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Degradation p-Chloronitrobenzene in Ozone-loaded System with Perfluorodecalin Solvent

Shiyin Li · Yiping Zhu · Xiaorong Li · Guoxiang Wang · Lixiao Ni

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Abstract Study was carried out for the removal of hazardous organic compound from aqueous solution by using water/perfluorodecalin loaded ozone two-phase system. p-Chloronitrobenzene was used as hazardous organics to examine the efficiency of the two-phase ozonation system. Effects of initial pH in water, stirring speed, initial molar ratio of O_3/p-chloronitrobenzene (M), and free radical scavenger on the removal rate of p-chloronitrobenzene were investigated respectively. It was revealed that ozone had low decomposed rate coefficient $k = 0.0035\ min^{-1}$ and solubility of 61.94 mg/L at 25°C in perfluorocarbon. In contrast to pH 2.0, higher level of pH (8.0) in water increased the removal rate of p-chloronitrobenzene in water/perfluorocarbon two-phase ozonation system. Removal rate of p-chloronitrobenzene was increased with the elevation of initial M value in water/perfluorocarbon two-phase ozonation system. Stirring speed was needed to control with proper level of speed in water/perfluorocarbon two-phase system. Compared to the conventional gas/water ozonation system, $NaHCO_3$ (20 mmol/L) had no obvious negative effect on the p-chloronitrobenzene degradation in water/perfluorocarbon ozonation system. Oxidation efficiency of ozonation in water/perfluorocarbon system was superior to that of in conventional gas/water system.

Keywords Ozonation · p-Chloronitrobenzene · Perfluorodecalin · Two-phase · Degradation

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Decomposition of odorous compounds, hazardous organics like pesticides and chlorinated organic carbons by ozone is one of the most efficient processes in water and wastewater treatments (Kim et al. 1997a, b). It is used in combination with biological activated carbon to remove natural organic matter as a precursor of disinfection by-products in drinking water treatment (Reungoat et al. 2010). Many studies on ozonation have been carried out in water to remove aquatic organic substances. However, ozone has relatively low solubility and stability in water,the aquatic concentrations of most target organics are very low and coexist with relatively higher concentrations of ozone scavengers like CO_2. The ozonation in water, therefore, is not necessarily an efficient process.

In order to provide higher ozonation process efficiency, many assistant methods of advanced oxidation (for example, UV, H_2O_2, etc.) have been investigated (Milena et al. 2008; Rosenfeldt and Linden 2007). Advanced oxidation processes (AOPs) involve the generation of free hydroxyl radicals, characterized by oxidative potential significantly higher compared to molecular ozone (Gromadzka and Wietlik 2007). However, reactions with free radicals are not selective and more likely to be hindered by competitive reactions. For that reason, new methods based on molecular ozone reactions, which allow for better ozone dissolution and stability in water as well as improvement of ozonation efficiency are investigated. One of them is

two-phase ozonation, sometimes called as ozone-loaded system (Bin 2006).

Extended research on solubility and stability of ozone indicates that ozone is strongly stabilised in organic solvents of low polarity. According to recent review paper (Bin 2006), ozone is approximately ten times better soluble in perfluorinated compounds non-polar solvents than in water. For the practical reasons non-polar phases used in ozonation process should be characterized by non-toxicity, high density and low vapor pressure. Additional benefit of perfluorinated solvents is their reusability. One of the perfluorinated hydrocarbons C-18 is Fluorinert FC40 characterized by ten times better ozone solubility than water (Ward et al. 2003). Perfluorodecalin ($C_{10}F_{18}$) has a number of medical applications stemming from its use in first-generation perfluorocarbon-based blood substitutes. It is used in retinal surgery, for treating lung disorders, as an ultrasonic contrast agent and in organ storage (Walker et al. 2003). Perfluorocarbon has average molecular weight 462, boiling point 142°C, density 1.95 g/mL,saturated vapor pressure 12.3 mmHg at temperature 25°C. According to the properties of perfluorocarbon, perfluorocarbon seems to be fit for non-polar solvents loaded ozone.

