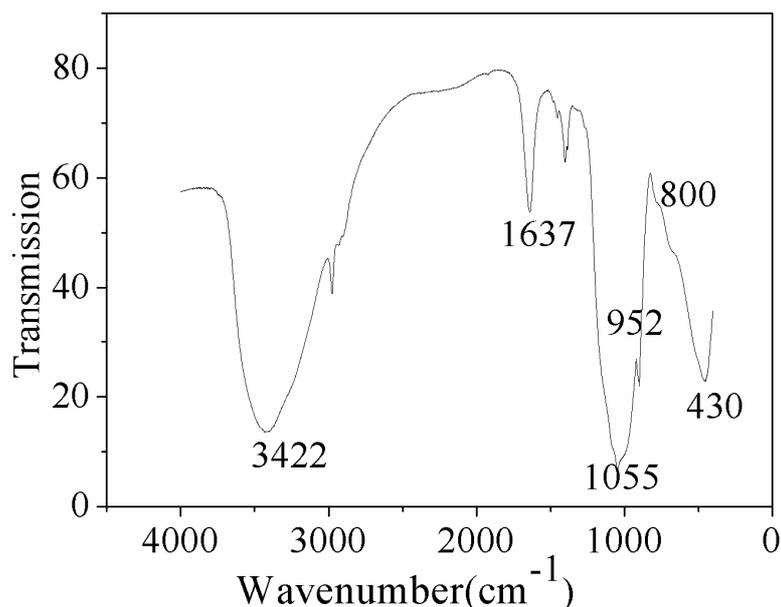
Ozonation experiments. The experiments of pCNB removal from aqueous solution under different conditions were carried out in a 1.2L reactor equipped with a magnetic stirrer. The experiments were in the bath mode at room temperature (20±1 °C). For comparative purpose both adsorption on iron silicate and the sole ozonation experiments in the absence of iron silicate were performed in the same system, under identical experimental conditions. For each experiment, 1L deionized water with the pH pre-adjusted by NaOH or HNO₃ was first transferred into the reactor. Then, the ozone gas which was produced from pure oxygen (Harbin Gas Co.Ltd., 99.999%, China) through CF-G-3-010g ozone generator (Qingdao guolin, China) was continuously injected into the aqueous solution and dispersed into solution by means of a silicon dispenser until to the desired concentration. The desired amounts of catalyst and pCNB stock solution were immediately dosed into the reactor. The reactor was quickly sealed and agitated by the magnetic stirrer. Samples were grabbed at certain intervals (0, 1, 3, 5, 10, and 15min) and quenched by sodium sulfite solution (0.1mol/L). The quenched samples were analyzed to determine the pCNB concentration using the method described below.

Analytical methods. The dissolved ozone concentration was measured by indigo method (Bader and Hoigné, 1981). The concentration of pCNB was determined by a 1200 high performance liquid chromatography (HPLC, Agilent, USA) provided with an UV-Vis detector. A reversed-phase 4.6mm×250mm C18 waters column was used at room temperature. Elution was carried out by pumping methanol and water (8:2v/v) at a flow rate of 1.0×10⁻³L/min. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis, carried out on a Bruker D8 Advance Diffractometer with Cu Kα radiation (λ = 1.5418 Å). The surface properties of the samples were measured by FT-infrared spectroscopy (FTIR) analysis on a Spectrum One Perkin Elmer Fourier transform infrared spectrum instrument (Japan) with a spectral range of 4000-400 cm⁻¹.

RESULTS AND DISCUSSION

Characterization of iron silicate. The XRD pattern of the as-synthesized iron silicate is shown in Fig. 1. It is interesting to note that there is no single, sharp, intense and well recognizable peaks above background, and no reactants can be identified, which indicate that the as synthesized iron silicate is an amorphous matter .