The purpose of this study was to investigate the stabilization of ozone in perfluorocarbon and water/perfluorocarbon systems. p-Chloronitrobenzene was used as the model hazardous organic compound to examine the efficiency of the water/perfluorocarbon two-phase ozonation system compared to that of the conventional gas/water ozonation system.

Materials and Methods

For all experiments, the non-aqueous solvent was perfluorocarbon, obtained from 3 M Co. Perfluorocarbon was purified and recycled using the same procedure as FC40 described previously (Bhattacharyya et al. 1995; Gromadzka and Nawrocki 2006). Two-phase ozonation was carried out in semi-continuous operational system using the scheme procedure as described in Fig. 1. Prior to reaction, the solvent was saturated with ozone by bubbling a mixture of O_2 and O_3 through it for about 30 min. The saturation concentration of O_3 in perfluorocarbon is 61.94 mg/L at 25°C. The initial concentration of compound in model solution was 20 mg/L for p-chloronitrobenzene. The working solution was adjusted to suitable pH with NaOH or H_2SO_4. A measured volume of water containing the hazardous organic (p-chloronitrobenzene, Sigma) was then added to the ozonated solvent in a reaction vessel and stirred intensely with magnetic stirrer. The ratio of volume of solvent loaded ozone to water was controlled. The stirring speed was adjusted by electrical current and was

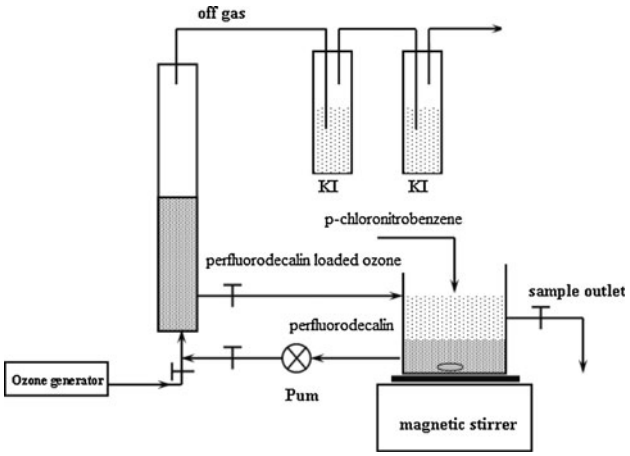

Fig. 1 Scheme of semi-continuous ozonation reactor

monitored by a tachometer. After an elapsed time, the remaining ozone in the system was quenched with $NaHSO_3$, and the phases were separated. In the aqueous phase, pH, compound concentration, total organic carbon (TOC) degradation rate were measured. The solvent phase was analyzed for compound concentration.

Experiments conducted using a continuous supply of ozone to the reactor followed the procedure above with the addition of a gas diffuser in the reactor from which O_3 flowed continuously at a rate of 0.05 m^3/h (T = 25°C, 48.82 mg/min). For single aqueous-phase reactions, O_3 was bubbled from the gas diffuser into a stirred volume of water containing p-chloronitrobenzene. No perfluorocarbon was presented for the single aqueous-phase reactions. To maintain virgin quality of the organic solvent, the perfluorocarbon was washed after every experiment and then reused. In short, the perfluorocarbon was washed with acetone, methanol to extract residual organics, followed by water washes combining with bubbling ozone to remove the previous solvents and acids.

Ozone was generated in ozone generator (WH-H-Y, China) using pure oxygen. Concentration of ozone in in-gas and off-gas was measured with iodometric method, and concentration of ozone in water was determined spectrophotometrically with indigo method (APHA 1998). Aqueous and perfluorocarbon was measured spectrophotometrically with spectrophotometer (UV 2201, SHIMADZU) at $\lambda = 254$ nm. The concentration of ozone was calculated by the use of Beer–Lambert law. The molar extinction coefficient of ozone is 3,300 L mol^{-1} cm^{-1} (Pera-Titus et al. 2004). Measurement of pH value of the aqueous solution in reactive system was carried out with a pH meter at temperature 25°C (Meter 6171, JENCO USA). The pH meter was calibrated with standard pH 6.86 and pH 4.00 buffer solutions. TOC in water phase was quantified using a TOC-5000 (SHIMADZU). Hydrochloric acid