In heterogeneous catalytic ozonation, the surface properties of the catalyst are very important for the degradation of organic pollutions [9]. Therefore, the catalyst was further characterized with FTIR. Fig.2 illustrates the FTIR spectra of the iron silicate. The broad bands at 3422cm⁻¹ assign to the OH stretching vibration of water. The bands at 1637cm⁻¹ are also assigned to OH bending vibrations in water. These surface hydroxylation groups may result in the surface functional group formation on the surface of the mineral. The stretching vibration of Si-O bond is overlapped up by the adsorption peak caused by the bending vibration of Si-O-Fe bond, indicated that ferric ion and its hydrolysis species have reacted with Na₂SiO₃ and its hydrolysis species to form iron silicate. The surface hydroxyl groups are very advantageous for the catalytic ozonation or catalytic ozone decomposition [10].

**Fig. 1.** XRD pattern of theiron silicate**Fig.2** FTIR spectra of iron silicate

Decomposition kinetics of ozone. To study catalytic activity of the iron silicate, the decomposition kinetics of ozone was performed both with and without the iron silicate at pH=7. In this experiment, initial ozone concentration was 1mg/L, and iron silicate concentration was fixed at 500mg/L. As demonstrated in Fig. 3, the decomposition of ozone followed first-order kinetics with and without the presence of the iron silicate. With the iron silicate addition to the water, the decomposition rate of aqueous ozone was obviously enhanced, which is 3.13 times compared to that without the presence of the catalyst. Hence, the as-synthesized iron silicate had a significant effect on the catalytic decomposition of ozone in aqueous solution.

Catalytic activity of iron silicate in the degradation of pCNB. Different processes of experiments were performed to investigate the catalytic activity of iron silicate for the degradation of pCNB, such as ozonation alone, iron silicate catalytic ozonation and adsorption of iron silicate. Fig.4 shows the removal curves of pCNB for the different experimental processes. Regarding the adsorption of pCNB on iron silicate, a 15min reaction can cause approximate 1% disappearance of pCNB. Regarding ozonation alone a 15min reaction showed that pCNB removal had reached only 47% . Thus, at the same time period, the pCNB removal rate of the simultaneous application of ozone and iron silicate was 99.7% which was much higher than that the sum of individual contributions of single ozonation and single

adsorption. these date indicate that the iron silicate had obvious activity in catalytic ozonation of pCNB in aqueous solution.

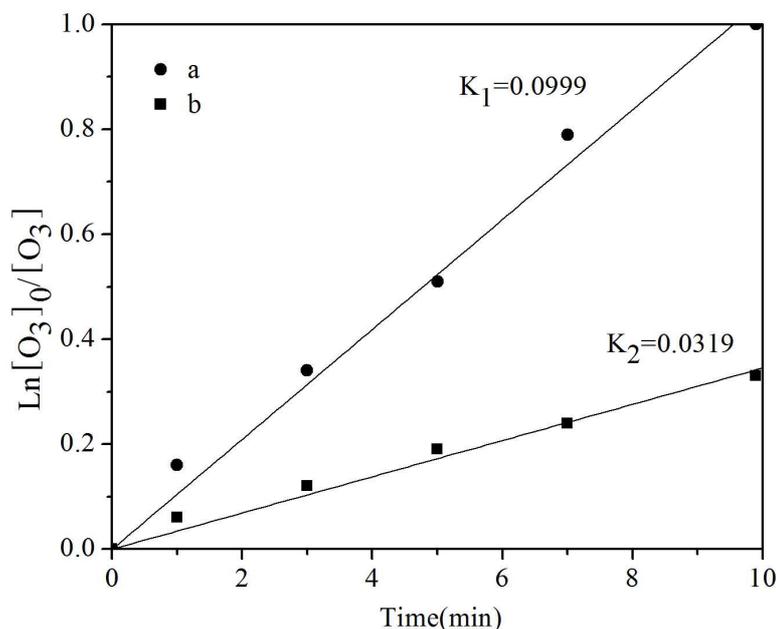


Fig. 3. iron silicate catalyzed decomposition of ozone , a: catalytic ozonation b: ozone alone $[O_3]_0=1\text{mg/L}$, $[\text{iron silicate}]_0=500\text{mg/L}$, $\text{pH}=7.0$, $t=293\text{K}$

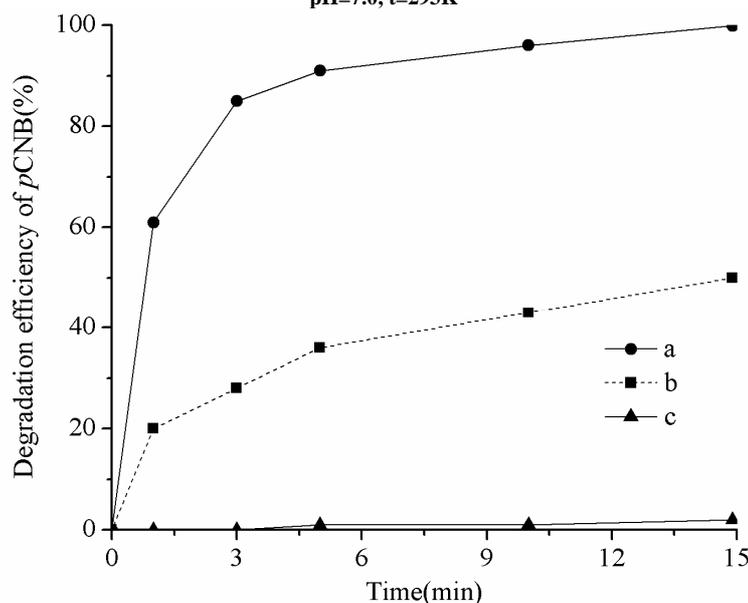


Fig. 4 Degradation of pCNB along with reaction time (a) catalytic ozonation with iron silicate, (b) ozonation alone and (c) iron silicate adsorption. Experiment conditions were: $[\text{pCNB}]_0=100\mu\text{g/L}$, $[O_3]_0=0.6\text{mg/L}$, $[\text{iron silicate}] = 100\text{mg/L}$, solution $\text{pH}=7.0$, the reaction time 15min

Influence of t-butanol and carbonate on the efficiency of degradation of pCNB. As we all known, the molecular ozone reaction with organic substrates follows two reaction mechanisms [11]: (1) direct reaction (molecular ozone oxidation), and (2) hydroxyl radicals oxidation. Since pCNB was hardly adsorbed on the surface of iron silicate (Fig.4), the removal of pCNB in water was due to some phenomenon rather than the total contribution of single adsorption and ozonation alone. It is presumed that hydroxyl radicals were formed during the processes of iron silicate catalytic ozonation. To support this hypothesis, some experiments were carried out in the presence of radical scavengers.

Experiments were carried out in the presence of t-butanol and carbonate as radical scavengers. Since OOCH_2COO and CO_3^{2-} can react with hydroxyl radicals, and these reaction form secondary radicals, which do not predominantly produce the $\text{HO}_2\cdot$ and $\cdot\text{O}_2^-$ radicals, then result in the termination of chain reactions. t-butanol is a relatively stronger radical scavenger than carbonate. The reaction rate constant of t-butanol and carbonate with hydroxyl radical are

$5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $7.9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ [12], respectively. As illustrated in Fig.5 and Fig.6, the influence of t-butanol is higher than carbonate. It is apparent that the presence of t-butanol had negative impact on both of ozonation alone and catalytic ozonation, which keep consistent with the free radical characteristics. The presence of t-butanol at a concentration of 15mg/L in water caused the degradation efficiency of pCNB decreases by 87% and 46% in the processes of catalytic ozonation and ozonation alone. However, the removal rate of pCNB did not decrease any more when keep on increasing the concentration of t-butanol. Carbonate had less scavenging effect than t-butanol. With the increasing of the concentration of carbonate the degradation rate of pCNB decreased gradually, which also proved the free radical mechanism. So, the result in Fig.5 and Fig.6 validated the formation of hydroxyl radicals during the catalyzed ozonation process.