(made in SHIMADZU Corporation) was used to take out carbon dioxide dissolved in samples. Total organic carbon (TOC) equals to the difference of TC and IC.

p-Chloronitrobenzene in perfluorocarbon phase was extracted by contacting a measured amount of the sample with a known amount of HPLC grade methanol. The system was shaken for 5 min and allowed to separate. Percent recovery was determined for p-chloronitrobenzene by extracting a known pollutant concentration and experimental samples were adjusted accordingly. p-Chloronitrobenzene in methanol or aqueous phase was determined by HPLC (Agilent LC-1100) with a UV/Visible detector and a ODS-C18 column. The detection was made with a 1.0 mL min^{-1} mobile phase (water–methanol, 20:80, H_3PO_4 was used to adjust pH value of water phase) at 254 nm for p-chloronitrobenzene. Calibration curves were linear from the detection limit 0.02 mg/L to at least 5 mg/L. RDS was less than 10%. The injection volume was 0.02 mL.

A distribution coefficient, K_d, describes the extent that p-chloronitrobenzene partitions between the perfluorocarbon phase and the aqueous phase. K_d is determined for p-chloronitrobenzene studied by the following equation: $K_d = C_{AS}/C_A$, where C_{AS} is the concentration of p-chloronitrobenzene in the perfluorocarbon phase and C_A is its concentration in the water phase. The concentration for the aqueous phase was measured by HPLC. The perfluorocarbon phase concentration can be determined by material balance. For the determination of K_d of p-chloronitrobenzene, 20 mL of perfluorocarbon was mixed intensely with 20 mL of p-chloronitrobenzene 20 mg/L aqueous solution. The system was shaken for 10 min and allowed to separate. The concentrations of the p-chloronitrobenzene in the aqueous phase and methanol were analysed by HPLC. Experiments of p-chloronitrobenzene recovery in perfluorocarbon were replicated at least five times. The average rate of p-chloronitrobenzene recovery is 98.5%. RDS was 6.97%.

Results and Discussion

The perfluorocarbon was used as organic solvent loaded ozone. It was connected with lower productivity of ozone generator (T = 25°C, 48.82 mg O_3/min, 0.05 m^3/h) used in our study. In all experiments the utmost concentration of ozone in perfluorocarbon was amounted to maximum 61.94 mg O_3/L (T = 25°C). At this condition, the highest concentration of ozone in deionised water was only about 4.13 mg/L. On the other hand, the low concentration of ozone measured in water was in proportion with lower saturation of perfluorocarbon with oxidant. According to literature data, the concentration of ozone in FC40 is usually 12 times higher than in water (Bhattacharyya et al. 1995; Ward et al. 2003). Despite lowest saturation of both phases with ozone, the ratio of $[O_3]_{perfluorocarbon}/[O_3]_{aqueous}$ obtained in our study is equal to 15. Therefore, the application of perfluorocarbon seems to be a better solution for aqueous systems.

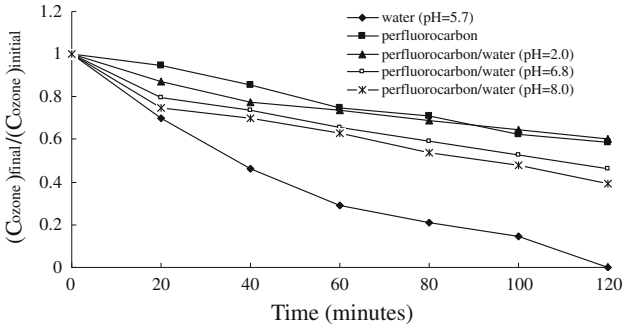

Fig. 2 Comparison of ozone stability in single phase and perfluorocarbon/water two-phase system

The research found that ozone was strongly stabilized in perfluorocarbon phase (Fig. 2). The measured concentration of ozone in perfluorocarbon was over 34.97 mg O_3/L after 2 h (i.e. about 58.07% of initial concentration), and about 3 mg O_3/L after 24 h from the saturation process. In a parallel set of experiments with deionised water (pH 6.8), after 3 h from saturation, ozone was not detected in aqueous samples. It proves that application of perfluorocarbon in ozonation system causes considerable increase of oxidant stability.