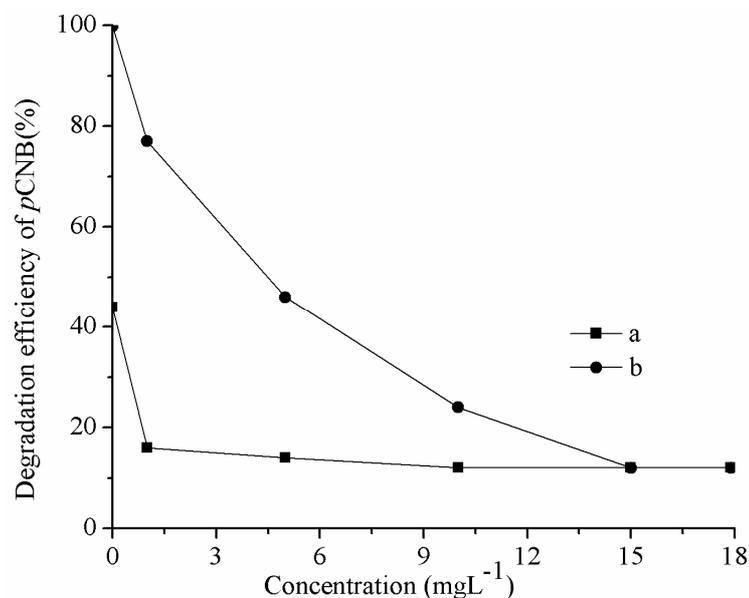


Fig. 5 Effect of t-butanol on the degradation efficiency of pCNB in the different processes (a) ozonation alone, and (b) iron silicate catalyzed ozonation. Experimental conditions: $[\text{pCNB}]_0=100\mu\text{g/L}$, $[\text{O}_3]_0=0.6\text{mg/L}$, $[\text{iron silicate}]=100\text{mg/L}$, solution pH=7.0, the reaction time 15min

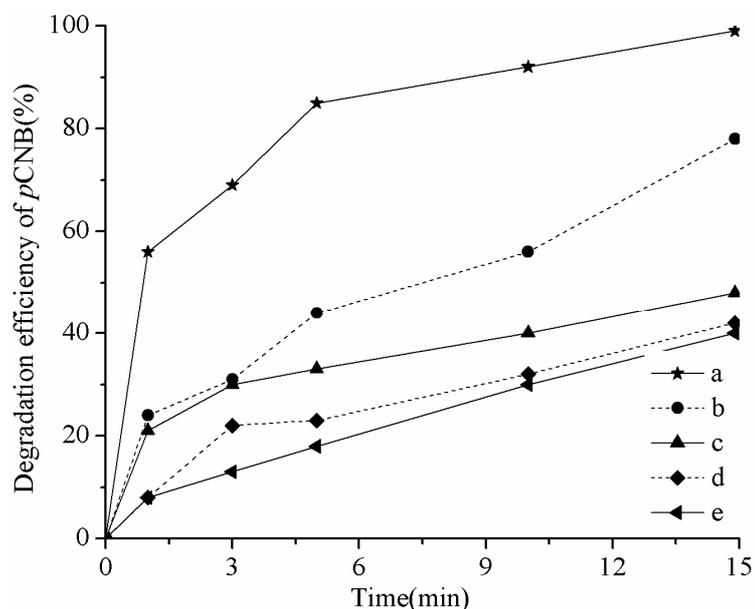


Fig. 6 Effect of carbonate on the degradation of pCNB (a) $[\text{HCO}_3^-]_0=0\text{mg/L}$, (b) $[\text{HCO}_3^-]_0=50\text{mg/L}$, (c) $[\text{HCO}_3^-]_0=100\text{mg/L}$, (d) $[\text{HCO}_3^-]_0=150\text{mg/L}$, and (e) $[\text{HCO}_3^-]_0=200\text{mg/L}$. Experimental conditions: $[\text{pCNB}]_0=100\mu\text{g/L}$, $[\text{O}_3]_0=0.6\text{mg/L}$, $[\text{iron silicate}]=100\text{mg/L}$, solution pH=7.0, the reaction time 15min

Effect of initial pH. Since pH is a key parameter for both ozone stability and catalyst surface properties in aqueous solution, it is important to examine the influence of pH on catalytic ozonation of pCNB.

From the Fig.7, it can be seen that the removal rate of ozonation alone is greatly increased with the increasing initial pH range from 3 to 9.5. Significantly, only in the initial pH range 2.5-7.1, the degradation efficiency of pCNB in the iron silicate catalytic ozonation processes can follow this positive influence rule and the increasing initial pH to 9.5 and 10 results in a reduction of the degradation efficiency compared to that of initial pH 7.1 in the same system.