In conventional ozonation process, decay of ozone is also strongly influenced by the pH of water solution (Camel and Bermond 1998). Moreover, the rate of ozone decomposition significantly increases in alkaline pH. As result of pH rise, the decrease of ozone concentration in perfluorocarbon/water phase is observed (Fig. 2). The concentration of ozone in perfluorocarbon remained at constant level (about 85% of initial concentration), while in aqueous phase oxidant concentration was only 15% of initial concentration at pH 2. The increase of pH value to 8 caused significantly higher losses of ozone, reaching about 40% after 2 h of contact time. Using the initial rate data from pH experiments and assuming a first-order ozone degradation rate in the perfluorocarbon/water (pH 6.8) two-phase and single water phase (pH = 5.7), the first-order ozonation rate constants were calculated by regression analysis using Origin 8.0 soft and all the correlation coefficients were larger than 0.9. The following ozone degradation rate constant (k) were obtained 0.0035 and 0.019 min^{-1}, respectively.

Since free radical scavengers exist naturally in water systems (Bhattacharyya et al. 1995), it is imperative to explore their effect on the new perfluorocarbon/water two-phase ozonation system. An experiment following the

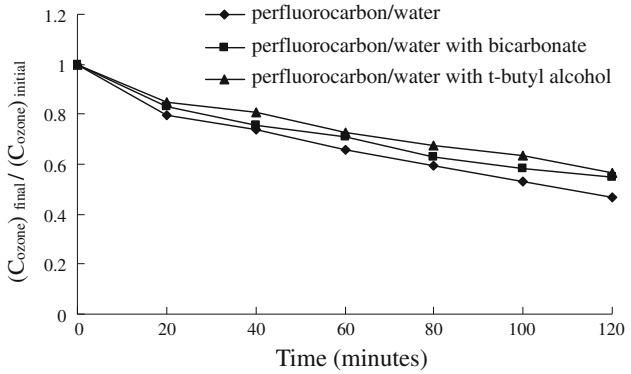

Fig. 3 Ozone decomposition in perfluorocarbon/water two-phase system (equal volumes perfluorocarbon and water, no mixing)

previous conditions was performed with the addition of 20 mM $NaHCO_3$ or 20 mg/L ter-butyl alcohol to the aqueous phase to prove this theory. Figure 3 shows the results obtained from the ozone decomposition experiment with the presence of $NaHCO_3$ or ter-butyl alcohol compared to that of without free radical scavengers. The additions of sodium bicarbonate or ter-butyl alcohol slightly increased the ozone stability, with an ozone decomposition of only 40% after 2 h.

The stirring speed was adjusted by electrical current and was monitored by a tachometer. The stirring speed affects directly on the mass transport of ozone and compounds between water phase and perfluorocarbon phase. Effects of stirring speed on ozonation of p-chloronitrobenzene in perfluorocarbon/water two-phase system are shown in Fig. 4. The results indicated that the degradation rate of total p-chloronitrobenzene was increased with the improvement of stirring speed. It was due to the increase of mass transport of ozone and p-chloronitrobenzene in perfluorocarbon/water two-phase system when stirring speed was accelerated. However, the concentration of ozone in water phase and perfluorocarbon phase was decreased when stirring speed elevated excessively in two-phase system according to the laboratorial test. Therefore, the stirring speed in perfluorocarbon/water two-phase system was controlled at 300 rpm in this study.

The determination of the partitioning coefficient (K_d) is important for understanding the degradation of the p-chloronitrobenzene in a two-phase perfluorocarbon/water system (Rivas et al. 2005). The experimentally determined K_d value (perfluorocarbon/water at pH 6.8) is 3.12. It suggested that p-chloronitrobenzene was mainly saved in perfluorocarbon phase in two-phase system.