For the ozonation alone system, the influence of initial pH on the degradation efficiency comes from the action of pH on the homogeneous ozonation. Since hydroxides ions may play a role of initiator of the chain reaction, in basic solution ozone decomposes into hydroxyl radicals more easily than neutral or acid circumstances[1]. For the concentration of hydroxyl radicals in basic solution is much higher than acid solution, more pCNB molecules can be oxidized in a basic solution. Compared the results of catalytic ozonation with the ozonation alone mentioned above, it can be found that the influence of initial pH on the degradation efficiency of catalytic ozonation of pCNB may come from the synergistic effect of homogeneous and heterogeneous catalytic ozonation, the latter of which is based on the introduction of heterogeneous catalytic surface.

Generally, in most cases of water treatment the water pH is around neutral, so iron silicate is a suitable catalyst to promote hydroxyl radicals generation and enhance the degradation of refractory organic pollutants. This is the value of the catalytic ozonation with iron silicate in water treatment.

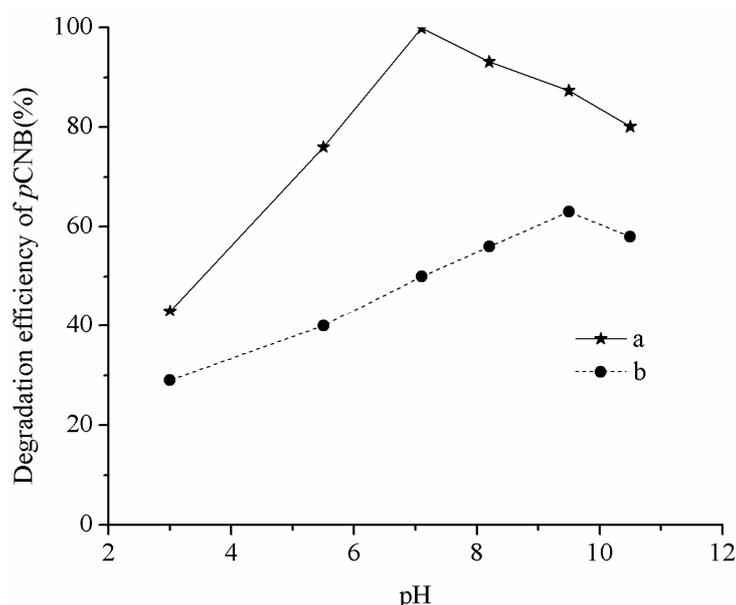


Fig. 7 Effect of initial pH on the iron silicate catalyzed ozonation of pCNB (a) iron silicate catalytic ozonation and (b) ozonation alone. Experiment conditions were: $[pCNB]_0=100\mu\text{g/L}$, $[O_3]_0=0.6\text{mg/L}$, $[\text{iron silicate}]=100\text{mg/L}$, the reaction time 15min, solution pH adjusted with NaOH or HNO_3

CONCLUSION

The aims of this study were to characterize iron silicate and to evaluate its efficiency as a catalyst for the decomposition of pCNB in aqueous solution. On the basis of the experimental results and discussion, the following conclusions could be drawn as following.

- (1) XRD and FTIR analyses confirmed that the Mn-O-Si bond is formed on the surface of the amorphous MS which contain abundant of functional groups.
- (2) The iron silicate had a significant effect on the catalytic decomposition of aqueous ozone.
- (3) Iron silicate showed remarkable activity for the decomposition of pCNB in aqueous solution compared with ozonation alone. The enhancement of removal rate of pCNB in catalytic ozonation process is due to the generation of hydroxyl radicals which is confirmed by the experiments with addition of t-butanol (0-15mg/L) and carbonate (0-200mg/L).
- (4) Furthermore, it was proved that the round neutral pH had better process removal efficiency than that at acidic pH or alkaline pH.

Acknowledgments

This work was financially supported by financially by the Natural Science Foundation of China (51308561).

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