At the condition of 20 mg/L p-chloronitrobenzene at various pH (2.0, 6.8 and 8.0 using NaOH and H_2SO_4 to adjust pH), studies were performed to determine the effect of the initial pH on the degradation of p-chloronitrobenzene in conventional gas/water and perfluorocarbon/water two-phase systems (Figs. 5, 6). Removal efficiency in conventional gas/water system was significantly lower than that of in perfluorocarbon/water two-phase system at same initial pH in water. As in aqueous solution of pH 2, ozone was very stable, low degradation rate (about 40%) for p-chloronitrobenzene was connected to the absence of hydroxyl radicals. The increase of ozonation efficiency to 74.4% ($[O_3]$/[p-chloronitrobenzene] = 15.43) in conventional gas/water ozonation system and to 79.5% ($[O_3]$/[p-chloronitrobenzene] = 2.58) after 10 min were observed in perfluorocarbon/water two-phase system at pH 8.0. Application of perfluorocarbon caused overly 5% increase of process efficiency after 10 min of ozonation time compared to conventional ozonation. Moreover, the amount of ozone consumed for the degradation of p-chloronitrobenzene in conventional gas/water system was 3–6 times higher than that of in perfluorocarbon/water two-phase system (Fig. 6).

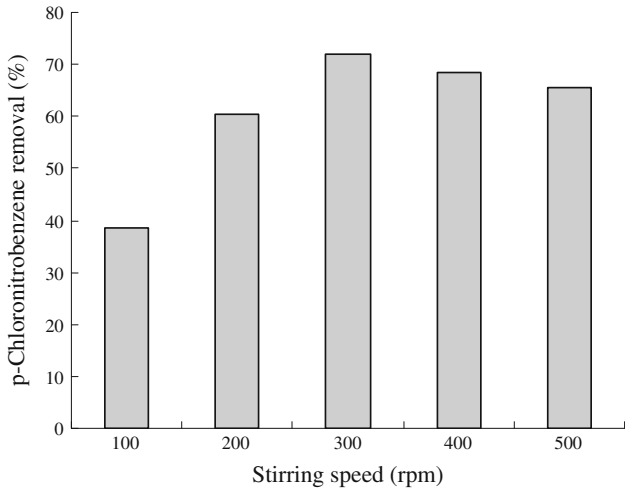

Fig. 4 Effects of stirring speed on ozonation of p-chloronitrobenzene in perfluorocarbon/water two-phase system

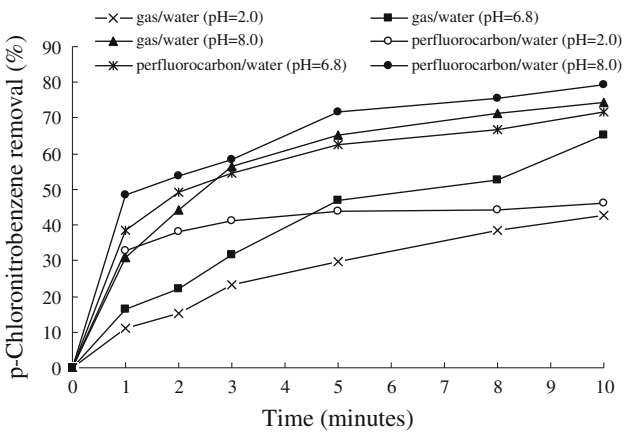

Fig. 5 Degradation of p-chloronitrobenzene in conventional gas/water and perfluorocarbon/water two-phase systems

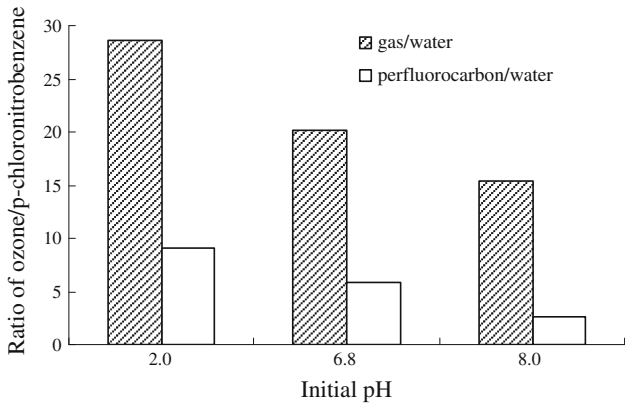

Fig. 6 The initial pH in water phase versus the ratio of ozone consumed with p-chloronitrobenzene degradated in gas/water and perfluorocarbon/water system, respectively

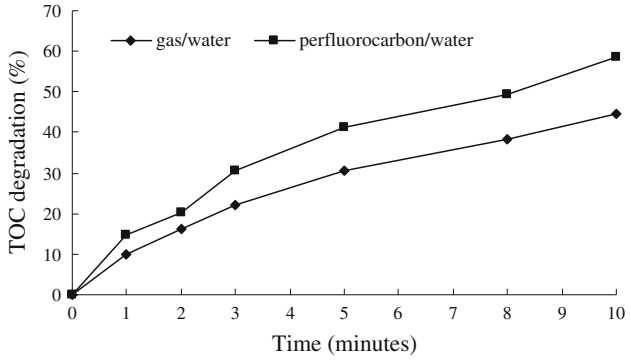

Fig. 8 TOC degradation of p-chloronitrobenzene in water phase for conventional gas/water and perfluorocarbon/water two-phase systems at initial pH = 6.8

The results showed that the perfluorocarbon/water system required less O_3 than that of the conventional gas/water system. p-Chloronitrobenzene with high K_d is mainly reacted with molecular ozone dissolved in perfluorocarbon phase at pH 2.0. Both direct ozone reactions in organic solvent as well as decomposition of ozone with the formation of reactive hydroxyl radicals at the water/organic solvent interface can occur at high pH in water/perfluorocarbon loaded ozone system (Chang and Chen 1995). The application of ozone-loaded system caused the increase of p-chloronitrobenzene degradation rate and process efficiency. It is in good agreement with the results previously presented (Bhattacharyya et al. 1995) as well as confirmed that compounds with high K_d react with molecular ozone directly in organic solvent.

The changes of pH and TOC in water phase with reactive time in perfluorocarbon/water two-phase ozonation system are showed in Figs. 7, 8 respectively. The results indicated that the initial pH and the degradation rate of TOC in aqueous phase were decreased with the prolong of reactive time in perfluorocarbon/water two-phase systems at initial pH = 6.8. The oxidation efficiency of ozonation in perfluorocarbon/water two-phase system was superior to that of ozonation in conventional gas/water two-phase system. It demonstrated that the intermediate oxidation products of p-chloronitrobenzene include highly polar acids which diffuse into the aqueous phase due to their high solubility (Gromadzka and Wietlik 2007). Further research is being conducted to characterize those organic acid intermediates.

Under the condition of initial pH 6.8, p-chloronitrobenzene 20 mg/L, 20 mM $NaHCO_3$ was used as free radical scavengers to investigate the effects on ozonation of p-chloronitrobenzene in gas/water and perfluorocarbon/water system (Fig. 9). The results showed that $NaHCO_3$ had slightly influence on the degradation of p-chloronitrobenzene in perfluorocarbon/water system, but had obviously adverse effect the degradation of p-chloronitrobenzene in conventional gas/water. It demonstrated that p-chloronitrobenzene was mainly reacted with molecular ozone dissolved in perfluorocarbon phase, and could be selectively oxidized in organic solvent loaded ozone system (Gromadzka and Wietlik 2007).

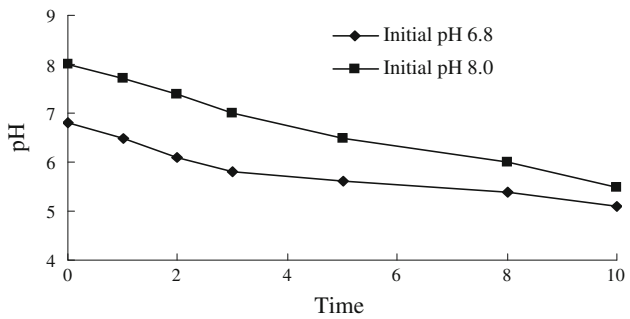

Fig. 7 The change of pH (water phase) with reactive time in perfluorocarbon/water two-phase ozonation system

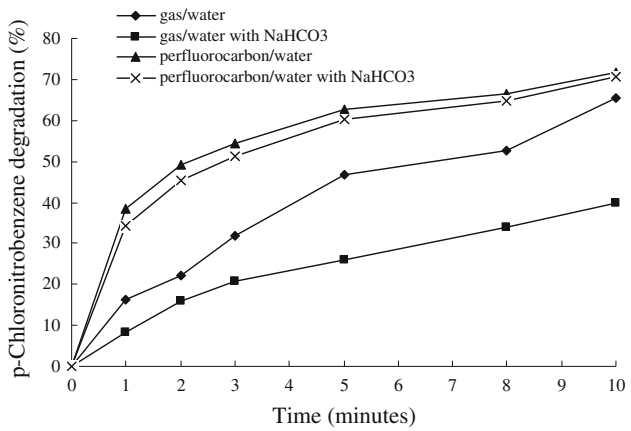

Fig. 9 Effect of sodium bicarbonate on ozonation degradation of p-chloronitrobenzene in gas/water and perfluorocarbon/water systems

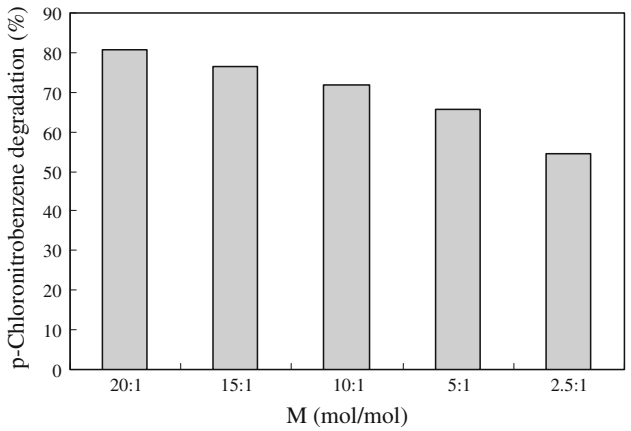

Fig. 10 The initial M values versus degradation of p-chloronitrobenzene in perfluorocarbon/water two-phase system

The volume of p-chloronitrobenzene aqueous solution was regulated in order to investigate the effects of the initial molar ratio of O_3/p-chloronitrobenzene (M) on ozonation of p-chloronitrobenzene in perfluorocarbon/water two-phase system (Fig. 10). In this experiment, the initial amount of ozone loaded in perfluorocarbon phase, the concentration of p-chloronitrobenzene in water (20 mg/L) and pH 6.8 were unchanged. The results indicated that the degradation rate of p-chloronitrobenzene was increased with the increase of initial M value in perfluorocarbon/water two-phase system. It demonstrated that the effective number of double bonds oxidized by each ozone molecule was higher at low reactant concentrations than that of at high reactant concentrations (Anthony et al. 2008).

In conclusion, the application of perfluorocarbon induced the increase of ozone solubility and stability. The influence of different pH values on ozone stability in perfluorocarbon was noteworthy. As results of pH rise, the decrease of ozone concentration were observed in perfluorocarbon phase. The amount of ozone consumed during oxidation of studied p-chloronitrobenzene was significantly lower in perfluorocarbon/water two-phase ozonation than that of in conventional gas/water ozonation system. The oxidation efficiency of ozonation in perfluorocarbon/water two-phase system was superior to that of ozonation in conventional gas/water two-phase system. $NaHCO_3$ had slightly influence on the degradation of p-chloronitrobenzene in perfluorocarbon/water loaded ozone two-phase system, but had obviously adverse effect the degradation of p-chloronitrobenzene in conventional gas/water two-phase ozonation system. p-Chloronitrobenzene was mainly reacted with molecular ozone dissolved in perfluorocarbon phase, and could be selectively oxidized in water/perfluorocarbon loaded ozone two-phase system. The degradation rate of p-chloronitrobenzene was increased with the increase of initial M value in perfluorocarbon/water two-phase system.

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